

Long-term records of atmospheric deposition of mercury in peat cores from Arctic, and comparison with bogs

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Long-term records of atmospheric deposition of mercury in peat cores from Arctic, and comparison with bogs in the temperate zone

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PhD dissertation
February 2004



Institute of Geological Sciences
University of Berne

Long-term records of atmospheric deposition of mercury in peat cores from Arctic, and comparison with bogs in the temperate zone

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Chapter 1:

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 8,000 years). *Journal of Environmental Monitoring*, **5**, 935-949.

Chapter 2:

Givelet N., Roos-Barraclough F., Goodsite M.E., Cheburkin A. K. and Shotyk W. (2004) Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the High Arctic of Canada recorded by peat hummocks. *Environmental Science & technology*, **38**, 4964-4972.

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The following papers have evolved from collaboration during my master thesis (DEA Dynamique de la Lithosphère, Grenoble) or my doctoral thesis:

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Arnaud F.; Revel-Rolland M.; Bosch D.; Winiarski T.; Desmet M.; Tribovillard N.; **Givelet N.** (2004) A 300 year history of lead contamination in northern French Alps reconstructed from distant lake sediment records. *Journal of Environmental Monitoring*, **6**, 448-456.

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-Abstract-

Because of the strong tendency of mercury (Hg) to bioaccumulate in the food chain, one of the greatest challenges faced by environmental mercury research in the Arctic is to *quantify the relative contribution of anthropogenic sources* of mercury to the contamination of this environment, as anthropogenically elevated mercury deposition over the past 150 years in Arctic ecosystems is potentially a serious environmental problem. To determine the magnitude of this concern, it is necessary to quantify the natural "background" of atmospheric mercury deposition and its variation over a millennial-scale period of time. A second problem is to understand the role which is played by the *unique climate* of the Arctic on the deposition of atmospheric mercury.

Total mercury concentrations were determined in peat cores from the High Arctic of Canada, the Faroe Islands and southern Ontario. The cores were dated using ^{210}Pb and ^{14}C. The mercury concentrations were used to calculate rates of atmospheric mercury accumulation in the peat in order to quantify rates of atmospheric deposition of mercury in the Arctic. In addition, rates of atmospheric mercury accumulation in the Arctic were compared with peat cores from the temperate zone of North America (southern Ontario).

Mercury concentration measurements and age dating of two peat hummocks from Bathurst Island, Nunavut indicate rather constant natural "background" mercury flux of ca. 1 µg m^{-2} per year from 5900 to 800 calibrated year BP. The values are well within the range of the Hg fluxes reported from other Arctic locations (Greenland and the Faroe Islands) but also by peat cores from southern Canada (Ontario) which provide a record of atmospheric Hg accumulation extending back to eight thousand years. Thus, pre-anthropogenic Hg fluxes in the Arctic were not significantly different from atmospheric Hg fluxes in the temperate zone. In pre-industrial times, therefore, the High Arctic was not more important as a sink for global atmospheric mercury than the temperate zone. Therefore, other processes have to be invoked as chief mechanism for transferring atmospheric Hg to the Arctic environment, possibly made more efficient in recent years by environmental changes, resulting in the mercury contamination of the Arctic food chain.

The beginning of mercury contamination from anthropogenic sources dates from AD 1475 at the Luther Bog in southern Ontario, corresponding to biomass burning for agricultural activities by Native North Americans. During the late 17th and 18th centuries, deposition of anthropogenic mercury was at least equal to that of mercury from natural sources. Anthropogenic inputs of mercury to the bogs have dominated continuously since the beginning of the 19th century.

The records from southern Ontario and the Faroe Islands show similar chronologies to one another, with mercury accumulation rates peaking in the 1950`s with 54 to 141 and 34 µg m^{-2} per year respectively. At both locations, in these (modern) samples, the Hg concentration profiles resemble those of lead (Pb), an element which is known to be immobile in peat bogs. The correlation between these two metals suggests that the predominant anthropogenic source of Hg (and Pb) was coal burning. While Hg accumulation rates have gone into strong decline since the late 1950`s, Hg deposition rates today still exceed the average natural background values by 7 to 13 times in southern Ontario. The increase in atmospheric mercury rates since the pre-industrial times in all these records is larger than the predicted by current global mercury cycling models.

- Introduction -

This doctoral dissertation consists of an Introduction and five chapters. The first four chapters are in the form of manuscripts which have either been published, accepted for publication, in review, or in preparation; the fifth chapter is an unpublished field report.

1. Introduction and background

Mercury (Hg) is primarily of interest as a long-range, persistent and toxic pollutant because of its ability to bioaccumulate in the food chain in the form of methylmercury (Morel *et al.*, 1998). Due to its high volatility, low chemical reactivity and low solubility in water, elemental mercury (Hg°) makes up approximately 98% of total atmospheric mercury and has a residence time in the atmosphere up to 2 years. This means that mercury vapour can be transported far beyond the regions in which it is emitted (Schroeder *et al.*, 1998). Environmental mercury levels have increased considerably since the on-set of the industrial age in the mid 1800's due to the increase in fossil fuel burning. Coal burning releases large amount of heavy metals such as lead and mercury into the atmosphere. Also, industrial emissions to the atmosphere such as mercury emission from chlor-alkaly factories and waste incineration increase the heavy metal burden of the atmosphere and the rates of atmospheric deposition to terrestrial and aquatic surfaces. Mercury is now present in a various environmental media and food all over the globe at levels that adversely affect humans and wildlife. Even regions with no significant mercury releases such as the Arctic, are adversely affected, due to transcontinental and global atmospheric transport of mercury.

1.1. Mercury contamination of the Arctic environment

Exposures are thought to be increasing, especially among indigenous Arctic populations who consume fish and piscivorus species contaminated by methylmercury (Wheatley *et al.*, 2000). Environmental mercury levels are thought to be elevated in Arctic, to generally increase with latitude, and to have increased over time (AMAP, 2002).

Several hypotheses have been addressed in a recent past to explain the contamination of the Arctic environment. For instance, it has been suggested that, as originally conceived for some volatile organic compounds (Wania *et al.*, 1993), there may be a latitudinal fractionation of mercury (Mackay *et al.*, 1995) which contributes to the continued mobilization of these compounds from warmer to colder climates (i.e. cold condensation), resulting in a natural geographical gradients in the atmospheric deposition rates. Mercury may condense over the Polar Regions due to the cold climate suggesting a natural high deposition rate in Polar Regions where it is ultimately deposited and stored. Moreover, record of atmospheric mercury deposited in a peat core from NW Spain extending back 4,000 years (Martínez Cortizas *et al.*, 1999) provided evidence of a causal relationship between net Hg accumulation and Holocene climate change, with cold climate phases appearing to promote the accumulation of atmospheric Hg in peat. Given this findings, it is reasonable to expect that cold climate in the Arctic region may promote the natural accumulation of atmospheric mercury, not only from recent anthropogenic sources, but also in pre-anthropogenic times.

More recent discoveries suggest that the Arctic experiences enhanced deposition of Hg as part of related mercury depletion events (MDEs) observed to occur each spring (Schroeder *et al.*, 1998). Gaseous elemental mercury (Hg°) in the Arctic atmosphere undergoes photochemically driven oxidation during polar sunrise, probably by reactive halogens, which converts elemental Hg to reactive gaseous mercury (RGM) which subsequently deposits rapidly on snow as follows:

$$Br + O_3 \rightarrow BrO + O_2 \text{ (i)}$$
$$BrO + Hg^{\circ} \rightarrow Hg^{2+} + Br \text{ (?) (ii)}$$

Some of the mercury deposited on the snow is released to the environment at snowmelt, becoming available just as the Arctic ecosystem becomes biologically active in springtime. Evidence suggests that this is a recent phenomenon that may occur throughout the Polar Regions. This enhanced deposition may mean that the Arctic plays a previously unrecognized role as an important sink in the global Hg cycle (Lindberg *et al.*, 2002).

The impact of climate change on Hg dynamics is the third emerging issue. Changes in physical climate in the past decades might actually have a greater impact on the Arctic Hg cycle than changes in global emissions: decreasing trend in multi-year ice coverage, related increases in annual ice coverage, later timing of snowfall and earlier timing of snowmelt, increasing ocean temperatures, and increasing atmospheric circulation and temperatures. Several data sets suggest that there has been a recent increase in Hg levels in Arctic biota despite a 20 year decrease in global atmospheric Hg emissions of 30% (Pacyna *et al.*, 2002). Environmental changes may have made Hg pathways more efficient in recent years by increasing transport of photooxidants and production of reactive halogens in the Arctic. Although poorly understood, these processes may be the chief mechanism for transferring atmospheric Hg to the Arctic food chain.

Environmental archives such as snow and ice, lake sediments and peat bogs provide a record from which we can reconstruct the natural contribution of heavy metals, determine rates of pollutant deposition and assess the rates of change that have occurred with increasing industrialization.

1.2. Archives of atmospheric metal deposition in the Arctic

Snow and ice

Quantitative measurements of trace metals in snow and ice from Greenland have been used to reconstruct historical records of atmospheric metal deposition (Boutron *et al.*, 1994; Boutron *et al.*, 1995). In contrast to the lead record which is now well documented for Greenland (Boutron *et al.*, 1998), much less is known about the historical records of atmospheric Hg deposition. To date, there is only one study for North America reporting Hg accumulation rates from a glacial ice core (Schuster *et al.*, 2002). The background metal concentrations in these ice cores may be so low (sub-pg/g), however, that the studies are severely challenged by generally inadequate analytical sensitivity and a variety of contamination problems; sample decontamination becomes an integral part of this work (Candelone *et al.*, 1994). Only those few laboratories with extreme ultraclean conditions can even be considered for use in these kinds of investigation. In addition, the geographic distribution of permanently frozen "snow and ice archives" is limited to high elevations and latitudes, thereby restricting such studies to these areas.

Lake sediments

Lake sediments have also been used as archives of metal pollution (e.g. Dillons and Evans, 1982; Evans and Dillon, 1982), and thee is a growing number of studies of Hg in lake sediments from Arctic and Subarctic regions (Lockhart *et al.*, 1995; Lucotte *et al.*, 1995; Hermanson, 1998; Lockhart *et al.*, 1998; Bindler *et al.*, 2001). However, lake sediments are influenced by both atmospheric and non-atmospheric inputs (Norton *et al.*, 1986). Also, interpreting the lake sediment record may be complicated by such processes as chemical diagenesis related to sulphate reduction at the sediment-water interface, bioturbation, resuspension and sediment focusing (Norton *et al.*, 1987; Norton *et al.*, 1990). Furthermore, decreased metal retention in the sediments due to recent acidification of lakes may further affect the historical trends (Dillon *et al.*, 1986).

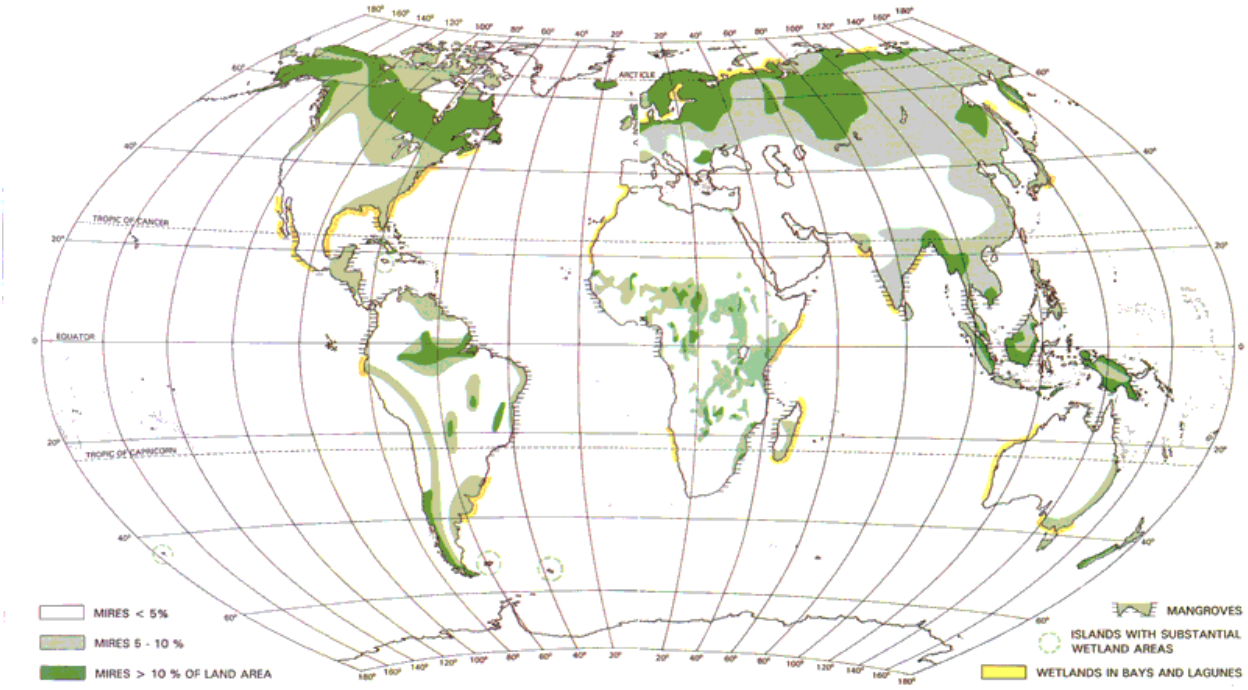


Fig. 1. Peatland distribution expressed as a proportion of the land surface for different parts of the world, based on Gore (1983) and Lappalainen (1996). This map provides a general idea of where peatlands are an important part of the landscape and is based on incomplete data. Redrawn from Lappalainen (1996) by permission of the International Peat Society in Charman (2002).

Peat bogs

Unlike glacial ice which is restricted to alpine and polar regions, peatlands are widely distributed across the globe (Fig 1), accounting perhaps 5% of the land area of the Earth (Kivinen *et al.*, 1981; Matthews *et al.*, 1987). The surface peat layers in ombrotrophic, raised bogs are hydrologically isolated from the influence of local groundwaters and surface waters, and are fed exclusively by atmospheric deposition (Damman, 1986). There have been numerous studies using peat bogs of the temperate zone (especially Europe and NE North America) as archives of atmospheric metal deposition (Glooschenko *et al.*, 1986; Jones *et al.*, 1993; Steward *et al.*, 1994; Shotyk, 1996; Shotyk *et al.*, 1997; Weiss *et al.*, 1999). To date, with the exception of superficial report by Headley (1996), and the brief report by Brown and colleagues (1994) which found most trace metal concentrations below the lower limit of detection, there is only one published study which use Arctic peat deposits from southern Greenland as archive of atmospheric metal deposition (Shotyk *et al.*, 2003).

2. Objectives

The ultimate objective of this research was to bridge the knowledge gap between the lack of temporal trends and deposition loads of mercury from long-range atmospheric transport in the Arctic of Canada and to try to understand the role which is played by the unique climate of Arctic on the geochemical cycle of mercury. To accomplish this, the main objective was to assess and quantify the changing rates of atmospheric mercury deposition on a millennial-scale period of time in the Arctic and to compare this with a record from the temperate zone in North America. This was accomplished using physical and chemical analysis of peat cores from hummocks peat on Bathurst Island (Chapter 2) and ombrotrophic *Sphagnum* peat bogs in southern Ontario (Chapter 1).

Specifically, we

1) quantified the changing rates of atmospheric mercury deposition in southern Ontario from the modern period through the pre-industrial period, into the pre-European times,
2) estimated the extent of anthropogenic contribution to the mercury deposition flux using the ratio of this element to selenium (Se) and bromine (Br) as reference elements for mercury,
3) identified the predominant sources of anthropogenic Hg contamination by comparison of the modern chronologies of lead and mercury,
4) quantified the rates of atmospheric mercury accumulation in the High Arctic of Canada, where such data was not available, focusing toward the rates of natural atmospheric mercury accumulation,
5) examined the potential for "cold condensation" effect for Hg.

A second objective of this research was to determine the anthropogenic contribution to the mercury deposition flux to the Faroe Islands and assess the importance of mercury from volcanism and mantle degassing as potential local or regional source of natural mercury to the environment. This was accomplished using physical, chemical and isotopic analysis of peat cores from ombrotrophic *Sphagnum* peat bogs on the Faroe Islands (Chapter 3).

Specifically, we

1) quantified the net rates of atmospheric mercury accumulation on the Faroe Islands using recent and pre-industrial peats,
2) separated the mercury inventory into its natural and anthropogenic component using bromine and selenium as reference elements to help to characterise pre-anthropogenic inputs
3) compared the chronologies of anthropogenic mercury accumulation with that of Pb,
4) identified the predominant anthropogenic sources of Hg and Pb to the Faroe Islands using Pb isotopes.

3. Results

These studies are based on the measurement of geochemical profiles in peat cores and on their interpretation as archives of past environmental change. Major and trace element concentrations in peat were analysed using x-ray fluorescence spectrometry (XRF). Mercury was measured in solid peat samples by atomic absorption spectroscopy (AAS) using an analytical protocol in-house developed (Appendix A). The relative degree of decomposition of the peat was determined by colorimetric measurement of alkaline peat extracts. Isotopic ratios of lead contained in peat were measured using inductively coupled plasma mass spectrometry. Dating of the peat was carried out using three different techniques: conventional ^{14}C atomic mass spectrometry dating, the bomb pulse curve of ^{14}C (AMS) and ^{210}Pb dating by gamma assay using the constant rate of supply model.

3.1. Hg deposition in North American peat cores

Southern Ontario

Peat cores from three ombrotrophic bogs in southern Ontario provide a complete, quantitative record of net rates of atmospheric Hg accumulation since pre-Industrial times: Sifton bog in the city of London, Luther bog which is a rural location, and Spruce bog which is comparatively remote, in Algonquin Park. For comparison with these modern values, a peat core from Luther bog extending back 8,000 years was used to quantify the natural variations in Hg fluxes for this region, and their dependence on climatic change and land use history.

The average background mercury accumulation rate during the pre-anthropogenic period (from 5,700 years B.C. to 1470 AD) was 1.4 ± 1.0 μg m^{-2} per year. The beginning of Hg contamination from anthropogenic sources dates from AD 1475 at



Fig. 2. Location map of sites discussed in the text: Bathurst Island (1), the Faroe Island (2), Iceland (3), southern Greenland (4) and northern Quebec (5).

the Luther Bog, corresponding to biomass burning for agricultural activities by Native North Americans. During the late 17th and 18th centuries, deposition of anthropogenic Hg was at least equal to that of Hg from natural sources. Anthropogenic inputs of Hg to the bogs have dominated continuously since the beginning of the 19th century. The maximum Hg accumulation rates decrease in the order Sifton Bog, in the City of London, Ontario (141 µg Hg m^{-2} per year), Luther Bog in an agricultural region (89 µg Hg m^{-2} per year), and Spruce Bog which is in a comparatively remote, forested region (54 µg Hg m^{-2} per year). Accurate age dating of recent peat samples using the bomb pulse curve of ^{14}C

shows that the maximum rate of atmospheric Hg accumulation occurred during 1956 and 1959 at all sites. At that time, anthropogenic mercury contributed at least to 85 % of the total Hg AR. Clearly, there is a gradient within southern Ontario of the intensity in anthropogenic Hg inputs, with Hg AR increasing in the order remote < rural < urban site. Assuming that inputs to the relatively remote Spruce Bog are more indicative of global changes in the atmospheric Hg cycle, the much greater Hg AR recorded by the Sifton bog in London, Ontario reflects the importance of regional and local sources.
In these (modern) samples, the Hg concentration profiles resemble those of Pb, an element which is known to be immobile in peat bogs. The association of these two metals, together with sulphur, suggests that the predominant anthropogenic source of Hg (and Pb) was coal burning. Support for this hypothesis is provided by the sulphur concentration profiles which show that the maximum S concentrations in all three peat cores coincide with the peaks in Hg and Pb; coal is enriched in all three of these elements.

Bathurst Island

Two sites were sampled in Polar Bear Pass National Wildlife Area on Bathurst Island (Fig. 2): Bracebridge Inlet (BI) and Museum Station (MS). Available evidence suggests that the Hg concentration measured in peat cores were supplied by the atmosphere, that there is no significant diagenetic remobilisation of Hg and that the selected section of the deposits from Bathurst Island have faithfully preserved a record of atmospheric mercury accumulation. Thus, mercury concentrations measurements and age dating of minerotrophic peat profiles from Bathurst Island provide the first millennial-scale record of the changing rates of atmospheric mercury deposition for this region of High Arctic. Given the ages calculated using the age-depth relationships, we estimate that the natural background atmospheric mercury deposition rates on Bathurst Island were rather constant, approximately 1 μg m^{-2} per year (range 0.5 - 1.5 μg m^{-2} per year) from 4000 cal. years BC to AD 1200.

The natural background Hg accumulation rates in the High Arctic of Canada and the temperate locations of southern Ontario and Maine (Appendix B) are similar: ca. 1 μg m^{-2} per year. Assuming that the re-emission of Hg from the bog is negligible (Lodenius, 1983), these rates reflect the natural range of atmospheric Hg fluxes.

Comparison of High Arctic and temperate atmospheric Hg fluxes

Pre-anthropogenic atmospheric mercury fluxes in the Arctic were approximately 1 μg m^{-2} per year, and this is not significantly different from atmospheric Hg fluxes in the temperate zone (Roos-Barraclough *et al.*, 2002; Givelet *et al.*, 2003; Shotyk *et al.*, 2003). Thus, there is no evidence supporting the hypothesis that the Arctic was an important natural sink in the global cycle of mercury during pre-industrial times (Lindberg *et al.*, 2002). Arctic climate, therefore may not favour atmospheric mercury deposition compared to warmer climates. Even though this region of the Arctic experienced significant climatic change throughout the last 6000 years, there is no evidence that these changes affected the rates of atmospheric deposition. If there is a link between Holocene climate change and rates of atmospheric mercury accumulation, as suggested by Martinez-Cortizas and colleagues (1999), the poor temporal resolution provided by the Bathurst Island cores prevent this link from being discerned. Recently, it has become apparent that processes other than cold condensation have to be invoked as the chief mechanism for transferring atmospheric Hg to the Arctic environment. Several processes may have been made more efficient in recent years by environmental changes such as global warming and these may have important consequences for mercury cycling in the Arctic food chain.

3.2. Hg deposition in North European peat cores

A 1-meter peat monolith collected from a blanket bog at Myrarnar, Faroe Islands (Fig. 2) provide a 6,000-year record of mercury supplied exclusively by atmospheric inputs (Chapter 3). The average rate of atmospheric mercury accumulation from 1520 BC to AD 1385 was 1.4 ± 1.0 μg m^{-2} per year. These natural fluxes are similar to the pre-anthropogenic rates obtained using peat cores from Switzerland, southern Greenland, southern Ontario, and NE USA. In contrast, the maximum rate of total mercury accumulation, dated AD 1951, was 35 μg m^{-2} per year of which 76 to 90% was estimated to anthropogenic. The age date of the maximum of deposition flux of Hg in the Faroe Island is consistent with peat cores from southern Greenland and Denmark which showed maximum Hg accumulation rates in AD 1953. Similarity between modern trends of Hg and Pb accumulation, combined with the isotopic composition of Pb, suggest that coal burning was the dominant source of both elements at that time. The peat core at Myrarnar confirms that Hg emissions from coal burning have been quantitatively more important than volcanic emissions, but also that they have gone into decline since the mid-1950`s.

4. Conclusion and perspectives

The results presented here and other recent studies using peat bogs archives dated using the bomb pulse curve of ^{14}C have shown that undisturbed peat bogs are excellent paleoenvironmental archives. These bogs certainly do record in a faithful way the changing chronologies of atmospheric mercury deposition. In fact, the historical records of net atmospheric mercury deposition appear to be so well preserved in the peat profiles that our ability to read and interpret these records is much less dependent upon physical and chemical processes taking place within the bog, and more on peat core sampling, handling, sectioning, sub-sampling, preparation and age dating. For detail reconstructions of atmospheric mercury and other metals deposition, therefore, a comprehensive protocol for working with peat cores is warranted (chapter 4).

There is a lot of evidence (AMAP, 2002), mainly from lake sediments, showing that mercury levels appears to be increasing over time in the Arctic. Increases in the accumulation rates of Hg have been observed in the uppermost, modern layers of lake sediments in Subarctic and Arctic (Hermanson, 1998; Lockhart *et al.*, 1998; Bindler *et al.*, 2001) and they have been attributed to recent increases in atmospheric emission and deposition of Hg from human sources. There are a number of geochemical reasons to seriously question those interpretations, specifically for lake sediments as some processes which may explain these trends have been largely ignored in the interpretation of the results. Increases in Hg concentration of the upper layers of lake sediments may be related to several processes, such as post depositional redistribution by diagenesis, physical mixing, or erosion. Changes in the watershed, or of the biogenic productivity may control the variation of mercury concentration throughout the sediment column. For instance, evidence from an Arctic lake deposit has shown that higher rates of phytoplankton productivity, possibly related to global warming in the 20th century, lead to an increase of Hg scavenging from the water column to the sediment and results in an increase profile of Hg concentration to the top of the core (Outridge *et al.*, 2003). Thus, limnological processes rather than atmospheric deposition may account for most of the Hg increase over the past 100 years in the lake sediments. In other words, lake sediment records of Hg accumulation have to be interpreted with great care.

Therefore it remains very unclear whether deposition of anthropogenic atmospheric mercury may account for the mercury contamination of the Arctic environment and how atmospheric mercury deposition rates have evolved in the Arctic during the past 150 years. It seems unlikely that the Arctic was an important natural sink in the global cycle of

Hg during pre-industrial times as net accumulation rates of atmospheric mercury in peat deposits from the High Arctic of Canada have been found to be very similar to accumulations rates measured from peat and lakes sediments archives at temperate location (Givelet *et al.*, Chapter 2) during the same time period. This suggests that the cold Arctic climate may not significantly favour a final deposition compared to warmer climate regions. However, no effort has been made to investigate the effect of recent global warming on the pathways of Hg in the Arctic today. There is an urgent need to assess modern (past 150 years) rates of atmospheric mercury deposition in the Arctic and the problem may be summarized as follows:

- **The evolution of atmospheric mercury deposition in Arctic during the past 150 years is poorly understood**

- The role which is played by the unique climate of the Arctic on the geochemical cycle of mercury is incompletely understood, especially **the effect of the recent global warming on the deposition of atmospheric Hg.**

Those issues are critical to understanding the effects of human activities on Hg cycling in the Arctic, and their implications for ecosystem health.

The ultimate objective is to bridge the knowledge gap between the lack of comprehensive temporal trends and deposition loads of mercury from long-range atmospheric transport in Arctic and to assess the effect of recent global warming on deposition of atmospheric Hg in the Arctic environment.

To accomplish this, the next main objective will be to assess and quantify the changing rates of atmospheric Hg deposition from the modern period (past 150 years) to the pre-industrial period in Arctic, and to reconstruct a detail paleoclimatic record for the same period of time. This will be accomplished using physical, chemical, and isotopic analyses of peat cores from a minerotrophic peat bog in Northern Quebec (Fig. 2) and an ombrotrophic *Sphagnum* peat bog in eastern Ontario (Chapter 5). This project will be the central focus of my postdoctoral project at the Institute of Environmental Geochemistry of the University of Heidelberg in Germany.

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The final thought is for **my family**, with a special mention to my mum and dad who have always believed in me and supported me in many ways and to **Marion**.

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Chapter 1

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 8,000 years)

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Abstract

Peat cores from three bogs in southern Ontario provide a complete, quantitative record of net rates of atmospheric Hg accumulation since pre-Industrial times. For comparison with modern values, a peat core extending back 8,000 years was used to quantify the natural variations in Hg fluxes for this region, and their dependence on climatic change and land use history. The net mercury accumulation rates were separated into "natural" and "excess" components by comparing the Hg/Br ratios of modern samples with the long-term, pre-anthropogenic average Hg/Br. The average background mercury accumulation rate during the pre-anthropogenic period (from 5,700 years B.C. to 1470 AD) was 1.4 ± 1.0 μg m^{-2} yr^{-1} (n=197). The beginning of Hg contamination from anthropogenic sources dates from AD 1475 at the Luther Bog, corresponding to biomass burning for agricultural activities by Native North Americans. During the late 17^{th} and 18^{th} centuries, deposition of anthropogenic Hg was at least equal to that of Hg from natural sources. Anthropogenic inputs of Hg to the bogs have dominated continuously since the beginning of the 19^{th} century. The maximum Hg accumulation rates decrease in the order Sifton Bog, in the City of London, Ontario (141 μg Hg m^{-2} yr^{-1}), Luther Bog in an agricultural region (89 μg Hg m^{-2} yr^{-1}), and Spruce Bog which is in a comparatively remote, forested region (54 μg Hg m^{-2} yr^{-1}). Accurate age dating of recent peat samples using the bomb pulse curve of ^{14}C shows that the maximum rate of atmospheric Hg accumulation occurred during AD 1956 and 1959 at all sites. In these (modern) samples, the Hg concentration profiles resemble those of Pb, an element which is known to be immobile in peat bogs. The correlation between these two metals, together with sulphur, suggests that the predominant anthropogenic source of Hg (and Pb) was coal burning. While Hg accumulation rates have gone into strong decline since the late 1950`s, Hg deposition rates today still exceed the average natural background values by 7 to 13 times.

1. Introduction

Mercury is a potentially toxic trace metal which is released from the Earth to the atmosphere, biosphere, and hydrosphere from a variety of natural processes. Degassing from hydrothermal systems, volcanism, soil erosion, biomass burning, and marine emissions are believed to dominate natural sources of Hg to the air (Schroeder *et al.*, 1998). By far the majority of Hg emitted from these natural sources is gaseous, elemental mercury (Hg^0). Because Hg is used in many industrial applications and also present in coal, natural gas and industrial and domestic waste, it is also emitted to the atmosphere during combustion for energy production or waste incineration. In contrast to the natural sources, at least one-half of anthropogenic Hg is emitted in various particulate forms (Mason *et al.*, 1994). Most of the mercury deposited from the atmosphere is either Hg^{II} or particulate mercury. Whereas particulate Hg is mainly deposited in the vicinity of its sources, Hg^0 is added to the global pool of atmospheric Hg: the volatility and low solubility of Hg^0, combined with its comparative stability in the atmosphere, are factors which contribute to the long atmospheric residence time (~1-2 years) of gaseous elemental Hg (Slemr *et al.*, 1992). Eventually, this species also will be deposited, but only after oxidation and washout, including non-industrial regions far from the original source. Because of the relatively rapid atmospheric scavenging and deposition of particulate mercury, Hg^0 is preferentially enriched in the air and, on average, accounts for 98 % of atmospheric mercury (Lamborg *et al.*, 2002). These facts, combined with the potential of methylated forms of Hg to bioaccumulate in aquatic ecosystems, renders Hg a trace metal of global environmental concern (Schroeder, 1994).

Increases in the accumulation rates of Hg have been observed in the uppermost, modern layers of lake sediment cores (Pirrone *et al.*, 1998; Swain *et al.*, 1992) and ombrotrophic bogs (Benoit *et al.*, 1994) in northeastern North America, and these have been attributed to recent increases in atmospheric Hg emissions (and deposition) related to human activities. In these studies, estimates of the "natural background" atmospheric deposition rates of Hg are poorly constrained, as they are derived from relatively short cores (less than one meter), which typically span only the last few hundred years of accumulation. These natural background accumulation rates of Hg are then assumed to represent the "pre-industrial" accumulation rates. However, age dating these materials is difficult, as the peats/sediments are usually too old to be age dated reliably using ^{210}Pb, and too young to be dated using ^{14}C. Not only are the natural background Hg accumulation rates inadequately quantified using this approach, but the extent to which these natural background accumulation rates have varied with time, and the natural processes which control this variation, often are not adequatly considered. To quantify the effects of human activities on atmospheric Hg deposition in southeastern Canada, an improved understanding is needed of the long-term, natural variations in the concentrations, fluxes and sources of Hg for this industrial region.

Ombrotrophic (Shotyk *et al.*, 1994) peat bogs receive metals only from the atmosphere. Because Hg supplied to peat bogs from the air is very well preserved in the peat column (Benoit *et al.*, 1998; Pheiffer-Madsen, 1981) peat cores from bogs can be used as long-term archives of atmospheric Hg deposition (Benoit *et al.*, 1994; Bindler, 2003; Martínez Cortizas *et al.*, 1999; Norton *et al.*, 1997; Roos-Barraclough *et al.*, 2003; Shotyk *et al.*, In press). Peat cores were collected from three ombrotrophic peat deposits in Southern Ontario (Fig. 1): Sifton Bog in the City of London, Ontario, Luther Bog which is in a rural location, and Spruce Bog which is comparatively remote, in Algonquin Provincial Park. The main goal of this study was to quantify the changing rates of atmospheric Hg accumulation from the modern period through the pre-industrial period, into pre-European times. To help put these results into perspective, the entire peat profile from Luther Bog (representing ca. 8,000 years of peat accumulation) has been studied in detail, to quantify the long-term, natural variation in atmospheric Hg

accumulation rates. Radiocarbon dating methods (the atmospheric bomb pulse of ^{14}C and conventional ^{14}C age dating) have been combined with ^{210}Pb to allow reliable age-depth models to be constructed for each of the peat profiles. To bridge the gap between ^{210}Pb and ^{14}C age dating, the probability distribution of ^{14}C age dates was used to model the age-depth relationship. In an effort to distinguish between natural and anthropogenic sources of Hg, the natural variation in Hg to bromine (Br) in ancient samples is used to calculate the amount of "excess" mercury in modern samples. Taken together, this is the first comprehensive, long-term study of changes in atmospheric Hg accumulation rates for this part of northeastern North America.

To compare with mercury in the three peat profiles, we have measured lead (Pb) which is transported primarily in the fine aerosol fraction (Puxbaum, 1991). Lead is known to be well preserved in ombrotrophic bogs (Shotyk *et al.*, 1998; Vile *et al.*, 1999; Weiss *et al.*, 1999), with bogs recording Pb chronologies which are comparable to lake sediment archives (Brännvall *et al.*, 1997; Norton *et al.*, 1997) and historical records of ancient Pb mining (Kempter *et al.*, 2000). Here, Pb is used to help identify the predominant source of anthropogenic Hg contamination.

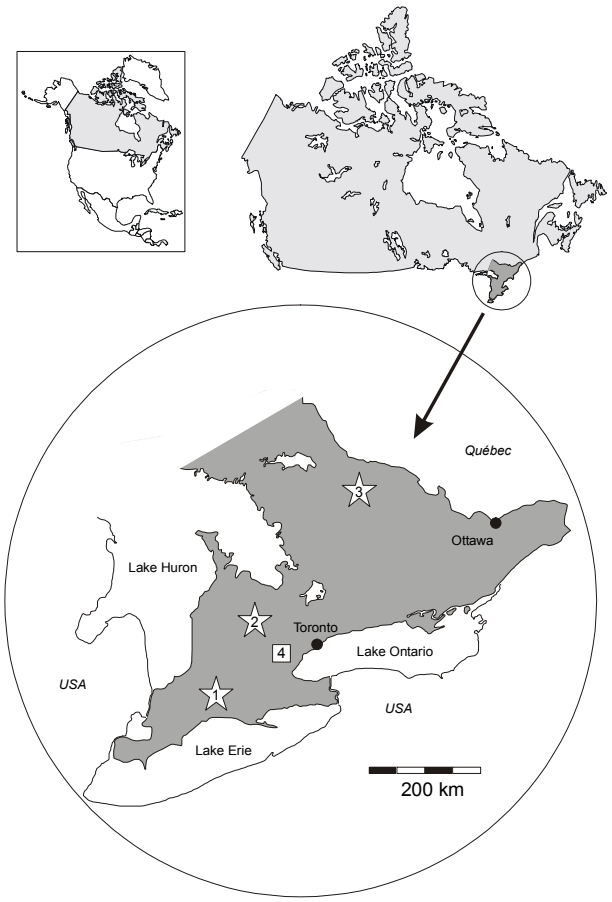


Fig. 1. Location map of peat cores collected in southern Ontario: Sifton Bog (1), Luther Bog (2) and Spruce Bog (3). The location of Crawford Lake is reported as (4).

2. Material

2.1. Luther Bog

Situated along a headwater tributary of the Grand River, Luther Marsh Provincial Wildlife Area lies near the southern fringe of the Dundalk Plateau, about 25 kilometres west the town of Orangeville, in a predominately agricultural region of southern Ontario (Fig. 1). The Dundalk plateau, with an elevation of approximately 480 meters above sea level, is the coldest off-shield region of southern Ontario, with temperatures and precipitation similar to those of Algonquin Park, 300 kilometres to the northeast (Sandilands, 1984).

Historically, Luther Marsh was a large peatland complex surrounding two small lakes and containing several streams. In 1954 the Grand River Conservation Commission constructed a dam across Black Creek, a headwater tributary of the Grand River, which created Luther Lake. Peat cores were collected on July 26, 2000 at a site (43 54.30N, 80 24.36W) which is characterised by vegetation typical of continental, ombrotrophic *Sphagnum* bogs. Visual inspection of the modern vegetation growing on the surface of the bog today, as well as the peat cores collected at this site, provided no botanical evidence that flooding had affecting the ombrotrophic zone of the bog in any way. A visit to the same site to collect peat cores in 1984 had drawn the same conclusion (W.S., personal observation). However, to overcome the uncertainty of possible impacts by past flooding at this site, peat cores were also collected at two other *Sphagnum* bogs in southern Ontario.

2.2. Spruce Bog Trail

Spruce Bog Trail is situated in Algonquin Park (Fig. 1), a 3000-km^2 nature preserve in predominately recreational region of rural southern Ontario, at an elevation of about 410 meters above sea level. Samples were collected on the northwest side, directly across from the boardwalk, on the far side of the peatland. The core was taken on July 10, 2000 in a very small (ca. 50 cm wide) *Sphagnum* lawn within a zone of dense growth of dwarf shrubs. This zone is between the floating mat and the forest, and the core was removed from the edge of the floating mat. This coring area (45 35.51N, 78 22.16W) was chosen because it is still open with respect to the surrounding forest and because it was firm and stable compared to the floating mat.

2.3. Sifton Bog

The Sifton Bog is an acidic *Sphagnum* peat bog located within the city of London, Ontario (Fig. 1) (population ca. 300,000). The bog covers an area of about 28 hectares and is formed in a large depression, left behind as a glacial block melted about 13,000 years ago. This bog rests on about 25 meters of glacial deposits of sands and gravels, which overlies Devonian limestones. The peatland today consists of a small pond surrounded by a floating mat of *Sphagnum* moss, flanked by a marginal hardwood swamp. Beyond the swamp are lowland and upland forest, respectively. The central portion of the bog contains as much as 10 meters of peat accumulation (Warner *et al.*, 1994). The sampling site (42 58.31N, 81 19.48W) was chosen in an area between the floating and the damp woods. The thickness of peat accumulation at the sampling site was about 6 meters at the time of collection (27 July, 2000).

3. Methods

3.1. Sample collection and preparation

The top most layers of peat were collected using a 1-meter titanium Wardenaar corer as a 15 x 15 cm monolith (Wardenaar, 1987). In addition to the short peat cores collected at all sites, a complete peat profile was taken at Luther Bog (ca. 600 cm) in 50 cm sections using a stainless steel Belarus corer (Belokopytov *et al.*, 1955). Unfortunately, a 50 cm section was lost during the coring session. Peat cores were removed from two holes, approximately 30 cm apart, in parallel overlapping fashion. The Luther Bog profile was reconstructed by correlating depth to depth using the bog surface as reference, assuming that samples from equal depths, but different hole, were the same distance from the bog surface. All samples were frozen at -18°C for storage and transport to Berne, Switzerland.

The Wardenaar and Belarus cores were cut in the laboratory (while frozen) into 1 cm and 2 cm slices respectively using a stainless steel band saw. The outside edges of each slice were cut away, dried overnight at 105°C in a drying oven and milled in a centrifugal mill with titanium sieve. The powdered samples (used for XRF and ^{14}C analyses) were manually homogenized and stored in airtight plastic beakers.

3.2. Analysis

One gram of dried, milled powder was analyzed for 22 selected major and trace elements, including lead, calcium (Ca), strontium (Sr), manganese (Mn), iron (Fe), bromine and selenium (Se), using the EMMA XRF spectrometer (Cheburkin *et al.*, 1996). Titanium (Ti) was measured using a new analytical spectrometer for Ti (NASTIA), which was described earlier (Shotyk *et al.*, 2002). The instrument were calibrated and checked for accuracy and precision as described elsewhere (Roos-Barraclough *et al.*, 2002). The XRF methods were validated using standard reference materials (Table 1). Calcium and Sr can be used to identify mineral weathering reactions in peat profiles, Mn and Fe redox processes, Br and Se atmospheric aerosols of marine origin, and Ti atmospheric aerosols of continental origin.

Four plugs were subsampled from the middle of each slice with a sharpened stainless

Table 1.
Summary of measurements of Hg, Br, Se and Ti in certified, Standard Reference Materials. Information values are indicated by *.

Element	Method	SRM	Measured value	Certified value
Hg	AAS	NIST 1515	31.8 ± 0.8 ng g^{-1}, n=27	31 ± 7 ng g^{-1}
Hg	AAS	NIST 1547	43.0 ± 0.7 ng g^{-1}, n=45	44 ± 4 ng g^{-1}
Br	Emma XRF	NIST 1515	2.02 ± 0.20 µg g^{-1}, n=3	1.8* µg g^{-1}
Br	Emma XRF	NIST 1547	12.92 ± 0.18 µg g^{-1}, n=2	11* µg g^{-1}
Br	Emma XRF	NIST 1575	9.3 ± 1.1 µg g^{-1}, n=9	9*µg g^{-1}
Se	Emma XRF	NIST 1632b	1.29 ± 0.43 µg g^{-1}, n=3	1.29 ± 0.11 µg g^{-1}
Pb	Emma XRF	NIST 1575	12.0 ± 1.1 µg g^{-1}, n=3	10.8 ± 0.5 µg g^{-1}
Ti	Nastia XRF	NIST 1635	189 ± 14 µg g^{-1}, n=11	200*µg g^{-1}

steel tube (16 mm diameter). Three of them were used for Hg analyses. These were air-dried overnight at room temperature in a class 100 laminar flow clean air cabinet. Mercury concentrations were measured by atomic absorption spectrometry (AAS) in solid peat samples (Salvato *et al.*, 1996) using the LECO AMA 254 as described in detail elsewhere (Roos-Barraclough *et al.*, 2002). The instrument was calibrated using liquid standards prepared from a Merck 1000 mg/l Hg standard solution. Precision was determined by measuring replicates of international standard reference materials, either NIST 1515 (Apple Leaves) or NIST 1547 (Peach Leaves), after every 10^{th} sample (Table 1). The mean relative standard deviation of the determination of Hg within a peat slice was 11.7% (n=3) which is primarily a reflection of the heterogeneity of the slices. The fourth plug was use to determine the dry bulk density. The height of each plug was measured to an accuracy of 0.1 mm and the volume calculated. After recording wet weights, plugs were dried at 105°C overnight and the dry mass was weighed to 1 mg.

The degree of decomposition of the peat was measured by colorimetry on alkaline peat extracts at 550 nm using a Cary 50 UV-visible spectrophotometer. The powdered peat samples (0.02g) were placed in test tubes and 8 % NaOH soln. (10 ml) was added. The samples were shaken then heated 95 ± 5°C for 1 hour, then made up to 20 ml with deionised water, shaken and left to stand for 1 hour before being re-shaken and filtered through Whatman no. 1 filter papers. Samples were diluted with an equal quantity of deionised water directly before colorimetric measurement. The percentage of light absorption (% absorbance) in these extracts was used as a proxy of peat humification (Caseldine *et al.*, 2000).

3.3. Age dating

Macrofossils of *Sphagnum* moss were collected, cleaned, and submitted for ^{14}C age dating by Acceleration Mass Spectrometry (AMS) at Århus University, Denmark, and at the ETH Zurich, Switzerland. In cases when it was not possible to identify macrofossils, bulk peat samples were used. Samples dated using AMS were prepared using a standard procedure for plant material (washed, acid-base-acid treatment) which removes humic matter that could overestimate the ^{14}C ages (Shore *et al.*, 1995). Selected bulk peat samples were also age dated using decay counting at the Institute of Environmental Physics, University of Heidelberg, Germany.

Age dates of plant macrofossils younger than AD 1950 can be obtained using ^{14}C by directly comparing the absolute concentration of ^{14}C in the sample to the general-purpose curve derived from annually averaged atmospheric $^{14}CO_2$ values in the northernmost northern hemisphere: post-1950 ^{14}C concentrations in the atmosphere are elevated compared to natural levels due to atomic

weapons testing. This approach which effectively matches the ^{14}C concentrations (percent modern carbon, or PMC) in successive plant macrofossils to the increase (since AD 1950) and subsequent decrease (since AD 1963) in ^{14}C concentrations is the so called "bomb pulse curve of ^{14}C" and has been successfully used to date peat accumulation in Denmark and in southern Greenland (Goodsite *et al.*, 2001). This comparatively new dating method has been found to provide high-resolution age dates which are accurate to ± 2 years.

The other ^{14}C calibrated ages were calculated using the Seattle CALIB program (Stuiver *et al.*, 1993) version 4.0 (Århus University) and version 4.3 (University of Heidelberg), and the program calibETH (ETH Zurich). The calibration curves used for the calibration were taken from Stuiver *et al.* (1998) and Niklaus *et al.* (1992) respectively. Due to irregular multimodal shapes of probability distributions of the major part of these dates, it was decided to present the results in the form of 95 % confidence intervals (2σ-ranges) of the highest probability (narrowest 95 % confidence intervals). The results of calibration of individual dates are presented in Table 2, 3 and 4 (Supporting information).

In addition to the ^{14}C age dating using the bomb pulse curve, the uppermost layers of the Spruce bog core was also age dated down to 65 cm using ^{210}Pb (CRS) model (Appleby *et al.*, 1988).

4. Results

4.1. Peat chronologies

Absolute chronologies were reconstructed for each of the three peat profiles (Fig.2) using calibrated ^{14}C dates (Luther and Sifton bogs), and both calibrated ^{14}C and ^{210}Pb dates (Algonquin bog); in each case, it is assumed that peat accumulation was continuous. The points included in the age-depth models were specified by taking the average depth of the peat slice together with the mid-point of the calibrated age. A significant challenge in dating peat accumulation is the gap which exists between the oldest reliable ^{14}C bomb pulse date (late 1950s) or ^{210}Pb date (ca. mid 19th century) to the first reliable conventional ^{14}C date (ca. 17th century). To bridge these gaps, composite probability distributions were used: for a given sample, these provide an estimate of the probability of each ^{14}C age. Assuming that the overlying samples are younger than the deeper samples, a best fit can be made using polynomial regression, linking the uppermost ^{14}C ages (obtained using the bomb pulse curve) to the deeper, conventional ^{14}C ages. Calibrated age ranges were considered only in visually assessing the fit of the regression line through the data. Moreover, the age of the top sample (the date of core collection, AD 2000) was used as a fixed point with 100 % confidence interval. A series of regression models were used to fit the age-depth plots. The choice of the model finally selected was based on best fit (r^2 values) of available age dates, and a consideration of the published range of peat accumulation rates.

For the Luther Bog profile (Fig. 2a), the age-depth relationship was constructed from the dated points using a third-degree polynomial regression from 0 to 45 cm and a sixth-degree polynomial regression from 45 cm to ~535 cm. The gap from the beginning of the oldest reliable ^{14}C bomb pulse date (AD 1956 at 20.0 cm) to the first reliable conventional radiocarbon date (AD 1631 to 1822; average age AD 1727 at 44.3 cm) was bridged by using the probability distribution for the sample from 24.9 cm. Specifically, the probability distribution of this sample shows that four age dates are possible (Fig. 2a). Of these four age dates, the three oldest ones do not lie on the age-depth trend. Therefore, the youngest age (AD 1935) was selected as being the most reasonable of the four, and this age was used to construct the age-depth relationship.

The age-depth relationship for Sifton Bog (Fig. 2b) was reconstructed using a second-degree polynomial regression from nine reliable points. Between 15.4 to 66.4 cm depths, the probability distribution profiles of three conventional radiocarbon dates were used. For Spruce Bog (Fig. 2c), the age-depth relationship was reconstructed using a third-

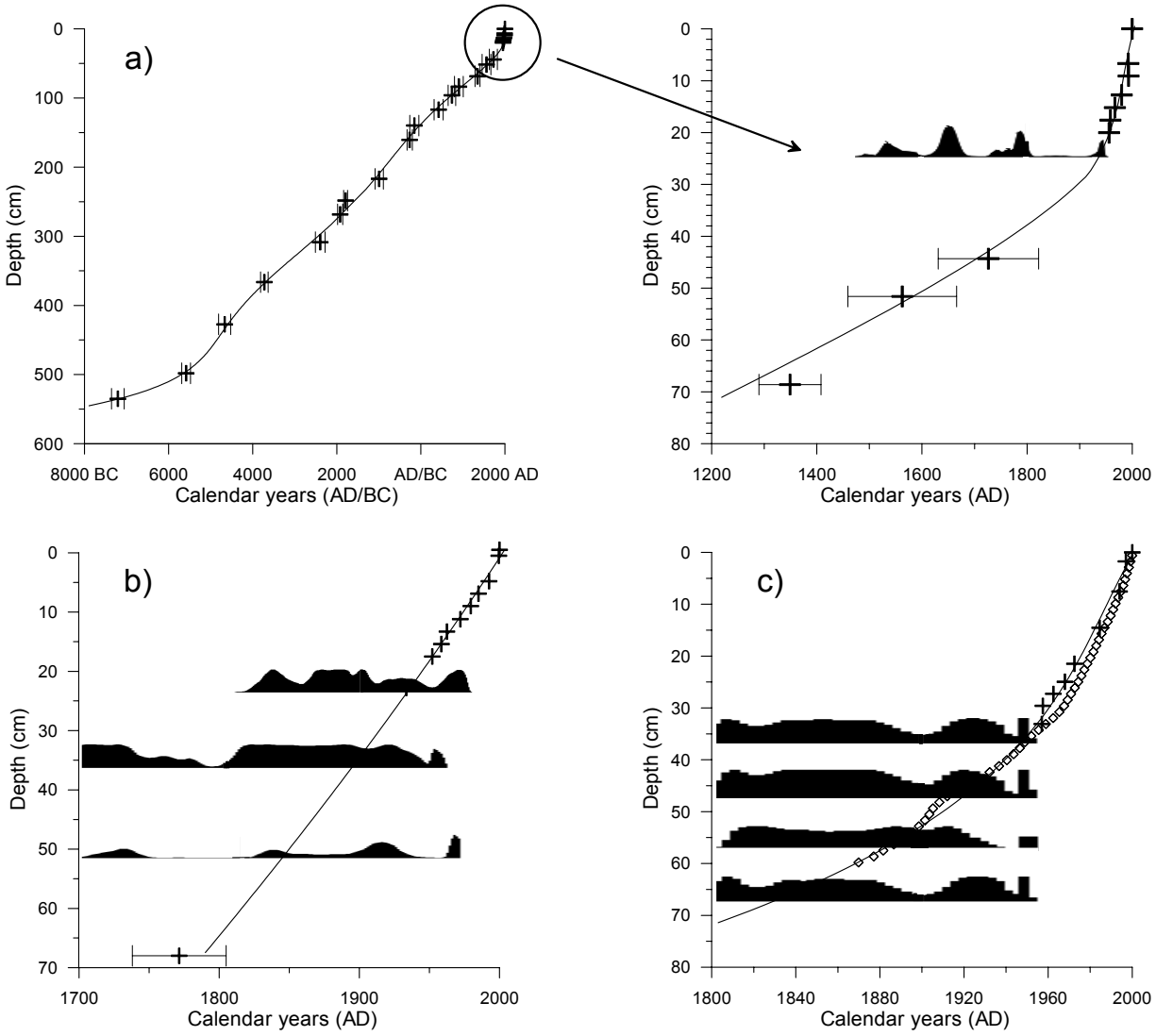


Fig. 2. Age-depth relationship for Luther Bog (a), Sifton Bog (b) and Spruce Bog (c). Calibrated age dates (obtained using ^{14}C) and their errors are reported as crosses (+), or as a composite of the probability distribution. Radiometric age dates obtained using ^{210}Pb (CRS model) are indicated by the diamonds (◇).

degree polynomial regression from the reliable age dated points from the surface to 33.1 cm depth. Below, the probability distributions of four conventional radiocarbon dates were used. Using this approach, sample depths for each peat profile were converted into calendar dates using the age-depth relationships.

4.2. Trophic status of the profiles

Visual inspection of the Luther bog core indicates that the profile consist of clay-rich sediments up to 560 cm; gyttja (a lacustrine organic-rich sediment), from 560 to 490 cm; and peat above 490 cm (Fig. 3). The concentrations of Ti and ash provide an index of the amount of mineral matter in the peat (Shotyk *et al.*, In press) which can be used to help distinguish between ombrotrophic peat (mineral matter supplied exclusively from the air) from minerotrophic peat (mineral matter from the air, as well as terrestrial and aquatic inputs). Calcium and Sr may be used to describe the trophic status of the peat profile (Steinmann *et al.*, 1996), and are also sensitive indicators of inputs to the peat profile from mineral-fluid interactions subsequent to peat formation. The concentrations of these parameters allow the following zones to be distinguished within the peat column, in

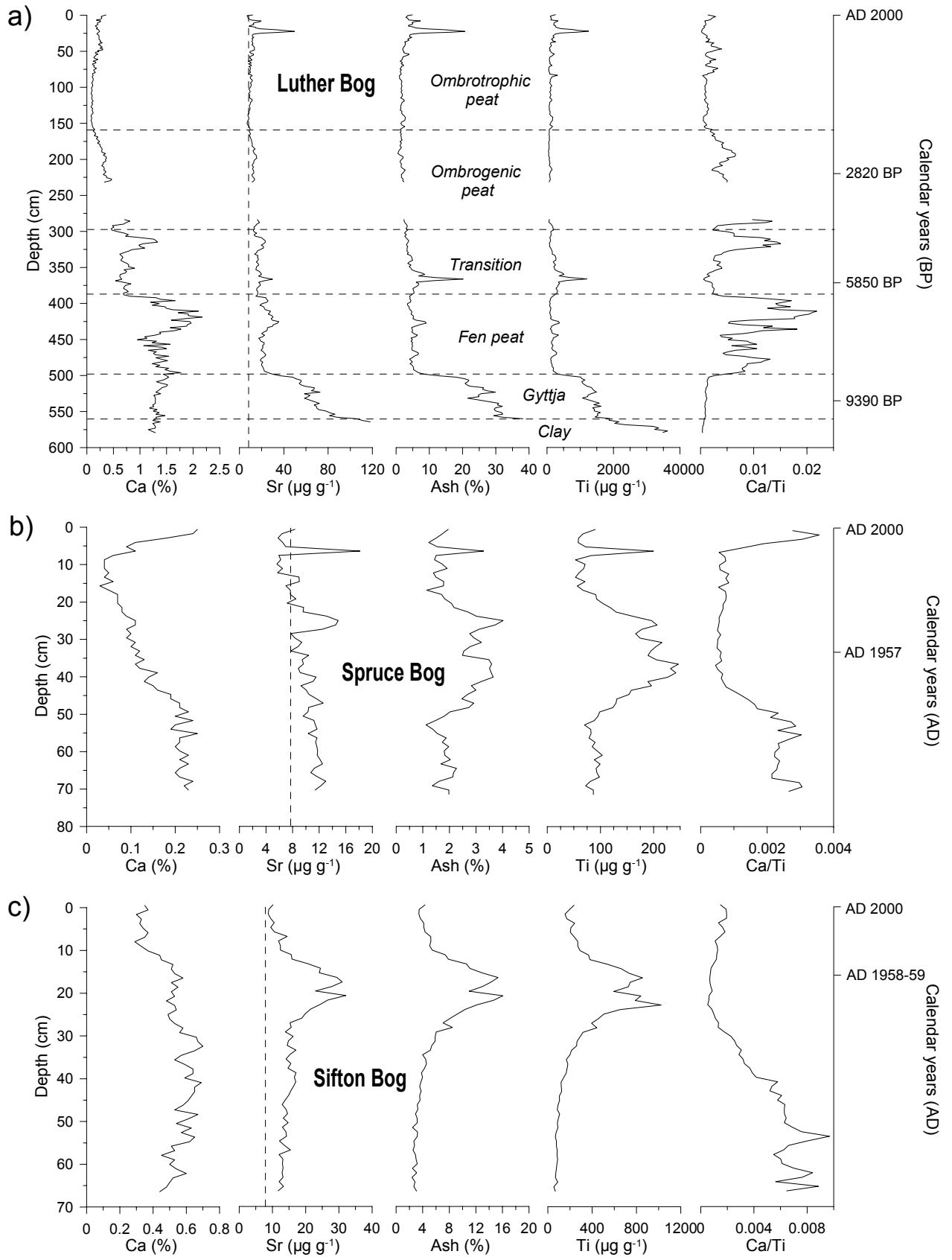


Fig. 3. Concentration profiles of elements discussed in the text and ash content in the Luther Bog (a), Spruce Bog (b) and Sifton Bog (c) and assigned peat/sediment type. The year of collection and selected calibrated age dates obtained by ^{14}C are shown for convinience. The vertical dashed line indicates the average Sr concentration in the ombrotrophic zone of Etang de la Gruère, a continental bog in the Jura Mountains of Switzerland.

ascending order (Fig. 3): clay, gyttja, minerotrophic fen peat, transitional peat, ombrogenic peat, and ombrotrophic peat. "Ombrogenic" peat consists of organic matter derived from ombrotrophic bog plants, but has since been overprinted with a minerotrophic signature because of the upward diffusion of Ca and Sr derived from chemical weathering of the underlying sediments. Taken together, the geochemical data, briefly summarised here, show that the uppermost 165 cm of the Luther profile are ombrotrophic and therefore that all elements were supplied to the peat in this section of the bog exclusively via the atmosphere.

The abundance and distribution of Ca, Sr, Ti and ash in the Spruce bog and Sifton peat cores are comparable to those in the ombrotrophic section of the Luther bog profile. In the peat cores from Spruce and Sifton bogs, therefore, these cores also have received their inputs from the atmosphere. As observed in the ombrotrophic section of the Luther bog profile, there is an exceptional zone of elevated ash content and lithogenic elements concentration in the uppermost layer of Spruce bog and Sifton bog at 35 and 20 cm respectively.

4.3. Mercury and lead concentration profiles in the three Wardenaar peat cores

Mercury concentrations are lowest in the top and bottom layers of the Wardenaar cores, with the maximum concentrations (189, 251 and 333 ng g^{-1} in Spruce Bog, Luther Bog and Sifton Bog respectively) at intermediate depths. Each peat core shows a unique variation in Hg concentrations with respect to depth (Fig. 4), with peaks in Hg concentration found at depths varying between 15 and 35 cm. Despite this, the chronologies of the changing Hg concentrations are remarkably similar, with maximum Hg concentrations dating from the late 1950`s in each core (Fig. 4). The Pb concentrations profiles resemble the Hg concentration profiles (r^2 = 0.72, 0.77 and 0.82 in the Luther bog, Spruce bog and Sifton bog profiles respectively) in the sense that the zones which contain elevated Hg concentrations, also are elevated with respect to Pb. As is true of Hg, therefore, Pb displays a similar chronology in each of the cores, with the maximum Pb concentration dating from the late 1950`s in each case. The coincidence of the Hg and Pb concentrations in the modern peat samples from the surface layers of all three bogs suggests that either these elements have a predominant source in common, that they behave similarly in peat bogs, or both.

4.4. "Background" Hg concentrations in the Luther Bog profile

For comparison with the Hg concentrations in modern peat samples from the surface layers of each of the bogs, it is important to establish the "natural background" Hg concentration for peat in this region. Analysis of the peat core from Luther Bog shows low and quite stable Hg concentrations below 150 cm, even in the transitional and minerotrophic peat sections, with values in the range of 13 to 35 ng g^{-1} from 150 to 495 cm (Fig. 5). Again, the peat samples from the fen, transitional, and ombrogenic zones are riched in Ca, out of proportion with Ti (Fig. 3); these peats, therefore, have been overprinted with chemical signatures indicating pronounced mineral-water interactions (Fig. 3). However, these reactions and processes have not measurably contributed Hg to the profile, and Hg concentrations are effectively constant (22.3 ± 4.0 ng g^{-1}) from 300 to 500 cm (Fig. 5). Because the concentrations of Hg in the transitional and minerotrophic peats are not significantly different from the ombrotrophic peat (which has received Hg only from the atmosphere), even in the transitional and minerotrophic, Hg was supplied exclusively by the atmosphere. Assuming that the Hg concentrations between 150 and 495 cm at Luther (13 to 35 ng g^{-1}) reflect the range in natural concentrations of Hg in ombrotrophic peat, the maximum Hg concentrations at Spruce Bog, Luther Bog and Sifton Bog exceed this range by factors of 6-13, 8-18, and 10-23 respectively.

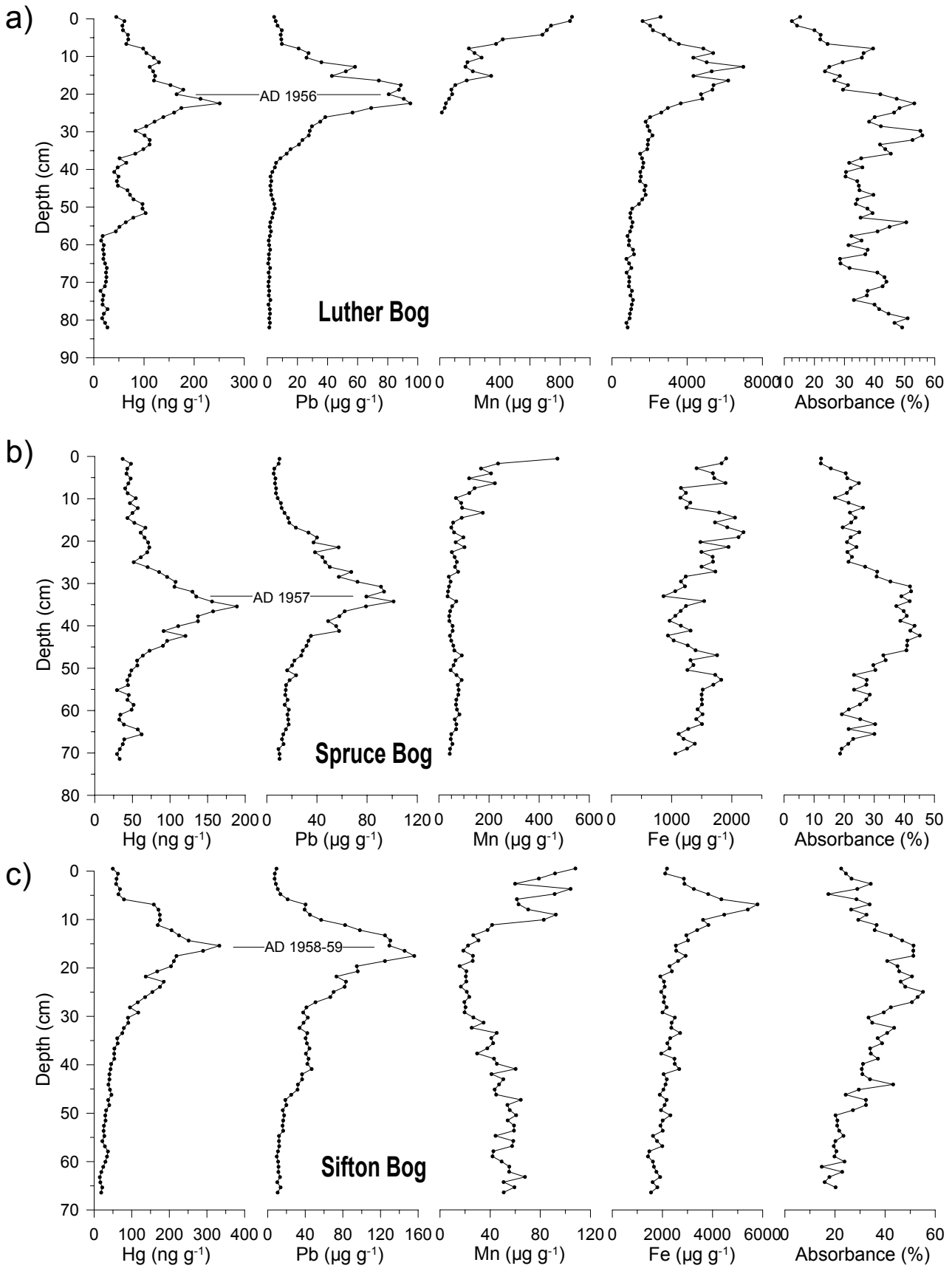


Fig. 4. Concentrations of Hg (ng g^{-1}), Pb (µg g^{-1}), Mn (µg g^{-1}) and Fe (µg g^{-1}), and degree of humification (corrected absorbance) for the Wardenaar peat profiles from Luther (a), Spruce (b) and Sifton bogs (c). The age dates represent those ^{14}C bomb pulse age dates (± 2 years) which are closest to the peaks in Hg concentration and are included for convenience.

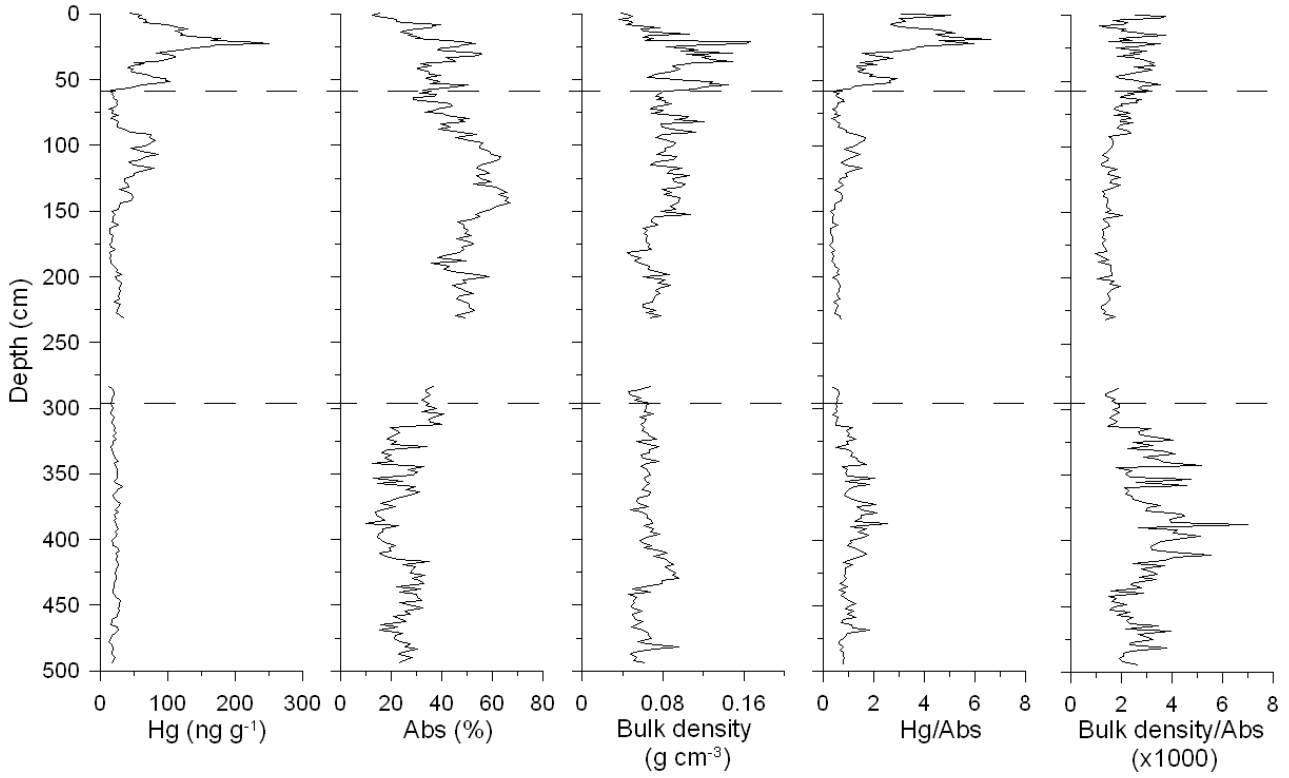


Fig. 5. Mercury concentrations (ng g^{-1}), degree of humification (corrected absorbance) and bulk density (g cm^{-3}) in the peat profile from Luther Bog. The ratio Hg/Abs is also shown to compensate the Hg concentrations for changes in peat decay. The ratio bulk density/Abs shows that these parameters provide a comparable index of the degree of humification for *Sphagnum*-dominated bog peats (above ca. 180 cm) but not for *Carex*-dominated fen peats (below ca. 250 cm).

5. Discussion

5.1. Effects of natural biogeochemical processes on Hg concentration profiles

Diagenesis of Fe and Mn within the peat profile

It has previously been shown that redox-related transformation of Fe and Mn in marine and lacustrine sediments may contribute significantly to Hg enrichments in the surface layers of these sediments, and it is important to know if these processes may have affected the Hg concentration profiles near the surface layers of the peat bogs. At the bog surface, Fe and Mn are deposited as soil dust particles, primarily as oxides and hydroxides derived from the chemical weathering of soils. In acidic, anoxic peat, these will react via reductive dissolution, releasing Fe(II) and Mn(II) to the porewaters which will diffuse upward into oxic zone, become oxidised and precipitate (Steinmann *et al.*, 1997). It is conceivable, therefore, that Hg may have become enriched in the surface layers of the peat profiles via absorption onto the reactive surfaces Fe and Mn oxides in the anoxic zone (Matty *et al.*, 1995). To evaluate this hypothesis, the distribution of Fe and Mn in the three Wardenaar cores is shown along with that of Hg in Figure 4. The surface layers of each core are clearly enriched in Mn: given the LLD of Mn in peat using the EMMA XRF (12 µg g^{-1}), the Mn concentration profile show that Mn concentrations in the top of each core may be as much as two orders of magnitude greater than the underlying peat layers. However, these pronounced Mn enrichments are restricted to the top of the peat core, and in each peat core they clearly overlie the zone of elevated Hg concentrations (Fig. 4). Thus, the distribution of Hg and the distribution of Mn are clearly separated in space and time at all sites. With respect to Fe, the maximum in Hg concentrations in each core also is below the

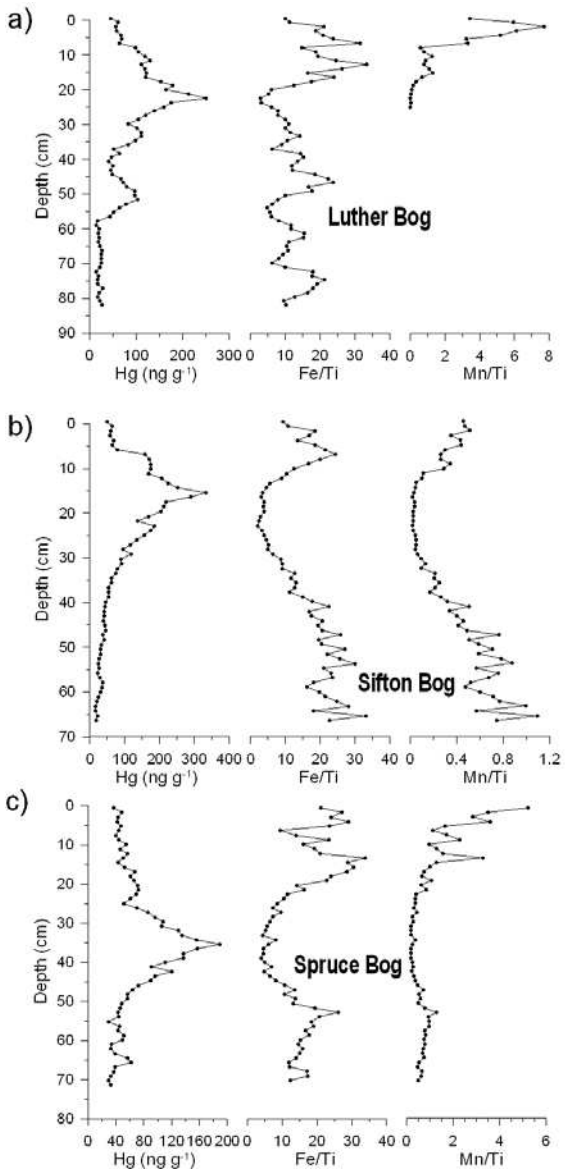


Fig. 6. Concentrations of Hg (ng g^{-1}), Fe/Ti and Mn/Ti ratio for the Wardenaar peat cores from (a) Luther Bog, (b) Sifton Bog, and (c) Spruce Bog. Note that the peaks in Hg concentrations correspond to minima in Fe/Ti in all three cores.

maximum Fe concentration (Fig. 4). Thus, in each of the three profiles, the maximum concentrations of Fe and Mn are separated in both space and time with respect to Hg (Fig. 4). The onset of changing Hg concentrations, therefore, precedes and pre-dates the changes in Mn and Fe concentrations.

Normalizing Mn and Fe to Ti emphasizes the change in Mn and Fe abundance, relative to the abundance of mineral matter (Fig. 6). In the peat core from Sifton Bog (Fig. 6b) and in the core from Spruce Bog (Fig. 6c), the maximum concentration of Hg corresponds to the minimum in Fe/Ti and Mn/Ti ratios. In these two peat profiles, therefore, there is no indication that the distribution of Hg has been affected in any way by redox-related transformations of either Fe or Mn.

Even in the case of the Luther bog (where a dam was constructed in 1954), the distribution of Hg does not correspond to that of Fe/Ti or Mn/Ti (Fig. 6a). The construction of the dam may have affected the hydrography of the bog by changing the level of the water table and therefore the depths at which redox processes take place within the peat column. The peaks in Fe/Ti at ca. 75 cm, 65 cm, and 45 cm may somehow be related to these hydrological changes to the peatland. However, even in these cases, the changes in Fe/Ti do not have a corresponding change in Hg concentration. The maximum Hg concentration, for example, at a depth of ca. 22 cm, corresponds to the minimum in Fe/Ti (Fig. 6a). Therefore, the distribution of Fe and Mn has not noticeably influenced the Hg concentration profiles in any of the cores. Although reductive dissolution of Mn and Fe in the peat cores is probably taking place (as seen in their chemical separation from Ti subsequent to deposition from the air as dust particles) this process has not dicernibly affected the distribution of Hg.

Other diagenetic processes

There are other factors which argue that the peaks in Hg concentration have not been caused by chemical diagenesis within the peat profile. First, given the differences in the structure and morphology of the three peat bogs studied, and the spatial variability within each peatland, each peat core shows a unique variation in Hg concentrations with respect to depth: the maximum Hg concentrations are found at depths of ca. 15 cm (Sifton Bog), 22 cm (Luther Bog), and 35 cm (Spruce Bog). Each of the peat bogs is a naturally acidic, organic-rich, ombrotrophic ecosystem. Considering that the climate regime is reasonably similar at all sites, the average depth to water table should also be similar in each of the bogs. Therefore, if the distribution of Hg concentrations within the peat profiles

was controlled or dominated by geochemical processes, there is no obvious reason why the maximum Hg concentrations should be found at different depths at each of the sites. However, the change in Hg concentrations with respect to time are similar, with Hg concentrations having reached their maximum concentrations during the late 1950`s at each site. The similar chronologies of Hg accumulation in the three peat cores, therefore, suggest that the changing rate of atmospheric Hg deposition is the dominating process affecting the Hg concentration profiles.

Second, many published studies have concluded that Pb is effectively immobile in acidic, ombrotrophic peat bogs, and that these bogs faithfully preserve a record of atmospheric Pb deposition (Shotyk *et al.*, 1998; Vile *et al.*, 1999; Weiss *et al.*, 1999). Given the pronounced differences between the geochemical behaviour of Hg and Pb, the correlation between the peaks in Hg and Pb concentrations (Fig. 4) cannot be mere coincidence. In fact, taking Pb to represent an immobile reference element, the similar distribution of Hg and Pb in these peat cores suggests that Hg too, is well preserved, and that these bogs do indeed serve as archives of atmospheric Hg deposition. Taken together, the available evidence suggests that

i) the Hg concentrations measured in the peat core were supplied exclusively by the atmosphere,
ii) that there has been no significant diagenetic remobilisation of Hg, and,
iii) that the peat bog has faithfully preserved a record of atmospheric Hg accumulation.

Effect of organic matter decay on Hg concentration profiles

In a recent study about Hg accumulation rates in Patagonian peat cores (Biester *et al.*, 2003), it has been suggested that humification processes and mass losses during the diagenesis of peat might have a strong influence on Hg concentrations or accumulation rates. Moreover, those authors suggested that bulk density is not an adequate parameter to express changes in peat humification, and that Hg accumulation rates should be corrected for humification to take into account mass loss during peat decay. In the present study, absorbance of alkaline extracts of peat was used as a measure of decay, and these data are compared with the Hg concentration profiles for the three Wardenaar cores in Figure 4. These data show that the changes in Hg concentration within the profile are disproportional to the changes in peat humification (as reflected by the absorbance measurements). For example, at the Luther Bog the peat samples between 100 and 150 cm are clearly more decomposed than the peat samples above 50 cm (Fig. 5); however, the peat samples above 50 cm contain far higher Hg concentrations (Fig. 5). Thus, the variation in degree of decomposition of peats from the Luther bog profile alone cannot explain the most significant changes in the Hg concentration profile (Fig. 5). To emphasise this, the Hg concentrations have been normalised to absorbance and this ratio (Hg/Abs) is found to be elevated in three zones: in the *Carex* fen peat (ca. 450 to 300 cm), around 100 to 150 cm (to be discussed later), and above 50 cm (Fig. 5). In contrast to the small changes in absorbance within the peat profile, the changes in Hg concentrations relative to absorbance (Hg/Abs) are far greater. As a result, physical processes such as organic matter decomposition cannot explain the magnitude of the variation in Hg concentrations with depth in these peat bog profiles. Also, the small variation in the ratio between bulk density and absorbance in the *Sphagnum* peats (Fig. 5) shows that other physical processes such as compaction also cannot explain the magnitude of the Hg concentration differences.

5.2. Predominant sources of atmospheric Hg

Lithogenic sources of Hg and Pb

In the upper part of all three profiles, Hg, Pb and Ti have some peaks in common (Figs. 3 and 4) and it is necessary to quantify to what extent atmospheric soil dust may be a potential source of Hg (and Pb) and to the bog. Recent research, for example, has demonstrated that

mineralised bedrock or/and bedrock with high natural background concentration in Hg and Pb constitutes significant sources of these elements to lake sediments in the south-eastern part of the Canadian Shield (Coker *et al.*, 1995). The lithogenic Hg and Pb fractions derived from atmospheric mineral matter can be estimated as the product of the concentrations of a conservative lithogenic element in a given profile (e.g. Ti), and the Hg/Ti or Pb/Ti ratio of the pre-anthropogenic, background period of the Luther bog profile. The pre-anthropogenic, natural background values of Hg/Ti and Pb/Ti are taken from the 60-290 cm section of the Luther bog profile which is ombrotrophic with respect to all three elements. These values are more representative of the pre-anthropogenic ratio of Hg/Ti and Pb/Ti ratios in atmospheric aerosols of southern Ontario than ratios obtained from compiled values published in the literature for the Upper Continental Crust (Wedepohl, 1995). Calculations of lithogenic Hg using the background Hg/Ti values, shows the atmospheric deposition of mineral matter cannot explain more than 0.2 % of the peak Hg concentrations, and no more than 15.5 % of the Pb. Clearly, natural inputs of Hg from soil dust represent a negligible source of Hg to the peat bog profiles. Further evidence supporting this conclusion is the notable peak in Ti concentration at a depth of ca. 375 cm in the Luther profile which has no corresponding peak in Hg concentration (Figs. 3 and 5).

The elevated Ti concentrations seen in all three peat cores (Fig. 3) indicate recent increases in the deposition of dust particles from the atmosphere. These changes are most likely caused by soil dust because of the extensive forest clearance for agriculture. During the period ca. AD 1800 to 1900, southern Ontario was more or less deforested by European settlers, and the increased rate of soil erosion would have created a significant increase in the release of dust particles to the air; the surface layers of these bogs bears witness to this process. Again, however, these inputs are not a significant source of Hg to the bogs. While there certainly are elevated concentrations of Hg and Pb in the samples which are enriched in Ti, these three elements only share a common chronology, and not a common source. In other words, the processes which have enhanced Ti inputs to the bog (enhanced fluxes of soil dust) are independent of those providing Hg and Pb (mainly coal-burning; see below): however, the chronology of the changing importance of these two processes is similar.

If the changing Hg concentrations seen in the recent peat layers of all three peat cores cannot be explained by chemical processes operating within the peat profiles, and if the changing rates of atmospheric soil dust cannot explain their distribution, then anthropogenic sources of Hg must be invoked to explain the increased rate of deposition of this element.

Distinguishing between natural and anthropogenic mercury sources

Hg in relation to Br and Se

To distinguish between natural and anthropogenic Pb in peat bog profiles, we have previously used scandium (Sc) as a conservative reference element to represent the natural Pb component contributed by atmospheric soil dust (Shotyk *et al.*, 1998). This approach is valid because atmospheric Pb deposition in pre-anthropogenic times was dominated by inputs of soil dust, and because Sc behaves conservatively both during chemical weathering in soil profiles, but also subsequent to deposition in the bog (Shotyk *et al.*, In press). It is highly desirable to have an analogous "reference element" for Hg, to quantify the natural inputs of Hg to the bog. In the case of Hg, however, the data and arguments given above show that soil dust inputs of Hg were insignificant in pre-anthropogenic times, and therefore that a reference element is needed whose inputs to the bog are independent of soil dust.

Bromine and selenium are two elements whose supply to the bog is independent of soil dust. The chemistry of Br and Se is very different to that of Hg: Br is probably supplied to the bog primarily as ionic bromide and Se perhaps as dimethyl selenide; both are ultimately supplied by the oceans. In contrast, Hg in the atmosphere in pre-anthropogenic

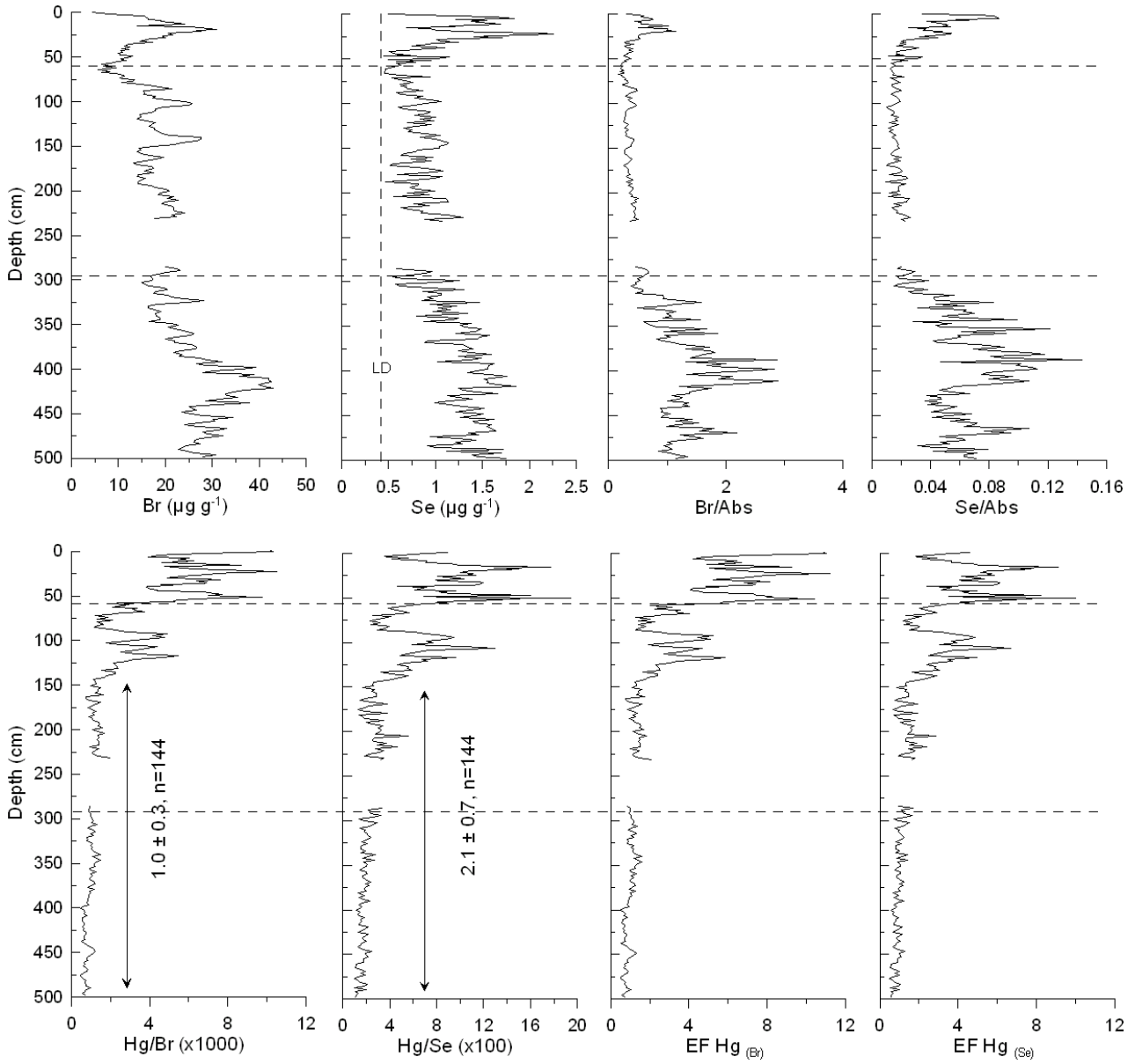


Fig. 7. Bromine and selenium concentration profiles (µg g^{-1}) for the Luther Bog peat profile. The Br/Abs and Se/Abs ratios show that the surface peat layers are enriched in Br and Se, out of proportion with the extent of humification. The Hg/Br and Hg/Se ratios show that these values were relatively constant for many thousands of years. The vertical dashed line indicates the analytical limit of detection for Se (0.4 ppm). Mercury enrichment factors (EF Hg) have been calculated using both the pre-anthropogenic Hg/Br and Hg/Se ratios to calculate the extent of enrichment (no. of times) relative to these pre-anthropogenic, background values.

times must have been present primarily as the volatile, unreactive, gaseous elemental form (Mason *et al.*, 1994; Schroeder *et al.*, 1998). The physical and chemical processes which affect and control their atmospheric transport and deposition also are very different. Despite these great differences, Hg/Br and Hg/Se ratios in ombrotrophic peat dating from pre-anthropogenic times were remarkably constant for thousand of years (Fig. 7): from 495 to 150 cm, the Hg/Br and Hg/Se ratios averaged 0.0010 ± 0.0003 and 0.021 ± 0.007, respectively (n=144). Therefore, even though these elements may have different atmospheric sources, chemical properties, and different modes of transport and deposition, their rates of accumulation in pre-anthropogenic peat were in constant proportions for thousands of years. The constant "background" ratios warrants an attempt to use Hg/Br and Hg/Se to try to quantify anthropogenic Hg. Further support for this approach is provided by the

peat core collected at Etang de la Gruère in the Jura Mountains of Switzerland, where the natural "background" Hg/Br ratio (Roos-Barraclough *et al.*, 2002; Roos-Barraclough *et al.*, 2003) was constant for several thousand years (average 0.0012 ± 0.0002 from ca. 14,500 to 800 yr B.P.).

Relative to the "background" values, the ratios Hg/Br and Hg/Se increase below 495 cm where the profile consists of gyttja and clays, as well as in samples from 150 to 85 cm and in all samples above 70 cm depth. The increases in Hg/Br and Hg/Se in the peat samples above 70 cm (dating from recent times) are of particular interest.

If Hg, Br and Se in peat are conserved during decomposition, then they will increase in concentration with increasing humification (as measured using corrected absorbance). In the Luther Bog profile from 300 cm to 60 cm depth, there is a constant botanical composition of peat, but variable degree of humification (Fig. 5): here, the Br/Abs and Se/Abs ratios are low and constant (Fig. 7). Thus, during decomposition, these elements appear to behave similarly and become enriched to the same extent; this is true also of Hg (Fig. 5). Humification processes operating with the peatland, therefore, affect Hg, Br and Se to the same extent, and as a first approximation, they are conserved during organic matter decay. In the *Carex* fen peat layers, the Br/Abs and Se/Abs ratios are clearly elevated, but here emphasis is placed on the corresponding ratios in ombrotrophic peat which are constant from ca. 200 to 50 cm (Fig. 7).

Calculating an Enrichment Factor for Hg (EF Hg) using Hg/Br and Hg/Se

Enrichment factors have been calculated for Hg (EF Hg) using the constant, pre-anthropogenic values for Hg/Br and Hg/Se. These EF calculations (Fig. 7) show that Hg is enriched in the Luther profile by a factor of up to 6 times, relative to "background" values. In the uppermost peat samples, however, the Br/Abs and Se/Abs profiles show that both Br and Se themselves are enriched, relative to "background" values (Fig. 7). Thus, the EF calculations underestimate the true extent of anthropogenic enrichment of Hg. The enrichments of Br and Se may be due to natural processes, anthropogenic inputs, or both. The topmost sample of the core is made up of living plant matter, but here the Br and Se concentrations are lower than in underlying samples (Fig. 7). Therefore, biological uptake of Br and Se by plants does not appear to be the dominant cause of the elevated Br/Abs and Se/Abs values in the surface layers of the bog. Possible anthropogenic sources of bromine (Thomas *et al.*, 1997) and selenium (Duce *et al.*, 1975) include bromine compounds added as gasoline Pb additives (to scavenge Pb from motors) and selenium release during coal burning and metal sulfide refining. The calculated EF values for Hg, therefore, are at best rather conservative estimates of anthropogenic Hg.

Separating total Hg into natural and anthropogenic components using Br

Because the ratio Hg/Br and Hg/Se in peat dating from pre-anthropogenic times was effectively constant, these ratios can be used to separate total Hg into its natural and anthropogenic components. With respect to Se, the concentrations of Se in the pre-anthropogenic section of the peat profile are typically ca. five times the LLD provided by EMMA XRF (0.4 ppm), but in some cases the Se concentrations in peat approach the LLD. In contrast, Br concentrations in the same peats are always at least a factor of ten above the LLD (0.7 ppm). Because measurements of element concentrations 10× LLD are more accurate than those approaching the LLD, Br was selected as the better reference element for Hg. Therefore, the natural Hg component in the peat cores was calculated using the Hg/Br ratio. Here, "excess Hg" is defined as the difference between the natural Hg component and the total Hg concentration:

$$[Hg]_{excess} = ([Hg]_{total}) - ([Hg]_{natural}) \quad (i)$$

$$\text{where } [Hg]_{natural} = ([Br]_{sample}) \times ([Hg]/[Br]_{background}) \quad (ii)$$

A similar approach was used previously to separate Pb in peat cores into its natural and anthropogenic components using the background Pb/Sc or Pb/Ti ratio (Shotyk *et al.*, 2002). Excess Hg calculated in this way cannot be attributed to the residual enrichment of Hg during the decomposition of organic matter because this effect is already taken into account by the Br concentrations: the Br concentrations (Fig. 7) vary with peat humification (Fig. 4) and by normalising the Hg concentrations to Br, therefore, this process is already considered. In the uppermost peat layer where Br/Abs reveals an enrichment of Br, out of proportion with humification (Fig. 7), however, excess Hg calculated as described above will certainly be underestimated. To have a better measure of excess Hg in the surface peat layers, a reference element for atmospheric Hg deposition is needed which has no significant anthropogenic contribution: we are not aware of any such element. For the moment, therefore, there is no choice but to use Br as a reference element for atmospheric Hg inputs, as imperfect as this may be.

Excess Hg in the peat core consists of Hg in a concentration range which exceeds that which can be attributed to the natural ratio of Hg to Br. This excess Hg may be due to Hg inputs from volcanic emissions (Roos-Barraclough *et al.*, 2002), changes in intensity of biogenic emissions including biomass burning, climate changes such as variations in temperature or rainfall (Roos-Barraclough *et al.*, 2002), or anthropogenic Hg inputs. Previous studies using peat cores from Swiss bogs (Roos-Barraclough *et al.*, 2002) have shown excess Hg due to climate change and volcanic emissions are small compared to the concentrations of excess Hg in modern peat samples dating from the Industrial Period.

Below 495 cm in the Luther Bog profile, excess Hg cannot be interpreted with respect to atmospheric inputs because the peat core at these depths consists of gyttja, a nutrient-rich sedimentary peat dominated by plankton and other plant and animal residues. The Hg/Br and Hg/Se ratios are elevated in this zone of the peat profile (not shown), as well as the Hg concentrations, possibly reflecting other Hg enrichment processes related to intense bacterial activity (bioaccumulation) at the gyttja/water interface during sedimentation in a quiet water environment. These natural Hg enrichment processes are beyond the scope of this paper.

5.3. Calculating net atmospheric Hg accumulation rates

To estimate the atmospheric Hg fluxes, net Hg accumulation rates (AR) were calculated using:

$$AR = 10 \times [Hg] \times BD \times GR \quad \text{(iii)}$$

where AR is the net accumulation rate of Hg ($\mu g\ m^{-2}\ yr^{-1}$), [Hg] the Hg concentration ($ng\ g^{-1}$), BD the bulk density of the peat ($g\ cm^{-3}$) and GR the growth rate ($cm\ yr^{-1}$). Growth rates were determined using ages calculated for each layer by the age-depth relationship of each core. The net rate of Hg accumulation (Hg AR) for the past 8,000 years derived from the Luther Bog peat profile is shown in Figure 8 and for the three Wardenaar peat cores in Figure 9. The error associated with the mercury accumulation rates for the last 50 years is calculated to be 21 %, based on conservative estimates of the errors associated with ^{14}C dates (ca. 5 %), Hg concentrations (ca. 5 %), and bulk density measurements (ca. 20 %). The error range for the samples pre-dating AD 1950 and too young to be dated using ^{14}C is more difficult to quantify because the age-depth model does not permit uncertainties to be calculated; however, these are assumed to be comparable to the others.

Natural background Hg accumulation rates

The Hg AR profile for Luther Bog shows total Hg deposition for the last 8,000 years (Fig. 8). Here, the net rate of atmospheric Hg accumulation during the Holocene (past ten thousand years) varied between 0.4 and 7.7 $\mu g\ m^{-2}\ yr^{-1}$ with an average accumulation rate of $1.4 \pm 1.0\ \mu g\ m^{-2}\ yr^{-1}$ (n=197) from 5,700 years BC to AD 1470. These values are consistent with natural Hg AR measured in peat cores from bogs in Sweden (Bindler, 2003), Switzerland (Roos-Barraclough *et al.*, 2002;

Roos-Barraclough *et al.*, 2003), Greenland (Shotyk *et al.*, In press) and Maine, USA (Roos-Barraclough, 2002). The variation exhibited by Hg AR is thought to be primarily due to Holocene climate change. For example, during a warm, dry period in southern Ontario (Yu *et al.*, 1997) from ca. 3,600 to 200 cal years BC, the natural rate of atmospheric Hg accumulation was particularly low and constant (Fig. 8). During the pre-anthropogenic period, an excess of Hg occurred only once, in peat from ca. 72 to 135 cm and dating from ca. 200 cal years BC to AD 1200 (Fig. 8).

Several physical and chemical properties of peat from ombrotrophic bogs have been used as proxy climate indicators (Blackford, 2000), including the degree of peat decomposition (Caseldine *et al.*, 2000). The increase in the absorbance values (degree of humification) of the Luther Bog peat core (Fig. 4) from 4000 to 0 cal. years BC (385 cm to 135 cm) reflects an increase in the degree of peat decomposition; this, in turn, indicates a period of low effective precipitation. The occurrence of this climate phase in the Luther Bog is consistent in timing (from other archival records) with the late middle Holocene warm and dry period in Ontario (Yu *et al.*, 1997). Recent paleohydrological studies of water levels at other sites in eastern North America indicate similar dry climate periods which are thought to be due to more frequent incursions of drier Pacific air into the northeast of North America (Almquist *et al.*, 2001; Shuman *et al.*, 2001).

Following this warm, dry phase, the subsequent period (ca. 200 cal years BC to AD 1200) shows a decrease in the degree of humification which reflects a shift in climatic conditions to a period of higher effective precipitation. Lake sediment records throughout the northeast USA document increasing lake levels by 2000 BP which suggests increased humidity and colder conditions; this has been interpreted as a response to a more southward displacement of the Arctic front relative to it's modern position (Gajewski, 1987; Harrison *et al.*, 1985). Of special interest here, an excess of Hg is observed throughout this period, with the Hg AR increasing by more than a factor of three from 1.4 to 4.6 $\mu g\ m^{-2}\ yr^{-1}$. These changes reflect an increase in atmospheric humidity in southern Ontario at that time, following the preceding warm and dry period: this must have led to a corresponding increase in wet deposition of atmospheric Hg which is recorded by the peat core from Luther Bog (Fig. 8). The elevated Hg fluxes for this period (Fig. 8), and the elevated Hg/Br and Hg/Se ratios (Fig. 7), are therefore interpreted as a direct reflection of climate change. The magnitude of the change in Hg AR from this period (a factor of three times) documents the sensitivity of natural 'background" Hg accumulation rates to Holocene climate change. Clearly, these variations must be duly considered when quantifying modern Hg accumulation rates for comparison with background values. Similar climate-driven Hg accumulation rate phenomena have been seen in others bogs (Martínez Cortizas *et al.*, 1999; Roos-Barraclough *et al.*, 2002).

In addition to direct effects of climate change on Hg accumulation rates, there are several possible indirect effects. For example, the change in climate may have led to changes in the relative abundance of dominant plant species growing on the bog surface at that time. Some bog plant species are particularly efficient at retaining Hg compared to others (Roos-Barraclough *et al.*, 2003) such that small differences in net rates of Hg accumulation may be partly due to changes in the abundance of predominant plant species. For example, the deposition of Hg associated with litterfall and throughfall may provide up to 60% of the total Hg deposited beneath a spruce forest canopy (Iverfeldt, 1990). Therefore, a change in vegetation such as a change of the relative abundance of bog plant species or greater tree cover, may have led to a long-term change in the efficiency by which Hg was deposited, captured and/or retained by the bog. While differential retention or release of Hg during organic matter decay may also play a role, this seems far less likely to be important because the relationship between Hg concentration and absorbance (Figs. 4, 5) suggests that Hg is very well retained by the peat. Also, experimental studies have shown

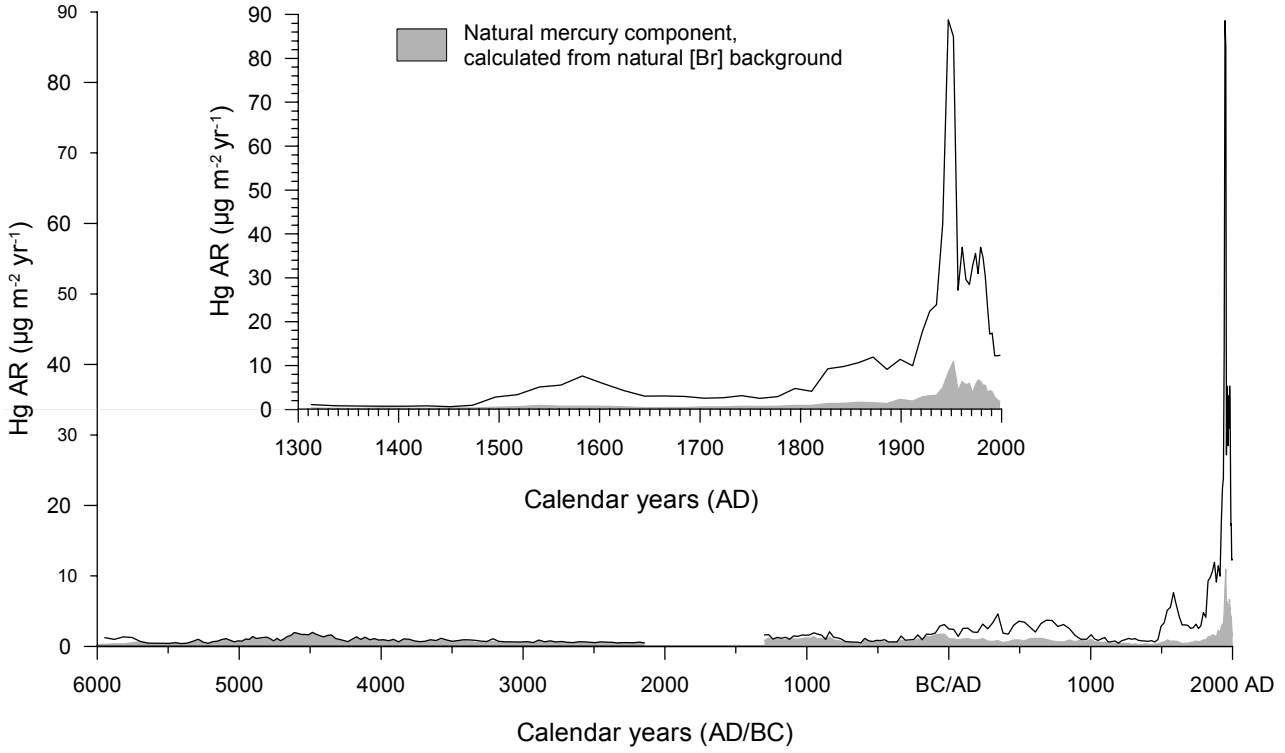


Fig. 8. Total (solid line) and natural (shaded area) Hg accumulation rates (past 8,000 years) in the Luther Bog profile calculated using the background Hg-Br relationship. Inset: past 700 years.

that little of the Hg deposited on peat bog surfaces is re-emitted to the air (Lodenius *et al.*, 1983).

The fluctuations in Hg AR due to Holocene climate change are dwarfed by the dramatic increases in Hg AR in peat samples dating from the modern period; these more recent changes are discussed in more detail below.

Excess Hg beginning in peat dating from the 15th Century AD

A notable peak of Hg AR (up to 5 time relative to "background") occurs from AD 1475 to AD 1650 and reaches a maximum flux of 7.7 µg m^{-2} yr^{-1} (Fig. 8, inset). Since AD 1475, Hg AR has been elevated and the Hg/Br and Hg/Se ratios have continuously been outside of their long-term average range. This excess of Hg relative to both Br and Se may be an entirely natural phenomenon such as enhanced Hg deposition from the global cycle of gaseous elemental Hg due to increased atmospheric humidity and its effects on Hg oxidation and precipitation scavenging, or an anthropogenic process such as local or regional scale changes in Hg emission rates due to gold and silver mining.

There are at least two regional anthropogenic sources of Hg which may have resulted in Hg contamination of the Luther bog profile in the late 15th century. First, this enrichment may be a reflection of Hg consumed and emitted by amalgamation associated with silver mining activities in Spanish America. Hylander *et al.* (2003) have recently reported that the onset of Hg use in South America dates from around AD 1550. The impact of fugitive Hg release from industrial silver production in Spanish America may explain part of the peak in Hg contamination observed in Luther profile from AD 1475 to AD 1650 (Fig. 8). However, at Caribou bog in Maine, about 1,000 km east of the Luther bog, onset of Hg contamination from anthropogenic sources began during the nineteenth century (Roos-Barraclough, 2002). No peak of HgAR is observed at that site in the period of industrial Hg use for silver recovery in South America. In addition, the peak in Hg concentration and Hg AR in the

Luther Bog correlates with smaller but significant peaks in Pb (Fig. 4) and S (not shown) concentrations during the same period. Taken together, those two observations suggest that a local source of anthropogenic Hg is probably needed to explain the Hg, Pb and S contamination observed in the Luther profile from AD 1475 to AD 1650.

Second, southern Ontario has its own unique record of regional scale human impacts. It is known from archaeological evidence that Iroquoians settled in the Grand River watershed of southern Ontario from AD 1370 to AD 1650. Although paleoecological evidence for impact of Iroquois farmers on the forests of southern Ontario is limited to few sites (Burden *et al.*, 1986; Clark *et al.*, 1995; McAndrews *et al.*, 1989), there is abundant archaeological evidence for their presence in the period between AD 900 and AD 1600 (Campbell *et al.*, 1994). High-resolution pollen and charcoal analyses from Crawford Lake (30 km SE of Luther Bog) by McAndrews and others (Clark *et al.*, 1995; Clark *et al.*, 1996; McAndrews *et al.*, 1989) reveal a pronounced change in the composition of upland forests around 1500 AD which was caused by deliberate forest burning by Iroquois for maize cultivation. The Iroquoian practiced long-fallow cultivation which involved clearing a plot of land by cutting the underbrush and girdling large trees, burning the residue, and planting crops for several years until the soluble nutrients supplied from the wood ashes became depleted. The cycle was repeated on other sections of land over a number of years until all the arable soils within a reasonable distance to the village were exhausted. Once this point had been reached, the village would be relocated to a new area and the process would begin over again (Campbell *et al.*, 1994).

Published studies from Manitoba, Canada, and the Amazon basin of Brazil have shown that forest fires can be significant sources of Hg emissions (Veiga *et al.*, 1994). It is quite possible, therefore, that the increase in Hg AR seen in the Luther Bog reflects biomass burning by Native North Americans. The peak in excess Hg dates from ca. AD 1580 when the Neutral population is estimated to have reached its maximum. The population of the Neutral has been variously estimated to range from 12,000 to 40,000 people (Noble, 1984). The lower estimates may reflect the devastating effects of European diseases and periods of famine which swept through the region between AD 1634 and 1640 (Trigger, 1982). The introduction of European diseases, for which native populations had little immunity, and intensified warfare during the beginning of the 17th century led to the collapse of the Huron and Neutral tribal in 1649 (Heidenreich, 1972) The Hg AR recorded by the peat core decreased from AD 1580 to reach a plateau around AD 1650, may reflect well the decline of biomass burning by at that time.

The partitioning of Hg released from biomass burning remains controversial. Combustion gases from fires would resemble those from fossil fuel burning (Veiga *et al.*, 1994), with up to 50 % of total Hg in the form of water-soluble Hg(II) (Pacyna *et al.*, 1991). Recent laboratory experiments (Friedly *et al.*, 2003), however, report that during biomass burning, mercury is emitted almost exclusively as elemental Hg (>95 %) and <5 % as particulate mercury. Thus, it remains unclear how the Hg released from regional biomass burning for native agriculture gave rise to the peak in Hg accumulation rate (AD 1580) in the Luther Bog. However, if 50 to 95 % of the Hg released was in the form of Hg^0, then the Hg recorded by the bog probably only reflects a fraction of the total emission flux, with much of the emitted Hg having been dispersed globally.

Modern Hg accumulation rates

During the late 17th and 18th centuries, the approach used here to calculate anthropogenic Hg in the Luther Bog profile indicates that the accumulation of Hg from anthropogenic sources was equivalent to or exceeded the inputs of Hg from natural sources (Fig. 8). All three bogs show that Hg contamination increased again at the beginning of the 19th century, with the greatest change seen at the beginning of the 20th century (Fig. 9). The chronology of Hg accumulation recorded by

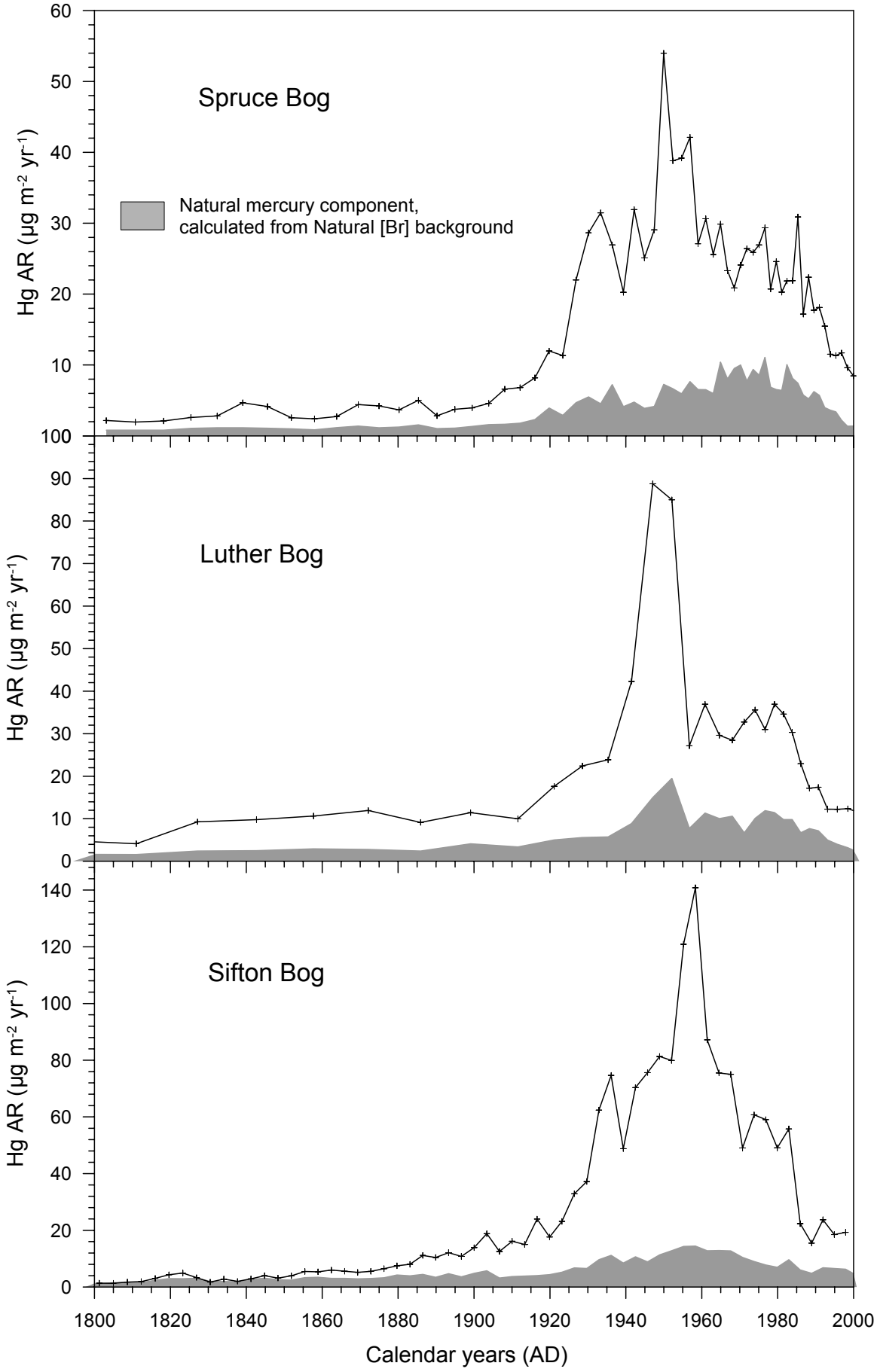


Fig. 9. Chronologies of total (solid line) and natural (shaded area) Hg accumulation rates for Spruce Bog, Luther Bog and Sifton bog. The difference between the total AR and the natural AR is an estimate of the anthropogenic contribution.

the three ombrotrophic bogs in southern Ontario is similar, with maximum rates of accumulation of anthropogenic Hg dating from the1950-60s at all three sites (Fig. 9). At that time, anthropogenic mercury contributed at least to 85 % of the total Hg AR and the greatest accumulation rates recorded by the bogs (54, 89 and 141 µg m^{-2} yr^{-1} at Spruce Bog, Luther Bog and Sifton Bog, respectively) are up to 39, 63 and 101 times greater than the average natural background rates. Clearly, there is a gradient within southern Ontario of the intensity in anthropogenic Hg inputs, with Hg AR increasing in the order remote < rural < urban site. Assuming that inputs to the relatively remote Spruce Bog are more indicative of global changes in the atmospheric Hg cycle, the much greater Hg AR recorded by the Sifton bog in London, Ontario reflects the importance of regional and local sources.

The Hg AR values today (10, 12 and 18 µg m^{-2} yr^{-1} at Spruce Bog, Luther Bog and Sifton Bog, respectively), are approximately 7, 9 and 13 times the average natural background values. The modern fluxes obtained using these peat cores can be compared with the direct measurements of atmospheric Hg deposition at regional Mercury Deposition Network (MDN) monitoring sites in southern Ontario. Wet deposition of mercury monitored at regional MDN sites in Ontario reported values of 7.4 µg m^{-2} yr^{-1} in 1998 at the Dorset site and 4.7 µg m^{-2} yr^{-1} in 2001 at the Edbergt site. Assuming that dry deposition constitutes no more than 40 ± 50 % of wet deposition (Lamborg *et al.*, 2002), these direct measurements indicate total mercury deposition rates ranging from 5.6 to 13.3 µg m^{-2} yr^{-1} which is in good agreement with the values reported by this study for the same period of time. The agreement between the two independent methods for quantifying atmospheric Hg deposition rates suggests that the approach described here (using peat cores from ombrotrophic bogs to reconstruct accumulation rates) is reasonable. Moreover, the retrospective approach using peat cores from bogs is especially valuable because it not only provides a detailed chronology of the changes extending back in time, but also because it yields the "natural background" rate of atmospheric Hg accumulation, against which modern values may be compared.

Because Br and Se have also been emitted by anthropogenic sources (Rahn *et al.*, 1985) such as gasoline additives (to scavenge Pb) and coal burning, respectively, the natural Hg component for the modern period has been overestimated by the peat cores. Given the changes in Br/Abs and Se/Abs seen in the top layers of the Luther Bog (Fig. 7), we estimate that the natural Hg component found in modern peats has been overestimated by at least by a factor of two, compared to the pre-anthropogenic period. As a result, the rates of anthropogenic Hg accumulation which we have calculated for the modern period in each of the peat cores (Fig. 9) represent conservative estimates.

Identifying the predominant source of anthropogenic Hg during the 20th century

The similarities in Hg accumulation chronologies among the three peat bogs from southern Ontario (Fig. 9) imply a common, predominant source. We note that the peat samples containing the greatest Hg concentrations and Hg accumulation rates (Fig. 9) are also the samples containing the highest Pb concentrations (Fig. 4). While traditional chloro-alkali plants were the predominant source of anthropogenic Hg to the global atmosphere in the recent past (Lindberg *et al.*, 1987), these did not emit Pb. While leaded gasoline was the single most important source of anthropogenic Pb to the global atmosphere (Schaule *et al.*, 1981) until recently, this was not a source of Hg. In fact, the predominant anthropogenic source that these two elements have in common is coal burning. In southern Ontario, therefore, the maximum rates of atmospheric Hg and Pb deposition, and the maximum contributions of these metals from anthropogenic sources, was due to coal burning, and this source peaked in the late 1950`s. Support for this hypothesis is provided by the sulphur concentration profiles (not shown) which show that the maximum S concentrations in all three peat cores coincide with the peaks in Hg and Pb; coal is enriched in all three of these elements. We note further

that a peat bog in Denmark and a minerotrophic fen in southern Greenland provide very similar chronologies of both metals (Shotyk *et al.*, In press), with maximum accumulation rates (also obtained using the bomb pulse curve of ^{14}C) dating from AD 1953. In that study (Shotyk *et al.*, In press), the isotopic composition of Pb in the most contaminated section of the Danish peat bog profile was found to be comparable with that of British coals lending further support to the importance of coal burning as a source of both metals.

5.4. Comparison with other archives

For comparison with the results presented here, we know of no published studies providing a record of atmospheric Hg deposition for North America extending so far back in time. However, there are several published chronologies of Hg contamination for the modern period, and the results presented here are generally in good agreement with those studies. For example, data from lake sediments in Minnesota(Engstrom *et al.*, 1997) indicate that mercury deposition peaked in the 1960`s, with recent declines appearing in both rural and urban sites. The emission budget by Pirrone (Pirrone *et al.*, 1998) suggests that atmospheric Hg deposition from local sources dominated from 1940 to 1960, with deposition subsequently dominated by long-range atmospheric transport. The results presented here also are consistent with other findings that indicate that a substantial fraction of anthropogenic Hg emissions are deposited locally near the source of pollution (Mason *et al.*, 1994).

The Upper Fremont Glacier (UGC) has yielded a high-resolution record of total atmospheric mercury deposition for the past ca. three centuries (Schuster *et al.*, 2002). The ice core taken from this site indicates a 20-fold increase in Hg accumulation rates between pre-industrial (ca. AD 1720) and industrial times which is comparable to the peat records from southern Ontario for the same period of time. The UGC core is the only other high-resolution record, along with the present study, reporting atmospheric mercury deposition in North America as far back in time as AD 1720. Without long-term records of atmospheric mercury deposition, it is difficult if not impossible to determine pre-industrial rates of atmospheric Hg accumulation, and to quantify the natural variation in "background" fluxes. Many of the studies published to date appear to have overestimated the natural "background" rates of atmospheric Hg deposition, and therefore may have underestimated the true impact of human activities on the geochemical cycle of mercury.

For example, lake sediment archives document smaller differences between anthropogenic and natural Hg fluxes. In many studies of peat and lake sediments archives by authors mentioned previously, accumulation rates of atmospheric mercury are reported to be in the range of 4 to 7 $\mu g\ m^{-2}\ yr^{-1}$ for the "natural background" and ranging between 10 to 50 $\mu g\ m^{-2}\ yr^{-1}$ for the modern period. In contrast, the peat cores studied here suggest that the maximum rates of net Hg deposition are between 54 and 141 $\mu g\ Hg\ m^{-2}\ yr^{-1}$, compared with a natural background of approximately 1.4 $\mu g\ m^{-2}\ yr^{-1}$ which was fairly constant for thousands of years. We see two important reasons for the discrepancies. First, unlike lake sediments, peat bogs receive Hg only from the atmosphere. Thus, the total amount of Hg retained by a peat core is a reasonable approximation of the total atmospheric input. In contrast, the Hg concentrations in lake sediments reflect not only direct inputs from the atmosphere, but also terrestrial and aquatic inputs. Second, many of the lake sediment Hg records do not provide high-resolution reconstructions. As a consequence, Hg concentrations are often averaged over longer time intervals which tends to "flatten" any peaks in concentration change (or flux). As a consequence, it is difficult to compare in detail the trace metal accumulation chronologies when there are large differences in the time increments being examined.

The results presented here and other recent studies using peat bog archives dated using the bomb pulse curve of ^{14}C have shown

that undisturbed peat bogs are excellent paleoenvironmental archives. These bogs certainly do record in a faithful way the changing chronologies of atmospheric mercury deposition. In fact, the historical records of net atmospheric Hg deposition appear to be so well preserved in the peat profiles that our ability to read and interpret these records is much less dependent upon physical and chemical processes taking place within the bog, and more dependent on appropriate and accurate methods for peat core sampling, handling, sectioning, sub-sampling, preparation, and age dating.

5.5. Implications for the global atmospheric Hg cycle

The changing fluxes of atmospheric Hg accumulation recorded by the peat bogs in southern Ontario, especially the decline since the 1960`s (Figure 9), is probably related to the introduction and growth of nuclear power, but also the regulatory developments or/and industrial process changes, including the introduction of filter technologies which retain particulate Hg (Pavlish *et al.*, 2003). In addition, residential home heating evolved from coal to oil and then to natural gas. While these trends are certainly positive and encouraging, they must also be viewed with caution and concern. Even though the various filtration technologies deal effectively with the removal of particulate Hg from flue gas streams, more volatile species such as gaseous elemental Hg are largely unaffected (Engstrom *et al.*, 1997; Trip *et al.*, 2000). As a result, the changing fluxes of atmospheric Hg accumulation recorded by the peat bogs (Fig. 9) do not necessarily document a decrease in total Hg emissions. Most likely, these changes primarily reflect strong declines in atmospheric emission of particulate Hg. The large differences in Hg AR between the three sites demonstrates the quantitative importance of local inputs of particulate and ionic Hg: the decline in Hg AR since the late 1950`s recorded by all three bogs certainly reflects a decrease in deposition of this fraction. However, these peat cores may provide little information about the changes in emissions of gaseous elemental Hg because it is volatile, much less reactive, and has a long atmospheric residence time. Peat cores from bogs in remote areas of Canada, for comparison with the results shown here, might provide more insight into the changing rates of atmospheric deposition of elemental Hg from anthropogenic sources. The effect of particle size distribution plays an important role in transferring Hg from the atmosphere to lakes (Pirrone *et al.*, 1996) and this phenomenon may have important implications for atmospheric Hg accumulation in remote areas such the Arctic.

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Supporting Information

Table 2.
Radiocarbon age dates (conventional ^{14}C years B.P.) and calibrated ages (calendar years B.P.) obtained from bulk peat samples and *Sphagnum* moss in selected samples from the Spruce Bog profile (Calendar dates calculated from Stuiver et al. 1998).

Average depth (cm)	Material dated	Dating method	Laboratory No.	Date (^{14}C yr BP)	$\delta\ ^{13}C$ (‰)	Date (Cal yr BC/AD)
-0.5		Year of collection				AD 2000
1.7	*Sphagnum*	^{14}C bomb pulse	AAR-7536	-880 ± 32	-28.90	AD 1996-8
7.5	*Sphagnum*	^{14}C bomb pulse	AAR-7537	-997 ± 39	-30.38	AD 1994
14.5	*Sphagnum*	^{14}C bomb pulse	AAR-7538	-1565 ± 37	-29.5	AD 1984-5
21.5	*Sphagnum*	^{14}C bomb pulse	AAR-7539	-2966 ± 29	-27.17	AD 1972-3
25.0	*Sphagnum*	^{14}C bomb pulse	AAR-7540	-3641 ± 30	-28.20	AD 1968
27.3	*Sphagnum*	^{14}C bomb pulse	AAR-7541	-3704 ± 32	-28.31	AD 1962-3
29.6	*Sphagnum*	^{14}C bomb pulse	AAR-7542	-1124 ± 36	-28.76	AD 1957-8
33.1	*Sphagnum*	^{14}C bomb pulse	AAR-7543	-899 ± 34	-28.74	AD 1957
35.4	*Sphagnum*	Conventional ^{14}C	AAR-7544	133 ± 37	-29.20	AD 1676-1779
37.7	*Sphagnum*	Conventional ^{14}C	AAR-7545	87 ± 41	-29.05	AD 1804-1939
45.9	*Sphagnum*	Conventional ^{14}C	AAR-7547	124 ± 37	-28.48	AD 1802-1839
56.3	*Sphagnum*	Conventional ^{14}C	AAR-7549	97 ± 34	-25.59	AD 1805-1935
65.6	*Sphagnum*	Conventional ^{14}C	AAR-7551	138 ± 37	-26.22	AD 1670-1780

Table 3.
Radiocarbon age dates (conventional ^{14}C years B.P.) and calibrated ages (calendar years B.P.) obtained from from bulk peat samples and *Sphagnum* moss in selected samples from the Sifton Bog profile (Calendar dates calculated from Niklaus et al. 1992 (ETH) and Stuiver et al. 1993 (Hd)).

Average depth (cm)	Material dated	Dating method	Laboratory No.	Date (14C yr BP)	$\delta\ ^{13}C$ (‰)	Date (Cal yr BC/AD)
-0.5		Year of collection				AD 2000
0.5	*Sphagnum*	^{14}C bomb pulse	ETH - 26273	-785 ± 45	-32.0 ± 1.2	AD 1999-2000
4.8	*Sphagnum*	^{14}C bomb pulse	ETH - 26274	-1050 ± 45	-32.8 ± 1.2	AD 1992-3
6.9	*Sphagnum*	^{14}C bomb pulse	ETH - 26275	-1580 ± 50	-30.3 ± 1.2	AD 1985
9.0	*Sphagnum*	^{14}C bomb pulse	ETH - 26276	-2025 ± 50	-29.5 ± 1.2	AD 1979-80
11.2	*Sphagnum*	^{14}C bomb pulse	ETH - 26277	-3140 ± 50	-30.0 ± 1.2	AD 1972
13.3	*Sphagnum*	^{14}C bomb pulse	ETH - 26278	-3345 ± 45	-28.7 ± 1.2	AD 1962-3
15.4	*Sphagnum*	^{14}C bomb pulse	ETH - 26279	-1460 ± 55	-28.2 ± 1.2	AD 1958-9
17.5	*Sphagnum*	Conventional ^{14}C	ETH - 26280	70 ± 50	-30.1 ± 1.2	AD 1804-1937
22.8	*Sphagnum*	Conventional ^{14}C	ETH - 26281	175 ± 55	-31.1 ± 1.2	AD 1656-1891
36.7	*Sphagnum*	Conventional ^{14}C	ETH - 26282	105 ± 45	-33.4 ± 1.2	AD 1802-1939
51.5	*Sphagnum*	Conventional ^{14}C	ETH - 26283	105 ± 45	-28.6 ± 1.2	AD 1802-1939
66.4	*Sphagnum*	Conventional ^{14}C	ETH - 26284	25 ± 45	-29.1 ± 1.2	AD 1813-1925
66.4+	Bulk peat sample	^{14}C decay counting	Hd - 21686	206 ± 24		AD 1738-1805

Table 4.
Radiocarbon age dates (conventional ^{14}C years B.P.) and calibrated ages (calendar years B.P.) obtained from bulk peat samples and *Sphagnum* moss in selected samples from the Luther Bog profile (Calendar dates calculated from Niklaus et al. 1992 (ETH) and Stuiver et al. 1993 (Hd)).

Average depth (cm)	Material dated	Dating method	Laboratory No.	Date (^{14}C yr BP)	$\delta^{13}C$ (‰)	Date (Cal yr BC/AD)
-0.5		Year of collection				AD 2000
6.7	*Sphagnum*	^{14}C bomb pulse	ETH - 26042	-1065 ± 45	-23.0 ± 1.2	AD 1992-1993
9.1	*Sphagnum*	^{14}C bomb pulse	ETH - 26043	-1030 ± 45	-19.5 ± 1.2	AD 1993
12.7	*Sphagnum*	^{14}C bomb pulse	ETH - 26044	- 1985 ± 45	-23.1 ± 1.2	AD 1979-1980
15.2	*Sphagnum*	^{14}C bomb pulse	ETH - 26045	-3980 ± 40	-27.3 ± 1.2	AD 1967
17.6	*Sphagnum*	^{14}C bomb pulse	ETH - 26046	-1470 ± 45	-29.9 ± 1.2	AD 1958-9
20.0	*Sphagnum*	^{14}C bomb pulse	ETH - 26047	-480 ± 45	-29.9 ± 1.2	AD 1956
24.9	*Sphagnum*	Conventional ^{14}C	ETH - 26049	245 ± 45	-26.8 ± 1.2	AD 1617-1692
44.3	*Sphagnum*	Conventional ^{14}C	ETH - 26052	220 ± 50	-30.0 ± 1.2	AD 1631-1822
51.6	*Sphagnum*	Conventional ^{14}C	ETH - 26053	315 ± 50	28.7 ± 1.2	AD 1459-1666
68.6	*Sphagnum*	Conventional ^{14}C	ETH - 26055	630 ± 50	-30.1 ± 1.2	AD 1290-1408
83.6	Bulk peat sample	Conventional ^{14}C	ETH - 25977	1130 ± 50	-28.3 ± 1.2	AD 800-1010
96.1	Bulk peat sample	Conventional ^{14}C	ETH - 25978	1310 ± 50	-31.6 ± 1.2	AD 649-829
116.9	Bulk peat sample	Conventional ^{14}C	ETH - 25941	1670 ± 50	-21.6 ± 1.2	AD 317-532
139.9	Bulk peat sample	Conventional ^{14}C	ETH - 25942	2150 ± 50	-21.9 ± 1.2	260-44 BC
160.7	Bulk peat sample	Conventional ^{14}C	ETH - 25943	2280 ± 50	-23.4 ± 1.2	328-200 BC
216.9	Bulk peat sample	Conventional ^{14}C	ETH - 25944	2825 ± 50	-25.9 ± 1.2	1088-890 BC
248.4	Bulk peat sample	^{14}C decay counting	Hd - 21554	3486 ± 24		1834-1739 BC
268.4	Bulk peat sample	^{14}C decay counting	Hd - 21553	3557 ± 37		1979-1855 BC
308.6	Bulk peat sample	Conventional ^{14}C	ETH - 25945	3935 ± 55	-24.5 ± 1.2	2508-2275 BC
366.3	Bulk peat sample	Conventional ^{14}C	ETH - 25946	4930 ± 60	-29.3 ± 1.2	3810-3629 BC
427.4	Bulk peat sample	Conventional ^{14}C	ETH - 25947	5815 ± 60	-26.2 ± 1.2	4807-4520 BC
498.2	Bulk peat sample	Conventional ^{14}C	ETH - 25948	6720 ± 65	-27.3 ± 1.2	5686-5474 BC
535.1	Bulk peat sample	^{14}C decay counting	Hd - 21694	8175 ± 71		7355-7052 BC

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Chapter 2

Atmospheric mercury accumulation rates between 5900 and 800 cal yr BP in the High Arctic of Canada recorded by peat hummocks

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Abstract

Geochemical studies of two peat hummocks from Bathurst Island, Nunavut reveal substantial inputs from soil dust (titanium), marine aerosols (bromine) and mineral-water interactions (uranium). Mercury, however, was supplied to these peat mounds exclusively by atmospheric deposition. Mercury concentration measurements and age dating of the peat profiles indicate rather constant natural "background" mercury flux of ca. 1 microgram per square meter per year from 5900 to 800 calibrated year BP. These values are well within the range of the mercury fluxes reported from other Arctic locations, but also by peat cores from southern Canada which provide a record of atmospheric Hg accumulation extending back to eight thousand years. Thus, pre-anthropogenic Hg fluxes in the Arctic were not significantly different from atmospheric Hg fluxes in the temperate zone. In pre-industrial times, therefore, the High Arctic was no more important as a sink for global atmospheric mercury than the temperate zone.

1. Introduction

Mercury (Hg) is primarily of interest as a long-range, persistent and potentially toxic pollutant because of its ability to bioaccumulate in the food chain in the form of methylmercury (Morel *et al.*, 1998). Environmental mercury levels have increased considerably since the on-set of the industrial age. Mercury is now present in a variety of environmental media in many parts of the world at levels that adversely affect humans and wildlife. Even regions such as the Arctic, with no significant mercury releases, are contaminated due to transcontinental and global atmospheric transport of mercury (AMAP, 1998). The present state of Hg contamination of the Arctic environment has been summarized in comprehensive reports (AMAP, 2002; NCP, 2003). Some of the main features of these reports are as follows: some Arctic population groups are among the most exposed populations in the world to certain environmental contaminants; contaminant levels in some Arctic birds and mammals exceed some thresholds associated with reproductive, immunosuppressive, and neurobehavioral effects; mercury seems to be increasing in aquatic sediments and in marine mammals.

Several hypotheses have been addressed in the recent past to explain the mercury contamination of the Arctic environment. For instance, it has been suggested that, as originally conceived for some volatile organic compounds (Wania *et al.*, 1993), there may be a latitudinal fractionation of Hg (Mackay *et al.*, 1995), which contributes to the continued mobilization of these compounds from warmer to colder climates (i.e. “cold condensation”), resulting in natural geographical gradients in the atmospheric Hg deposition rates. Mercury, especially oxidized forms of airborne Hg, may condense over the Polar Regions due to cold climate which predicts naturally high deposition rates in Polar Regions where Hg is ultimately deposited and stored. More recent discoveries suggest that the Arctic experiences enhanced deposition of Hg due to related mercury depletion events (MDEs) which are observed to occur each spring (Schroeder *et al.*, 1998). Gaseous elemental mercury (Hg°) in the Arctic atmosphere undergoes photochemically driven oxidation during polar sunrise, probably by reactive halogens, and is converted to reactive gaseous mercury (RGM) which rapidly deposits on snow. Some of the mercury deposited on the snow is released to the environment at snowmelt, becoming available just as the Arctic ecosystem becomes biologically active in springtime. This enhanced deposition may mean that the Arctic plays a previously unrecognised role as an important sink in the global Hg cycle (Lindberg *et al.*, 2002). However, evidence suggests that this is a recent phenomenon that may occur throughout the Polar Regions. The impact of climate change on Hg dynamics is the third emerging issue. Changes in physical climate in the past decades might actually have a greater impact on the Arctic Hg cycle than changes in global emissions. Several data sets suggest that there has been a recent increase in Hg levels in Arctic biota despite a 20 year decrease in global atmospheric mercury emissions of 30% (Pacyna *et al.*, 2002). Environmental changes such as reduced sea ice cover may have made mercury pathways more efficient in recent years by increasing transport of photooxidants and production of reactive halogens in the Arctic. Although poorly understood, these processes may be the chief mechanism for transferring atmospheric Hg to the Arctic food chain.

Time series derived from Arctic lake sediments are relatively scarce, but provide evidence of increasing Hg accumulation rates in many but not all areas of the Arctic (Hermanson, 1998; Lockhart *et al.*, 1998; Bindler *et al.*, 2001). The increases have been interpreted as evidence of recent increases in atmospheric emission and deposition of mercury from human activities. There are a number of reasons to critically examine these interpretations. For example, these time series by no means extend far enough back in time to determine extent of natural variations in atmospheric mercury deposition rates and the causes to which they are due. Natural variability in the deposition of atmospheric mercury can be only obtained using long-term records of mercury deposition which can help

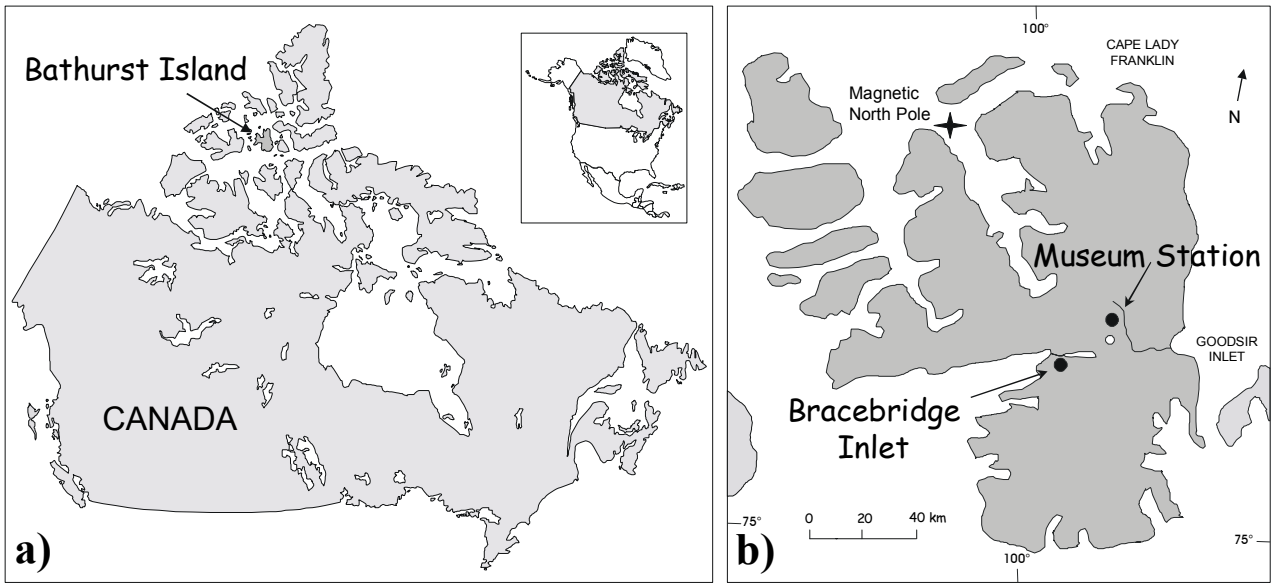


Fig. 1. Bathurst Island in the High Arctic of Canada (a). Location of the coring sites of Bracebridge Inlet and Museum Station in Polar Bear Pass National Wildlife Areas indicated by the black points (b). The cores were taken in July 2000. Details are available in the Post Expedition Field Report (Goodsite et Shotyk, 2001).

us to understand transport processes and delivery pathways.

Recent studies have shown that minerotrophic (i.e. groundwater-fed) peatlands may provide meaningful, reliable records of atmospheric mercury deposition (Roos-Barraclough *et al.*, 2003; Shotyk *et al.*, 2003). In this study, peat cores collected from minerogenic peat deposits on Bathurst Island (75 degrees of north latitude) in the High Arctic of Canada were used as archives of atmospheric mercury deposition.

Here, we present the first comprehensive long-term record of atmospheric Hg accumulation rates in dated peat deposits for the High Arctic of Canada. In particular, focus is directed toward pre-anthropogenic rates of atmospheric Hg deposition. The record obtained from two sites on Bathurst Island is interpreted and compared to records from other location in the Arctic as well as from temperate zone in North America and Europe in order to try to understand the role which is played by the Arctic on the geochemical cycle of mercury.

2. Material and methods

2.1. Study sites

A number of peat deposits on Bathurst Island (Fig. 1a) were studied in detail. Most of the necessary geological background, including description of peat depth and stratigraphy and some ^{14}C age dates, was already available in extensive reports and publications (Blake, 1964; Blake, 1974; Blake, 1974). Two sampling sites were selected (Fig 1b): Bracebridge Inlet (75° 38’50 N, 99° 20’00 W) and Museum Station (75° 45’00 N, 98° 18’00 W) in Polar Bear Pass National Wildlife Area are approximately 20 kilometres apart. The coring site at Bracebridge Inlet (BI) took place at the apex of a peat polygon, with an elevation of approximately 130 meters above sea level, located 5 kilometres from the ocean. The surface layer of the peat deposit was fractured into large blocks along gullies, probably resulting from the melting of this layer. Comparable features have been frequently observed at the advanced stage of this typical Arctic peatland (AMAP, 1998). The sampling site at Museum Station (MS), at

an elevation of approximately 90 meters above sea level, located more inland, is a peat mound with living vegetation at the top. It was not possible to determine in the field if the vegetation growing on the hummock today was representative of plants which formed the hummock, or if this was simply modern vegetation growing on a dried-out ancient hummock.

The climate in the Bathurst Island region today has commonly been described as polar maritime desert, with sparse vegetation, cold temperatures, moderate wind speeds, and low precipitation (Maxwell, 1981; Edlund *et al.*, 1989). Mean January temperatures are -32.1°C and -33.4°C recorded respectively at Resolute (on southern Cornwallis Island) and at Rea Point (on eastern Melville Island). July mean temperatures for the same stations are +6.8°C and +4.1°C. Prevailing winds are predominantly from the northwest and/or parallel to the inter-island channels. Total annual precipitation ranges from 60 to 130 mm. Half of the Arctic maritime precipitation falls as snow or rain from July to September. On average, there are 74 days of above freezing temperatures each year. Land areas are most consistently free of snow cover between late June and early August. Polar Bear Pass is a 5 km wide, 20 km long valley, formed by a prominent east-west trending thrust fault. Ridges bounding the valley consist of sedimentary rocks; sandstone, dolomite, shale, and limestones; ranging in age from Ordovician to Devonian, although the floor valley and the lower southern slopes are covered with Quaternary marine silts (Sheard *et al.*, 1983).

2.2. Sample collection, preparation and analysis

At BI, the non-frozen layer was cut away as blocks from the surface by hand using a serrated, stainless steel knife. After removing and wrapping the blocks, the underlying frozen layer was collected using a motorized SIPRE type-drilling machine (Noernberg *et al.*) built especially for the expedition. At BI, 90 cm of peat was recovered: the first 14 cm as blocks of non-frozen peat, and the other 76 cm as cores of frozen peat. At MS, only 70 cm of peat was found: 30 cm blocks of non-frozen peat were collected from the surface, and 30 cm was recovered as frozen peat core by drilling. All samples were frozen at -18°C at the Polar Continental Shelf Project for storage and subsequent transportation to Berne.

In the laboratory, cores were cut (while frozen) into 1 cm slices using a stainless steel band saw. The outside edges of each slice were cut away, dried overnight at 105°C in a drying oven and milled in a centrifugal mill with titanium sieve. The powder samples (used for XRF and ^{14}C analyses) were manually homogenized and stored in airtight plastic beakers. One gram of dried, milled powder was analysed for 22 selected major and trace elements, including rubidium (Rb), zirconium (Zr), potassium (K), bromine (Br), chlorine (Cl), selenium (Se), uranium (U) and yttrium (Y) using the EMMA XRF spectrometer (Cheburkin *et al.*, 1996). Titanium (Ti) was measured using the new TITAN XRF spectrometer for Ti (Cheburkin *et al.*). The instruments were calibrated and checked for accuracy and precision as described elsewhere (Roos-Barraclough *et al.*, 2002). Four plugs were subsampled from the middle of each slice with a sharpened stainless steel tube (16 mm diameter). Three of them were used for Hg analyses. These were air-dried overnight at room temperature in a class 100 laminar flow clean air cabinet. Mercury concentrations were measured by atomic absorption spectrometry (AAS) in solid peat samples (Salvato *et al.*, 1996) using the LECO AMA 254 as described in detail in Roos-Barraclough et al. (2002). The instrument was calibrated using liquid standards prepared from a Merck 1000 mg/l standard solution. Precision was determined by measuring replicates of international standard reference materials, either NIST 1515 (Apple Leaves) or NIST 1547 (Peach Leaves), after every 10th sample. The average of theses analyses are 33.0 ± 0.8 ng g^{-1} (n=32) and 40.3 ± 2.5 ng g^{-1} (n=33) which are in excellent agreement with the certified values of 31 ± 7 ng g^{-1} and 44 ± 4 ng g^{-1} respectively. The mean relative standard deviation of the determination of Hg within a peat slice was 11.7% (n=3) which is primarily a reflection of

the heterogeneity of the slices. The fourth plug was use to determine the dry bulk density. The height of each plug was measured to an accuracy of 0.1 mm and the volume calculated. After recording wet weights, plugs were dried at 105°C overnight and the dry mass weighted to 1 mg.

2.3. Age dating of the peat

Twenty samples from the upper layers of both cores have been studied with respect to their botanical content to try to select macrofossils of Sphagnum moss. The conclusion is that the samples are relatively uniform and well decomposed, consisting of 70-80% small debris, 10-30% of sedge roots and a few have small woody twigs. Only two moss stems have been found in the samples studied which look like Tomenthypnum nitens (D. Vitt, personal communication). It was impossible to identify enough macrofossils for age dating. Therefore, selected powdered bulk samples of both cores were age dated using ^{14}C Accelerator Mass Spectrometry (AMS) at Århus University, Denmark and at the ETH Zurich. The bulk samples have been given a standard base-acid-base treatment prior to dating.

Age dates of bulk peat samples younger than AD 1950 were obtained using 14C by directly comparing the absolute concentration of ^{14}C in the sample to the "bomb pulse curve of ^{14}C" as described in detail elsewhere (Goodsite *et al.*, 2001).

The other ^{14}C calibrated ages were calculated using the Seattle CALIB program (Stuiver *et al.*, 1993) version 4.0 (Århus University) and the program calibETH (ETH Zurich). The calibration curves used for the calibration were taken from Stuiver et al. (1998) and Niklaus et al. (1992) respectively. Due to the irregular multimodal shapes of probability distribution of part of these dates, it was decided to present the results in the form of 95% confidence interval (2σ-ranges) of the highest probability (narrowest 95% confidence intervals). The results of calibration of individual dates are presented in Table 1 & 2.

3. Results

3.1. Peat chronology

The 14 radiocarbon dates for the Bracebridge Inlet core are stratigraphically consistent. An age-depth model was constructed from the dated point (Table 1) using a 2nd degree polynomial regression (figure 2a). Below approximately 35 cm, there is no increase in age with depth. This phenomenon is due to the unique evolution of peat polygon which is typical of Arctic peat formation.

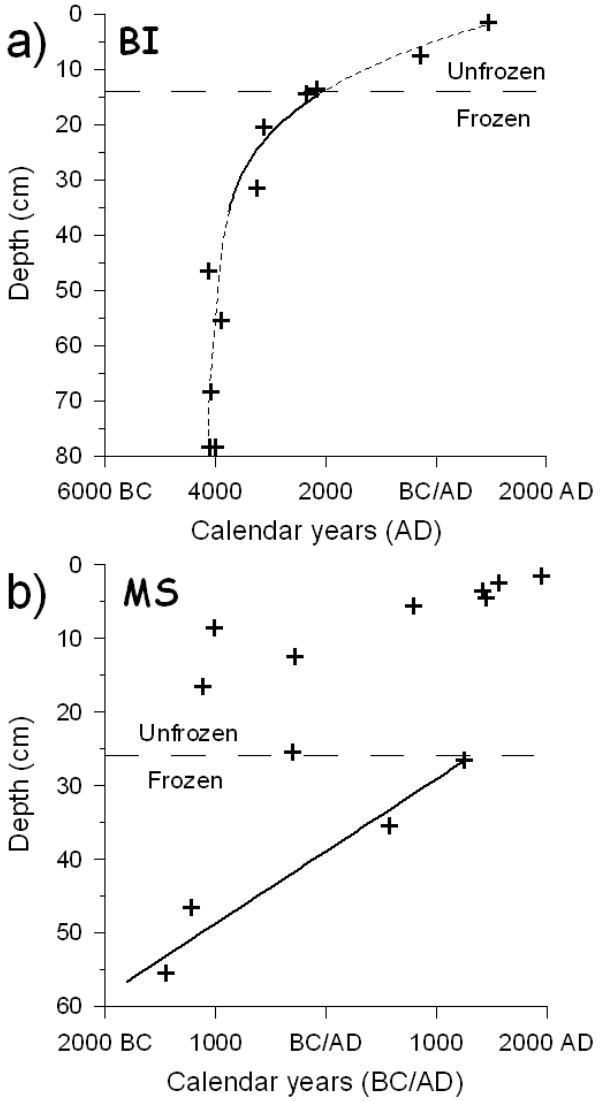


Fig. 2. Age-depth relationships constructed for peat cores at Bracebridge Inlet (a) and Museum Station (b). The bold line show the selected sections of the age-depth relationships which provide a composite paleoenvironmental record from 5900 to 800 calibrated years

Table 1.
Radiocarbon age dates (conventional ^{14}C years BP) and calibrated ages (calendar years AD/BC) obtained from bulk peat samples for the Bracebridge Inlet peat profile (Calendar dates calculated from Niklaus et al. 1992 (ETH) and Stuiver et al. 1998 (AAR)).

Average depth (cm)	Material dated	Dating method	Laboratory No.	Date (^{14}C yr BP)	$\delta^{13}C$ (‰)	Date (Cal yr AD/BC)
1.5	Bulk peat sample	Conventional ^{14}C	AAR-7497	1'090 ± 41	-27.22	**AD 896-998**
7.5	Bulk peat sample	Conventional ^{14}C	ETH-25935	2'240 ± 50	-24.0 ± 1.2	**BC 393-184**
13.5	Bulk peat sample	Conventional ^{14}C	ETH-25936	3'755 ± 55	-29.0 ± 1.2	**BC 2326-2012**
14.5	Bulk peat sample	Conventional ^{14}C	ETH-25937	3'900 ± 55	-26.1 ± 1.2	**BC 2493-2197**
20.5	Bulk peat sample	Conventional ^{14}C	AAR-7498	4'436 ± 42	-26.76	**BC 3263-2973**
31.5	Bulk peat sample	Conventional ^{14}C	ETH-25974	4'585 ± 60	-31.0 ± 1.2	**BC 3386-3093**
43.5	Bulk peat sample	Conventional ^{14}C	ETH-25975	4'365 ± 60	-29.9 ± 1.2	**BC 3109-2878**
46.5	Bulk peat sample	Conventional ^{14}C	ETH-25938	5'305 ± 60	-24.7 ± 1.2	**BC 4255-3985**
55.5	Bulk peat sample	Conventional ^{14}C	ETH-25939	5'110 ± 60	-25.5 ± 1.2	BC 4003-3772
68.5	Bulk peat sample	Conventional ^{14}C	ETH-25940	5'230 ± 60	-24.4 ± 1.2	BC 4228-3947
78.5	Bulk peat sample	Conventional ^{14}C	ETH-25976	5'180 ± 65	-32.0 ± 1.2	BC 4104-3900
78.5	Bulk peat sample	Conventional ^{14}C	AAR-7499	5'295 ± 50	-26.79	BC 4223-4001

Table 2.
Radiocarbon age dates (conventional ^{14}C years BP) and calibrated ages (calendar years AD/BC) obtained from bulk peat samples for the Museum Station peat profile (Calendar dates calculated from Niklaus et al. 1992 (ETH) and Stuiver et al. 1998 (AAR)).

Average depth (cm)	Material dated	Dating method	Laboratory No.	Date (^{14}C yr BP)	$\delta^{13}C$ (‰)	Date (Cal yr AD/BC)
0+	Bulk peat sample	Conventional ^{14}C	ETH-26003	540 ± 55	-25.9 ± 1.2	AD 1370-1450
1.5	Bulk peat sample	^{14}C bomb pulse	AAR-7494	-312 ± 36	-26.37	AD 1956
2.5	Bulk peat sample	Conventional ^{14}C	ETH-25925	305 ± 50	-30.0 ± 1.2	AD 1467-1671
3.5	Bulk peat sample	Conventional ^{14}C	ETH-25926	525 ± 50	-29.9 ± 1.2	AD 1378-1465
4.5	Bulk peat sample	Conventional ^{14}C	ETH-25927	475 ± 50	-28.9 ± 1.2	AD 1394-1517
5.5	Bulk peat sample	Conventional ^{14}C	ETH-25928	1'210 ± 50	-26.4 ± 1.2	AD 690-897
8.5	Bulk peat sample	Conventional ^{14}C	ETH-25929	2'855 ± 55	-25.8 ± 1.2	BC 1139-893
12.5	Bulk peat sample	Conventional ^{14}C	ETH-25930	2'225 ± 50	-29.3 ± 1.2	BC 392-164
16.5	Bulk peat sample	Conventional ^{14}C	ETH-25931	2'920 ± 55	-30.8 ± 1.2	BC 1263-973
25.5	Bulk peat sample	Conventional ^{14}C	ETH-25932	2'300 ± 55	-25.9 ± 1.2	BC 423-192
26.5	Bulk peat sample	Conventional ^{14}C	AAR-7495	788 ± 42	-25.61	**AD 1218-1280**
35.5	Bulk peat sample	Conventional ^{14}C	ETH-25933	1'495 ± 50	-25.9 ± 1.2	**AD 493-653**
46.5	Bulk peat sample	Conventional ^{14}C	ETH-25934	3'005 ± 50	-25.3 ± 1.2	**BC 1329-1112**
55.5	Bulk peat sample	Conventional ^{14}C	AAR-7496	3'175 ± 43	-27.22	**BC 1502-1409**

The peatland evolved from a low-centre polygon with high organic accumulation rate in a wet environment to a high-centre polygon with lower organic accumulation rate in a dryer environment which eventually led to the cessation of the peat growth. This evolution may be related to the combination of two phenomena: a change to cooler/dryer climate and the advanced stage of lowland polygon development (Short *et al.*, 1980). Because there is no significant difference in the age dates below 35 cm, organic matter accumulation during the "low centre" stage of the peat formation must have included physical addition of organic matter from the sides of the pool, in addition to plant growth. As a consequence, this section of the peat core (i.e. below 35 cm) cannot be used in any paleoenvironmental reconstruction.

At MS, the radiocarbon dates are not progressively older with depth (Table 2). Above 26 cm depth in the unfrozen section of the profile, dates are chaotic, possibly reflecting inputs of older organic material into desiccation cracks. This may have been caused by erosion or alteration of surrounding organic accumulation which was redeposited in the peat deposit by aeolian processes thereby incorporating older carbon in more recent sediment. Alternatively, the phenomenon may have been caused by the perturbation of stratigraphic horizons related to permafrost dynamics (Gajewski *et al.*, 1995). Therefore, this section of the MS peat deposit (i.e. above 26 cm) is not suitable for a paleoenvironmental reconstruction. From 26 cm to 57 cm depth, four consistent and therefore reliable age dates were obtained (Table 2), allowing an age-depth model to be reconstructed using a first-degree polynomial regression (figure 2b).

Taken together, the two selected peat sections from Bathurst Island (14-35 cm from BI and 26-57 cm from MS) provide a composite paleoenvironmental record from 5900 to 800 calibrated year BP.

3.2. Ash, moisture contents and lithogenic elements concentrations

The moisture content (Fig. 3) for both profiles is very different in the upper unfrozen layers compared to the underlying frozen layers. Specifically, it averages respectively 45 and 55% in the upper unfrozen parts and 75 and 90% in the lower frozen parts of MS and BI profiles. Similar to the zone of water table fluctuation, the limit between unfrozen peat and permafrost-affected may peat represent the interface between aerobic (above) and anaerobic (below) conditions.

The ash content and concentration of lithogenic elements provide an overview of the trophic status for both profiles. At BI (Fig 3a), ash content exhibits a C-shape distribution, being highest in the surface layers (0-14 cm depth, up to 65%) and in the bottom layers overlying the mineral substrate (82-87 cm depth, up to 82%). In between, the inorganic fraction varied between 45 and 84%, presenting an exceptional zone of elevated of ash content at 45 cm depth. At MS (Fig 3b), ash content exhibits a quasi-linear distribution throughout the profile ranging between 31 and 81%. These values are typical of minerotrophic Arctic peat deposits and reflect low rates of organic matter accumulation, but high rates of dust deposition.

The distribution of the elements K, Rb, Ti and Zr (Fig. 4a) in BI profile closely follows ash distribution, being highest in the top and basal peat layer, and low between (2 plateaux) with a peak in concentration around 45 cm depth. These elements are primarily associated with the inorganic fraction, e.g. they are present in the mineral fraction such as clay, mica and feldspars. Their concentrations can be explained in terms of mineral matter abundance and mainly reflect the chemical composition of local rocks and soils. The abundance of K, Rb, Ti and Zr in the MS profile (Fig. 4b) is comparable to these in BI profile. Moreover, the distribution of those elements in the MS profile mirror the ash content profile, suggesting that as for BI, the elemental distribution in the MS profile is mainly controlled by the trophic conditions in the peatland. In contrast, the halogens, in

particular Br, display a negative correlation with ash, thus suggesting a strong affinity with the organic fraction (Fig. 5).

3.3. Hg concentrations

At BI (Fig. 3a), total Hg ranges from 30 to 76 ng g^{-1} with a maximum concentration at the surface. At MS, total Hg ranges (Fig. 3b) from 25 to 75 ng g^{-1} with the largest increase in Hg beginning at 10 cm. The maximum concentration is at the top of the hummock. In the underlying frozen peat, Hg concentrations are relatively uniform (28 ± 4 ng g^{-1}).

To compare those two profiles, and to take in account the difference in bulk density (Fig. 3), the Hg concentrations profiles are corrected for variation in the bulk density and expressed on a volumetric basis. At MS, the Hg concentration increases gradually from 60 cm with 4 ng cm^{-3} to 69 ng cm^{-3} at the surface, representing an increase of 17 times. At BI, there is a relatively constant Hg concentration in the deeper layers from 90 cm to 20 cm depth, with an average value of 4 ng cm^{-3}. Following this zone, there is a pronounced increase (ca. 7×) from 6 ng cm^{-3} at 20 cm to 39 ng cm^{-3} at the surface.

4. Discussion

The two most important sources of atmospheric aerosols to the peat hummocks are mineral dust from weathering of crustal rocks and sea salts from oceans. The age dates shown in Fig. 2 show that the unfrozen peat blocks are a mixture of old and young organic material. The moisture contents (Fig. 3) show that these blocks also have been desiccated. For these reasons, the Hg concentrations in the unfrozen, top layers cannot be unambiguously interpreted, and will not be further discussed here.

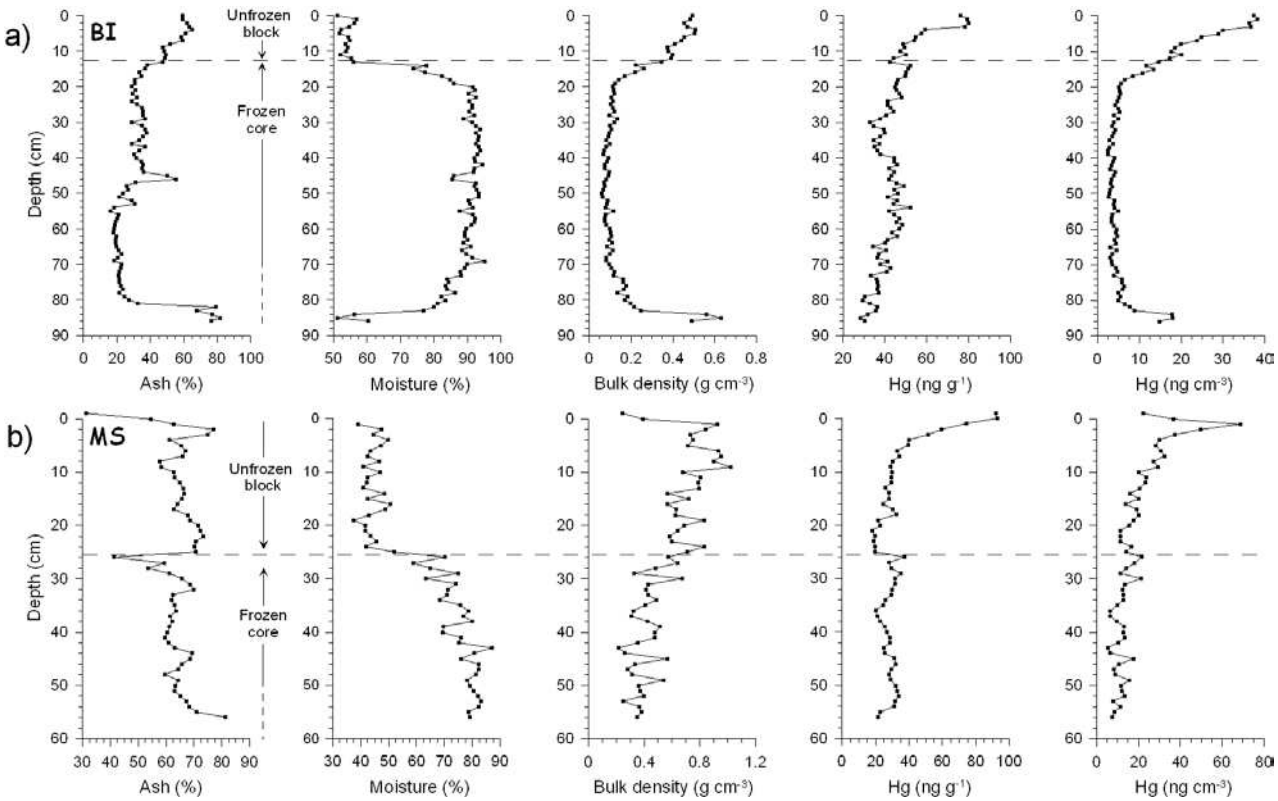


Fig. 3. Ash content, moisture content (%), bulk density (g cm^{-3}), gravimetric (ng g^{-1}) and volumetric (ng cm^{-3}) concentrations of mercury in the peat profiles from Bracebridge Inlet (a) and Museum Station (b).

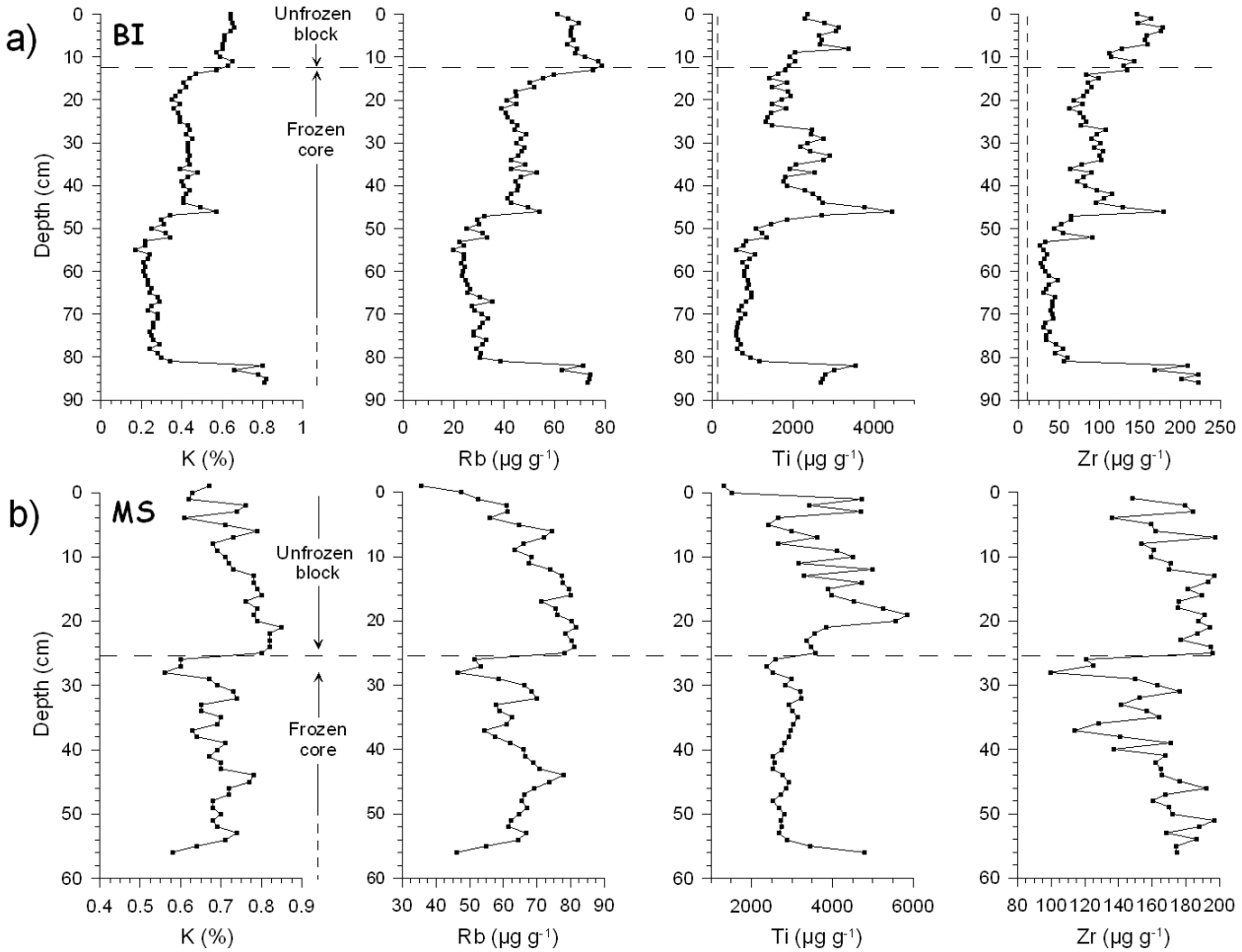


Fig. 4. Concentration profiles of the elements discussed in the text in the Bracebridge Inlet deposit (a) and Museum Station deposit (b). The vertical dash lines indicate the average Ti and Zr concentrations in the ombrotrophic zone of Luther Bog, a continental bog in southern Ontario.

4.1. Atmospheric transport: primary pathway of mercury deposition

Atmospheric soil dust

The distribution of the conservative, lithogenic elements such as Ti and Zr, is associated with the mineral fraction and reflects the abundance of mineral material in the peat core. The concentrations of these elements in the BI core indicate some change in atmospheric soil dust fluxes, organic matter loss during decomposition or both. However, comparing the concentration profiles of Ti and Zr with that of Hg shows that mineral dust inputs have not affected Hg deposition. For example, the notable peak in ash content, Rb, Zr, Ti and K concentration at a depth of ca. 46 cm has no corresponding peak in Hg concentration (Fig. 3). The Hg concentrations are independent of the amount of mineral matter in the peat cores, clearly indicating that the variation in mineral matter supply is not a viable explanation of the magnitude of the variation in Hg concentration with depth. This corroborates results of previous studies (Roos-Barraclough *et al.*, 2003; Shotyk *et al.*, 2003) showing that even in predominantly minerotrophic peatlands, Hg may be supplied independently of soil dust particles.

Marine aerosols

Bromine, chlorine and selenium concentrations in the peat profiles from Bathurst Island (Fig. 5) are elevated compared

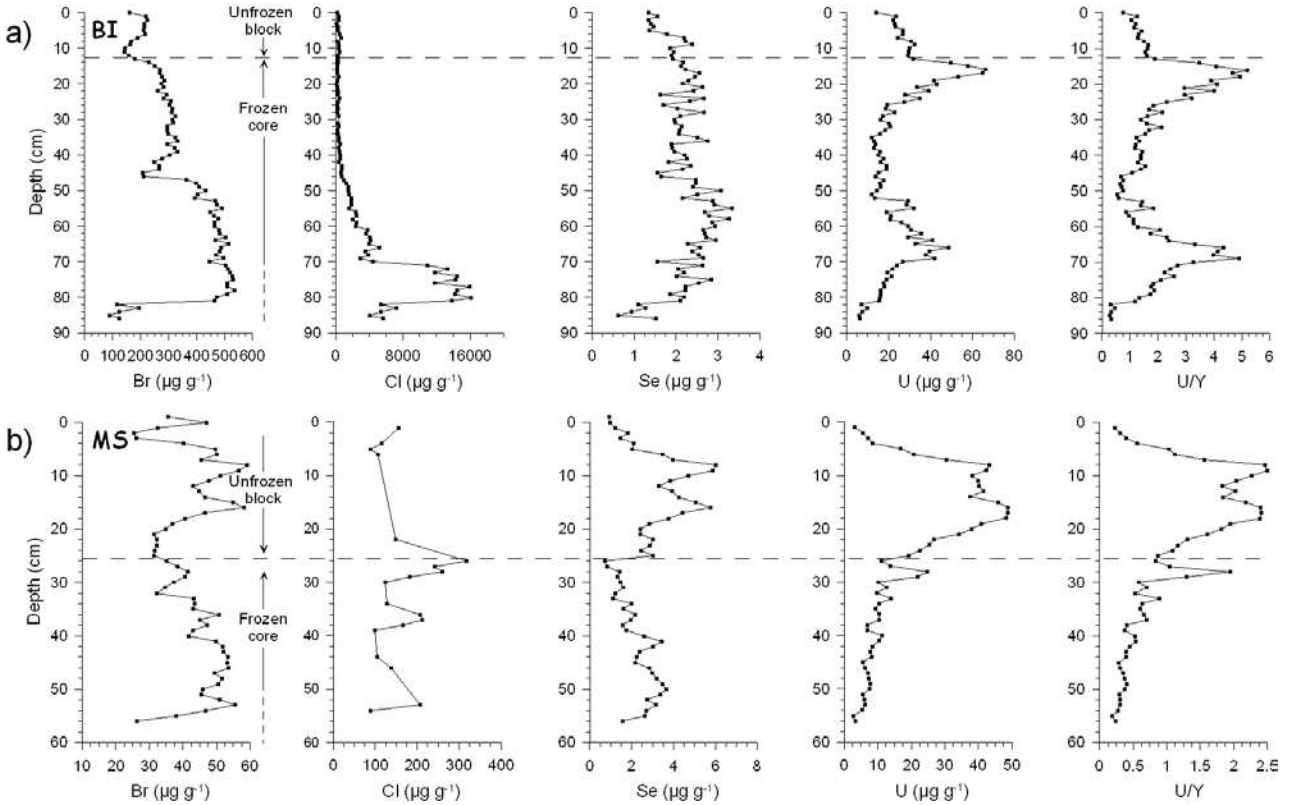


Fig. 5. Concentrations of bromine, chlorine, selenium, uranium (µg g^{-1}), and U/Y ratio for the peat profiles of Bracebridge Inlet (a) and Museum Station (b) peat deposits. Note that the peaks in U concentrations and U/Y ratio do not correspond to changes in gravimetric either volumetric Hg concentrations.

to ombrotrophic continental peat bogs from southern Ontario (Givelet *et al.*, 2003) and central Europe (Roos-Barraclough *et al.*, 2002). While elevated concentrations in Br, Cl and Se reveals the influence of sea salt spray at both locations (Chagué-Goff *et al.*, 1996), this may be a natural source of Hg to the cores and should be considered further.

The ranges in concentrations of Se in the peats are similar at two sites. On average, Se concentrations are not significantly different and are about twice that of the southern Ontario peat profiles (Givelet *et al.*, 2003). In contrast, the peat deposit at BI contains on average eight times more bromine than at MS. Compared to the southern Ontario bogs, the Br concentrations at BI and MS are twenty-two and three times greater respectively. Moreover, the average Cl concentration in the layers above 70 cm at BI exceeds by more than four times the highest Cl concentration at MS. Taken together, the elevated concentrations of Cl and Br in the BI core compared to the MS core reflects elevated inputs of dissolved marine salts because of the proximity of BI site to the ocean (Fig 1).

Below 70 cm depth at BI, chlorine is thought supplied not only by marine aerosols but also by upward diffusion into the peat column from the underlying marine silts; evidence of this is provided by the Cl/Br ratio (not shown). Despite the natural supply of marine salts from sea spray being much greater at BI compared to MS, the average Hg concentrations in the peats are not significantly different between the two sites (Fig 3). The lack of correspondence between the Br, Cl, Se concentrations and Hg concentrations in the peat profiles from Bathurst Island suggests that Hg concentrations were not controlled by inputs of marine aerosols. While sea salt spray may be a natural source of Hg to the cores, the relative importance of this source must have been relatively small and constant over time.

4.2. Natural geochemical processes and their effects on the Hg concentration profiles

Diagenetic processes

It has been suggested that processes in minerogenic peat deposits may contribute to Hg enrichments in peat layers. Minerotrophic peats from southern Greenland, for example, are enriched in Hg, Se, Cu and U which are all redox-sensitive elements (Shotyk *et al.*, 2003). Uranium (Fig. 5) is highly enriched in both peat profiles from Bathurst Island, relative to its abundance in superficial materials from the Island which range from 1.3 to 8.3 ppm with mean of 4.2 ppm (Bednarski, 1999). Uranium concentrations are even elevated in the upper unfrozen layer of MS, reaching more than 45 ppm and are enriched far out of proportion with ash (Fig. 3). Normalising the U concentrations to the Y, a conservative lithogenic element, the U/Y ratio illustrates the pronounced enrichment of this metal with decreasing depth. Uranium in BI profile exhibits two strong enrichments, one immediately below the permafrost, and the other much deeper in the profile, reaching up to 60 and 50 ppm respectively. The U/Y ratio reveals the shape of the U enrichment (Fig. 5). Uranium is commonly enriched in anoxic, minerotrophic peat due to reductive dissolution of U (VI) to U (IV). Uranium (Fig. 5) and mercury (Fig. 3) concentrations profiles at both sites of Bathurst Island show that these elements behave very differently. The U/Y profiles reveal highly intense and variable mineral-water interactions, but the processes have not noticeably affected the Hg concentration profiles. The Hg concentration profiles therefore, have not been influenced by mineral-water interactions. Instead, the Hg concentrations profiles can best be explained by atmospheric deposition.

Effect of permafrost on mercury profiles

Chagué-Goff and colleagues (1997) have shown that permafrost may greatly influence peat geochemistry in perennially frozen peatlands and that variations of the depth to permafrost may lead to mobilisation of some elements and enrichments of others immediately above the permafrost table. Here, however, we consider only mercury concentrations in those sections of the peat profiles which are permanently frozen.

Taken together, the available evidence suggests that:

i) the Hg concentrations measured in the frozen section of the peat cores were supplied exclusively by the atmosphere,
ii) that there is no significant diagenetic remobilisation of Hg due to mineral-water interactions,
iii) that these minerotrophic peat profiles from Bathurst Island have faithfully preserved a record of atmospheric Hg accumulation dating from pre-industrial times.

4.3. Atmospheric Hg accumulation rates in the High Arctic of Canada

To estimate the atmospheric fluxes, Hg accumulation rates (AR) expressed in $\mu g\ m^{-2}\ yr^{-1}$ can be calculated using:

$$AR = 10 \times [Hg] \times BD \times GR \quad (i)$$

where [Hg] is the Hg concentration ($ng\ g^{-1}$), BD the bulk density of the peat ($g\ cm^{-3}$) and GR is the growth rate ($cm\ yr^{-1}$). Given the ages calculated using the age-depth relationships from selected sections of the BI and MS cores, we estimate that the natural background atmospheric mercury deposition rates on Bathurst Island were approximately 1 $\mu g\ m^{-2}\ yr^{-1}$ (range 0.5 to 1.5 $\mu g\ m^{-2}\ yr^{-1}$) from 4000 calibrated years BC to AD 1200. Assuming that the re-emission of Hg from the bog surface is negligible (Lodenius *et al.*, 1983), these rates reflect the natural range in atmospheric fluxes for this region of the High Arctic. Slight variations in the rates of atmospheric mercury accumulation, both for MS and BI (Fig. 6), may be due mainly to variations in bulk density within individual peat slices rather than changing rates of atmospheric mercury deposition. However, those variations are small with respect to the average atmospheric mercury accumulation rates.

Comparison with other archives of Hg accumulation rates

In all previous studies of Hg deposition in the Arctic environment, natural background accumulation rates of Hg were assumed to be represented by samples dating from pre-AD 1800 or pre-AD 1850 (Hermanson, 1998; Lockhart *et al.*, 1998), or estimated using a downward extrapolation of the modern sediment accumulation rates (Bindler *et al.*, 2001). To date, there is no data on pre-industrial atmospheric Hg deposition rates in ancient, archival materials from the Artic. In contrast, the Bathurst Island peat profiles (Fig. 6) provide the first millennial-scale record of the natural rates of atmospheric mercury accumulation in the High Arctic. Natural mercury accumulation rates from peat deposits on Bathurst Island are comparable to values reported using lake sediments from Cornwallis Island (1.8 µg m^{-2} yr^{-1}) (Lockhart *et al.*, 1998) and from AD 100 to 1850 in west Greenland (1-5 µg m^{-2} yr^{-1}) (Bindler *et al.*, 2001).

The values reported in the present study are within the natural range of Hg accumulation rates recorded by a Swiss peat bog dated from ca. 14500 to 1000 calendar years (Roos-Barraclough *et al.*, 2002; Roos-Barraclough *et al.*, 2003) and for peat samples from southern Greenland dating from 1500 BC to AD 1800 (Shotyk *et al.*, 2003). Moreover, the natural variation in the pre-anthropogenic Hg fluxes in the High Arctic and southern Greenland (0.5 to 1.5 µg m^{-2} yr^{-1}) is well within the range of the corresponding fluxes in southern Ontario (Givelet *et al.*, 2003), north-eastern USA (Roos-Barraclough, 2002), and central Europe (Roos-Barraclough *et al.*, 2002; Roos-Barraclough *et al.*, 2003), where average annual temperature are much higher.

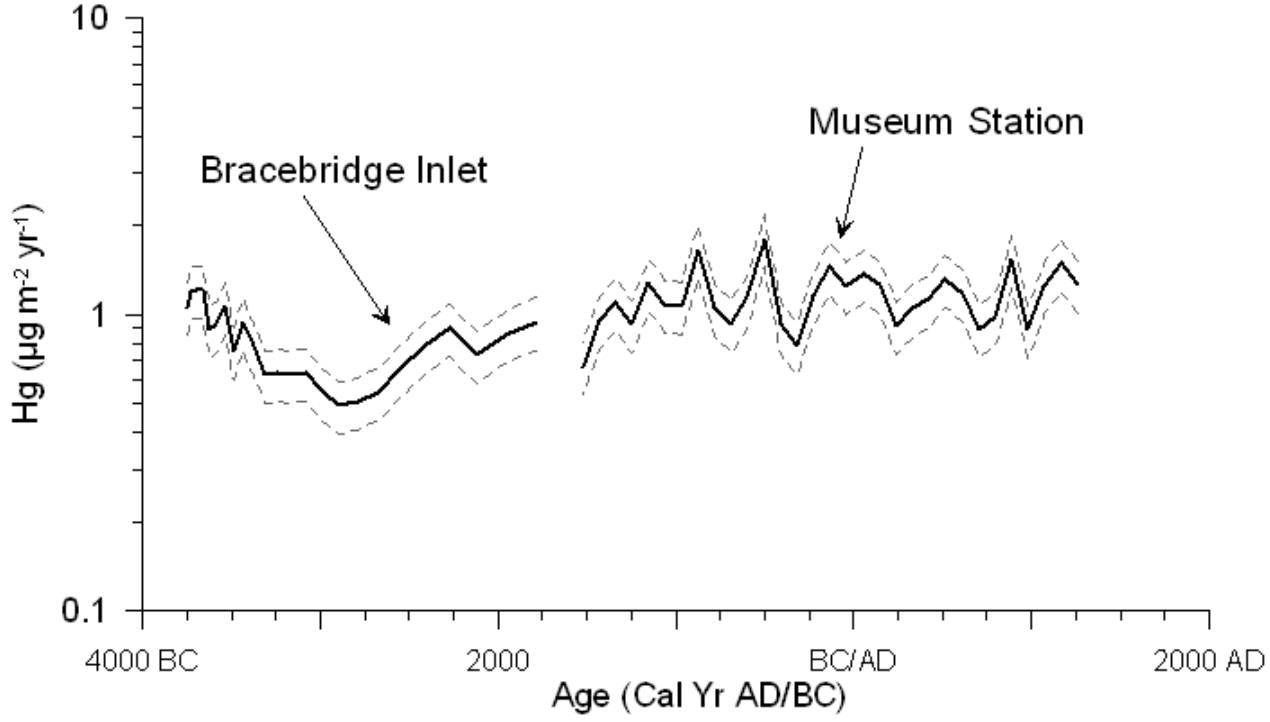


Fig 6. Chronologies of total mercury accumulation rates for Bracebridge Inlet and Museum Station. The upper dash line represents the estimated flux +21%, the lower dash line the estimated flux –21%. Twenty one percent is the error associated with the Hg fluxes calculation, based on conservative estimates of the errors associated with the ^{14}C age dates (ca. 5%), Hg concentrations (ca.5%) and the bulk density determination (ca. 20%).

Implication for the global atmospheric Hg cycle

Pre-anthropogenic atmospheric Hg fluxes in the Arctic were approximately 1 $\mu g\ m^{-2}\ yr^{-1}$, and this is not significantly different from atmospheric Hg fluxes in the temperate zone (Roos-Barraclough *et al.*, 2002; Givelet *et al.*, 2003; Shotyk *et al.*, 2003). Thus, there is no evidence supporting the hypothesis that the Arctic was an important natural sink in the global cycle of mercury during pre-industrial times (Lindberg *et al.*, 2002). Arctic climate, therefore may not favour atmospheric Hg deposition compared to warmer climates. Even though this region of the Arctic experienced significant climatic change throughout the last 6000 years, there is no evidence that these changes affected the rates of atmospheric deposition. If there is a link between Holocene climate change and rates of atmospheric Hg accumulation, as suggested by Martinez-Cortizas and colleagues (1999), the poor temporal resolution provided by the Bathurst Island cores prevent this link from being discerned. Recently, it has become apparent that processes other than cold condensation have to be invoked as the chief mechanism for transferring atmospheric Hg to the Arctic environment. Several processes may have been made more efficient in recent years by environmental changes such as global warming, resulting in the mercury contamination of the Arctic food chain. There is evidence, mainly from lake sediments, showing that mercury fluxes may have increased over the past 100 years in the Arctic. While these are generally attributed to increases in emission and deposition of mercury from human sources, global atmospheric mercury emissions are thought to have decreased by 30% (Pacyna *et al.*, 2002). Given this discrepancy and other considerations, there are a number of other reasons to seriously question the conventional interpretations. Natural, geochemical processes which may help to explain temporal trends in Hg accumulation, but these are often not given due to consideration. Therefore, it remains very unclear whether deposition of anthropogenic atmospheric mercury can account for increasing mercury contamination of the Arctic environment. Clearly, there is an urgent need to assess modern (past 150 years) rates of atmospheric mercury deposition in the Arctic using other archives of atmospheric mercury deposition including peat deposit and ice cores.

Acknowledgments

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Chapter 3

Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands since 5420 ^{14}C yr BP recorded by a peat core from a blanket bog

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Abstract

A monolith representing 5420 ^{14}C years of peat accumulation was collected from a blanket bog at Myrarnar, Faroe Islands. The maximum Hg concentration (498 ng/g at a depth of 4.5 cm) coincides with the peak in concentration of total Pb (117 µg/g) and the maximum concentration of anthropogenic Pb (111 µg/g). Age dating of recent peat accumulation using ^{210}Pb (CRS model) shows that the maxima in Hg and Pb concentrations occur at AD 1954 ± 2. These results, combined with the isotopic composition of Pb in that sample (^{206}Pb/^{207}Pb = 1.1720 ± 0.0017), suggest that coal burning was the dominant source of both elements. From the onset of peat accumulation (4286 B.C.) until AD 1385, the ratios Hg/Br and Hg/Se were constant ($2.2 \times 10^{-4} \pm 0.5 \times 10^{-4}$ and $8.5 \times 10^{-3} \pm 1.8 \times 10^{-3}$, respectively). Since then, Hg/Br and Hg/Se values increased, also reaching their maxima in AD 1954. The age date of the maximum concentrations of anthropogenic Hg and Pb in the Faroe Islands is consistent with peat cores from Greenland and Denmark which showed maximum concentrations in AD 1953 (dated using the atmospheric bomb pulse curve of ^{14}C).
The average rate of atmospheric Hg accumulation from 1520 B.C. to AD 1385 was 1.27 ± 0.38 µg/m^2/yr (n=39). The average rate of *natural* Hg accumulation for the same period was 1.32 ± 0.36 µg/m^2/yr and 1.34 ± 0.29 µg/m^2/yr calculated using Br and Se, respectively. These fluxes are similar to the pre-anthropogenic rates obtained using peat cores from Switzerland, southern Greenland, southern Ontario, and NE USA. In contrast, the maximum rate of total Hg accumulation was 34.4 µg/m^2/yr. The greatest fluxes of *anthropogenic* Hg accumulation were 26.1 and 30.8 µg/m^2/yr calculated using Br and Se, respectively. The rate of atmospheric Hg accumulation in 1998 (15.9 µg/m^2/yr) is comparable to the values obtained by atmospheric transport modelling for Denmark and Greenland of 18 and 12 µg/m^2/yr, respectively, for 1995. The Br and Se data suggest that 72 to 91% of this Hg is anthropogenic.

1. Introduction

There is concern about the concentrations and chemical speciation of Hg in the food chain of the Faroe Islands, and their possible impacts on human health. Marine foods constitute an important part of the Faroese diet, including meat and blubber from pilot whales. Muscle tissue of these whales contain on average 3.3 µg g^{-1} Hg, half of which is potentially toxic methylmercury (Weihe *et al.*, 1996). The average dietary intake of Hg approaches the Provisional Temporary Weekly Intake of 0.3 mg (Weihe *et al.*, 1996). In one out of eight human births, Hg concentrations in maternal hair exceed the limit of 10 µg g^{-1}, the threshold of neurobehavioral dysfunction; Hg concentrations in umbilical cord blood have similar implications (Weihe *et al.*, 1996). Cord-blood Hg concentrations show associations with deficits in language, attention, and memory, while fine motor function deficits are associated with maternal hair Hg (Grandjean *et al.*, 1997).

It is unclear how much of the present day Hg flux to the Faroe Islands is from anthropogenic sources (Larsen *et al.*, 1999). As volcanic and mantle degassing are thought to be important natural sources of Hg to the global atmosphere (Rasmussen, 1994; Nriagu *et al.*, 2003), Icelandic emissions represent a potentially important natural source of atmospheric Hg to the Faroe Islands, only 450 km to the SE (Fig. 1). If the fluxes of atmospheric Hg to the Faroes are naturally high, local inhabitants may have been exposed to elevated Hg ever since settlement in the 6th to 9th centuries A.D. (Hannon *et al.*, 2000). The total estimated global flux of Hg from volcanic emissions, degassing and "unmeasured SO_2 emissions" is estimated to be 112 t yr^{-1}. Fluxes from geothermal sources are not very well quantified and the global flux believed to range between 1.4 and 60 t yr^{-1} (Nriagu *et al.*, 2003).

The natural rates of atmospheric Hg accumulation and their temporal variation can be obtained using archival records. Ombrotrophic bogs are the only archive on the Faroe Islands that can provide a long-term record of Hg supplied exclusively by atmospheric inputs. Peat is an excellent medium for strongly adsorbing and complexing Hg^{2+} (Oechsle, 1982; Lodenius *et al.*, 1983), and ombrotrophic bogs have been studied extensively as archives of the changing rates of atmospheric Hg deposition (Boyarkina *et al.*, 1980; Pheiffer-Madsen, 1981; Jensen, 1991; Norton *et al.*, 1997; Benoit *et al.*, 1998; Martínez Cortizas *et al.*, 1999; Biester *et al.*, 2002). A peat core from a Swiss bog has been used to reconstruct in detail the record of atmospheric Hg accumulation extending back 14,500 calendar years (Roos-Barraclough *et al.*, 2002). A subsequent study from a nearby bog yielded a very similar chronology of atmospheric Hg accumulation (Roos-Barraclough *et al.*, 2003). Using the same approach, peat cores from ombrotrophic bogs have also been used for high-resolution reconstruction of atmospheric Hg deposition in Denmark and Greenland (Shotyk *et al.*, 2003), southern Ontario, Canada (Givelet *et al.*, 2003) and northeastern USA (Roos-Barraclough, 2002).

The main objectives of the present study were to 1) quantify net rates of atmospheric Hg accumulation on the Faroe Islands using a) recent peats dated using ^{210}Pb and b) pre-industrial peats dated using ^{14}C, 2) separate the Hg inventory into its natural and anthropogenic components using Br and Se as reference elements to help characterize pre-anthropogenic Hg inputs, 3) compare the

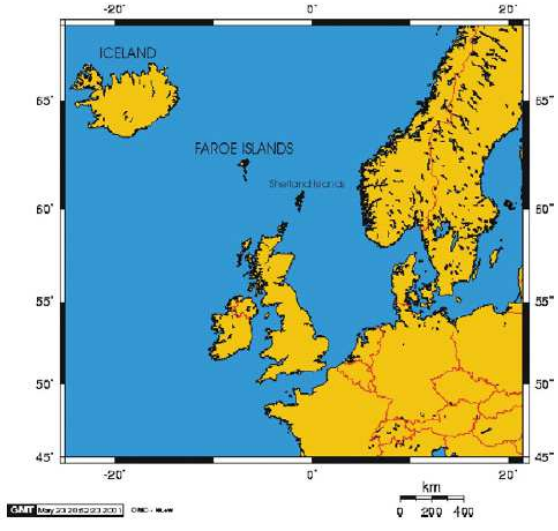


Fig. 1. Faroe Islands location map

chronology of anthropogenic Hg accumulation with that of Pb, an element whose atmospheric geochemical cycle is largely dominated by human activities, and 4) identify the predominant anthropogenic sources of Hg and Pb to the Faroe Islands using Pb isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb).

2. Materials and methods

Several Faroe Island peat bogs, including Myrarnar (Fig. 2) have been studied in detail for their tephrachronological records (Persson, 1971; Mangerud *et al.*, 1986; Dugmore *et al.*, 1998; Wastegard *et al.*, 2001). Thus, descriptions of suitable sites were readily available, and these were prioritized during our sampling campaign in May of 2000. Site selection criteria included the topography and morphology of the peatlands themselves, depth of peat accumulation (indicated by probing with a metal rod), character of peat (visual inspection of the botanical composition, degree of decomposition, moisture content, and abundance of mineral material), possible disturbances to the hydrology of the peatland (such as ditching or peat cutting), and distance of the peatland from human activity. A summary of our fieldwork activities, as well as detailed descriptions and photos of the sites, is available as a .pdf file from the senior author.

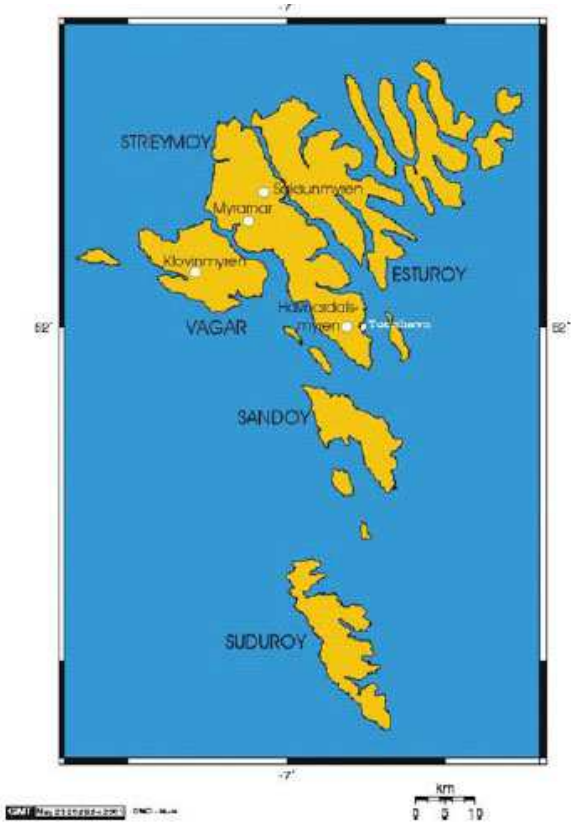


Fig. 2. Location of sites investigated

Approximately 4 km northeast of Vestmannahavn, on Streymoy, Myrarnar was described by Persson (1971). He reported 125 cm of peat accumulation, but provided no age date of the basal peat layer. Volcanic ash was found at depths of 20-23 cm (1050 ±120 AD) and 73-87 cm (ca. 1500 BC). Local inhabitants indicated that there was no peat cutting in recent history. Average annual precipitation at Torshavn (1961 to 1990) was 1284 mm and average annual temperature was 7.0^{o} C (Danish Meteorological Institute, Technical Report 98-14).

Core MYR2 was taken at a site intermediate between small hummocks and hollows using a Ti Wardenaar corer. All peat was very decomposed except for the grassy surface. Roots similar to those of *Scirpus* or *Trichophorum* were visible throughout the core.

2.1. Sample preparation

The MYR2 core was cut while frozen at -18°C into 1 cm slices using a stainless steel band saw. A plexiglass template 10 x 10 cm was used to allow the outside edges of each peat slice to be trimmed away using a Ti knife and discarded. Subsamples of the interior of each slice were dried at 105°C and ground to a fine powder using a Ti centrifugal mill (Ultracentrifugal Mill ZM 1-T, F. K. Retsch GmbH and Co., Haan, Germany). Bulk density was determined in cylindrical plugs (20 mm diameter) which were removed from the centre of the frozen slices by means of a hand operated stainless steel press. The height of each plug was measured to 0.1 mm and the volume calculated. Plugs of known volume were oven dried at 105°C overnight and the dry mass was recorded to 1 mg.

Selected samples were squeezed (while in plastic sample bags) to extract pore water; these were filtered with a 0.2 µm membrane filter under vacuum and major anions and

cations were measured using ion chromatography (Steinmann *et al.*, 1997).

2.2. Degree of humification of peat

The powdered peat samples (0.02g) were placed in test tubes and 10 ml of 8% NaOH was added. The samples were shaken then heated at 95 ± 5°C for 1 hour, then made up to 20 ml with deionised water, shaken and left to stand for 1 hour before being re-shaken and filtered through Whatman no. 1 filter papers. Samples were diluted with an equal quantity of deionised water directly before colorimetric measurement at 550 nm wavelength using a Cary 50 UV-visible spectrophotometer. The time between extraction and colorimetric measurement was as short as possible, as the extracts fade over time (Blackford *et al.*, 1993).

2.3. Trace elements

One gram of dried, milled peat was analyzed for selected trace elements using the EMMA macro XRF analyser (Cheburkin *et al.*, 1996). The lower limits of detection for the elements reported here, on a dry weight basis, are Mn 12, Fe 5, Ga 0.5, Se 0.4, Br 0.7, Rb 0.5, Sr 0.6, Y 1.0, Zr 1.5 and Pb 0.4 $\mu g\ g^{-1}$. Calibration of the instrument using international, certified, standard reference materials (SRMs), and the accuracy and precision of the trace metal measurements are described by Cheburkin et al. (1996). The accuracy and precision of the Br and Se data are given by Roos-Barraclough et al. (2002) and (2003), respectively.

Calcium and Ti were quantified using a new analytical spectrometer which consists ^{55}Fe annular radioisotope source placed on top of the end cup of the streamline cryostat of the Si(Li) detector, sample holder, shaping amplifier with shaping time of 20 microseconds, a 10 bit ADC, and an interface to PC computer. The Si(Li) detector is 50 mm^2 with resolution of 175 eV at 5.9 keV @ 1000 counts per second. Acquisition time is 600 sec for samples having Ti less than 20 ppm, but may be reduced for higher Ti concentrations. Regular 32 mm Spectro Cups with 5 micron Prolene film on the bottom were used as sample vials. The distance between the bottom of the sample and the Be window of the Si(Li) detector was 5 mm. The peak area of Ti K-alpha was normalized to the intensity of scattering radiation (both coherent and Compton) to eliminate the effects of variation in peat density and air contents of the peat samples. The analyser was calibrated for Ti using NIST 1632b Bituminous Coal, NIST 1635 Sub-bituminous Coal, SARM 19 Coal, and SARM 20 Coal. The lower limits of detection for Ca and Ti were 10 $\mu g\ g^{-1}$ and 7 $\mu g\ g^{-1}$, respectively. Inaccuracy was approximately 12 percent relative for Ti concentrations higher than 20 ppm. Reproducibility of the analyses was less than 2 percent relative, including spectra processing at the level of 30 ppm of Ti. In addition to measuring Ca and Ti quantitatively, this instrument measured Al, Si, S and Cl semi-quantitatively using NIST 1515 Apple Leaves, NIST 1547 Peach Leaves and NIST 1575 Pine Needles for calibration.

2.4. Mercury

A hand operated stainless steel press was used to remove three plugs (20 mm diameter) from the central portion of each slice. Plugs were air-dried overnight in a Class 100 laminar flow clean air cabinet, analysed for Hg, and the results of the three plugs were averaged (Roos-Barraclough *et al.*, 2002; Givelet *et al.*, 2003). Mercury concentrations were determined in solid peat samples with a LECO AMA 254. Samples in Ni boats entered a sealed furnace where they were dried, then thermally decomposed in a stream of oxygen. Gases from the decomposition were swept into the stream of oxygen through a catalyst furnace at 750°C, which fully decomposes the gases and traps NO_2, SO_2 and halogens. Mercury was trapped on a gold amalgamator at the end of the furnace. The amalgamator was heated to 500°C to release the Hg, which was measured by AAS at 254 nm. The detection limit of the instrument was 0.01ng Hg and the working range was 0.05 to 600 ng Hg, with reproducibility better than 1.5%.

Calibration of the LECO instrument was performed using liquid standards prepared from a 1000 mg l^{-1} standard solution (Merck). Working standards were made to contain 10 ng ml^{-1} and 1000 ng ml^{-1}. A ten-point calibration was made from 0.00 to 29 ng Hg. Evaluation of various instrument (temperature, time) and sample (botanical composition, water content, bulk density) parameters were evaluated with in-house standards (OGS 1878 P) and bulk peat samples from various cores. The accuracy and precision were determined by measuring after every 10th sample, a certified standard reference materials: these were either NIST 1547 Peach Leaves (certified value 31 ± 7 ng g^{-1}; measured value 30.9 ± 0.9 ng g^{-1}, n = 12) or NIST 1515 Apple Leaves (certified value 44 ± 4 ng g^{-1}; measured value 42.8 ± 0.6 ng g^{-1}; n = 12). The mean relative standard deviation of Hg within a peat slice was 7.4% (n = 3).

As an independent check on the validity of the analytical method described above, Hg concentrations were measured in eleven selected subsamples using hydride generation atomic fluorescence, following acid dissolution, at the University of Maine, Orono. Samples were dried at 40°C and a 0.4 to 0.5 gram aliquot digested using a microwave-assisted acid digestion. Mercury was brought into solution through leaching with nitric and hydrochloric acids and closed vessel heating by microwave, followed by oxidation with permanganate/persulfate solutions. Hydroxy-lamine hydrochloride was added to the digestate, which was then brought to 100 ml with deionised water. The solutions were filtered and analyzed using cold vapor atomic absorption with a flow injection mercury system (FIMS). Approximately 3 500 µl aliquots of the digestate were combined with a solution of stannous chloride and with blank acid matrix to convert the Hg in solution to elemental Hg vapor which is swept to the detector using an Argon carrier gas. The signal produced by the UV lamp is converted to a signal peak, which is measured against a 5-point calibration curve to determine concentration. Precision and accuracy are routinely checked with standard reference material (SRM) analyses, blanks, duplicate analyses, replicate samples, spike recoveries, and periodic check of standards during a run. One SRM and one duplicate were digested per 10 samples, a blank was prepared every 10 samples, and 1 of every 10 samples was a replicate. One check standard is run for every 10 analyses.

2.5. Age dating using ^{210}Pb

Dried, milled samples from the uppermost ca. 20 cm were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Liverpool University Environmental Radioactivity Laboratory, using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby *et al.*, 1997). ^{210}Pb was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV g-rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to establish secular equilibrium. ^{137}Cs and ^{241}Am were measured by their emissions at 662keV and 59.5keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low energy γ-rays within the sample.

2.6. Age dating using ^{14}C

Plant macrofossils were ^{14}C dated with Accelerator Mass Spectrometry (AMS). The macrofossils were taken from the centers of selected one-cm slices at the Institute of Plant Science, University of Berne, where they were also cleaned and dried at 60°C. Within one week from selection they were processed using a standard procedure for plant material (washed, acid-base-acid treatment) at the Dating Laboratory, University of Aarhus. A summary of these age dates is given in Table 1, Supporting Information (SI).

A sample from the bottom slice (72 cm+) was dried, milled and homogenized, then age dated using ^{14}C AMS (ETH Zurich) at 5415 ± 60 ^{14}C yr BP (ETH-23508). The calibrated age of this sample (4359 to 4212 cal years B.C.) implies a long-term, average rate of peat

accumulation of approximately 72 cm / 6286 years = 0.012 cm yr^{-1}.

2.7. Stable Pb isotopes

Selected samples were evaporated in Savillex beakers after acid HNO3-HBF4-H2O2 microwave digestion (Krachler et al., 2002). Dried samples were redissolved in 2.4N HCl. Lead was consequently separated using 3-4 µl EiChrom Sr-resin and 6N HCl elution in the clean laboratory in Heidelberg. Procedure details will be given in a separate publication (Kober et al., in prep.). Lead isotope ratios were determined using an Isoprobe multi-collector ICP-MS at the Imperial College/Natural History Museum Joint Analytical Facility (JAF), London. Mass fractionation was corrected using NBS 997 Tl as an internal standard (Rehkämper and Mezger, 2000). The Pb/Tl ratios were kept constant and above 2 to avoid possible peak overlaps of the dopant. The 205Tl/203Tl ratio used for mass bias correction was optimised daily using repeated measurements of spiked NBS 981 Pb solutions and the values of Galer and abouchami (1998). Long term reproducibility determined over a five month period (n=42) was 263 ppm for $^{206}Pb/^{204}Pb$, 322 ppm for $^{207}Pb/^{204}Pb$, 314 ppm for $^{208}Pb/^{204}Pb$, 222 ppm for $^{207}Pb/^{206}Pb$ and 263 ppm for $^{208}Pb/^{206}Pb$ (Weiss *et al.*, 2003). Procedural blanks were insignificant compared to the total amount of Pb in the samples and no blank correction was necessary. Baseline correction was done using an on peak zeroing procedure. Interference contributions by Hg on ^{204}Pb was corrected using ^{200}Hg but were well below 0.1% for all measurements. One additional sample (Myr Neo 11) was measured by classical thermal ionisation mass spectrometry (TIMS) on a MAT Finnigan 261 in Heidelberg (Kober *et al.*, 1999) after the same resin extraction.

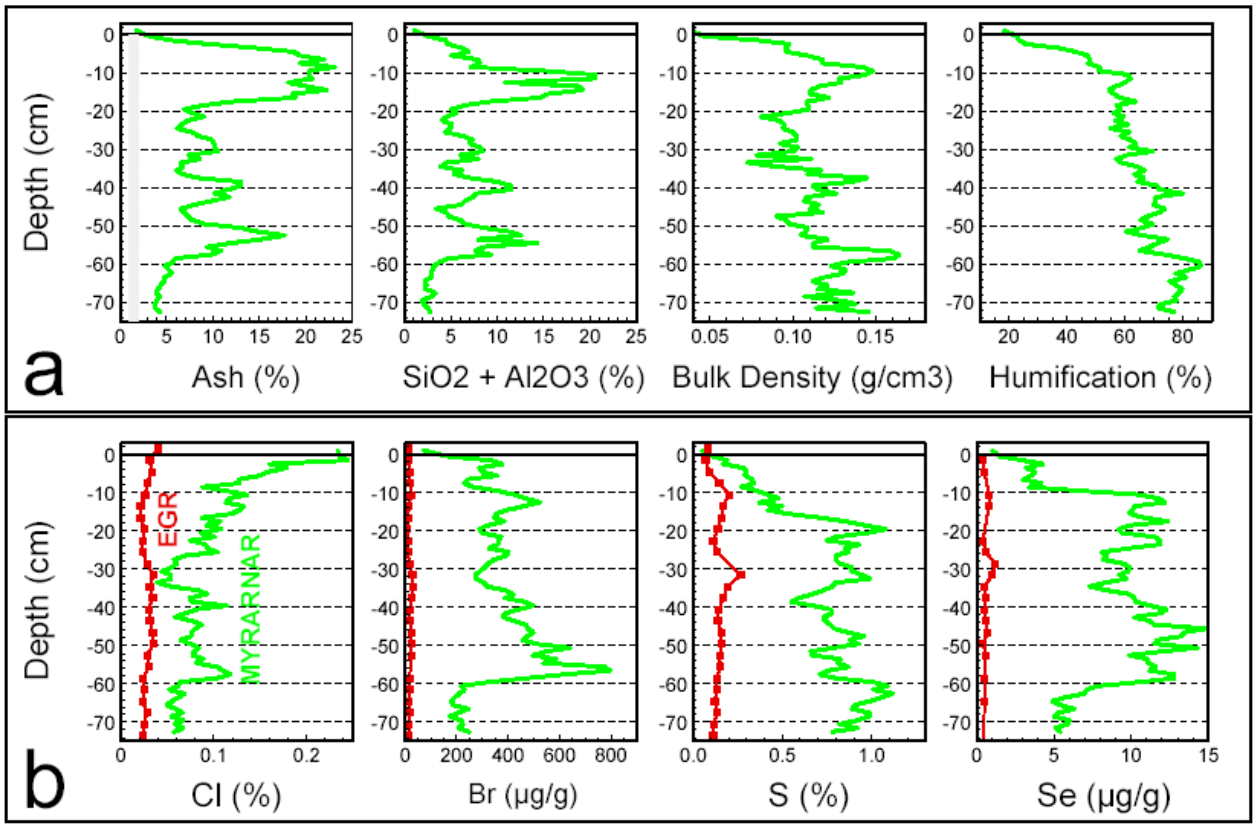


Fig. 3. a) Ash content (%), concentrations of SiO_2 + Al_2O_3 (%), dry bulk density (g/cm^3), and peat humification (%) in the MYR2 peat core. b) Concentrations of Cl, Br, Se and Se in the continental, ombrotrophic peat bog at EGR are indicated for comparison.

3. Results

3.1. Geochemistry of the peat profile

Description of the volcanic ash particles

The MYR2 peat core contained abundant white to gray mineral grains approximately 0.5 to 3 mm in diameter. These grains were particularly abundant in the samples from 3-9, 10-20, 23-32, 34 43, and 56-59 cm, with grains less commonly seen in the slices from 45-46, 47-48, and 53-54 cm. Grains from depths of 12-13, 30-31, 41-42 and 56-57 cm were examined using an optical microscope as well as SEM/EDAX. The particles were either gray, ashy masses, or almost pure white grains. Some grains revealed fresh surfaces (41-42 cm) whereas others were highly pitted (56-57 cm). Gas vesicles were obvious in the 30-31 cm and 41-42 cm slices. An EDAX analysis of a grain selected from 12-13 cm showed that Si, Al, Fe, and Ca are the dominant elements, followed by Ti and Na. Analyses of individual grains using the EMMA microXRF analyser (Cheburkin *et al.*, 1997) indicated that Rb and Sr were the most abundant trace elements.

Ash content, bulk density, and humification

The ash content of the peat profile (Fig. 3a) reflects the abundance and distribution of the volcanic ash grains. Silica plus alumina together account for most of the ash in the MYR2 core (Fig. 3a). In contrast to the MYR2 core, typical *Sphagnum* peats from continental ombrotrophic bogs contain 1-2% ash.

Despite the mineral grains in the peat profile, the bulk density of the peat samples is within the typical range for ombrotrophic peats (Fig. 3a). The topmost 10 cm are poorly decomposed, compared to deeper, underlying layers (Fig. 3a).

Marine-derived elements: Cl, Br, S, and Se

The vertical concentration profiles for Cl, Br, S, and Se are shown in Figure 3b. The average concentration of Cl^- in the pore waters at Myrarnar is ca. 18 mg/l, comparable with the long-term average rainwater value (ca. 21 mg l^{-1}) for this area (Danish Meteorological Institute, Technical Report 98-14). For comparision, the concentrations of Cl^- in the pore waters of a continental *Sphagnum* bog (EGR in the Jura Mountains of Switzerland) is approximately 0.3 mg l^{-1} (Steinmann *et al.*, 1997). Given the similar levels of precipitation (1300 mm per year in the Jura Mountains and 1280 mm per year on the Faroe Islands), the differences in chloride concentrations in the porewaters (0.3 at EGR versus 18 mg l^{-1} at Myrarnar) indicates that inputs of marine aerosols to Myrarnar are approximately 60 times higher than in the continental peat bog. Concentrations of Br, S, and Se also are much greater in the MYR2 peat core compared with the continental Sphagnum bog at EGR (Fig. 3a), again showing the importance of marine aerosols to the blanket bog.

Conservative lithogenic elements: Ti, Ga, Y, Zr

Concentrations of Ti, Ga, Y, and Zr are found at discrete depths, in particular at ca. 10, 31, 39, and 52 cm (Fig. 4a), indicating episodic supply. Of the lithogenic elements measured in the MYR2 profile, Zr is the most conservative during chemical weathering (Goldich, 1938): we use this element as a surrogate for the distribution of mineral matter in this peat core. The concentrations of Ti, Ga, Y, and Zr are far higher in the MYR2 profile compared with EGR, indicating that volcanic sources of mineral matter dominate inputs to the MYR2 peat profile.

Mobile lithogenic elements: Ca, Sr, Mn, Fe

The distributions of Sr and Mn (Fig. 4b) generally follow the conservative elements Ti and Zr (Fig. 4a) which suggests that Sr and Mn too, are also supplied primarily by volcanic sources. The Ca/Sr and Ca/Ti ratios (Fig. 5a), however, show that the peat samples below 58 cm are enriched in Ca, relative to overlying sample: this probably reflects minerotrophic inputs of Ca from chemical weathering of the bedrock and soil under the peat. Thus, the MYR2 profile is truly ombrotrophic only to a depth of 58 cm, below which it becomes

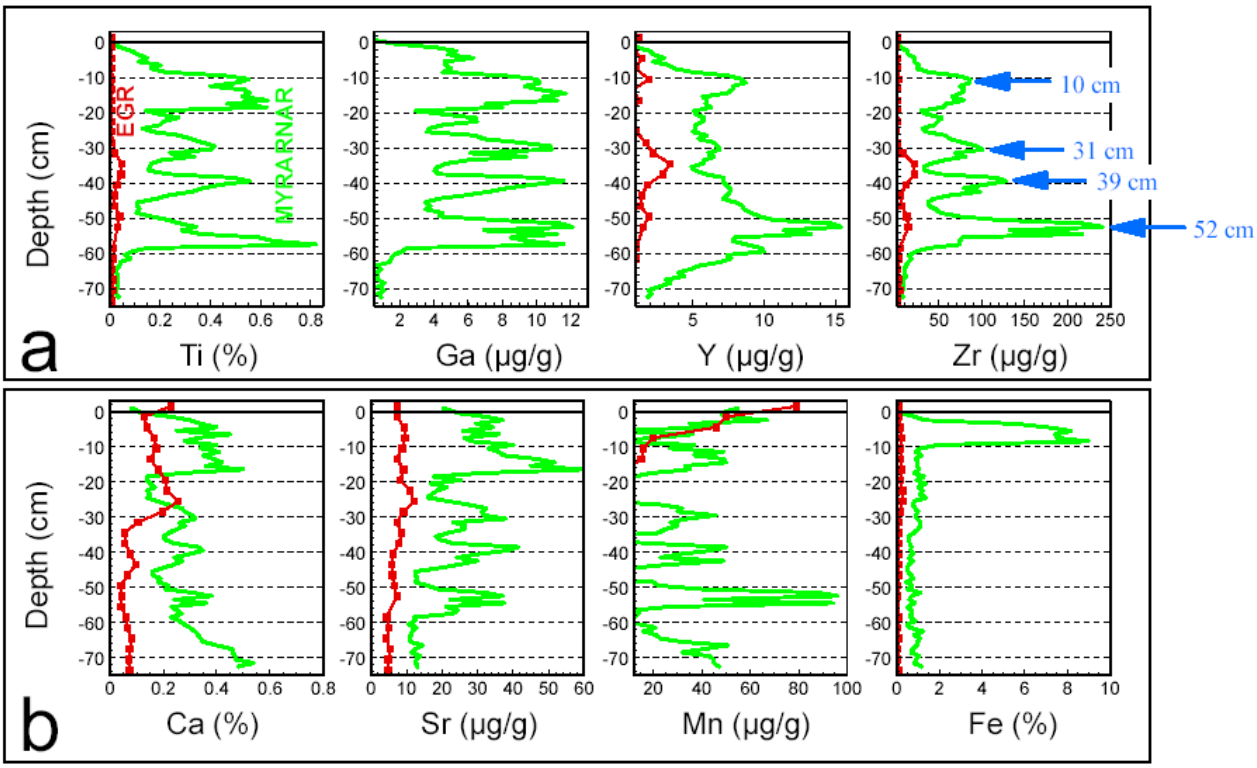


Fig. 4. a) Concentrations of Ti (%), Ga (µg/g), Y (µg/g), and Zr (µg/g) in the MYR 2 peat core. The arrows indicate the depths at which the maximum concentrations of volcanic ash particles are found (10, 31, 39, and 52 cm). b) Concentrations of Ca (%), Sr (µg/g), Mn (µg/g), and Fe (%). Concentrations of these elements in the continental, ombrotrophic peat bog at EGR are indicated for comparison.

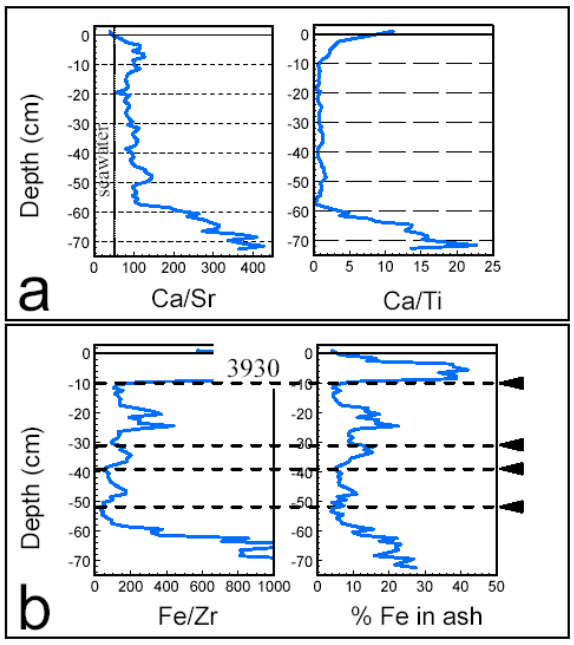


Fig. 5. a) Ca/Sr, and Ca/Ti in the MYR 2 peat core. b) Fe/Zr and Fe concentration in the ash fraction (%) of the MYR2 peat core. Black arrows and dashed horizontal lines indicate the depths at which the maximum concentrations of volcanic ash particles are found.

increasingly minerotrophic.

The average concentration of Fe in MYR2 (1.3 %) is approximately a factor of ten greater than in typical ombrotrophic peats. Iron concentrations reach approximately 9% at a depth of 7.5 cm (Fig. 4b). The near surface peak argues against a local terrestrial or aquatic source, and in favour of an atmospheric one. The Fe/Zr ratio (Fig. 5b) shows that Fe is enriched in the peat immediately above the peaks in ash contents (indicated by the black arrows in Fig. 5b). The Fe may have been mobilised from the volcanic ash particles and translocated because of the anoxic, acidic, organic-rich waters.

Fallout radionuclides ^{137}Cs, ^{210}Pb, ^{241}Am

The radionuclide concentrations are given in Table 2 (SI). The distribution of supported and unsupported ^{210}Pb shown in Fig. 6a shows that no unsupported ^{210}Pb was found below a depth of 10 cm. The maximum concentrations of ^{137}Cs and ^{241}Am are found at 3-4 and 4-5,

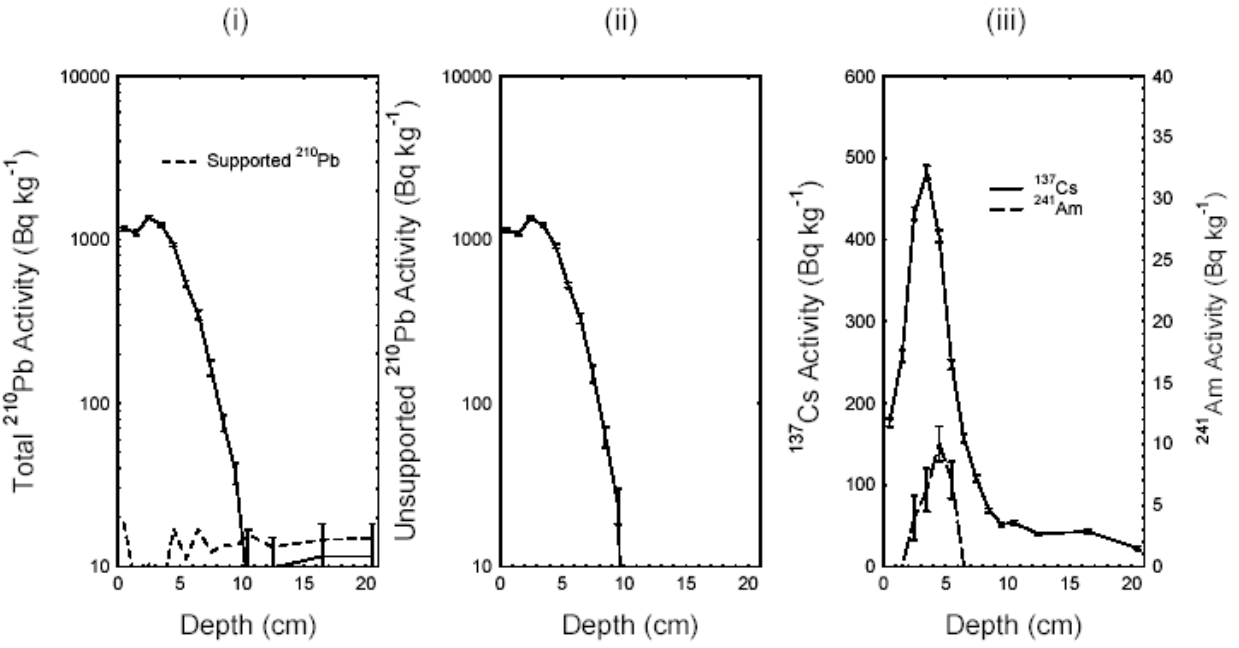


Fig. 6a. Fallout radionuclides in Myranar core MYR2 showing (i) total and supported ^{210}Pb, (ii) unsupported ^{210}Pb, (iii) ^{137}Cs and ^{241}Am activities versus depth.

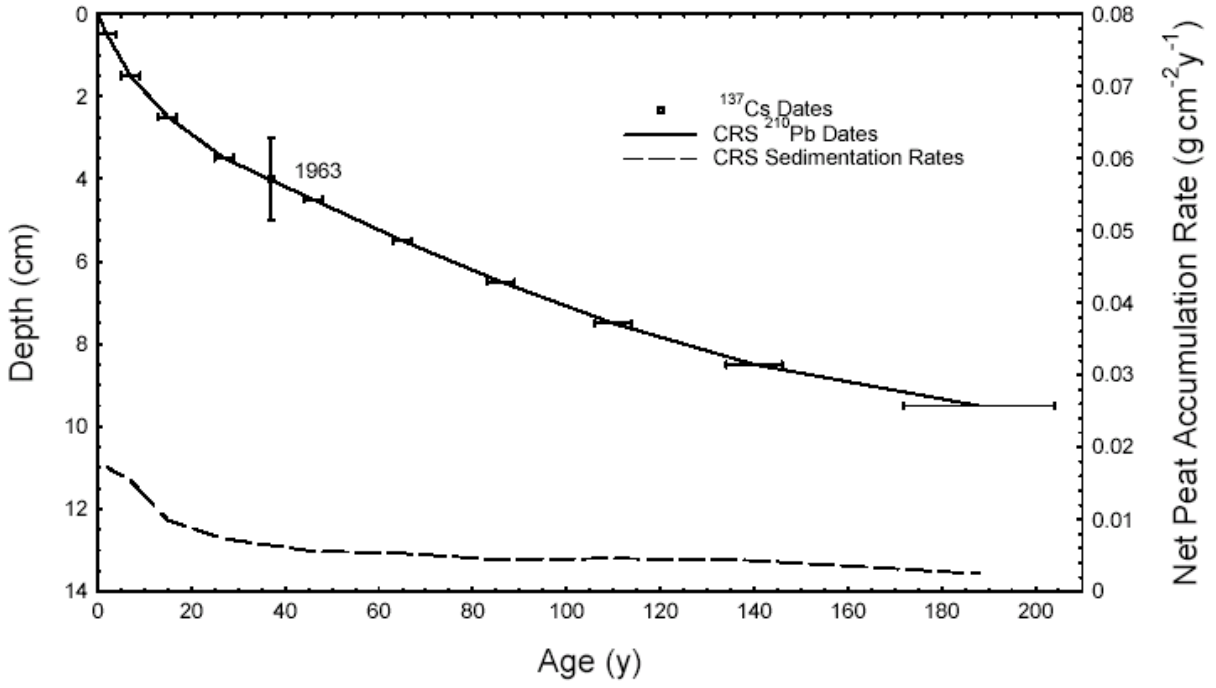


Fig. 6b. Radiometric chronology of Myranar core MYR2 showing the CRS model ^{210}Pb dates and sedimentation rates together with the 1963 depth determined from the ^{137}Cs/^{241}Am stratigraphy.

respectively (Fig. 6a). The Constant Rate of Supply model was used to calculate the ^{210}Pb ages (Fig. 6a). The position of AD 1963 was determined using the ^{137}Cs stratigraphy.

Mercury

The Hg concentrations obtained using AAS are shown in Fig. 7 along with the selected samples (red diamonds) measured using AFS. Figure 7 also shows the volumetric Hg concentrations and selected ^{14}C age dates in calibrated years B.P. The depths at which maxima in Zr concentrations are found (solid black arrows) are interpreted as volcanic ash inputs. The peaks in volcanic ash at 10 and 39 cm have corresponding peaks in Hg concentrations, but the volcanic ash peaks at 31 cm and 52 cm do not (Fig. 7). The largest peak in Hg concentrations in the MYR2 profile (4-5 cm and dating from AD 1954 ± 2) does not have a corresponding peak in volcanic ash.

Lithogenic and anthropogenic Pb

Lead has a concentration maximum (117 µg g^{-1}) at a depth of 4-5 cm in the MYR2 profile (Fig. 8). This Pb peak does not have a corresponding peak in Ti concentration (Fig. 4a) which argues against a volcanic source. To emphasise the change in Pb relative to Ti, the Pb concentrations were separated into "lithogenic" and "anthropogenic" components as follows:

$$[Pb]_{lithogenic} = [Ti]_{sample} ¼(Pb/Ti)_{background}$$

where the "background" Pb/Ti ratio was determined using the samples below 39.5 cm; these samples pre-date the Roman Period and we assume that the average Pb/Ti in these samples (0.001) represents "natural Pb" values. "Anthropogenic" Pb was then calculated as

$$[Pb]_{anthropogenic} = [Pb]_{total} - [Pb]_{lithogenic}$$

The elevated Pb concentrations in the uppermost layers of the MYR2 peat profile are predominately anthropogenic, with the maximum concentration of anthropogenic Pb (115 µg g^{-1}) dating to AD 1954 ± 2. The ^{206}Pb/^{207}Pb ratio (Fig. 8) shows that Pb became much less radiogenic *after* the maximum concentration of anthropogenic Pb. Prior to the

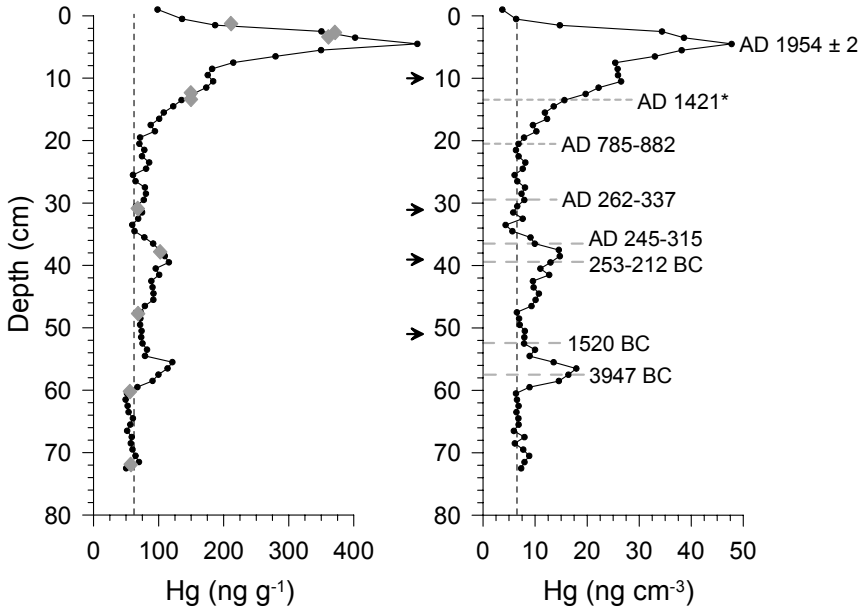


Fig. 7. Gravimetric (ng/g) and volumetric (ng/cm^3) Hg concentrations. The values indicated by the solid lines were obtained using AAS of solid samples, and the concentrations indicated by the diamonds using AFS following acid digestion (see text for details). Black arrows and dashed horizontal lines indicate the depths at which the maximum concentrations of volcanic ash particles are found. Selected ^{14}C age dates are shown (from Table 1). The age date of AD 1954 ± 2 was determined using ^{210}Pb (Table 3).

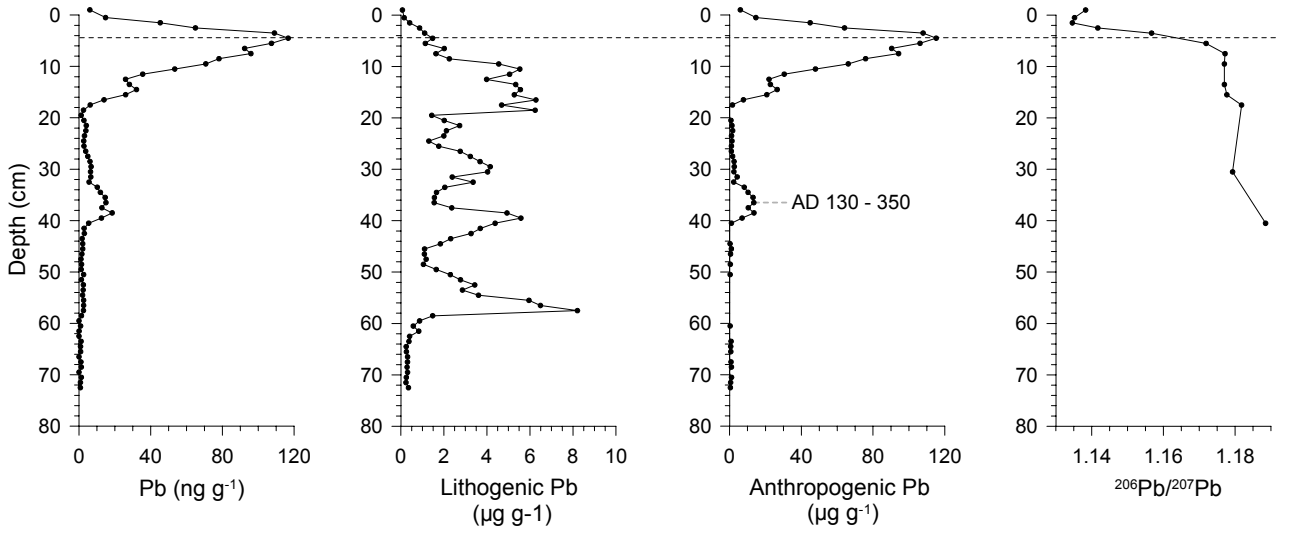


Fig. 8. Concentrations (µg/g) of total Pb, lithogenic Pb, and anthropogenic Pb (see text for description of the calculation), and isotopic composition of Pb (summarised as the ratio $^{206}Pb/^{207}Pb$). The peak in anthropogenic Pb at a depth of 36 cm dates from the Roman Period.

maximum in anthropogenic Pb (AD 1954), the $^{206}Pb/^{207}Pb$ ratio exceeded 1.17 in each sample; these values are comparable to the values for British coals summarised by Farmer et al. (1999). In contrast, after 1954 the $^{206}Pb/^{207}Pb$ ratios declined to values as low as 1.135 which approach the gasoline lead ratios published by Monna et al. (1997). These data show clearly that there have been at least two sources of anthropogenic Pb to the atmosphere, with a significant change in predominant source in the mid-1950`s.

Whether the "background" Pb/Ti ratio is used to calculate "lithogenic" Pb, or the Pb/Ti ratio of crustal rocks (14.8/4010 µg g^{-1} according to Wedepohl (1995)), a second peak in anthropogenic Pb appears in the profile, reaching a maximum at a depth of 36-37 cm. This sample dates from AD 130-350, and is undoubtedly due to long-range transport of atmospheric Pb contamination from Roman Pb mining and smelting (Hong *et al.*, 1994; Shotyk *et al.*, 1998).

3.2. Development of an age-depth model

An age depth model for the MYR2 core was created which employs both the ^{210}Pb and ^{14}C ages. Specifically, the ^{210}Pb age dates were used to calculate peat accumulation rates for the top 9.5 cm (Table 3, SI) and the ^{14}C ages from 13.5 cm to 52.5 cm (Table 1, SI). The peat accumulation rates obtained using the ^{210}Pb chronology are listed in Table 3 (SI). The six ^{14}C age dates between 13.5 cm (AD 1385) and 52.5 cm (1530 B.C.) plotted against depth yields a linear peat accumulation rate of 0.014 cm yr^{-1} ($r^2 = 0.877$).

The rate of peat accumulation recorded by the MYR2 core is approximately one-third the long-term rate of peat accumulation at Etang de la Gruère (Shotyk *et al.*, 2001), a continental ombrotrophic bog in Switzerland. Also, the MYR2 peat accumulation rates are approximately one-fifth the long-term peat accumulation rates found in blanket peat bogs from NW Scotland and the Island of Foula in Shetland (Shotyk, 1997). There is no obvious reason for the much lower peat accumulation rates in the MYR2 core.

The rates of peat accumulate between 52.5 cm (1530 B.C.) and 57.5 cm (3885 B.C.) is so low (0.002 cm yr^{-1}) that there must have been a hiatus in peat accumulation.

4. Discussion

4.1. Non-atmospheric sources of Hg and Pb to the peat profile

The Ca/Sr and Ca/Ti ratios (Fig. 5a) suggest that the peat above 58 cm is ombrotrophic, whereas it is minerotrophic below. In contrast, Hg (Fig. 7) and Pb (Fig. 8)

concentrations do not increase with depth in the peat samples below 58 cm. Therefore, unlike Ca which is also supplied to the deeper peat layers by terrestrial/aquatic sources, Hg and Pb have been supplied exclusively by atmospheric deposition since peat accumulation began ca. 4286 BC. Similar observations have been made in peat cores from other bogs. For example, at EGR in Switzerland, even though Ca, Sr, Fe, Mn are clearly elevated in the minerotrophic fen peats because of the chemical weathering of calcareous basal sediments, this process has neither contributed significantly to the inventory of Pb (Shotyk *et al.*, 2001) nor Hg (Roos-Barraclough *et al.*, 2002). Even at the predominately minerotrophic peatland of Tourbière des Genevez in the Swiss Jura, both Pb (Shotyk *et al.*, 2002) and Hg (Roos-Barraclough *et al.*, 2003) are supplied exclusively by atmospheric deposition.

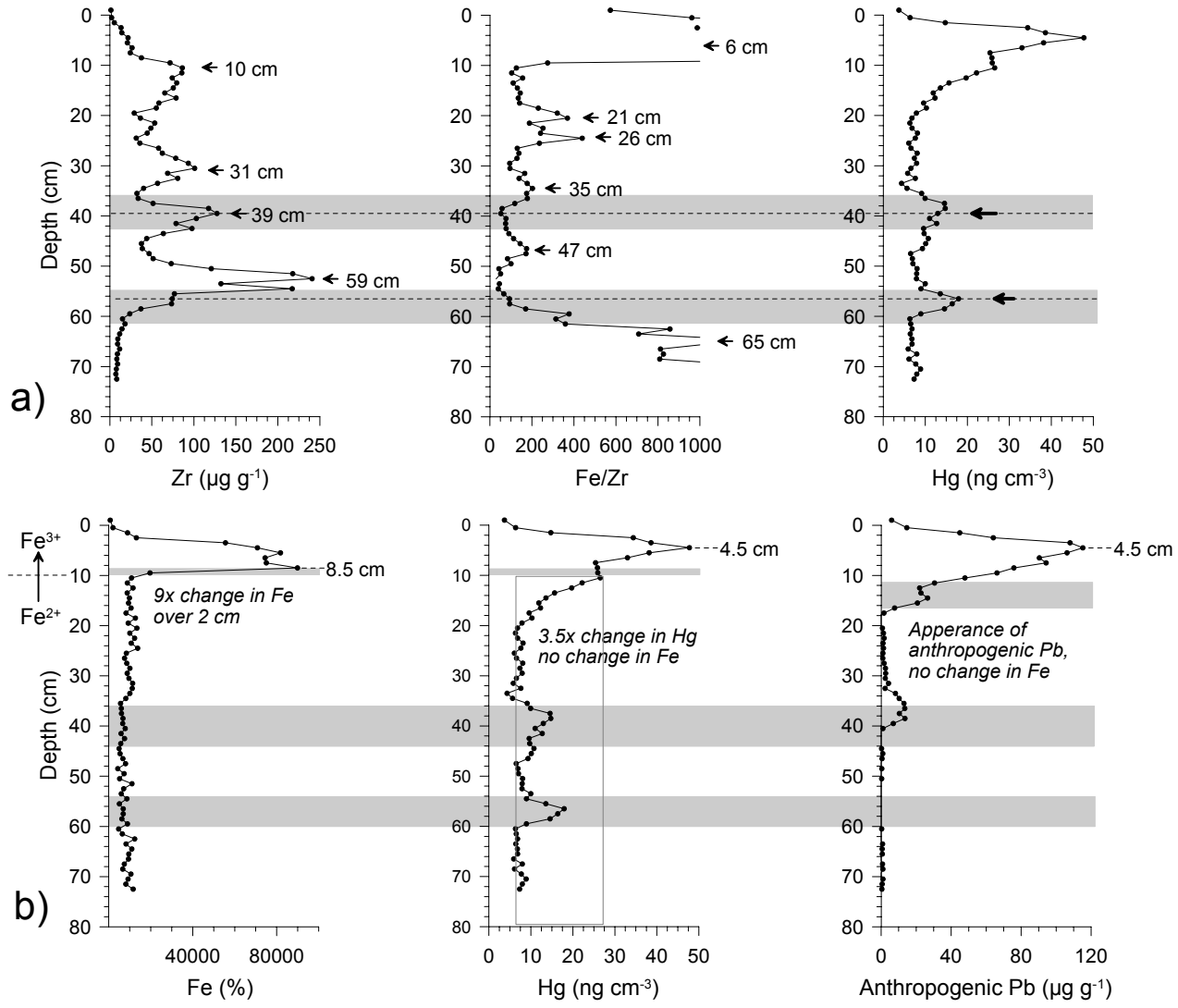


Fig. 9. a) Comparison of Zr concentrations (µg/g) with Fe/Zr and volumetric Hg concentrations (ng/cm^3). Notice that two of the peaks in Zr concentration have corresponding peaks in Hg concentration. Peaks in Fe/Zr tend to overlie the peaks in Zr, indicating diagenetic Fe mobilisation. However, the peaks in Fe/Zr do not have corresponding peaks in Hg concentrations. b) Concentrations of Fe (%), volumetric Hg concentrations (ng/cm3), and anthropogenic Pb (µg/g). There is a three-fold change in Hg concentrations which precede and pre-date the nine-fold changes in Fe concentrations. The appearance of anthropogenic Pb (15.5 cm) and the maximum in anthropogenic Pb (4.5 cm) are much greater and vertically more extensive than the changes in Fe concentration (nine-fold over a distance of only 2 cm).

4.2. Diagenesis of Hg and Pb within the peat profile

Mercury may become adsorbed onto Fe and Mn oxides which are formed when Fe (II) and Mn (II) in the anoxic zone of sediments diffuse upward and become oxidized (Gobeil *et al.*, 1999). Peatlands may have a shallow oxic zone, depending on the seasonally dependent depth to water table (Shotyk, 1988). The strong Fe enrichment at MYR2 (Fig. 4b) and the highly variable Fe/Zr ratio (Fig. 5b) indicates reductive dissolution of Fe-bearing minerals, upward migration of dissolved ferrous Fe, and oxidation and precipitation as Fe hydroxides in the surface layers. Compared to the peaks in Zr concentration at 52, 39, 31, and 10 cm (original inputs of mineral matter), there are overlying peaks in Fe/Zr (diagenetic formation of Fe hydroxides) at 47, 35, 25, and 5.5 cm (Fig. 9a). Therefore, there have been a number of periods of Fe diagenesis which are preserved as peaks in Fe/Zr. However, none of the ancient peaks in Fe/Zr (65, 47, 35, 25, and 21 cm) have a corresponding Hg peak.

In the near-surface peat layer, Fe concentrations increase from 1.1 % Fe (10.5 cm) to 8.9 % Fe (8.5 cm), a distance of only 2 cm (Fig. 9b). The zone of greatest Fe enrichment is broad, with all samples from 3-9 cm containing more than 5% Fe. Mercury concentrations, on the other hand, reach their maximum concentration at 4 to 5 cm. In addition, the increase in Hg concentrations begins at a depth of approximately 20 cm which is 10 cm below the increase in Fe (Fig. 9b). Also, the increase in Hg concentration pre-dates the Fe peak by a considerable margin: based on the age dating, the start of the increase in Hg concentrations (ca. 20 cm) dates from AD 779-893 (Table 1, SI) whereas the increase in Fe concentration (ca. 10 cm) dates from approximately AD 1812 (Table 3, SI). Finally, we note that Hg concentrations increase by a factor of three from ca. 20 cm to 10 cm, while there is no change in Fe concentrations over the same distance (Fig. 9b).

Lead concentrations also begin to increase deeper in the profile than Fe (Fig. 9b). Except for the peak in anthropogenic Pb centred at 36 cm (and dating from the Roman Period), there is no anthropogenic Pb below 16 cm (Fig. 8). Also, Pb is not significantly enriched (Pb EF < 1) in the peat samples below 16 cm. Therefore, the onset of anthropogenic Pb, the increase in anthropogenic Pb and Pb EF, all precede and pre-date the changes in Fe concentrations.

These and other factors argue against the pronounced peak in Hg concentration (4-5 cm) having been caused by chemical diagenesis. First, the isotopic composition of Pb (Fig. 8) shows a pronounced change beginning 5 cm below the peat surface; if Pb had been migrating upward in the profile and adsorbed by Fe hydroxides, the change in isotopic composition would not be so sharp. Second, Pb is immobile in peat bog profiles (Vile *et al.*, 1995; Shotyk *et al.*, 1996; MacKenzie *et al.*, 1997; Shotyk *et al.*, 1997; MacKenzie *et al.*, 1998; Vile *et al.*, 1999; Weiss *et al.*, 1999; Weiss *et al.*, 1999), with bogs recording Pb chronologies which are comparable with lake sediment archives (Brännvall *et al.*, 1997; Farmer *et al.*, 1997; Martínez-Cortizas *et al.*, 1997; Norton *et al.*, 1997) and historical records of ancient Pb mining (Kempter *et al.*, 1997; Kempter *et al.*, 1999; Kempter *et al.*, 2000; Novak *et al.*, 2003). The coincidence of the Hg (Fig. 7) and Pb (Fig. 8) concentration peaks suggests that Hg also is immobile. Third, the maximum Hg concentration in the MYR2 core occurred at AD 1954 ± 2 which is not significantly different from the peak in Hg concentration in the Storelung bog in Denmark (AD 1953 ± 2), and in the minerotrophic peat core from Tasiusaq in southern Greenland (AD 1953 ± 2), both of which were age dated using the atmospheric bomb pulse curve of ^{14}C (Shotyk *et al.*, 2003). The synchronicity of atmospheric Hg accumulation in these different geochemical settings suggests that the dominant changes in Hg concentration are not the result of chemical diagenesis, but rather due to the changing rates of atmospheric Hg deposition.

4.3. Distinguishing between natural and anthropogenic Hg using Br and Se

Anthropogenic Pb can be distinguished from natural Pb in peat bog profiles using the

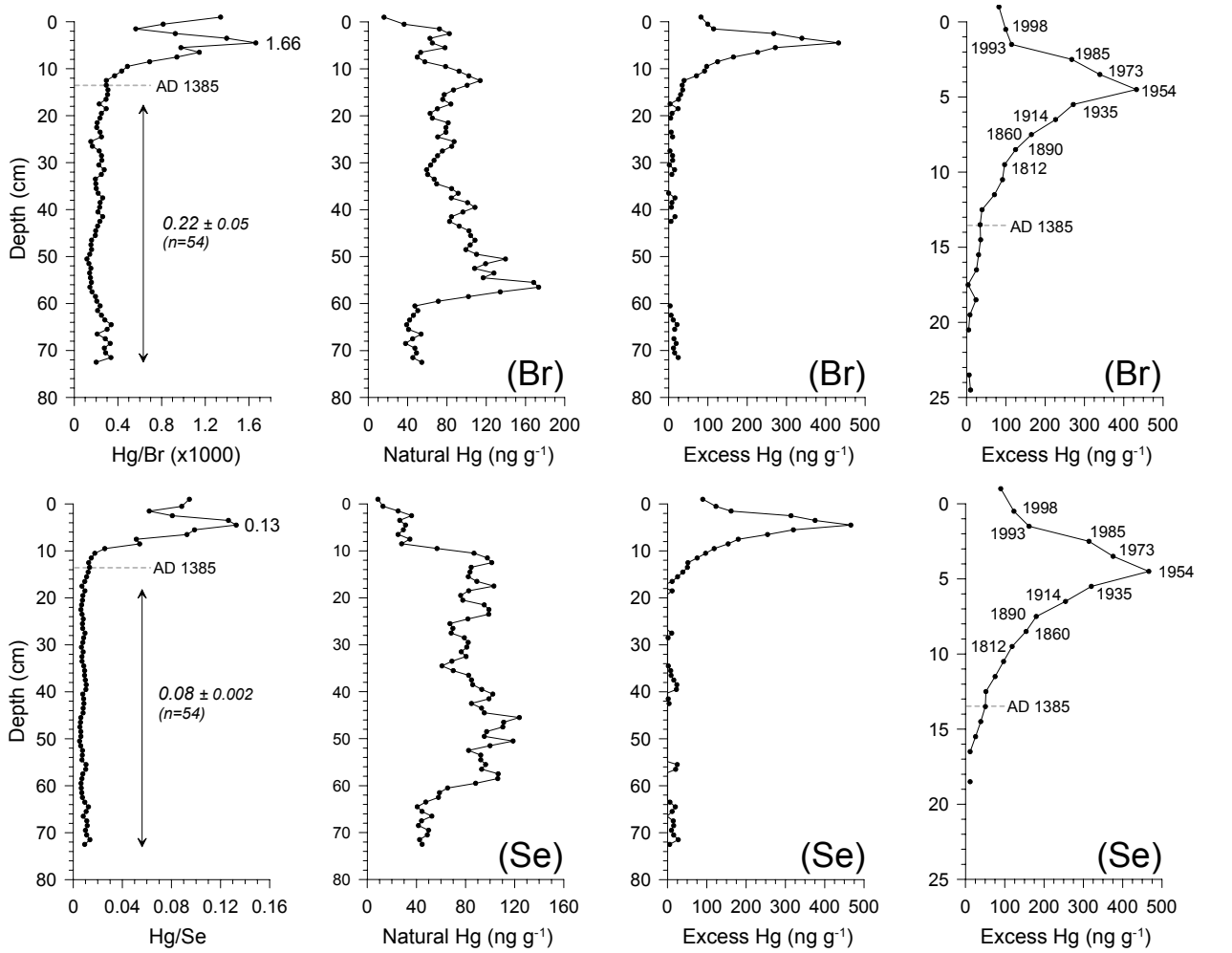


Fig. 10. a) Hg/Br ratio and concentrations of natural and excess Hg (ng/g) calculated using Br concentrations and the "background" Hg/Br ratio (see text). b) Hg/Se ratio and concentrations of natural and excess Hg (ng/g) calculated using Se concentrations and the "background" Hg/Se ratio (see text).

"background" ratio of Pb to Ti to calculate the natural variation in Pb deposition supplied by atmospheric soil dust: this ratio is determined using ombrotrophic peats dating from pre-anthropogenic time (Shotyk *et al.*, 2001). This practice works well for Pb because the atmospheric Pb flux in pre-anthropogenic times was dominated by soil dust (Shotyk *et al.*, 1998), and Ti is a good surrogate for the concentration of mineral particles. In contrast, more than 95% of atmospheric Hg is in the vapour phase (Schroeder *et al.*, 1998; Lin *et al.*, 1999). Therefore, normalising Hg concentrations in peat to a lithogenic element such as Ti is unreasonable. However, the ratio of Hg/Br in peat dating from pre-anthropogenic time has been found to vary over a narrow range, and this ratio has been used to calculate "excess" Hg (Roos-Barraclough *et al.*, 2002; Givelet *et al.*, 2003; Roos-Barraclough *et al.*, 2003). Excess Hg may be either volcanic (sharp peaks in Hg concentrations from pre-anthropogenic time), or "anthropogenic" Hg (much larger, and broader peaks from Industrial times).

The Hg/Br and Hg/Se ratios (Fig. 10) were fairly constant for thousands of years: Hg/Br = $2.2 \times 10^{-4} \pm 0.5 \times 10^{-4}$ and Hg/Se = $8.5 \times 10^{-3} \pm 1.8 \times 10^{-3}$ (n=54). Considering the different geochemical behaviour of Br and Se, the similarity in these ratios is remarkable. Some natural peaks in Hg/Br and Hg/Se may correspond to volcanic emissions (Fig. 10). However, the ratios increase dramatically within the Industrial Period. If Br and Se are deposited as marine aerosols, efficiently retained by the peat (or at least retained at a rate proportional to deposition), and are

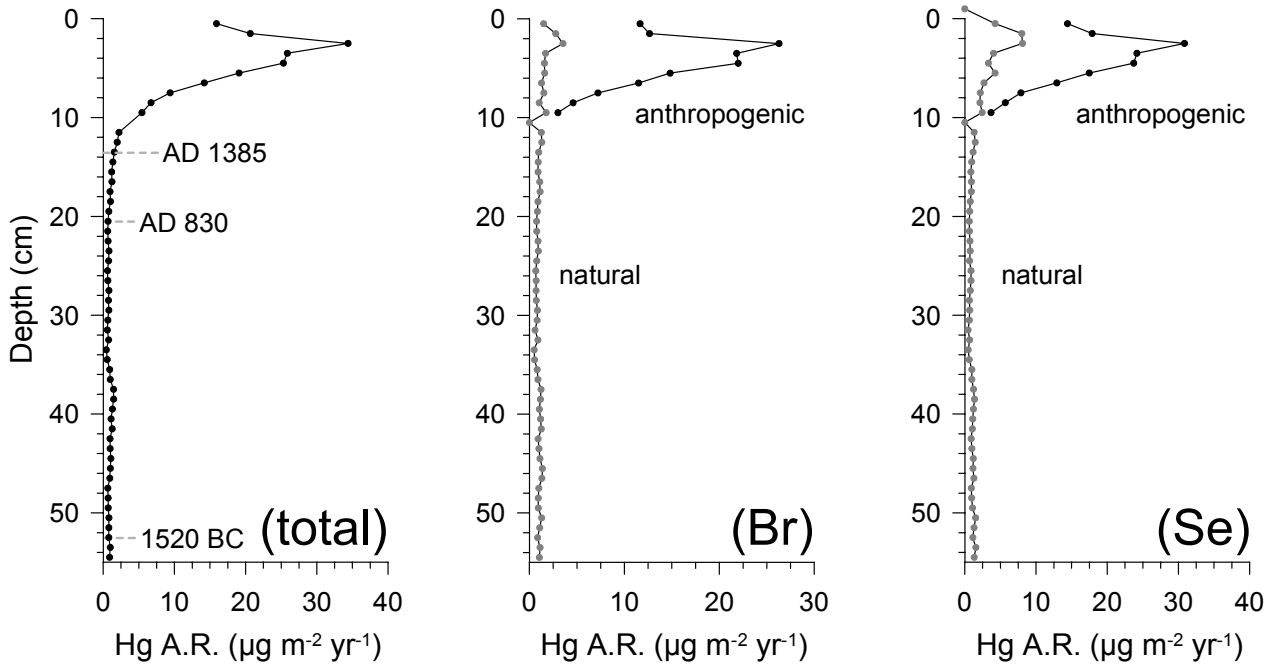


Fig. 11. Accumulation rates of atmospheric Hg (µg m^{-2} per year): total, natural, and anthropogenic. Natural and anthropogenic fluxes of Hg calculated using Br and Se concentrations, and Hg/Br and Hg/Se ratios, as described in the text.

conserved during chemical diagenesis in the peat, the Hg/Br and Hg/Se profiles suggest that aerosol deposition since the beginning of the Industrial Revolution has been strongly enriched in Hg.

The concentration of "natural" Hg can be calculated as the product of the total concentration of either Br or Se, and the corresponding "background" Hg/Br or Hg/Se ratio (Fig. 10). The concentration of "excess" Hg can then be calculated as the difference between total Hg concentrations, and natural Hg (Fig. 10). Excess Hg is similar using both approaches and a linear regression yields [Excess Hg (Se)] = 1.081 * [Excess Hg (Br)] + 4.69 (r^2 = 0.956, n = 74). The concentration of excess Hg is most abundant in peats dating from the Industrial Period, and is most likely derived from anthropogenic sources.

4.4. Rates of atmospheric Hg deposition from natural and anthropogenic sources

The rate of atmospheric Hg accumulation is calculated using the total Hg concentrations, the bulk density, and the rates of peat accumulation (Fig. 11). The average rate of atmospheric Hg accumulation from 1520 B.C. to AD 1385 was 1.27 ± 0.38 µg m^{-2} per year (n=39), with much higher accumulation rates found in modern peat samples (Fig. 11). The fluxes of "natural" Hg are calculated in the same way, but substituting "natural Hg" concentrations which are calculated as the product of the Hg/Br and Hg/Se ratios and the Br and Se concentrations, respectively. The average rate of natural Hg accumulation from 1520 B.C. to AD 1385 was 1.32 ± 0.36 µg m^{-2} per year and 1.34 ± 0.29 µg m^{-2} per year using Br and Se, respectively (Fig. 11). The agreement between the "background" Hg accumulation rats calculated using these three approaches indicates that both the Hg/Br and Hg/Se ratios are good predictors of natural Hg concentrations. The difference between "natural" Hg accumulation rates and the total Hg flux is attributed to anthropogenic contributions (Fig. 11). The rate of natural Hg accumulation calculated using Br is clearly elevated at the top of the peat core; this is true also of Se, but to a lesser extent (Fig. 11). This change may reflect increases in Br concentrations due to organic matter decay (see below), elevated Br deposited rates from anthropogenic sources (such as scavengers

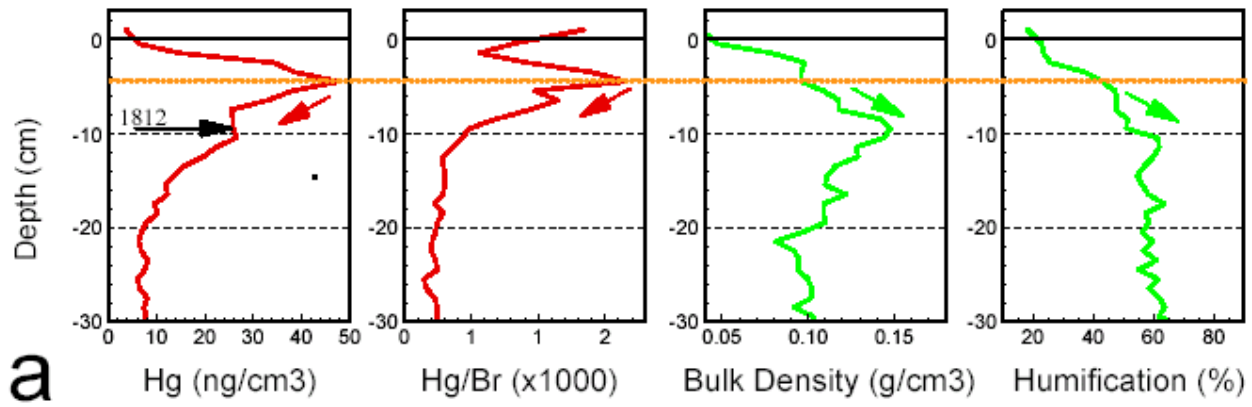


Fig. 12. Comparison of volumetric Hg concentrations (ng/cm3), Hg/Br (x1000), peat bulk density, and humification (%). Notice that the changes in Hg concentrations and Hg/Br ratio within the top 10 cm of the profile do not correspond to the changes in bulk density or humification.

used with gasoline lead additives), or both. As a result, the calculated rates of anthropogenic Hg accumulation are a *conservative* estimate of this parameter, as the natural accumulation rates of Hg may be overestimated.

For comparison with the background values, the maximum rate of total Hg accumulation is 34.4 µg m^{-2} per year: this value exceeds the average Hg accumulation rate from 1520 B.C. to AD 1385 by 27.1 times. The greatest fluxes of anthropogenic Hg accumulation are 26.1 and 30.8 µg m^{-2} per year calculated using Br and Se, respectively (Fig. 11): these exceed the average rate of natural Hg accumulation (Br, Se) by 26.1 and 30.8 times, respectively. Taken together, these data suggest that the greatest rates of atmospheric Hg deposition exceeded the background values by a factor of 26-31 times.

4.5. Effects of organic matter decay on the apparent rates of Hg accumulation

Biester et al. (2003) suggested that bulk density is not an adequate parameter to express changes in peat humification, and that Hg accumulation rates should be corrected for humification. In Fig. 12 the changes in volumetric Hg concentrations, Hg/Br, bulk density, and humification are shown for the top 30 cm of the MYR2 peat profile. These graphs emphasise the fact that volumetric Hg concentrations, the Hg/Br ratio, and the Hg/Se ratio (not shown) achieve their maxima at a depth of 4-5 cm. In contrast, bulk density and humification increase from the top of the core to reach their maxima at 9-10 and 10-11 cm, respectively (Fig. 12). The maximum Hg concentration and Hg/Br and Hg/Se ratios, therefore are independent of the maximum in bulk density and humification. Whereas the maximum in Hg concentration, Hg/Br, and Hg/Se date from AD 1954, the maximum in bulk density dates from AD 1812 ± 16 (Table 3, SI) and the maximum in peat humification pre-dates this. Thus, the maximum extent of Hg enrichment cannot simply be explained by decay processes. Moreover, these data suggest that the effect of organic matter decomposition is adequately considered if the rate of atmospheric Hg accumulation is calculated as the product of the volumetric Hg concentrations (ng cm^{-3}) and the peat accumulation rate (cm yr^{-1}). Increases in bulk density are compensated by decreases in peat accumulation rate.

4.6. Determining the predominant source of anthropogenic Hg using Pb isotopes

The predominant sources of atmospheric Pb to the peat core can be identified by comparing the $^{208}Pb/^{206}Pb$ ratio with the $^{206}Pb/^{207}Pb$ ratio (Fig. 13). The deepest sample measured (MYR Neo 42) shows the most radiogenic signature. However, this signature does not lie within the field of pre-anthropogenic Pb as defined by the occurrence

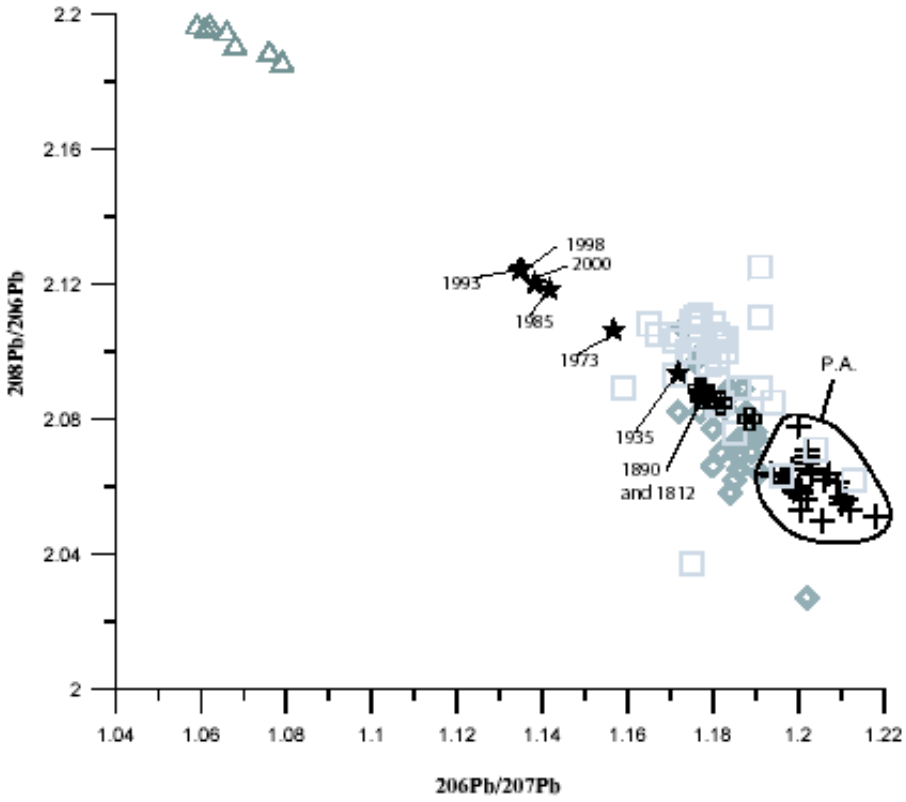


Fig. 13. Three isotope plot ($^{208}Pb/^{206}Pb$ vs.$^{206}Pb/^{207}Pb$) diagram with the least radiogenic samples (triangles) corresponding to leaded gasoline from England in 1995 (Monna et al., 1997) and the most radiogenic samples (+) representing "pre-anthropogenic" values for sediments (Shotyk, 2001; Sun, 1980). Values for U.K. coals from Farmer et al. (1999) are from England (diamonds) and Scotland (squares). Peat samples dating from the 19th and early part of the 20th century most closely resemble U.K. coal, whereas the most recent peat samples (past 30 years) can only be explained by the addition of Pb-bearing aerosols derived from the combustion of leaded gasoline.

of Sahara dust in aerosol samples or in sediments (Rosman *et al.*, 1997; Alleman *et al.*, 2000), even though the sample pre-dates the Roman Period. The discrepancy can be explained by local inputs of natural Pb having less radiogenic signatures than crustal rocks and the pre-anthropogenic soils and sediments derived from them. While the geology of the Faroe Islands is well described (Larsen *et al.*, 1999), there is limited data describing the isotopic composition of Pb in the basalts which correspond to our sampling location (Gariepy *et al.*, 1983). Therefore, it is not possible to constrain in a quantitative way the relative importance of local soil inputs of Pb to the peat.

The sample from 13.5 cm which dates from AD 1330-1440 has $^{206}Pb/^{207}Pb$ = 1.177. This value could be explained by a mixture of natural lead from local soil dust, as well as soil dusts transported from further a field. In addition, Medieval lead mining and coal burning in the United Kingdom may have also contributed to this value.

Samples after AD 1812 contain significant concentrations of anthropogenic Pb (Fig. 8) and are less radiogenic than the underlying peats (Fig. 13). However, these highly contaminated samples fall into two categories. First, the lowest $^{206}Pb/^{207}Pb$ ratios are found in peat samples dating from 1993 to 1998 (Fig. 13). The data shown in Fig. 13 indicates that these Pb isotope ratios can only be explained by the introduction of lead-bearing aerosols from leaded gasoline combustion. Second, the samples pre-dating 1973 are more radiogenic, with $^{206}Pb/^{207}Pb$ ratios (1.1712 to 1.1770 from AD 1812 to AD 1935) comparable to British

coals (Fig. 13). In this group of samples, therefore, coal combustion was the predominant source of anthropogenic Pb. In fact, much of this anthropogenic Pb pre-dates by a considerable margin the introduction of leaded gasoline (in North America) in 1923 (Nriagu, 1990).

The maximum concentration of anthropogenic Pb dates from 1954 (Fig. 8), and this Pb was supplied primarily by coal burning (Fig. 13). The maximum concentration of anthropogenic Pb (Fig. 8), however, also corresponds with the maximum concentration of Hg (Fig. 9) and the maximum Hg/Br and Hg/Se ratios (Fig. 10). Taken together, the Hg, Pb, and Pb isotope data show that the predominant source of anthropogenic Hg to the peat core was coal burning, and this source reached its maximum in AD 1954.

4.7. Implications for the global atmospheric Hg cycle

In general, the results presented here are in good agreement with the global historic primary production over the last 500 years as reported by Hylander and Meili (2003). This is a good indication of the global character and long residence time of elemental Hg in the atmosphere, and why similar chronologies and accumulation rates are found in archives collected from areas with no significant local or regional source. The MYR2 peat core, however, provides poor temporal resolution and cannot be compared quantitatively with annual mercury production records (Hylander *et al.*, 2003). Hylander and Meili (2003) that approximately one-half of the mercury produced during the past five centuries has been used to recover silver and gold. The appearance of anthropogenic Hg dating from Medieval times in peat bogs from Spain (Martínez Cortizas *et al.*, 1999), Switzerland (Roos-Barraclough *et al.*, 2002; Roos-Barraclough *et al.*, 2003) and the Faroe Islands (this study) is probably a consequence of metallurgical uses of mercury.

Nriagu and Becker (2003) have estimated the total global flux of Hg from volcanic emissions at approximately 100 t yr^{-1}. In contrast, emissions of Hg from coal burning worldwide was estimated at 3,000 t yr^{-1} (Joensuu, 1971): this estimate was based on global coal consumption of 3 x 109 t yr^{-1}, but coal consumption today exceeds 4 x 109 t yr^{-1}. Taking 1 µg g^{-1} as a representative concentration of Hg in coal (Joensuu, 1971; Valkovic, 1983; Swaine, 1990), the total mass of Hg mobilised by coal burning today is approximately 4,000 t yr^{-1}. The peat core at MYR2 confirms that Hg emissions from coal burning have been quantitatively more important than volcanic emissions, but also that they have gone into decline since the mid-1950`s. The age date of the maximum concentrations of anthropogenic Hg and Pb in the Faroe Islands is consistent with peat cores from Greenland and Denmark which showed maximum concentrations in AD 1953 (dated using the atmospheric bomb pulse curve of ^{14}C). The decline in Hg accumulation rates since the 1950`s appears to be inconsistent with the progressive increase in coal consumption worldwide and the potential mobilisation of Hg from coal burning. However, the development and introduction of pollution control technologies, with their emphasis on removal of fly ash particles and SO_2, may have caused a shift in the kind of Hg which is being emitted from these facilities, with a decrease in the relative proportion of particulate Hg which is readily scavenged by precipitation.

The pre-industrial annual flux of Hg to the continents has been estimated at 4 Mmoles (Lamborg *et al.*, 2002). If this value is taken to represent the continental land mass (total 147 x 106 km^2), then an average, pre-industrial flux of 5.5 µg m^{-2} per year is implied. For comparison, the minimum pre-industrial flux recorded by the MYR2 core is approximately 1 µg m^{-2} per year which is also the minimum Hg accumulation rate recorded by the peat bog at EGR (Roos-Barraclough *et al.*, 2002) as well as peat cores from Greenland (Shotyk *et al.*, 2003), southern Ontario (Givelet *et al.*, 2003) and NE USA (Roos-Barraclough, 2002). The pre-industrial flux calculated by Lamborg et al. (2002), therefore, may be too large by a factor of five times. Thus, the true impact of human activities on the emissions of Hg to the global atmosphere may have been

underestimated by to the same extent. Compared to the "natural background" rate of atmospheric Hg accumulation, the maximum rate of atmospheric Hg accumulation in Switzerland, Denmark, Greenland, southern Ontario, and NE USA are as much as 30 to 50 ¼ greater. The difference between the long-term rate of atmospheric Hg accumulation and the maximum rates of Hg accumulation provide quantitative insight into the true impact of human activities on the atmospheric Hg cycle.

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Supporting Information

Table 1.
AMS ^{14}C dating of plant macrofossils and peat fractions from MYR peat core from Myrarnar, Faroe Islands.

Average depth (cm)	Material dated	Dating method	Laboratory No.	$\delta^{13}C$ (‰)	Conv. ^{14}C age (BP)	Calibrated age (68% conf. Inter.)
5.5	*Sphagnum*	Conventional ^{14}C	AAR - 8006	-26.48	265 ± 65	AD 1760-1810
13.5	Peat fraction <2mm	Conventional ^{14}C	AAR - 8007 - 2	-28.00	520 ± 44	AD 1330-1440
20.5	*Sphagnum*	Conventional ^{14}C	AAR - 8008	-28.10	1184 ± 37	AD 780-890
29.5	*Sphagnum*	Conventional ^{14}C	AAR - 8009 - 1	-26.32	1725 ± 39	AD 250-390
29.5	Peat fraction <2mm	Conventional ^{14}C	AAR - 8009 - 2	-28.08	2532 ± 47	800-540 BC
36.5	*Selaginella*	Conventional ^{14}C	AAR - 8010	-25.40	1770 ± 50	AD 130-540
39.5	*Selaginella*	Conventional ^{14}C	AAR - 8011	-25.07	2217 ± 43	370-200 BC
52.5	*Selaginella*	Conventional ^{14}C	AAR - 8012	-26.22	3260 ± 55	1610-1450 BC
57.5	*Selaginella*	Conventional ^{14}C	AAR - 8013	-24.94	5104 ± 47	397063800 BC
13.5	Plant root	^{14}C bomb pulse	AAR - 7802	-25.33	-44 ± 38	AD 1955
20.5	Plant root	Conventional ^{14}C	AAR - 7803	-25.12	105 ± 36	AD 1810-1920
29.5	Plant root	Conventional ^{14}C	AAR - 7804	-25.55	126 ± 36	AD 1800-1890
36.5	Plant root	Conventional ^{14}C	AAR - 7805	-25.03	229 ± 38	AD 1760-1810
39.5	Plant root	Conventional ^{14}C	AAR - 7806	-25.00	119 ± 39	AD 1800-1890
52.5	Plant root	Conventional ^{14}C	AAR - 7807	-24.54	534 ± 41	AD 1340-1440
57.5	Plant root	Conventional ^{14}C	AAR - 7808	-24.97	29 ± 36	AD 1951

Table 2.
Fallout radionuclide concentrations in Myranar core MYR2

Depth		^{210}Pb Total		^{210}Pb Unsupported		^{210}Pb Supported		^{137}Cs		^{241}Am	
cm	g cm^{-2}	Bq kg^{-1}	±	Bq kg^{-1}	±	Bq kg^{-1}	±	Bq kg^{-1}	±	Bq kg^{-1}	±
0.5	0.04	1159.4	24.4	1141.0	24.5	18.3	2.7	176.3	5.0	0.0	0.0
1.5	0.12	1102.2	34.7	1095.2	35.0	6.9	4.1	256.8	7.4	0.0	0.0
2.5	0.21	1361.1	28.4	1350.8	28.6	10.3	2.7	431.8	7.5	4.0	1.8
3.5	0.32	1227.7	31.7	1221.0	31.9	6.7	3.4	482.3	8.4	6.3	1.8
4.5	0.44	929.2	24.3	912.3	24.5	16.9	2.8	403.8	7.6	10.0	1.5
5.5	0.54	537.6	21.2	526.5	21.4	11.2	2.8	246.9	6.0	7.0	1.5
6.5	0.64	346.9	23.6	330.0	23.9	16.9	3.5	156.9	5.9	0.0	0.0
7.5	0.75	163.5	17.6	151.3	17.8	12.3	3.1	107.7	4.5	0.0	0.0
8.5	0.89	75.8	8.6	62.2	8.8	13.6	1.8	68.6	2.9	0.0	0.0
9.5	1.05	37.3	5.7	24.1	5.9	13.2	1.6	52.0	2.1	0.0	0.0
10.5	1.22	6.8	9.9	-8.9	10.2	15.7	2.2	53.1	2.5	0.0	0.0
12.5	1.53	9.9	5.2	-3.3	5.4	13.2	1.5	40.2	1.6	0.0	0.0
16.5	2.06	11.6	6.8	-3.1	7.1	14.6	2.1	42.7	2.6	0.0	0.0
20.5	2.52	11.6	6.8	-3.3	7.1	14.9	2.1	22.5	2.4	0.0	0.0

Table 3.
^{210}Pb chronology of Myranar core MYR2

Depth		Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	y	±	g cm^{-2} y^{-1}	cm y^{-1}	± (%)
0.0	0.00	2000	0				
0.5	0.04	1998	2	2	0.017	0.25	3.2
1.0	0.08	1996	4	2	0.016	0.20	3.6
1.5	0.12	1993	7	2	0.015	0.14	4.1
2.0	0.16	1989	11	2	0.013	0.13	3.8
2.5	0.21	1985	15	2	0.010	0.10	3.6
3.0	0.26	1979	21	2	0.0086	0.083	3.9
3.5	0.32	1973	27	2	0.0073	0.067	4.2
4.0	0.38	1964	36	2	0.0064	0.053	4.5
4.5	0.44	1954	46	2	0.0056	0.053	4.8
5.0	0.49	1945	55	2	0.0054	0.053	5.7
5.5	0.54	1935	65	2	0.0053	0.050	6.6
6.0	0.59	1925	75	2	0.0049	0.048	8.4
6.5	0.64	1914	86	3	0.0044	0.043	10.2
7.0	0.70	1902	98	3	0.0045	0.042	12.8
7.5	0.75	1890	110	4	0.0046	0.037	15.5
8.0	0.82	1875	125	5	0.0044	0.033	18.9
8.5	0.89	1860	140	6	0.0043	0.026	22.3
9.0	0.97	1836	164	11	0.0034	0.021	26.2
9.5	1.05	1812	188	16	0.0025	0.021	30.0

Table 4.
Isotopic composition of selected peat samples, MYR2 core. *sample was measured by TIMS.

Depth (cm)	Sample ID	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{206}Pb	Total
1	Neo 01	17.738	15.583	37.606	0.8785	1.1383	2.1201	6.0
-0.5	Neo 02	17.688	15.582	37.577	0.8809	1.1352	2.1244	14.8
-1.5	Neo 03	17. 657	15.562	37.503	0.8813	1.1346	2.1239	45.3
-2.5	Neo 04	17.774	15.567	37.651	0.8759	1.1417	2.1184	65.0
-3.5	Neo 05	18.043	15.599	38.004	0.8645	1.1567	2.1063	109.0
-5.5	Neo 07	18.307	15.621	38.326	0.8533	1.1719	2.0936	107.4
-7.5	Neo 09	18.383	15.616	38.348	0.8495	1.1772	2.0860	95.9
-9.5	Neo 11*	18.423	15.655	38.463	0.8496	1.1770	2.0880	70.1
-13.5	Neo 15	18.404	15.637	38.443	0.8496	1.1770	2.0888	28.1
-15.5	Neo 17	18.396	15.620	38.381	0.8491	1.1777	2.0854	26.0
-17.5	Neo 19	18.470	15.629	38.505	0.8462	1.1818	2.0848	6.2
-30.5	Neo 32	18.428	15.626	38.452	0.8480	1.1793	2.0867	6.4
-40.5	Neo 42	18.557	15.614	38.600	0.8414	1.1885	2.0800	5.4
Reproducibility (pp)		263	322	314	222		263	

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Chapter 4

Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical, and isotopic analyses

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Abstract

For detailed reconstructions of atmospheric metal deposition using peat cores from bogs, a comprehensive protocol for working with peat cores is proposed. The first step is to locate and determine suitable sampling sites in accordance with the principal goal of the study, the period of time of interest and the precision required. Using the state of the art procedures and field equipment, peat cores are collected in such a way as to provide high quality records for paleoenvironmental study. Pertinent field observations gathered during the fieldwork are recorded in a field report. Cores are kept frozen at -18 °C until they can be prepared in the laboratory. Frozen peat cores are precisely cut into 1 cm slices using a stainless steel band saw with stainless steel blades. The outside edges of each slice are removed using a titanium knife to avoid any possible contamination which might have occurred during the sampling and handling stage. Each slice is split, with one-half kept frozen for future studies (archived), and the other half further subdivided for physical, chemical, and mineralogical analyses. Physical parameters such as ash and water contents, the bulk density and the degree of decomposition of the peat are determined using established methods. A subsample is dried overnight at 105 °C in a drying oven and milled in a centrifugal mill with titanium sieve. Prior to any expensive and time consuming chemical procedures and analyses, the resulting powdered samples, after manual homogenisation, are measured for more than twenty-two major and trace elements using non-destructive X-Ray fluorescence (XRF) methods. This approach provides lots of valuable geochemical data which documents the natural geochemical processes which occur in the peat profiles and their possible effect on the trace metal profiles. The development, evaluation and use of peat cores from bogs as archives of high-resolution records of atmospheric deposition of mineral dust and trace elements have led to the development of many analytical procedures which now permit the measurement of a wide range of elements in peat samples such as lead and lead isotopes ratios, mercury, arsenic, antimony, silver, molybdenum, thorium, uranium, rare earth elements. Radiometric methods (the carbon bomb pulse of ^{14}C, ^{210}Pb and conventional ^{14}C dating) are combined to allow reliable age-depth models to be reconstructed for each peat profile.

1. Introduction

The use of peat cores from bogs in paleoenvironmental studies has increased dramatically during the last decade (MacKenzie *et al.*, 1988; Vile *et al.*, 1995; Farmer *et al.*, 1997; Martínez Cortizas *et al.*, 1999; Novak *et al.*, 2003; Monna *et al.*, 2004). The reasons for this are not only that peat cores from ombrotrophic bogs are excellent archives of many kinds of atmospheric particles: soil dust, volcanic ash, phytoliths, anthropogenic aerosols, and many trace elements but peat bogs are also economically attractive archives because the concentrations of trace elements such as mercury (Hg) and lead (Pb), are sufficiently high that they are much more accessible by conventional methods of analysis than other archives of atmospheric deposition such as ice cores. Unlike glacial ice, which is restricted to Alpine and Polar regions, peatlands are widely distributed across the globe, accounting perhaps 5% of the land area of the Earth (Charman, 2002). There is growing evidence that undisturbed bogs have faithfully preserved the historical records of a wide range of trace metals, despite the low pH and abundance of dissolved organic acids in the waters, and the seasonal variations in water table (and impact which this may have on redox state). In the case of a metal such as lead, for example, the historical record of atmospheric Pb deposition is so well preserved in undisturbed bogs (Shotyk *et al.*, 1998) that our ability to read and interpret the peat bog records is largely independent of chemical processes taking place within the bog itself, but can depend to a large extent on the methods used to collect, handle, and prepare the samples for analysis (Shotyk *et al.*, 2002). Moreover, the lack of a commonly used, validated protocol has hindered the interpretation and comparison of peat core metal profiles from different laboratories within the international community. Therefore, to compare the published peat bog records with one another or to other archives (e.g. lake sediments, ice cores, tree rings), and for detailed reconstructions of atmospheric metal deposition, a comprehensive protocol for working with peat cores is warranted.

Since the first cores for chemical analysis were collected at Etang de la Gruère in the Jura Mountains, Switzerland, in the autumn of 1990(Shotyk *et al.*, 1994), many changes and developments have been made with respect to the practical aspects of this work. The present paper shows that the effects of core compression during sampling, the spatial resolution obtained by core cutting, as well as the accuracy and precision of peat core slicing can very much affect the vertical variation in trace element concentrations and enrichment factors (EF). Moreover, in this paper we have summarized the refinements made to the methodological procedures and analyses which have been developed by our research group over the years, to share these with the international community. We hope that the protocol described here can serve as a guideline for future paleoenvironmental studies using peat cores from bogs. Improvements to the description of the coring sites and the cores themselves, the accuracy and precision of slicing techniques and sub-sampling, as well as the physical and chemical analytical methods employed and the dating methods used to model the age-depth relationship, will help to ensure that the results obtained by different research teams are directly comparable.

2. Background to the problem

Comparison of two peat bog records of atmospheric lead pollution from Etang de la Gruère in Switzerland (EGR) have shown that while the general agreement between the two cores (EGR, cores 2F and 2K) is very good, there are also some differences (Shotyk *et al.*, 2002). One difference is revealed by the concentration profiles of anthropogenic Pb. The 2F core reveals two pronounced peaks of nearly identical Pb EF during the 20th century, but in the 2K core the more recent of these two is less pronounced (Fig. 1). Here, possible reasons for this difference are explored: differential core compression during sample collection, the relative thick peat slices (3 cm) used to represent the individual samples, and

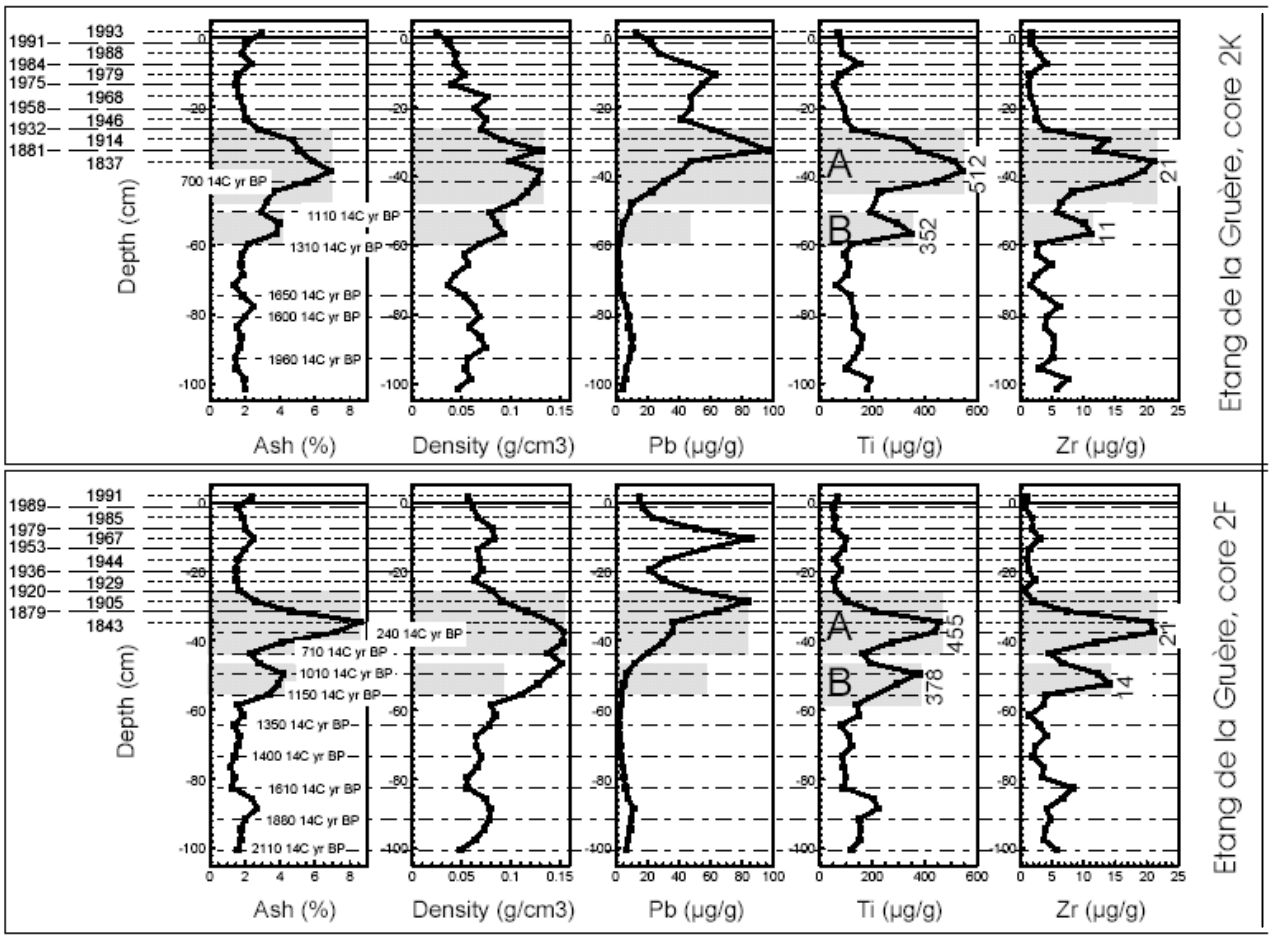


Fig. 1. a) Ash content, bulk density, concentrations of Pb, Ti, and Zr in the 2K core. b) ash content, bulk density, concentrations of Pb, Ti, and Zr in the 2F core. Maximum concentrations of Ti and Zr are indicated beside the peaks identified by the shaded bars. Age dates shown on the left hand side of box b) were obtained using ^{210}Pb, age dates within box b) are radiocarbon ages, expressed as conventional radiocarbon years Before Present.

from the imprecision of the cutting technique used to section the cores.

2.1. Effects of core compression on anthropogenic Pb concentrations

A summary of some physical and chemical properties of the two peat cores is given in Figure 1. In general, both profiles contain a zone of enhanced peat humification from ca. 20 to 60 cm which is visible upon inspection of the cores in the field (darker colour, finer texture, fewer visible plant remains). This zone is also revealed in each core by the elevated bulk density values at these depths, as well as reduced pH values and lower yields of extractable porewater (Fig. 2). However, there are some discernible differences between the two cores. First, the ash content profile shows significantly higher maximum ash content in the 2F core (8.6 %) compared with 2K (6.9 %). Second, the maximum bulk density in the 2F core (0.15 g cm^{-3}) exceeds that of 2K (0.13 g cm^{-3}). Both of these changes suggest that the 2F core experienced compression in the vertical direction, relative to the 2K core. At the time which core 2F was collected (26. August, 1991), the bog surface was very dry; with the depth to water table approximately 70 cm below the peat surface. During these conditions, it is very difficult to obtain a peat monolith without compressing the core, especially with the abundance of roots of *Ericaceous* shrubs and *Eriphorum* fibres which dominate the near surface layers of the

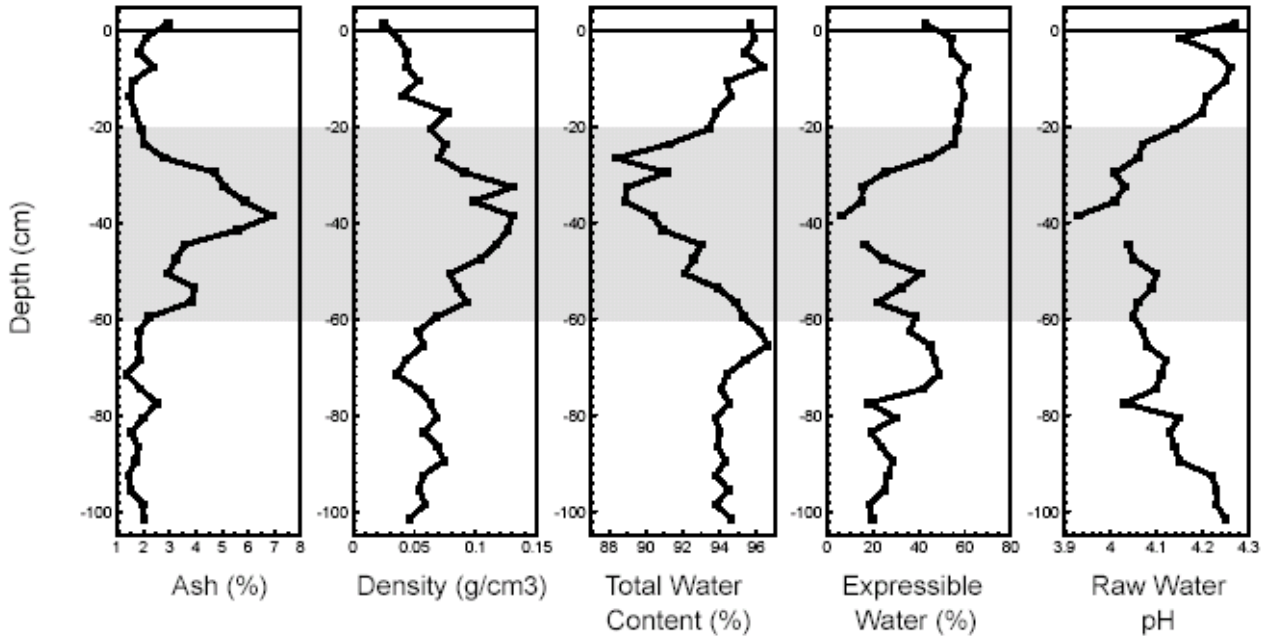


Fig. 2. Ash concentration, bulk density, total water content, expressible water, and raw water pH, 2K core.

peat profile. Comparison of the ash content and bulk density profiles introduces (Fig. 1) the suspicion that the 2F core was compressed, relative to 2K, during core retrieval.

The abundance and distribution of total Pb concentrations exhibit striking differences: in 2F, there are two nearly identical peaks in Pb concentration, whereas in the 2K core the deeper, older peak is clearly superior (Fig. 1). The concentrations of Pb at these depths exceed the LLD (0.4 μg g^{-1}) by more than two orders of magnitude, and in this concentration range the accuracy and precision of the Pb measurements using EMMA XRF are better than 5 % (Cheburkin *et al.*, 1996). Thus, the difference in the abundance and distribution of Pb cannot be explained in terms of analytical error. Titanium and Zr both show two pronounced peaks in each core, but the ratios between the two peaks differ (Fig. 1): in the 2K core, the ratio of Ti and Zr in peak A to peak B are 1.5 and 1.9, respectively; the corresponding ratios in 2F are 1.2 and 1.5, respectively. Thus, soil-derived mineral material is relatively more abundant in the A peak of the 2K core than the A peak of the 2F core. To say it another way, Pb, Ti, and Zr are relatively more abundant in the B peak of core 2F compared with core 2K. This difference may simply reflect the extent of natural variation with a given area at a given time, as observed previously using *Sphagnum* mosses collected from a given bog during a single year (Weiss *et al.*, 1999). However, if both Pb and Ti have been accidentally increased at any point in the 2F peat core by vertical compression while coring, then both elements would increase in concentration to the same extent, and this would have no net effect on anthropogenic Pb calculated as described earlier. Thus, the direct effect of compression in the 2F peat core on the concentrations of Pb and Ti cannot explain the differences in the relative abundance of anthropogenic Pb between the two cores.

2.2. Effects of core compression on the age-depth relationship

To further evaluate the possibility that the 2F core may have been compressed and to try to understand the possible importance of this process, the age depth relationship has been plotted for the entire length of both cores (Fig. 3a) and for only the uppermost layers which were dated using ^{210}Pb (Fig. 3b). Both graphics show clearly that there has been some

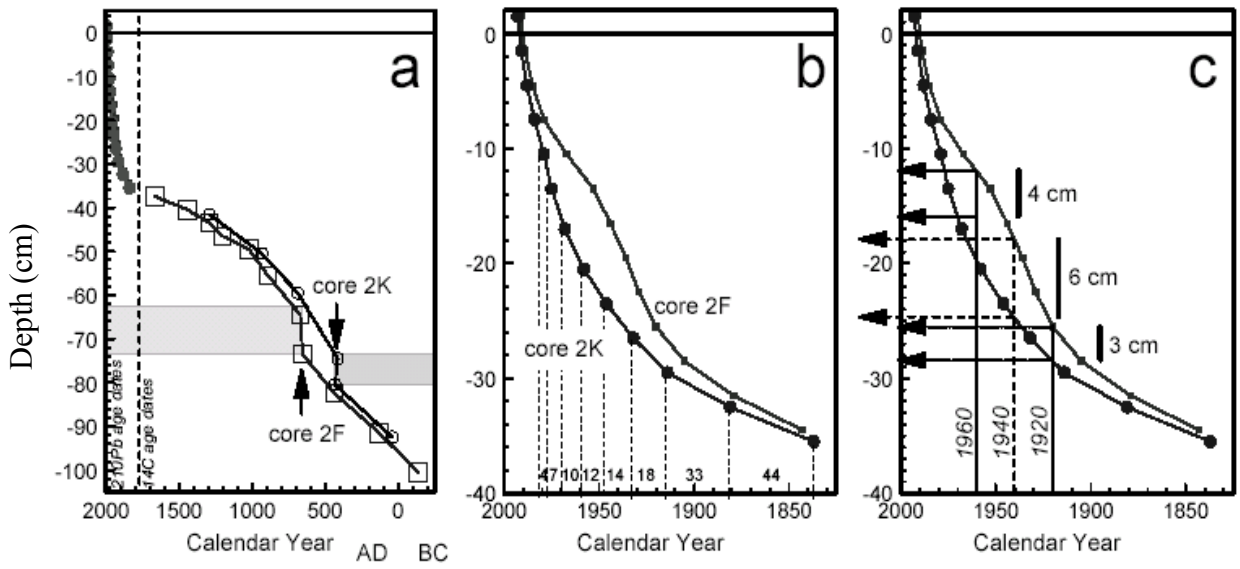


Fig. 3. a) Age-depth relationship in the two peat cores. Vertical dashed line distinguishes ^{210}Pb from ^{14}C age dates. Notice that both ^{14}C curves show an inflection, indicated by the arrows, but that this section is deeper in the 2K core (shaded bar on right) compared to 2F (shaded bar on left). b) ^{210}Pb age dates of the two peat profiles. Numerical values between vertical dotted lines indicate the number of calendar years represented by each slice. c) Assuming that the ^{210}Pb age should represent the same depth in each peat core, the dotted line indicates the vertical displacement (cm) between the two cores at AD 1920, the dashed line at AD 1940, and the solid line at AD 1960.

vertical displacement of the 2F core, relative to 2K. First, the arrows in Fig. 3a show an inflection point where age does not measurably change with depth; in the 2F core, this is found between 64 and 74 cm, but in the 2K core from 74 to 81 cm. The change in ^{210}Pb age with depth shows that the 2F core has certainly been compressed, relative to 2K, in particular in the range ca. 10 to 30 cm (Fig. 3b).

Also shown in Fig. 3c is the incremental age, in calendar years, for the individual slices of 2K samples pre-dating ca. 1980. This information is included to emphasize the increase in age of each peat slice with increasing depth. In the range where the 2F core was compressed, the individual peat slices represent from 4 to 33 years of peat accumulation. The effect of compression on age therefore becomes increasingly important with depth, as a greater proportion of older material becomes compressed into a given volume. The extent of compression can be estimated by assuming that any given ^{210}Pb age should be found at the same depth in each core. Assuming this ideal case, the vertical difference between the two cores is approximately 3 cm at 1920, 6 cm at 1940, 12 cm at 1960, and 4 cm at 1980 (Fig. 3c).

Despite these differences and the causes to which they are due, compression of the peat core will affect the activity of ^{210}Pb and the concentrations of Pb and Sc, all to the same extent. Compression of the peat core alone, therefore will not affect the chronology or intensity of the changes in anthropogenic Pb concentrations.

2.3. Effects of hand slicing of peat cores on the chronology of anthropogenic Pb

When the two peat cores were sectioned, they had been removed from the bog and were cut fresh, at ambient temperature, by hand using a bread knife. A measuring tape was attached to the cutting board and used to guide the eye while positioning the knife blade. While the intended thickness of each slice was 3 cm, no effort was made to determine the accuracy or precision of the cuts. Using the

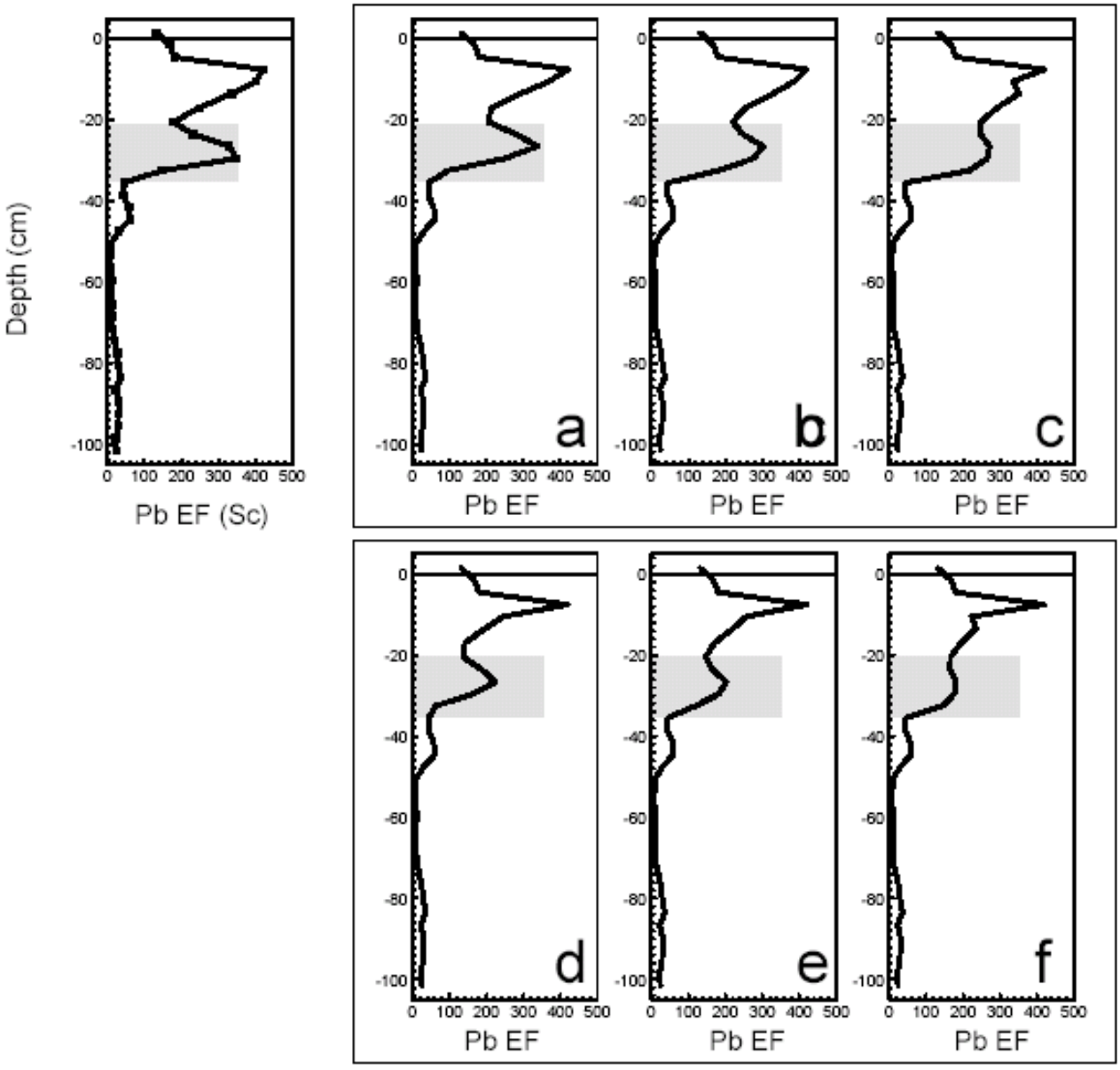


Fig. 4. Modelling the Pb EF using a moving average calculation which varies the position and thickness of peat slices.

green plant material as a guide to the location of the living, biologically active layer, this section was cut away first, and is the first sample of each core. Strictly speaking, however, this material is living plant matter, and not peat. After cutting away the living layer, the top of the core became the "zero" depth, and all subsequent cuts, in increments of ca. 3 cm, were made relative to this point. Given the differential compression between the two cores and the differences in age-depth relationship, modelling of curve smoothing and combined smoothing plus compression scenarios indicates that the thickness and position of peat core slicing can significantly affect the intensity of a peak in anthropogenic Pb (Fig. 4) by incorporating overlying and underlying material of lower anthropogenic Pb concentration. Not only could this process affect the calculated concentration of anthropogenic Pb per slice, but also the chronology of the enrichment, as determined using ^{210}Pb, as material of younger and older age becomes incorporated into any given slice.

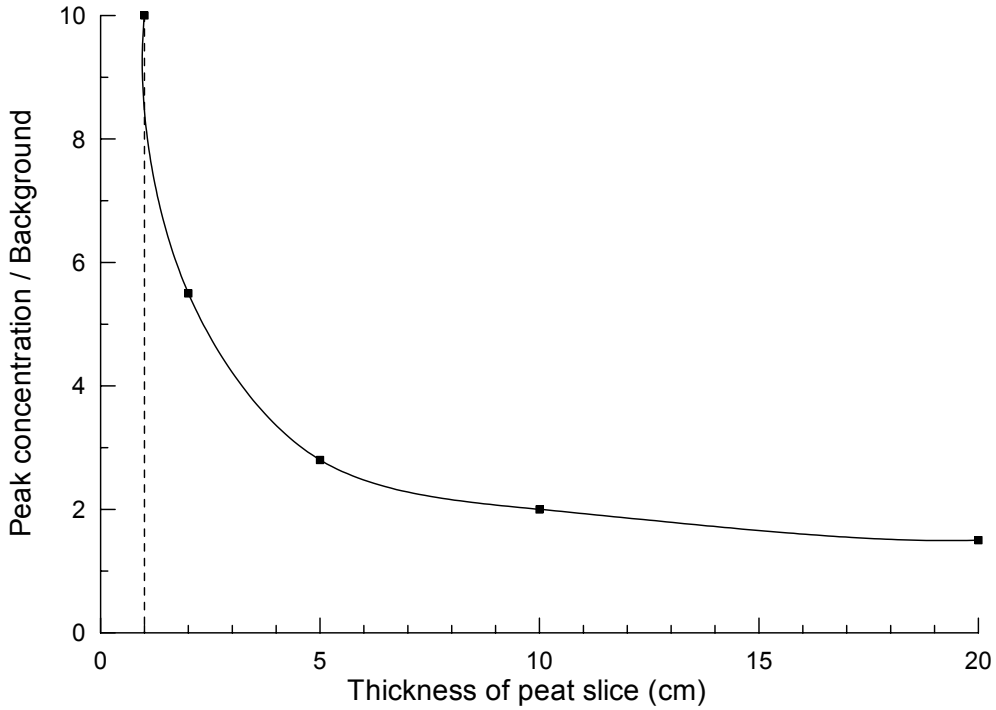


Fig. 5. Signal/noise ratio versus the thickness of the slice. The magnitude of the peak depends on the thickness of the peat slice.

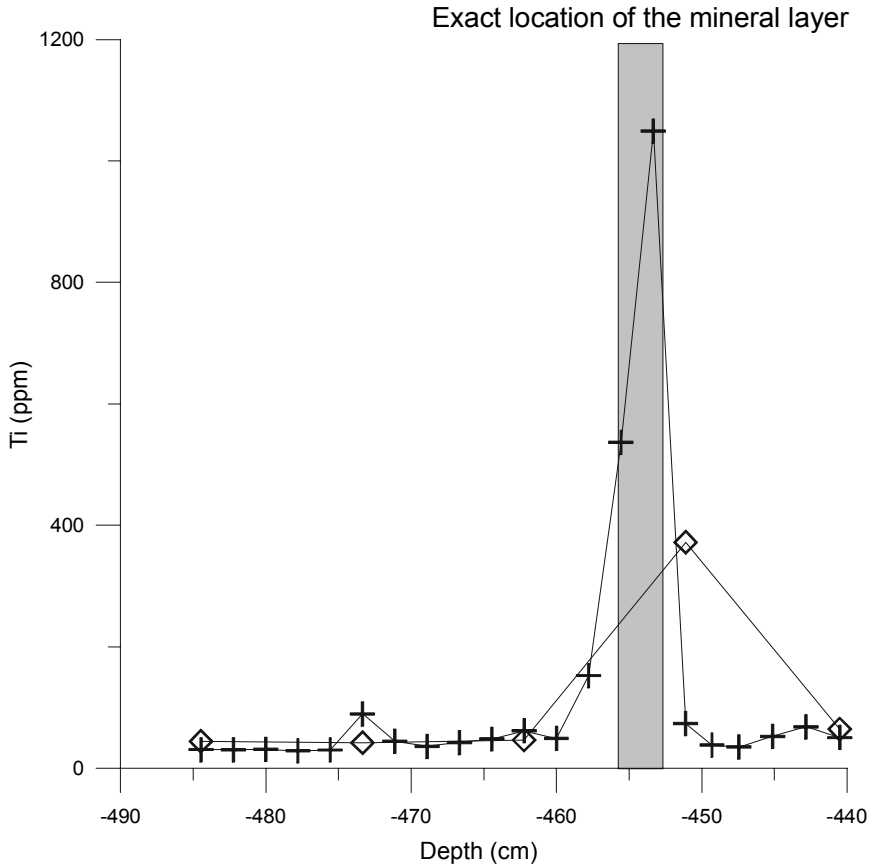


Fig. 6. Concentration of Ti (ppm) between 440 and 490 cm depth from a peat core from the Black Forest, Germany.(Cheburkin *et al.*) Titanium concentrations were measured in every second sample, cut into 1 cm slices; those are reported as crosses (+) whereas average Ti concentrations for five samples (10 cm peat section) are indicated by diamonds (◇).

2.4. Effect of the thickness of a peat slice on the signal resolution

The resolution and magnitude of any given peak depends on the thickness of the slice (Fig. 5). The thinner the slice is, the better will be the resolution of the record. Moreover, as shown in Figure 1, over a small vertical distance (ca. 50 cm), there are extreme changes in Pb concentration, as well as significant changes in ash content and bulk density. Therefore the thickness of the slices is of greatest importance in the uppermost peat layers which represent the most critical time period in terms of pollution reconstruction (i.e. the past two centuries since the start of industrialisation). However, even in the lower peat layers, the thickness of the slices is also important. For example, short-lived events such as the deposition of volcanic ash can be clearly resolved using 1 cm slices (Fig. 6). Thicker slices, however, not only provide poorer resolution (Fig. 6), but they also prevent the event from being accurately age-dated.Taken together, the available evidence suggested that the protocol used during the past decade had to be improved. Specifically, cutting the cores very precisely into 1 cm slices will maximize the signal/noise ratio of the peaks in metal concentration and therefore greatly contribute to improving the accuracy, reproducibility and reliability of peat bog archives (Figure 7).

3. Improvements and proposed protocol

Since EGR 2F and 2K cores were collected in 1991 and 1993, respectively, several changes have been made in the collection, handling and preparation of peat cores to improve the accuracy and precision of peat bog records of atmospheric dust and trace

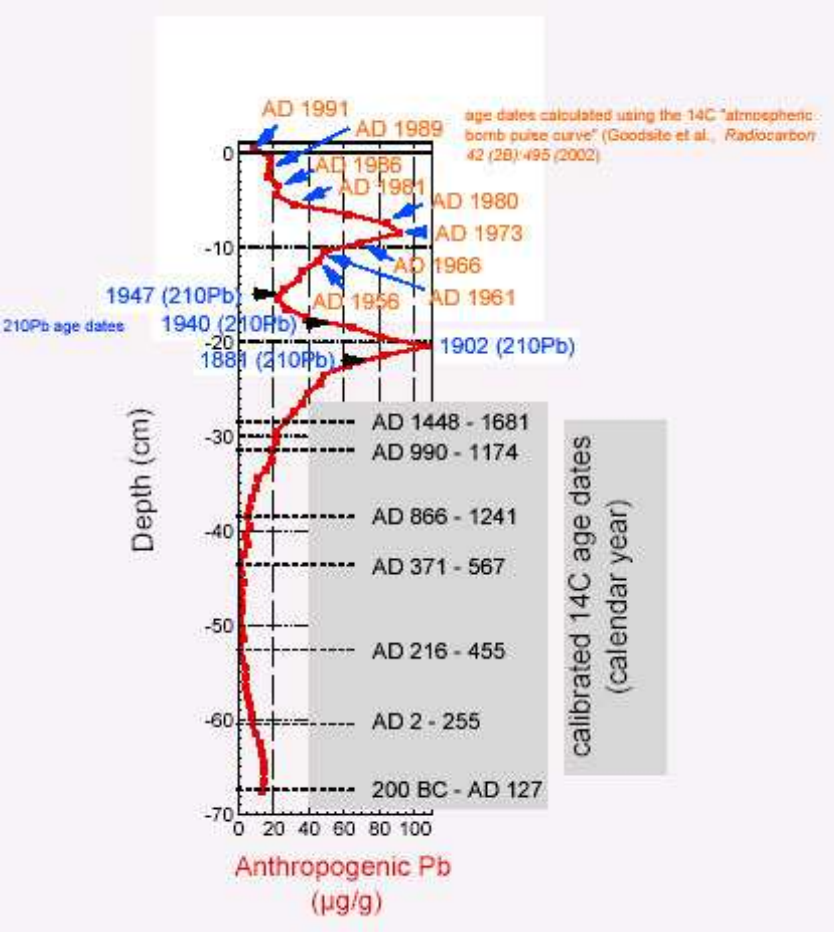


Fig. 7. Concentration of Pb (ppm) for the Wardenaar peat profile 2G from Etang de la Gruère, Switzerland (Shotyk, unpublished). This core was collected the same year as the EGR 2F core (i.e. 1991). It shows the kind of resolution which can be obtained using 1 cm slices (compare the 2F and 2K cores (Fig. 1) which were cut into 3 cm slices) and accurate age dating.

metal deposition. The most important changes are summarised below.

3.1. Field sampling strategy

The success of paleoenvironmental studies using peat cores as archives largely depends on the ability to select appropriate peatlands which have preserved high-quality paleoenvironmental records. Therefore careful selection of sites and coring locations within the sites are critical elements of field research. Although, the strategy will vary depending on the purpose of the study and the site itself, several general considerations can be helpful to design suitable field sampling strategies and for retrieving peat cores. Since comprehensive field observations are a very valuable aspect of the survey, pertinent information that should be recorded are listed and discussed below.

Site selection

To reconstruct the deposition history of atmospheric particles using peat cores, selection criteria should include the morphology of the peatland (topography and depth of peat accumulation), character of peat (visual inspection of the botanical composition, degree of decomposition, moisture content and abundance of mineral matter), possible damages to the peatland and to the peatland hydrology (peat cutting, drainage, dams), possible use of the peatland for forestry or agriculture, and distance from human activities.

Not all peatlands are appropriate for the reconstruction of the changing rates of atmospheric metal deposition and it is worthwhile to pay particular attention on the selection of the peatland. The quality of the paleoenvironmental record for many trace elements is mainly controlled by the trophic status of the peatland as revealed by e.g. the botanical composition and abundances of mineral matter. Ombrotrophic ("rain-fed") bogs should be favored over other types of peatlands, as they receive water solely from atmospheric precipitation (rain, snow) falling onto their surface. Ideally, the most valuable part of a bog is the raised dome. Neither groundwater nor surface water runoff from other areas can reach the raised part of the bog, as it is above the level of the local groundwater table. Moreover, ombrotrophic bogs provide records with better time resolution than minerotrophic deposits, mainly due to the lower degree of organic decomposition. Both biological and chemical characteristics that can be used in the field and in the lab to establish the existence of an ombrotrophic zone are presented elsewhere in detail (Shotyk, 1996). The mineralogical and chemical composition of the basal sediment on which the peatland is resting should be also considered. Weathering of minerals from the underlying rocks and sediments could be an important source of ions which migrate upward into the peat by diffusion (Shotyk *et al.*, 1994). There is a great difference between the trophic status of peat profile in a bog forming on calcareous versus granitic substratum, with carbonate weathering clearly supplying more metals to the basal peat layers. Therefore, ombrotrophic bogs underlain by granites are chemically less affected by upward diffusion of ions and should be favoured over bogs growing on carbonate rocks.

If ombrotrophic bogs are common in temperate and boreal latitudes, they are scarce in sub-Arctic and Arctic latitudes (Charman, 2002). Therefore at high latitudes, minerotrophic peat deposits may have to be used as archives of atmospheric metals even though they are fed both by atmospheric and terrestrial inputs. Recent studies have shown that at some predominantly minerotrophic peatlands, mercury and lead may be supplied exclusively by the atmosphere and therefore can still provide a record of the changing rates of atmospheric deposition of those elements (Givelet *et al.*, ; Shotyk, 2002; Roos-Barraclough *et al.*, 2003; Shotyk *et al.*, 2003). Such reconstructions, however, must be interpreted with great caution and on an element-by-element basis because some metals of interest e.g. nickel (Krachler *et al.*, 2003) and uranium (Krachler *et al.*) are certainly enriched in minerotrophic peat due to weathering inputs.

Before selecting the exact site for collecting peat profiles at a peatland, the site morphology must be known. If this is not the case, it could be established by depth profiling at least two transects at 90°. This process will help selecting the deepest ombrotrophic part of a bog or the deepest organic accumulation of a minerotrophic peat deposit. Comparison of mercury and lead fluxes to hummocks and hollows of ombrotrophic bogs suggest that cores from both locations are recording trends in atmospheric deposition of Hg and Pb, but that hollow cores are recording lower input values than hummock cores, apparently due to a larger component of dry and occult (fog) deposition at hummocks than at hollows (Norton *et al.*, 1997). Therefore sampling sites located in "lawns", or at the transition between hollow and hummock are considered to be optimal and therefore recommended.

Prior to peat core collection, permission to retrieve geologic and environmental samples should be secured from the owner of the land if necessary. This is especially important in the case of nature reserves and other protected areas where many of the remaining central European raised bogs are found.

Core collection

The low density and the unsaturated environment of the topmost layers of a peat bog make the collection of good quality peat cores challenging. It is difficult to cut these layers as they are easily trampled and compressed. Moreover, the upper layers of a peat bog represent the past decades which is the most critical and interesting period in terms of atmospheric pollution, not only for trace metals and organic contaminants, but also for fallout radionuclides. The main concern about this section is to collect surface layers as an undisturbed continuous peat profile extending as far back in time as possible in an effort to reach "natural background" values. By using procedures developed by our research group, all fieldwork is completed in such a way as to minimize the impact on the environment, utilizing the latest techniques and best available technology for sampling, handling and preparing the materials.

Modified Wardenaar corer

The topmost layers of peat can be collected using a 10 cm × 10 × 100 cm Wardenaar peat profile cutter (Belokopytov *et al.*, 1955) which is commercially available. Our 1 m Wardenaar corer with XY dimensions 15 cm × 15 cm, was home-made using a Ti-Al-Mn alloy and includes a serrated cutting edge; this new cutting edge cuts more easily through dwarf shrubs (e.g. *Ericaceous* shrubs) and *Eriphorum* root fibres. This feature, combined with the larger cross sectional area means that any given slice undergoes less compression in the Z (vertical) dimension. Moreover, the enlargement of the XY dimensions to 15 cm of the new Wardenaar corer compared to the older version (10 cm) provides enough peat sample material to conduct a wide range of analyses and still to be able to preserve part of the material as an archive for futures work, even using thin slices (i.e. 1 cm). The state of the art of the modified Wardenaar corer and the best way to collect a good quality peat core from the surface layers of a bog are described in detail elsewhere (Noernberg *et al.*).

During extraction, some compression of the peat core is unavoidable. However, the compression can be measured, using the bog surface as a reference. After extraction, the Wardenaar corer is laid horizontally on the bog surface, on a large sheet of plastic; the top half of the Wardenaar corer is removed, exposing the peat monolith. This core is described visually in the field (length, colour, texture, plant remains, moisture, special layers) and photographed. The core is inspected for modern plants of the bog surface which may have "contaminated" the outside of the core; these are carefully removed using a small knife. The exposed surface and two sides of the core are wrapped in polyethylene cling film. A wooden core box built specifically for the Wardenaar core is lined with plastic (a large sheet, or two large sheets, is made using plastic garbage bags). The plastic-lined wooden core box is placed over

the peat core. Two people lift the bottom half of the Wardenaar corer, flip it carefully backward 180°, allowing the peat core to slide down into the box. The surface of the core is wrapped in polyethylene cling film, with the film pressed down around the sides of the core and ends using a plastic spatula. The core is covered with plastic, labelled and the lid attached using screws. In this way, handling of the core in the field is kept to a minimum.

Belarus corer

A Belarus (Macaulay) peat sampler is used for deeper peat layers (Belokopytov *et al.*, 1955). Two versions of this corer are actually used: stainless steel and titanium (Ti). The titanium corer, which is much lighter, was constructed using the same alloy as for the Wardenaar corer.

Cores are removed from two holes adjacent to the hole from the Wardenaar core, approximately 20 cm apart, in parallel overlapping design. Peat cores are carefully packed onto plastic-semi tubes which are lined with polyethylene cling film: while still in the peat corer, the peat sample (a semi-cylinder ca. 50 cm long and 10 cm wide) is wrapped with polyethylene cling film and a plastic semi-tube is placed on top; the corer is gently flipped backwards 180°, and holding the semi-tube, the core is carefully slid away from the corer. Again, the cores are described and photographed without touching them. The core is wrapped with polyethylene cling film, labelled, and packed in rows in a transport aluminium box.

Motorized corer for frozen peat

A unique peat sampler was designed and built by Mr. Tommy Nørnberg for obtaining continuous samples of frozen peat in the Arctic. Up to 10 meters of frozen peat in 70 cm sections can be removed using this corer. The sampler and the coring technique is described in detail elsewhere (Noernberg *et al.*).

Cores are kept cool until they can be frozen: this is done soon as possible after collection, and kept frozen at –18 °C until they can be prepared in the laboratory. Cores collected from frozen peat deposits are shipped frozen back to the laboratory.

Field observations

Pertinent field observations that should be gathered during the fieldwork include sampling date and time, sampling site significance and location. The precise location of the core collection should be indicated on a topographical map and the GPS coordinates recorded. Because it may be very useful to return to the coring site at some future date, burying a plastic soda pop bottle containing a handful of steel just below the surface of the coring site will allow the exact site of core collection to be found later, using a metal detector. This also helps to avoid possible further peat collection at the same location, as the peat stratigraphy may have been affected by the coring session. Notes on colour, component, length, depth, core compression and other details (e.g. layers of wood, charcoal) are also information that should be recorded. As noted earlier, core compression during sample collection can be a problem, because of secondary effects on the metal concentration profiles and/or the age-depth relationship. Therefore, coring in spring or early summer when the peatland is at its wettest is recommended. Additional pertinent information that should be recorded includes maximum depth of peat accumulation at the collection site and possible disturbance. Collection of representative surface plant species may serve as a valuable reference for the plant material which constitutes the fossil botanical assemblage of the peat cores.

In order to achieve consistency in recording such data, a field report should to be written. This primarily provides a public report of the fieldwork, detailing how and where peat and other geologic or environmental samples were taken for subsequent dating and analysis. The Field Report format developed by M.E. Goodsite is highly recommended (Goodsite *et al.*, 2001) and is available for downloading for free use

at http://www.rzuser.uni-heidelberg.de/~i12/eergebnisse.htm.

3.2. Samples preparation

To have a rapid, approximate description of the geochemistry of a peat core, a sacrificial core may be sliced immediately in the field using a serrated stainless steel knife into 3 cm slices. Using plastic gloves, each slice is placed in a plastic bag and the bag squeezed by hand to express the pore water. The pore waters may be analyzed for pH, major element cations and anions, and DOC (Shotyk *et al.*, 1994). Slicing the core by hand with a knife has some advantages, as it can provide a rapid survey of the geochemistry of the peat profile if the pore waters are analysed. However it only provides an approximate description of the geochemistry, and this preparation procedure is not suitable to reconstruct high-resolution records of atmospheric metal contamination.

Slicing the cores

With respect to high-resolution records, Wardenaar, Belarus and Nørnberg peat cores are cut frozen in the lab into 1 cm increments using a stainless steel band saw with stainless steel blades. The width of the blade is 1 mm, so ca. 10% of each slice is lost during cutting. The accuracy of the thickness of theses slices is better than ± 1 mm. For Belarus and Nørnberg cores, a slicing system was designed and constructed as described elsewhere (Noernberg *et al.*). A similar system made of an Omega SO 200a band saw and a precision cutting table is used to slice the Wardenaar cores. Because the cores are large and long, they are heavy (~23 kg) and the cutting table is necessary for precise cutting. The individual slices are subsequently placed on a polyethylene cutting board and the outer 1 cm of each slice is trimmed away using a 13 × 13 cm polyethylene plate and either an acid rinsed ceramic knife or a Ti knife (Fig. 8). The outside edges are systematically discarded, as those could have been contaminated during the sampling and preparation procedures by layers enriched in mineral matter such as tephra layers (e.g. Faroe Island cores), or where there are very high metal concentrations (due to intense atmospheric pollution). The cutting board and knife are rinsed with deionised water three times between each slice. Then slices are packed into labelled zip-lock plastic bags for storage and further preparation.

Sub-sampling Strategy

Great care has to be focused on the orientation of each slice during the slicing session with respect to its original position when it was in the peat monolith. To guarantee the reconstruction of high-resolution records, peat material for a given analysis should be sub-sampled along a conceptual micro-core within the Wardenaar core and therefore at a similar location within the oriented slices.

A sub-sampling strategy is defined for each individual core depending of the main objective of the study. An example of the approach we use is shown in Figure 8. Two 6 × 6 cm squares are removed using a polyethylene plate. The squares are divided into four triangles by cutting each square along its diagonal. Each triangle is identified with respect to its position within the peat slice, packed into labeled bags and reserved for previously defined analyses (Fig. 8). Part of the material is archived at -18 °C for possible future studies, and the remainder of the sub-samples will be processed for physical, chemical, mineralogical and isotopic analyses.

Drying and milling

The peat samples are dried at 105 °C in acid-washed Teflon bowls, and macerated in a centrifugal mill equipped with a Ti rotor and 0.25 mm Ti sieve (Ultra centrifugal Mill ZM 1-T, F.K. Retsch GmbH and Co., Haan, Germany). This yields a very fine, homogeneous powder with average particle size of ca. 100 µm (and Gaussian particle size distribution). For finer powder (e.g. for slurry sampling AAS), the direction of the sieve can be reversed. For samples rich in mineral matter (e.g. tephra layers) and for organic-rich sediments, an agate ball mill is used instead.

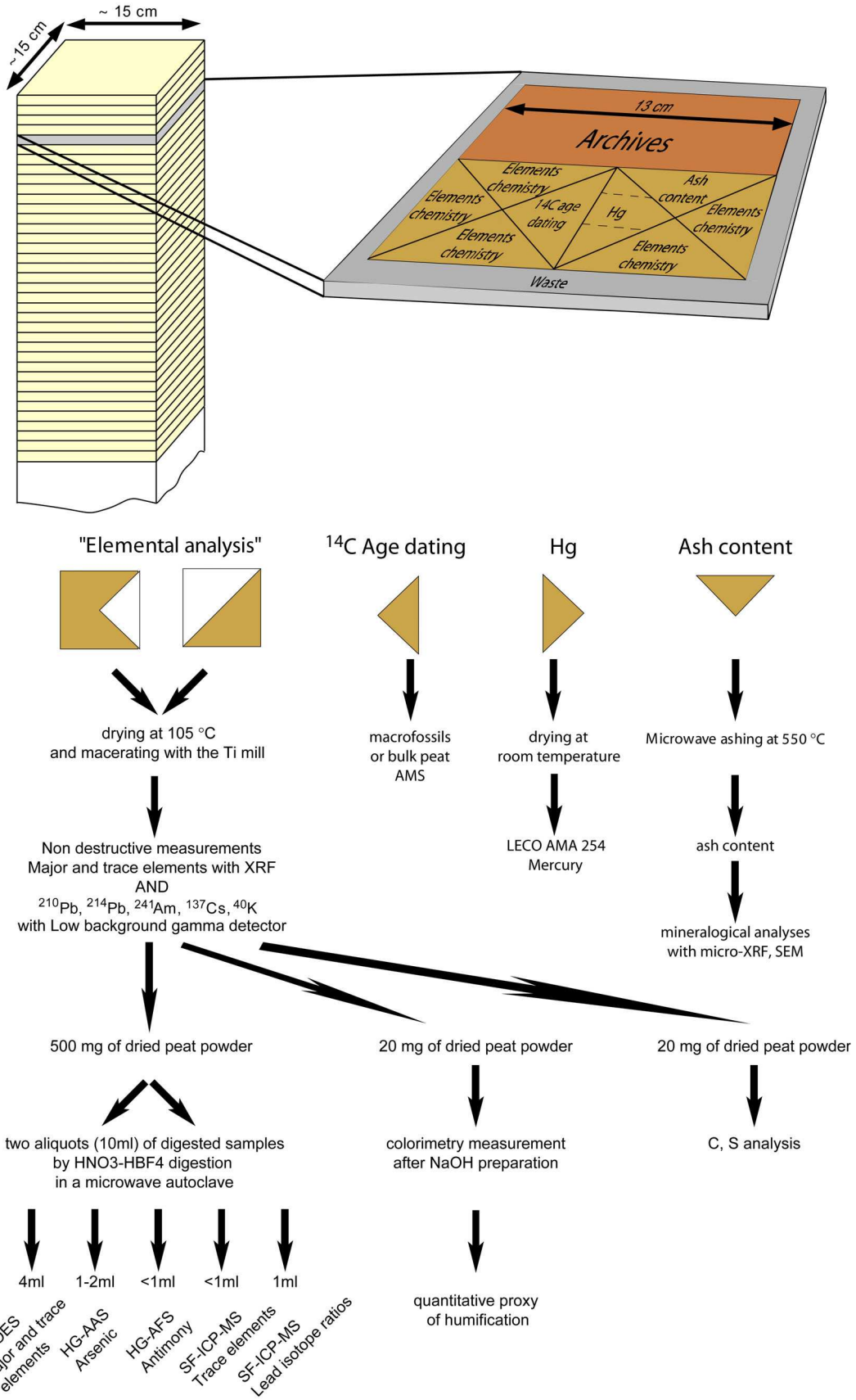


Fig. 8. Analytical flow chart and sub-sampling strategy for a peat slice from a Wardenaar core. The outside edges of the slices are systematically removed to waste to ensure that only the uncontaminated part of each sample is used for study. Part of the slice is archived for possible future studies. Peat triangles are sub-sampled, oriented to ensure that, for any given analysis, the sub-samples are taken from the same position in each slice.

The powdered samples are manually homogenised and stored in airtight plastic beakers. The milling is carried out in a Class 100 laminar flow clean air cabinet to prevent possible contamination of the peat samples by lab dust. In the laboratory, all of the sample handling and preparation is carried out using clean laboratory techniques. Peat powder stored for longer than one year in humid conditions should be re-dried prior to analysis following similar procedures for certified standard reference materials (e.g. plant SRMS from NIST, BCR, or IAEA).

3.3. Analyses

Physical analyses

The precision of the bulk density measurements is of great importance for the reconstruction of records of metal contamination as the bulk density data is used to calculate the rates of metal accumulation. Until recently, the centers of the peat slices were sub-sampled using a sharpened stainless steel tube (16 mm diameter) and these plugs used to determine the dry bulk density. The height of each plug was measured to an accuracy of 0.1 mm and the volume calculated. After recording wet weights, plugs were dried at 105 °C overnight and the dry mass was weighed to 1 mg. Later, in order to decrease the discrepancy of the diameter of the plugs induced by the operator, a hand-operated stainless steel press was used to recover plugs of 20 mm diameter with an accuracy of 0.1 mm (Noernberg *et al.*). However, with respect to the heterogeneity of peat material within a slice, especially the upper layers of modern accumulation, and the unknown, possibly important uncertainties in the measurement of the volume and weight of a small plug of peat material, we found that the determination of bulk density was an important source of error in the calculation of rates of metal accumulation. For example, the calculation of Hg accumulation rates in a peat core from southern Ontario using the minimum and the maximum value of bulk density determined using four plugs for each slice show the

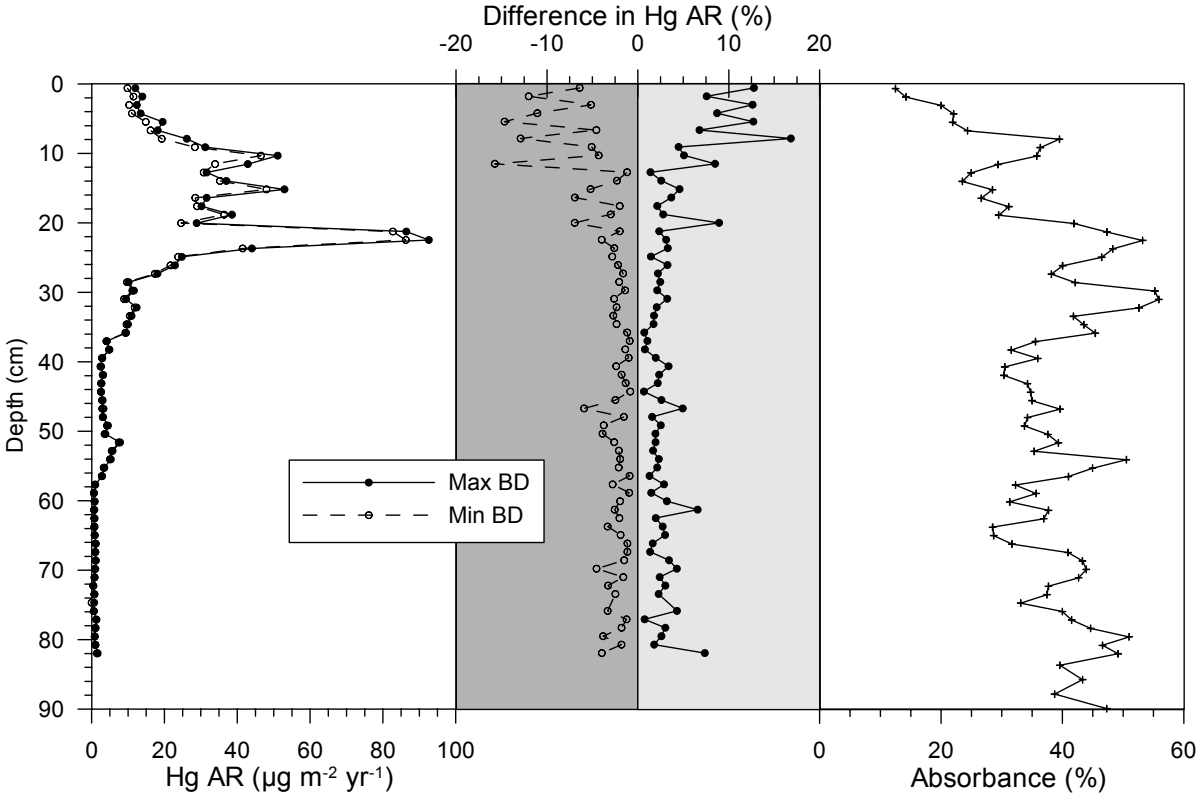


Fig. 9. Comparison of mercury accumulation rate profiles calculated using a) minimum bulk density value and b) maximum bulk density value for a peat core from southern Ontario, Canada. The corrected absorbance is an indicator of the degree of peat humification.

calculated Hg accumulation rates of mercury may be ± 10 % of the accumulation rate value calculated using the average bulk density value of the four plugs (Fig. 9). This is mainly explained by the heterogeneity of the peat material within a given slice, especially in the surface peat layers which are poorly decomposed. Therefore the use of larger volume samples, such as the 6 × 6 cm rectangle as recommended in the previous section, should improve the quality of the bulk density measurement because they are more representative of the slice, thereby also improving the accuracy of the rate of metal accumulation calculation.

The degree of decomposition of the peat is measured by colorimetry on alkaline peat extracts at 550 nm using a Cary 50 UV-visible spectrophotometer. The powdered peat samples (0.02g) are placed in test tubes and 8 % NaOH soln. (10 ml) is added. The samples are shaken then heated 95 ± 5 °C for 1 hour, then made up to 20 ml with deionised water, shaken and left to stand for 1 hour before being re-shaken and filtered through Whatman no. 1 filter papers. Samples are diluted with an equal quantity of deionised water directly before colorimetric measurement. The percentage of light absorption (% absorbance) in these extracts may be used as a proxy of peat humification (Caseldine *et al.*, 2000).

Chemical analyses

The development, evaluation and use of peat cores from ombrotrophic bogs as archives of high-resolution reconstructions of atmospheric deposition of mineral dust and trace elements have led to the development of many analytical procedures which now permit the measurement of a wide range of elements in peat samples.

Prior to any expensive and time consuming chemical procedure and analysis, measurement of major and trace elements in peat samples using the non-destructive and relatively inexpensive X-Ray Fluorescence (XRF) method is performed on all peat samples first. This method provides invaluable geochemical data that helps to document the natural geochemical processes which occur in the peat profiles and their possible effect on the distribution of trace elements. Calcium (Ca) and strontium (Sr), for example, can be used to identify mineral weathering reactions in peat profiles, manganese (Mn) and iron (Fe) redox processes, bromine (Br) and selenium (Se) atmospheric aerosols of marine origin. Titanium (Ti) and zirconium (Zr) are conservative, lithogenic elements whose abundance and distribution reflects the variation in mineral matter concentration in the peat core (Shotyk *et al.*, 2001). One gram of dried, milled peat may be analysed for these and other major and trace elements simultaneously (Y, K, Rb, Cr, Ni, Cu, Zn, As and Pb) using the EMMA XRF (Cheburkin *et al.*, 1996; Cheburkin *et al.*, 1999). Titanium (Ti) may be analysed precisely using the new TITAN XRF spectrometer which provides a lower limit of detection for Ti of only 1 $\mu g\ g^{-1}$. Both instruments measure the sample in powder form. Because the method is non-destructive, these same samples can be used again for other measurements (Fig. 8). Complete details about the design and construction of this instrument are presented in a separate publication (Cheburkin *et al.*).

Mercury

Solid peat samples can be analysed for Hg using a direct mercury analyser (LECO AMA 254) (Roos-Barraclough *et al.*, 2004). The main advantage of this approach is that no acid digestion of the peat sample is necessary. After air-drying overnight in a Class 100 laminar flow clean air cabinet, three subsamples, previously removed from a determined portion of each slice, are analysed for total Hg, and the results of the three subsamples are averaged (Fig. 8). The detection limit of the instrument is 0.01 ng Hg and the working range is 0.05 to 600 ng Hg, with reproducibility better than 1.5%.

Acid digestion procedures

Other elements in solid peat samples can be quantified for a wide selection of trace elements using instrumental neutron activation

analysis (INAA). As no certified reference material for trace elements in ombrotrophic peat was available until recently, INAA data served as a reasonable benchmark for the development of other analytical procedures requiring dissolution of peat samples. In this context, several digestion procedures for the acid dissolution of peat have been developed and evaluated using open vessel digestion as well as closed vessel digestion procedures on a hot plate or using microwave energy. No matter which digestion approach is considered, it is essential to completely destroy the silicate fraction of peat in order to release the trace elements that are hosted in the silicates. This can be achieved by the addition of HF or HBF_4 to the acid mixture, whereas the use of HBF_4 provides many advantages in that context and thus is highly recommended (Krachler *et al.*, 2002; Krachler *et al.*, 2002).

Quantification of trace elements

Trace elements in these digestion solutions have been determined using ICP-MS, ICP-OES, HG-AAS and HG-AFS (Krachler *et al.*, 1999; Krachler *et al.*, 1999; Krachler *et al.*, 1999; Krachler *et al.*, 2001; Krachler *et al.*, 2002; Chen *et al.*, 2003). The large variety of analytical instruments available allowed several inter-method comparisons which greatly benefit the quality of the analytical results (Fig. 8). Both ICP-MS and ICP-OES were used to analyse more than 25 elements, whereas work to date with HG-AAS and HG-AFS mainly focused on the determination of low concentrations of arsenic and antimony in peat (Chen *et al.*, 2003; Shotyk *et al.*, 2004). Using ICP-MS, a powerful multi-element technique with low detection limits, it has been possible to establish complete chronologies of Ag, Tl, Pb, Cd; (Shotyk *et al.*) Mo, U, Th; (Krachler *et al.*), the REE (Krachler *et al.*, 2002) and V, Cr, Ni (Krachler *et al.*, 2003). A method has also been developed to determine major elements in acid digested peat samples using ICP-OES and this has been successfully applied to the determination of Al, Ca, K, Mn, Ti, Fe, Na, Sr, Mg concentrations. Again, measurements of international, certified, standard reference materials yielded results which are in good agreement with the certified values.

Lead isotope measurements

Lead isotope ratios in peat can largely help to identify the predominant anthropogenic sources of Pb. Lead isotopes measurements can be performed using ICP-MS. We recently developed a method using sector field inductively coupled mass spectrometry (SF-ICP-MS) after acid digestion of peat powders using a high-pressure and high-temperature microwave autoclave (Krachler *et al.*). The accuracy and precision of the ICP-SMS protocol was further evaluated using thermal ionisation mass spectrometry (TIMS) of selected samples and an in-house peat reference material. In general, the Pb isotope ratios determined using ICP-SMS deviated from the TIMS values by less than < 0.1%. Given the throughput of the ICP-SMS compared to the TIMS (which requires chemical separation of Pb), the ICP-SMS approach offers great promise for environmental studies to fingerprint the predominant sources of anthropogenic Pb. In a few cases when improved accuracy and precision are needed, the Pb isotopes ratios in these selected samples may also be measured using thermal ionisation mass spectrometry (TIMS).

Quality control

Decreasing limits and thresholds require accuracy, comparability and traceability of analytical measurements for the determination of elemental content in peat material. Certified Standard Reference Materials of coals and plants from the National Institute of Science and Technology (USA), the International Atomic Energy Agency (Vienna), South Africa, the European Community, Poland, the Czech Republic, and China are analysed in triplicate as blind standards. However, to guarantee accuracy, quality control, quality assurance or validation of a measurement by means of certified reference material, the assessment of analytical results in certified reference materials must be as accurate as

possible and every single step has to be fully evaluated. To date, the lack of a common certified peat reference material has hindered the quality assurance of the generated analytical data from different laboratories in the international community. There are ongoing efforts to fill the lack of a common certified peat reference material for working with peat material by developing a multi-element reference material for low-ash peat to be used by the international community (Barbante *et al.*, 2000; Yafa *et al.*, 2003).

Mineralogical analyses

Mineralogical analyses of the inorganic fraction could be of particular importance to identify the origin and type of anthropogenic and natural particles deposited on the surface of the peat bog. However because of the very low inorganic content in ombrotrophic peat, it is very difficult to extract the deposited atmospheric particles. Moreover in the case of a general study also including bulk peat geochemistry, there may be only a small quantity of peat available for mineralogical analyses. Finally the extraction method used is dependent on the type of mineral investigated because the reagents and temperature used could modify the minerals by oxidation (e.g. sulphides) or dehydration (e.g. clays). However, prior to mineralogical analyses, samples should not be milled. Many methods for extracting minerals grains from the bulk peat matrix are available from the literature, some of them designed for the extraction of specific fractions such as tephra glasses (Persson, 1971; Dugmore *et al.*, 1992) or recent anthropogenic particles.

One method used in our laboratory and proposed by Steinman and Shotyk (Steinmann *et al.*, 1997) is to ash the peat at 550 °C, remove the carbonates and other inorganic components formed during the ashing process using dilute HCl. These samples are then ready for optical microscopy and could also be analysed after preparation using Scanning Electron Microscope (SEM w/EDAX). Another approach is to digest the peat with 65% H_2O_2 in a Teflon beaker on a hot plate. Every ca. three days, the reagents are poured off and a new solution of 65% H_2O_2 is added until there is no visible trace of organic matter. However, this procedure is time-consuming and could last more than two weeks. It is possible to use an ultrasonic bath to mechanically extract the minerals before and after each H_2O_2 attack. Individual mineral grains which are large enough could be also directly analysed by microscopic techniques such as microbeam XRF (Cheburkin *et al.*, 1997).

Age dating

Establishing high quality chronologies is a critical feature of paleoenvironmental studies, especially for the last few hundred years which have witnessed so many changes. A reliable and detailed chronology is essential if peat bogs are to be compared with other high-resolution archives such as polar ice, laminated lake sediments, tree rings, bryophytes, including herbarium specimens. Multiple techniques can be used to develop peat chronologies including analyses of short-lived radioisotopes (^{210}Pb, ^{137}Cs, ^{241}Am, ^{14}C bomb pulse), historical pollen, chronostratigraphic markers, tephra layers, and fly-ash particles (Renberg *et al.*, 2001).

<u>Radiocarbon age dating</u>

It should be relatively straightforward to establish radiocarbon-based chronologies for most Holocene peats used for paleoenvironmental reconstructions. However, there are a number of problems to be considered in radiocarbon dating peat. In the past, ^{14}C age dating was typically done using the decay counting method on bulk samples. This method had the disadvantage of wasting a large amount of material, because several grams of dry peat was needed. Moreover, radiocarbon age dating of bulk samples can be problematic as it may lead to ^{14}C age inversions in cases where older peat layers have been penetrated by younger plant roots (Weiss *et al.*, 2002). Therefore macrofossils of *Sphagnum* moss, specifically selected and cleaned are ideal for radiocarbon dating as mosses have no root systems and therefore

cannot introduce younger carbon to lower layers. Careful sample selection and cleaning (removing roots of other plants), pre-treatment (washed water followed by an acid-base-acid treatment) circumvents other potential problems such as the mobility of carbon in the peat profiles. However some movements of carbon can occur, especially of dissolved organic carbon; the translocation of younger carbon to deeper horizons by vascular plant roots or the possible "reservoir" effect involving translocation of older carbon to contemporary vegetation also are real concerns.

Age dates of plant macrofossils younger than AD 1950 can be obtained using ^{14}C by directly comparing the absolute concentration of ^{14}C in the sample to the general-purpose curve derived from annually averaged atmospheric $^{14}CO_2$ values in the northernmost northern hemisphere: post-1950 ^{14}C concentrations in the atmosphere are elevated compared to natural levels due to atomic weapons testing. This approach which effectively matches the ^{14}C concentrations (percent modern carbon, or PMC) in successive plant macrofossils to the increase (since AD 1950) and subsequent decrease (since AD 1963) in ^{14}C concentrations is the so called "bomb pulse curve of ^{14}C" and has been successfully used to date peat accumulation in Denmark and in southern Greenland (Goodsite *et al.*, 2002). This comparatively new dating method has been found to provide high-resolution age dates which are accurate to ± 2 years.

Radiometric age dating

^{210}Pb is widely used for dating environmental records in natural archives such as lake sediments, peat bogs and marine sediments spanning the last 130 years or so (Appleby *et al.*, 1988). Assessing ^{210}Pb dates in conjunction with dates from longer time-scale dating methods such as ^{14}C can be beneficial in a number of respects. Age dating peat profiles by combining independent dating methods helps to provide a reliable long time-scale chronology. The main advantage of ^{210}Pb age dating is that it can be done in-house using low background gamma spectrometry and therefore eventually reduces the cost of age dating. In contrast, ^{14}C age dating of plant macrofossils can be done only at those labs with Acceleration Mass Spectrometry (AMS) facilities.

When building up an age dating strategy, an important question is what are we trying to date? The age dating strategy will be different if we try to provide dates for a few events such as the concentration peaks in a record or if we establish a chronology for an entire record. In the case of dating specific events, the optimum strategy would be to direct all the effort at these particular periods (Mauquoy *et al.*, 2002). Therefore great attention is required in selecting material sent to the laboratory, to be sure that the most important events are dated. To establish a precise chronology for the entire peat profile, a regular interval of sample selection will guarantee the generation of an accurate age-depth model and therefore of a reliable peat chronology.

Modelling the age-depth relationship

Chronology reconstruction is based on a series of radiometric dates, sometimes supplemented by other markers (e.g. tephra layers…). As independent check, various models can be applied, all of which have underlying assumptions, even if they are not explicitly stated. The choice of model varies but is most often subjective, favouring linear model based on R^2 values, using central calibrated dates, and assuming continuous peat accumulation often without evaluating this assumption.

Without a large number of dates there is no convincing reason for preferring one regression to another or for using the same regression for all profiles (Telford *et al.*). We are forced to return to a subjective evaluation of curve fitting as well as our knowledge of peatland system. If we want to estimate maximum possible error then we should perhaps evaluate the age-depth function obtained from a range of models which would give us an error range. Of course, this still excludes the error ranges on the calibrated

ages used to generate the age-depth relationship. As far we are aware, there is no available method to deal with these errors, because the probability distribution of calibrated ages is non-normal (Bennet, 1994).

3.4. Conclusion

The protocol described here is time consuming and expensive. There is no need to apply it to poor quality cores. We recommend that for the study of the uppermost layers a peat bog, three Wardenaar cores should to be collected. The first one could be used to investigate the quality and the suitability of the peat deposit for paleoenvironmental purposes. This core could be visually inspected, described, and cut by hand in the field. Measurement of the pH and the calcium concentration in the porewater can be used to determine the trophic status of the peat profile, and the chlorine concentration to reveal the influence of marine aerosols. As first approximation of the chronology, Pb could be measured using XRF which would clearly indicate the beginning of industrialisation. In Europe, this approach would also identify the Roman period, if this is present in the peat core. If the core is in good agreement with the selection criteria define during the first step of the study (ombrotrophic peat deposit, time period of interest), then the second core should be cut into 1 cm slices and the protocol proposed in this paper could be followed. The third core should be storage intact at -18 °C as an "archive" which could be used in future studies.

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Chapter 5

POST EXPEDITION FIELD and STATUS REPORT

LONG-TERM RECORDS OF ATMOSPHERIC MERCURY DEPOSITION RECORDED BY PEAT DEPOSITS FROM EASTERN CANADA

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Photo 1. The Great Whale River near the village of Whapmagoostui/Kuujjuarapik, Northern Quebec

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PREFACE

This report is submitted to the respective agencies that have supported the project or have substantial interest in the results. It primarily provides a public record of fieldwork, detailing how and where peat and other geologic or environmental samples were taken for later dating and analysis. Additionally, the present status of samples is given.

The present project have been founded by the Geological Survey of Canada as part of the Metal in the Environment Program

"Source apportionment and natural archives of metals in Northern Canada" to P.M. Outridge (Project leader, Geological Survey of Canada)

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By using procedures developed by our research group (Head: Prof. Dr. William Shotyk, Institute of Environmental Geochemistry, University of Heidelberg, Germany) specifically for our project, all field work was completed in such a way as to minimize the impact on the environment, utilizing the latest techniques and best available technology for sampling, handling and analysis of the materials.

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The field trip described in this report would not have been possible without the financial support provided by the Geological Survey of Canada. Special thanks to **Dr. Peter Outridge**, project leader and **Dr. Roger McNeely** for their continuous support and assistance. Very special thanks to **Rog** for his participation in the peat core collection at Mer Bleue Bog, which is sincerely appreciated.

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Thanks to the Centre d'études nordiques (CEN) de l'Université Laval, with special thanks to **Claude Tremblay**, **Steve** and **Chantal** for accommodation at the Whapmagoostui-Kuujjuarapik research station as well as for technical assistance, providing us excellent equipment for reaching our sampling sites.

Special thanks to **Prof. Dr. Najat Bhiry** for having make me discover the Kuujjuarapik's area palsa bogs, and advice me on the selection of the most suitable sampling sites for this study, as well as her research team; **Dr. Mustapha Touazi** and **Mathieu Lahaye**; for their great assistance during the days we spent all together in the field.

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Thanks to forwarding companies for their assistance in the shipment of the equipment from Germany to Montreal and Kuujjuarapik and back: Air Inuit Cargo in the person of **Yves Pelletier**, Colbeck & Clarke, Cargolution at Dorval airport and Agotrans at Frankfurt airport.

In Germany:
The Institute of Environmental Geochemistry of the University of Heidelberg, more specifically **Prof. Dr. William Shotyk**, for his constant help and support during the preparation of this field trip and for providing all the equipment for peat collection; and also **Stephan Rheinberger** and **Gaël Le Roux** for their help with logistics.

In Denmark:
The Environmental Chemistry group at the Department of Chemistry of the University of Southern Denmark in Odense in the person of **Prof. Christian Lohse** and **Dr. Mike Goodsite**.

Very special thanks to my other team member, **Tommy Nørnberg**, for being invaluable in the field and for the good time we had together in Canada when not digging peat.

ABSTRACT

Peat cores, plant material, sediment and water samples were collected from a palsa bog field in the vicinity of Whapmagoostui / Kuujjuarapik in North Quebec.

Short peat cores from a thermokarst depression were collected as a peat monolith using a titanium Wardenaar corer. Material from unfrozen surface peat layers of the palsa bog was cut away using a Wardenaar corer, and deeper, frozen peat layers were recovered by drilling with a Nørnberg corer, a custom-made, motorized SIPRE-type coring device. Considering the results recently obtained by Dr. Najat Bhiry and Yann Arlen-Pouliot, we expect that the peat recovered will extend back to the pre-industrial and pre-anthropogenic times, possibly as far as 5,500 years BP. By measuring Hg concentrations and age dating the profile, the natural background as well as the present day levels of atmospheric Hg accumulation will be obtained, to help determine the importance of long- range transport of anthropogenic mercury to the Subarctic. Radiocarbon dating methods (the atmospheric bomb pulse of ^{14}C and conventional ^{14}C age dating) will be combined with ^{210}Pb to allow reliable age-depth relationship to be reconstructed for each peat profile. In an effort to distinguish between natural and anthropogenic sources of Hg, the natural variation in Hg to bromine and selenium in ancient samples will be used to calculate "excess" of mercury in modern samples.

For comparison with the cores from the Subarctic, peat cores were also collected from the ombrotrophic peat bog of Mer Bleue Bog in eastern Ontario. In addition to the short Wardenaar peat cores collected, complete peat profiles were taken (ca. 550 cm). It is hoped that these peat cores will provide a long-term high-resolution record of atmospheric Hg deposition for the last 8,500 years.

Disclaimer

The ideas and opinions expressed in this report are the author alone. They do not necessarily reflect the opinions or ideas of the funding agencies, employers, or corporate sponsors.

Respectfully submitted by

Nicolas Givelet

Berne, Switzerland, October 24, 2003

I. PROJECT OUTLINE

1.1. Introduction and background

Mercury (Hg) is primarily of interest as a long-range, persistent and toxic pollutant because of its ability to bioaccumulate in the food chain in the form of methylmercury (Morel *et al.*, 1998). Due to its high volatility, low chemical reactivity and low solubility in water, elemental mercury (Hg°) makes up approximately 98% of total atmospheric mercury and has a residence time in the atmosphere up to 2 years: This means that mercury vapour can be transported far beyond the regions in which it is emitted (Schroeder *et al.*, 1998). Environmental mercury levels have increased considerably since the on-set of the industrial age in the mid 1800's. Mercury is now present in a various environmental media and food all over the globe at levels that adversely affect humans and wildlife. Even regions with no significant mercury releases such as the Arctic, are adversely affected, due to transcontinental and global atmospheric transport of mercury. Exposures are thought to be increasing, especially among Arctic indigenous populations who consume fish and piscivorus species contaminated by methylmercury (Wheatley *et al.*, 2000). Environmental mercury levels are thought to be elevated in Arctic, to generally increase with latitude, and to have increased over time (AMAP, 2002).

Several hypotheses have been addressed in the recent past to explain the contamination of the Arctic environment. For instance, it has been suggested that, as originally conceived for some volatile organic compounds (Wania *et al.*, 1993), for mercury (Mackay *et al.*, 1995), there may be a latitudinal fractionation which contributes to the continued mobilization of these compounds from warmer to colder climates (i.e. "cold condensation"), resulting in a natural geographical gradients in the atmospheric Hg deposition rates. Mercury, especially oxidized forms of airborne Hg, may condense over the Polar Regions due to cold climate suggesting a natural high deposition rate in Polar Regions where it is ultimately deposited and stored.
More recent discoveries suggest that the Arctic experiences enhanced deposition of Hg related to mercury depletion events (MDEs) observed to occur each spring (Schroeder *et al.*, 1998). Gaseous elemental mercury (Hg°) in the Arctic atmosphere undergoes photochemically driven oxidation during polar sunrise, probably by reactive halogens, which converts elemental Hg to reactive gaseous mercury (RGM) which subsequently deposits rapidly on snow as follows:

$$Br + O_3 \rightarrow BrO + O_2 \text{ (i)}$$
$$BrO + Hg^\circ \rightarrow Hg^{2+} + Br \text{ (?) (ii)}$$

Some of the mercury deposited on the snow is released to the environment at snowmelt, becoming available just as the Arctic ecosystem becomes biologically active in springtime. Evidence suggests that this is a recent phenomenon that may occur throughout the Polar Regions. This enhanced deposition may mean that the Arctic plays a previously unrecognized role as an important sink in the global Hg cycle (Lindberg *et al.*, 2002).
The impact of climate change on Hg dynamics is the third emerging issue. Changes in physical climate; decreasing trend in multi-year ice coverage, related increases in annual ice coverage, later timing of snowfall and earlier timing of snowmelt, increasing ocean temperatures, and increasing atmospheric circulation and temperatures: these factors and processes in the past decades might actually have a greater impact on the Arctic Hg cycle than changes in global emissions. Several data sets suggest that there has been a recent increase in Hg levels in Arctic biota despite a 20 year decrease in global atmospheric Hg emissions of 30% (Pacyna *et al.*, 2002). Environmental changes may have made Hg pathways more efficient in recent years by increasing transport of photooxidants

and production of reactive halogens in the Arctic. Although poorly understood, these processes may be the chief mechanism for transferring atmospheric Hg to the Arctic food chain.

There is a lot of evidence (AMAP, 2002), mainly from lake sediments, showing that mercury levels appears to be increasing over time in the Arctic. Increases in the accumulation rates of Hg have been observed in the uppermost, modern layers of lake sediments in Subarctic and Arctic (Hermanson, 1998; Lockhart *et al.*, 1998) and they have been attributed to recent increases in atmospheric emission and deposition of Hg from human sources. There are a number of geochemical reasons to seriously question those interpretations, specifically for lake sediments as some processes which may explain these trends have been largely ignored in the interpretation of the results. Increases in the upper layers of lake sediments may be related to several processes, such as post depositional redistribution by diagenesis, physical mixing, or erosion. Changes in the watershed, or of the biogenic productivity may control the variation of mercury concentration throughout the sediment column. For instance, evidence from an Arctic lake deposit has shown that higher rates of phytoplankton productivity, possibly related to global warming in the 20th century, led to an increase of Hg scavenging from the water column to the sediment and results in an increase profile of Hg concentration to the top of the core (Outridge *et al.*, 2003). Thus, limnological processes rather than atmospheric deposition may account for much or most of the Hg increases over the past 100 years in the lake sediments. In other words, lake sediment records of Hg accumulation have to be interpreted with great care.

Therefore it remains very unclear whether deposition of anthropogenic atmospheric mercury may account for the mercury contamination of the Arctic environment and how atmospheric mercury deposition rates have evolved in Arctic during the past 150 years. It seems very unlikely that Arctic was an important natural sink in the global cycle of Hg during the pre-industrial time as net accumulation rates of atmospheric mercury in peat deposits from the High Arctic of Canada have been found to be very similar to accumulations rates measured from peat and lakes sediments archives at temperate location during the same time period (Givelet *et al.*). This suggests that the cold Arctic climate may not significantly favour a final deposition compared to warmer climate regions. However, no effort has been made to investigate the effect of recent global warming on the pathways of Hg in the Arctic today. There is an urgent need to assess modern (past 150 years) rates of atmospheric mercury deposition in the Arctic.

Peat cores from ombrotrophic bogs are excellent archives of atmospheric mercury deposition as they receive all their inputs from the atmosphere; this is a fundamental difference compared with lake or marine sediments which receive metals by atmospheric as well as non-atmospheric sources. In other words, ombrotrophic peat bogs are faithful archives of atmospheric mercury deposition. Recent studies presented evidences that atmospheric Hg is also well preserved in the peat column of minerogenic peat deposits (Shotyk *et al.*, 2003).

We propose to use modern peat from the Arctic to answer the question: are atmospheric mercury fluxes really increasing in the Arctic? One shortcoming from the study of peat deposits in the High-Arctic of Canada (Givelet *et al.*), after extensive dating using ^{14}C AMS and ^{210}Pb method, is that there is no modern peat material in the cores collected on Bathurst Island. Moreover, results from southern Ontario (Givelet *et al.*, 2003) show that records from temperate latitudes during modern period are largely affected by local/regional sources and it is not known to what extend they provide a record of global atmospheric Hg deposition. Therefore, a peat core from a remote location, far from anthropogenic emission sources is required and will provide very different information than from southern Ontario. Kuujjuarapik (55° North latitude), on the east shore of the Hudson Bay in the Subarctic of the Northern Quebec, is a remote site, far from sources and highly influenced by air

masses from Arctic. Kuujjuarapik is the most meridional site where MDE's have been observed and measured throughout the Arctic (Poissant *et al.*, 2001).

Finally, to investigate the possible relation between changes in physical climate, especially recent global warming, and the geochemical cycle of mercury, we propose to reconstruct a detailed paleoclimatic record using the same peat cores from Arctic and to compare it with the high-resolution record of atmospheric Hg deposition.

Summary of the problem:

- **The evolution of atmospheric mercury deposition rates in the Arctic during the past 150 years is poorly understood,**

- **The role which is played by the unique climate of the Arctic on the geochemical cycle of mercury is incompletely understood,** especially the effect of recent global warming on the deposition of atmospheric Hg.

Those issues are critical to understanding the effects of human activities on Hg cycling in the Arctic, and its implications for ecosystem health.

1.2. Research objectives

The ultimate objective is to bridge the knowledge gap between the lack of comprehensive temporal trends and deposition loads of mercury from long-range atmospheric transport in Arctic and to assess the effect of recent global warming on deposition of atmospheric Hg in the Arctic environment.

To accomplish this, the main objective is to assess and quantify the changing rates of atmospheric Hg deposition from the modern period (past 150 years) to the pre-industrial period in Arctic, and to reconstruct a detail paleoclimatic record for the same period of time. This will be accomplished using physical, chemical, and isotopic analyses of peat cores from a minerotrophic peat bog in Northern Quebec and an ombrotrophic *Sphagnum* peat bog in eastern Ontario.

Specifically, the following step will be taken:

1) **Quantify the changing rates of atmospheric mercury deposition** in Arctic over the past 150 years and during pre-industrial times,
2) Reconstruct a **detailed paleoclimatic record for this region of Arctic** using indicators of effective precipitation (e.g. degree of peat humification and bromine), soil dust flux (e.g. titanium), biological productivity of the oceans (e.g. selenium),
3) Estimate the **extent of anthropogenic contribution** to the Hg deposition flux using the ratio of this element to selenium (Se) and bromine (Br) as "reference elements" for Hg
4) Identify the **predominant sources of atmospheric** Hg contamination using precise measurements of the isotopic composition of Pb,
5) Compare the rates of atmospheric Hg accumulation in Arctic with results from a temperate zone of eastern Ontario.

1.3. Expedition plan

The primary goal of the expedition can be summarized as follow:

- To locate and determine the suitability of sampling sites in the vicinity of Kuujjuarapik and at the Mer Bleue Bog. According to the studies by Prof. Dr. Najat Bhiry and other published work, both the vicinity Kuujjuarapik and Mer Bleue will provide suitable peat cores for reconstructing long-term records of climate change and atmospheric deposition of trace elements

- To obtain two complete profiles of peat accumulation in addition to three one meter Wardenaar cores at each location.

- To collect plant samples, surface water samples, obtain pH measurements and make observations at each coring site.

II. GENERAL INFORMATIONS

2.1. Fieldwork team

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Photo 2. Tommy Nørnberg (left) and Nicolas Givelet (right) on the way to the palsa bogs field, southeast of the village of Kuujjuarapik, north Quebec

2.2. Scientific co-investigators

This project already established international collaboration and will include the participation and expertise of the following persons.

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2.3. Accommodation

The expedition team was accommodated at the Whapmagoostui-Kuujjuarapik research station, Centre d'études Nordiques (http://www.cen.ulaval.ca/english/station.html) during our stay in Northern Quebec and in various hotels in Montreal and Ottawa for the Mer Bleue Bog part of the trip.



Photo 3. The CEN research station at Whapmagoostui-Kuujjuarapik

2.4. Logistics

Forwarding companies; Agotrans Air Cargo and Colbeck & Clarcke; and Air Inuit Cargo (http://www.airinuit.com/) were responsible for the transport of the equipment to Montreal and Kuujjuarapik respectively from Heidelberg and back.

Colbeck & Clarke c/o Cargolution
800 Stuart Graham
Suite 332
Dorval, Québec, H4Y 1J6
Canada
Tel: 001 514 636 1576
Fax: 001 514 636 8799

Air Inuit Cargo
800 Stuart Graham
Porte 47-53
Dorval, Québec
Canada
Tel: 001 819 638 8163 post 221

Budget car rental at Dorval Airport provided a rental a van for the field trip to the Mer Bleue Bog.

2.5. Equipment

All the equipment as well for the transport as for sampling was provided by Prof. Dr. William Shotyk, Director of the Institute of Environmental Geochemistry of the University of Heidelberg in Germany.

For detailed information, see the list of the equipment in Appendix I.

Motorboat, ATVs and trailer, used for fieldwork in North Quebec, were rented to the Centre d'Etudes Nordiques at the research station of Kuujjuarapik-Whapmagoostui.

III. PEAT CORE SAMPLING

The fieldwork described in this report took place from July 14 to July 24, 2003. During these two weeks, peat cores were collected in the vicinity of Kuujjuarapik, North Quebec (July 14 – 21, 2003) as well as at Mer Bleue Bog near Ottawa, Ontario (July 22, 2003).

3.1. Palsa bogs - Kuujjuarapik

The sampling site in the vicinity of Kuujjuarapik was selected based on results of a two year study conducted by Prof. Dr. Najat Bhiry and her team at the University Laval in Quebec, Canada. The aim of their work is to understand the dynamic and evolution of palsa bogs (permafrost peatlands) related to climate variations, based on macrofossils analyses (Arlen-Pouliot et *al.* In preparation). Regarding the results of this study, especially the chronology the resolution and the type of the peat accumulation, this site have been selected has a valuable and suitable site for the reconstruction of long-term high-resolution records of atmospheric mercury and lead deposition in Subarctic.

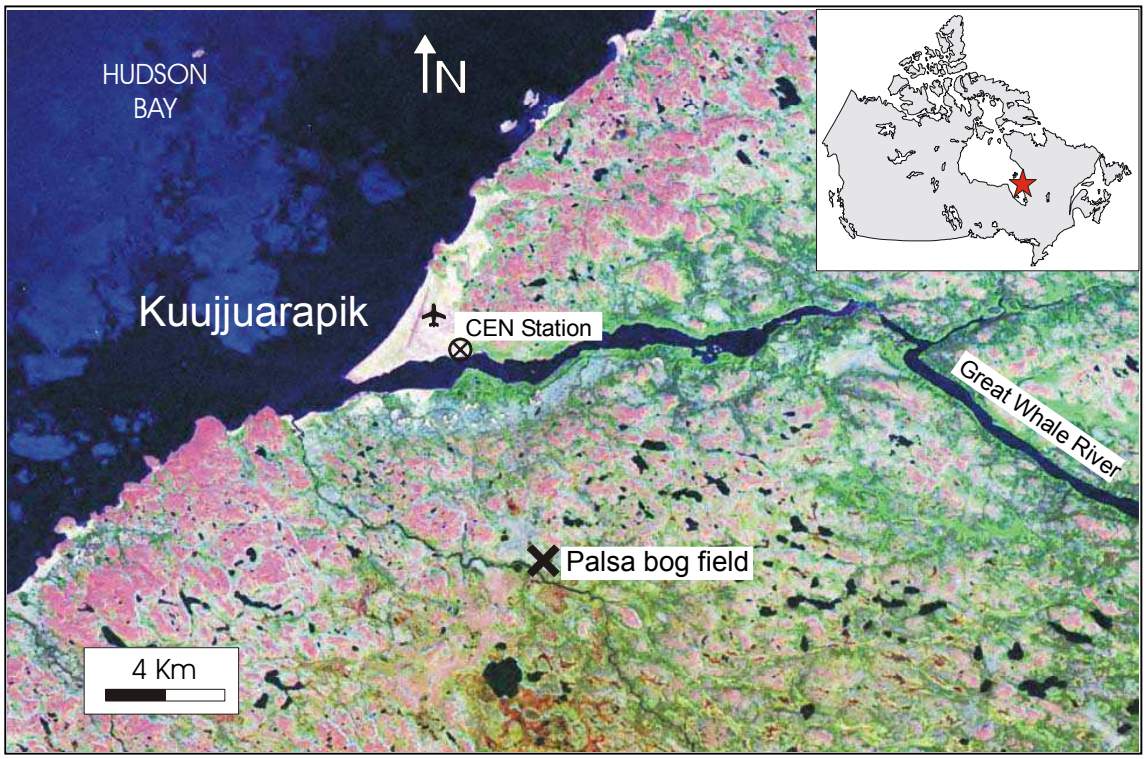


Figure 1. Satellite photo of the vicinity of Kuujjuarapik reporting the location of the palsa bog field sampled during this fieldwork

A palsa bog is a bog composed of individual or coalesced palsas, occurring in an unfrozen peatland. Palsas are mounds of perennially frozen peat and mineral soil, up to 5 m high, with a maximum diameter of 100 m. The surface is highly uneven, often containing collapse scar bogs, which are circular or oval-shaped wet depression in a perennially frozen peatland; the collapse scar bog was once part of the perennially frozen peatland, but the permafrost thawed, causing the surface to subside; the depression is poor in nutrients, as it is not connected to the minerotrophic fens in which the palsa or peat plateau occurs. It results in thermokarst depressions.

The study area is located in the Subarctic, about 5 km southeast of the communities of Whapmagoostui/Kuujjuarapik, some 5 km inland from the eastern shore of the Hudson Bay (Figure 1).

The morphology of the palsa closely reflects the shape of the ice-rich core heaved by the growth of a thick ice lenses in thick marine clay silts of the Tyrrell Sea.

3.1.1 Transportation

As the sampling site is located on the other side of the Great Whale River from the CEN research station (figure 1), we had to cross the river (photo 4) everytime we went to the palsa bogs. The research station provided a motorboat. Then we had to drive ATVs (photo 5) for about 40 minutes, following a trail in the forest. All the equipment was placed in a trailer. During the first three days of reconnaissance and sampling, we had to walk about 1.2 km (30 minutes) throughout the wetlands along the shore of the River to reach the palsa bogs field. On the last day, after a successful reconnaissance, another trail leading few hundreds of meters of the bogs was used.



Photo 4. Crossing the Great Whale River. Mathieu Lahaye (left), Tommy Nørnberg (middle) and Mustapha Touazi (right)



Photo 5. ATV and trailer used to reach the palsa bogs field

3.1.2 Peat cores collection protocol

A modified Wardenaar peat profile sampler, that removed a peat monolith approximately 15×15×110 cm (Wardenaar, 1987), was used to collect samples for unfrozen surface peat layers of the thermokarst depression. The corer is push down into the bog using a sledgehammer (Photo 6). After extraction, the Wardenaar corer was laid horizontally on the bog surface, and the top half of the corer removed, exposing the peat monolith. The core was described visually in the field and photographed. The core was wrapped in polyethylene film and packed into a wooden box specifically built for Wardenaar cores.



Photo 6. The Wardenaar corer is pushed down using a sledge hammer

The non-frozen upper layers of the palsa bogs were cut away by hand using a serrated, stainless steel knife. After removing and wrapping the blocks, the underlying frozen layer was collected using the Nørnberg peat corer (Photo 7). This specific corer was designed and built by M. Tommy Nørnberg for obtaining continuous samples of frozen peat in 60-70 cm sections. Cores where wrapped in polyethylene and loaded in black plastic PVC tubes which were sealed at one end, capped and labelled.



Photo 7. Nørnberg peat corer held by it inventor. Sampler and sample technique is described elsewhere (Noernberg *et al.*)

3.1.3 Summary of collected samples

This section presents a list of all samples collected at the different sites of the palsa bogs as well as the precise location of those sampling sites pointed on an aerial photo of the studied palsa bogs field. A detail description of samples collection is given in the following section.

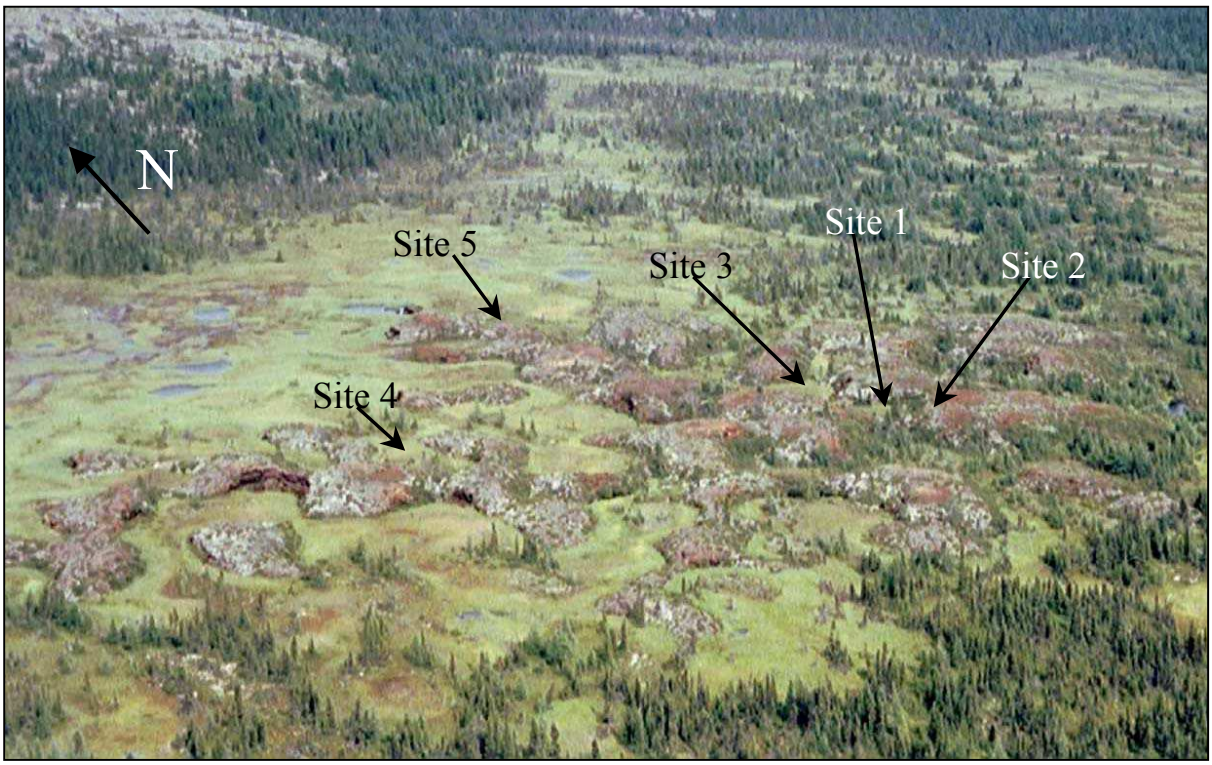


Photo 8. Aerial view of the palsa bogs field reporting the different sampling sites

Site 1
NQT 01, 0-101 cm, Wardenaar core
NQT 02, 0-95 cm, Wardenaar core (Sampled for Prof. Dr. Najat Bhiry)

Site 2
NQP 01, 0-56 cm, Wardenaar block
NQP 02, 54-119 cm, Nørnberg core
NQP 03, 119-177 cm, Nørnberg core
NQP 04, 177-193 cm, Nørnberg core

Site 3
NQT 03, 0-107 cm, Wardenaar core

Site 4
NQT 04, 0-105 cm, Wardenaar core

Site 5
CP 01, 0-37 cm, block
CP 02, 37-107 cm, Nørnberg core
CP 03, 107-175 cm, Nørnberg core
CP 04, 175-225 cm, Nørnberg core

PE 01, 37-95 cm, Nørnberg core (Sampled for Prof. Dr. Najat Bhiry)
PE 02, 95-148 cm, Nørnberg core (Sampled for Prof. Dr. Najat Bhiry)
PE 03, 148-216 cm, Nørnberg core (Sampled for Prof. Dr. Najat Bhiry)

3.1.4 Day by day Chronology

July 15, 2003

We flew by helicopter to the palsa bogs, 5 km southeast of Kuujjuarapik, for a first reconnaissance in company of Najat Bhiry, Mustapha Touazi and Mathieu Lahaye. Najat presented the palsa bog profile and the thermokarst depression (photo 11) recently studied by her graduate student Yann Arlen-Pouliot. This profile, about 1.8 meter depth, represent up to 5,000 years of peat accumulation from 360 to 5,400 years before present.

July 16, 2003

Because the aluminum box containing the sampling equipment had not yet arrived in Kuujjuarapik, we decided to survey another bog area located on the right shore of the Great Whale River, about 4 km east from the village of Kuujjuarapik. The reconnaissance was unfortunately unsuccessful as no real trails lead to those sites. The easiest way to reach those sites would have been the river.

July 17, 2003

This day was dedicated to a complete reconnaissance and selection of the sampling sites at the palsa bogs field, southeast of Kuujjuarapik.

July 18, 2003

The aluminum box arrived by the cargo aircraft in the morning. We picked it up at the airport in the early afternoon and went directly to the sampling site. This day was dedicated to the collection of modern peat accumulation from a thermokarst depression.

NQT 01 (site 1)

Coordinates:	55°13'31.5" N
	77°41'44.4" W
Elevation:	~116 m asl
Length:	101 cm
Compression:	10 cm
Surface water pH:	4.1

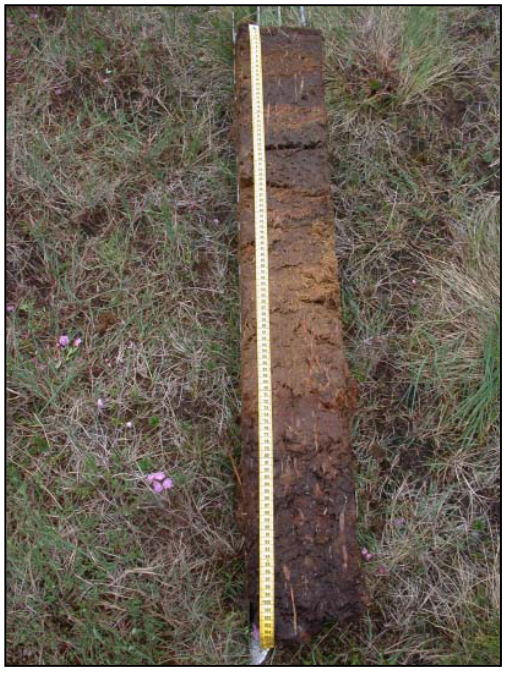


Photo 9. NQT 01 peat core

NQT 02 (site 1)

Coordinates:	55°13'31.5" N
	77°41'44.4" W
Elevation:	~116 m asl
Length:	95 cm
Compression:	11 cm
Surface water pH:	4.1



Photo 10. NQT 02 peat core

Two Wardenaar cores were collected from a thermokarst depression at site 1 (photo 8 and 11). A previous peat monolith was collected from this site and studied in detail for macrofossils by Yann Alen-Pouliot. The two cores were sampled about 30 cm far from each other and labelled NQT 01 (photo 9) and NQT 02 (photo 10). The corer was cleaned before and between each core in a nearby pond.

The interface between modern peat (last 400 years) and old peat (remains of palsa peat) is expected to be at 80 cm depth at that site, based on visual observation of a change in the colour and decomposition of the material.
Peat core NQT 02 was provided to Prof. Dr. Najat Bhiry for her own research. Results of both studies will be compared in an advanced stage of those studies.

July 19, 2003

During this day, we expected to collect a complete profile from the palsa bog studied at site 2 (photo 8). Unfortunately, it wasn't very successful due to technical problem with the engine of the Nørnberg corer. Only the unfrozen part of the accumulation of this palsa bog was sampled as a block.

The Wardenaar corer was pushed into the unfrozen layer using a sledge hammer until the surface of the permafrost. As the peat material was dryer and with less cohesion than a typical peat core from an actively growing peat bog, it was decided to dig out the corer using a shovel. A 56 cm long block (photo 12), labelled NQP 01, was removed from the accumulation representing the unfrozen part of the palsa bog accumulation. We unsuccessfully tried to collect the rest of the accumulation using the Nørnberg corer.

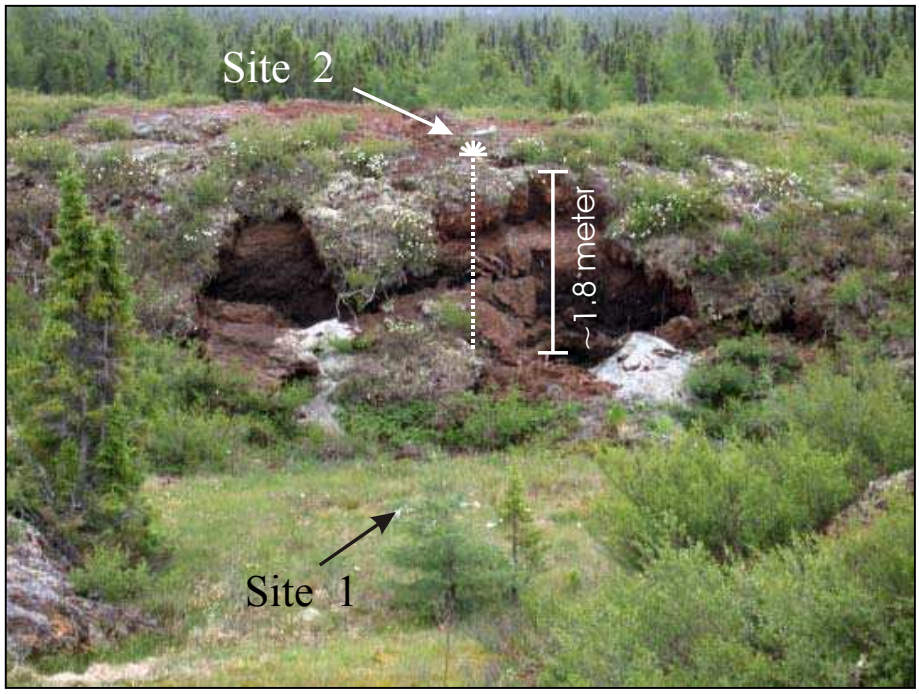


Photo 11. View of sampling sites 1 and 2. At sampling site 2, a complete peat profile have been collected (white dot line), in the neighwood of the profile (white bold line) recently studied by Najat Bhiry and Yann Arlen-Pouliot

NQP 01 (site2)

Coordinates:	55°13'31.0" N
	77°41'44.3" W
Elevation:	~106 m asl
Length:	56 cm
Compression:	0 cm

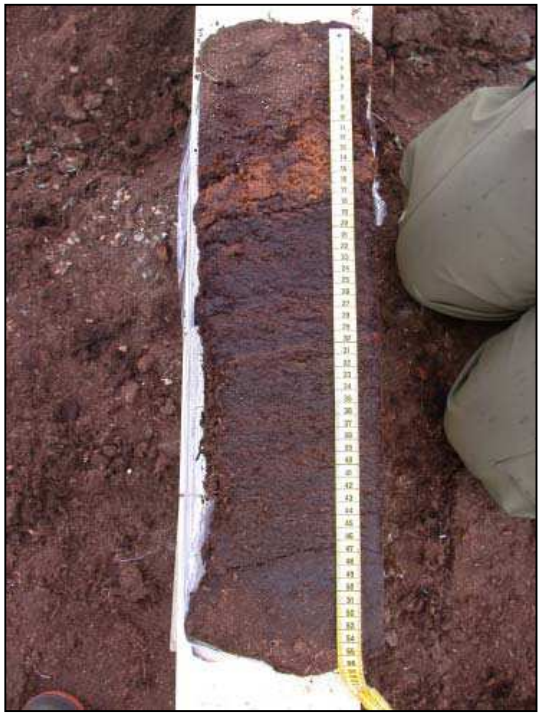


Photo 12. NQP 01 peat block

A second thermokarst depression, site 3 (photo 8), was sampled, about 30 meters north far from the previous thermokarst depression (site 1). Only one Wardenaar core (NQT 03) was collected at that site. The interface between the modern accumulation and remain material from old palsa wasn't clear: 76 cm or 100 cm depth. The core was initially 116 cm long but was cut at 107 cm long to fit in the wooden box.



NQT 03 (site3)

Coordinates:	55°13'32.0" N
	77°41'44.4" W
Elevation:	~98 m asl
Length:	107 cm
Compression:	4 cm

Photo 13. NQT 03 peat core

July 20, 2003

A third thermokarst depression, site 4 (photo 8), was sampled, in the western part of the palsa bogs field. One Wardenaar core, labelled NQT 04 (photo 14), was collected at that site. A transition at 95 cm depth from a light brown colour to a dark brown colour of the material may be the interface between modern peat accumulations and remain material from old palsa bog.



NQT 04 (site4)

Coordinates:	55°13'33.0" N
	77°41'49.6" W
Elevation:	~102 m asl
Length:	105 cm
Compression:	10 cm

Photo 14. NQT 04 peat core

The rest of the profile in the palsa at site 2 (photo 8) was collected using the Nørnberg corer (Tommy had repaired the engine in the morning). The hole, where the block labelled NQP 01 was collected, was enlarged using a shovel and the interface between unfrozen and frozen peat carefully digged out using a large titanium knife in order to prevent against any possible contamination of the top of the underlying core. The complete frozen part of the profile was then sampled in 3 sections as described in Figure 2 down to 193 cm, where the marine silt sediment were reached.



Photo 15. Tommy and Mathieu sampling the palsa bog at site 2 using the Nørnberg corer

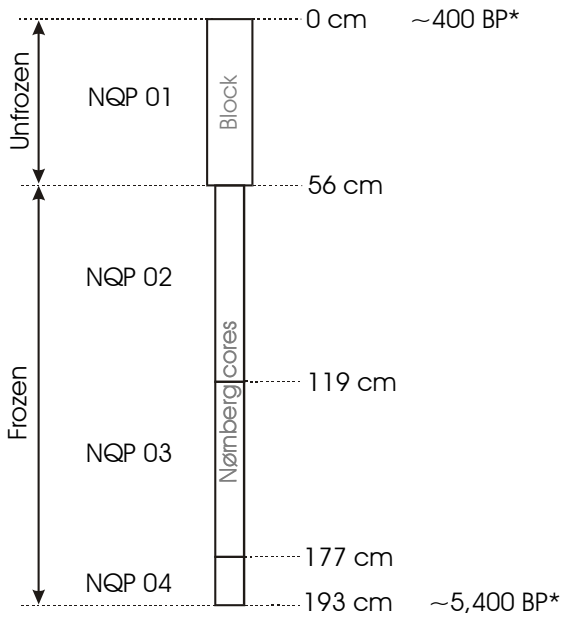


Figure 2. Scheme of the block and Nørnberg core sections collected at the site 2 versus depth.

A collapsed palsa, site 5, (photo 8) was also sampled. Two profiles were collected about 30 cm from each other using the Nørnberg corer. The basal marine silt sediment wasn't reached due to technical problems caused by the infiltration of water into the hole. About 200 cm of peat was collected at that site (figure 3), the first 37 cm as a block of unfrozen peat, and the other 180 cm as Nørnberg cores of frozen peat. The peat profile labelled PE was provided to Prof. Dr. Najat Bhiry for her own study.

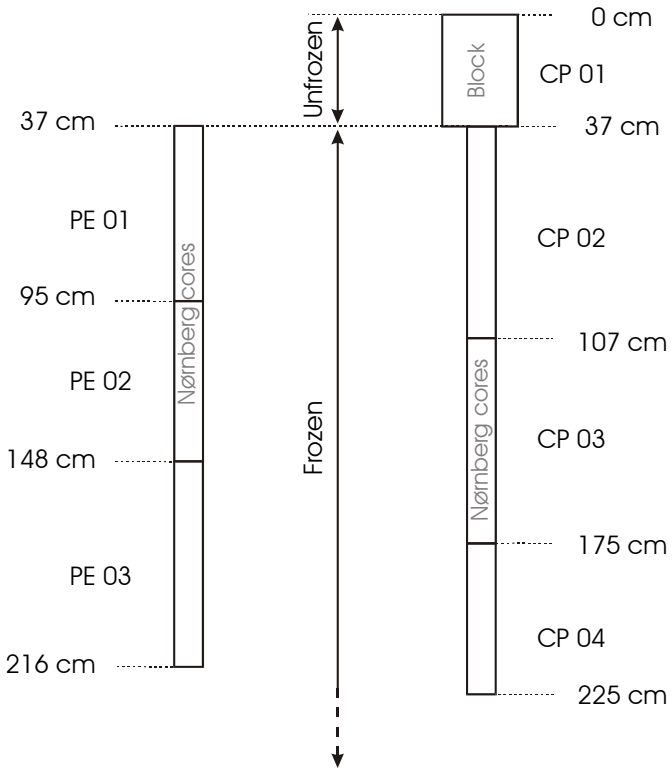


Figure 3. Scheme of the block and Nørnberg core sections collected at the collapsed palsa bog (site 5) versus depth.

All samples were stored frozen as soon after our return at the research station in Kuujjuarapik.

July 21, 2003

During this day, we cleaned and packed the field equipment before shipment. The aluminum box was returned to the airport for shipment to Montreal (Air Inuit). Before leaving, we ensured that the box was well stored in a freezer room. Tommy and I flew back to rainy Montreal in the mid afternoon.



Photo 16. Air Inuit dash8 at Kuujjuarapik airport

3.2. The Mer Bleue Bog - Ottawa

The Mer Bleue Bog is a Provincial Conservation Area situated in the eastern portion of the National Capital Region less than 10 km from Ottawa in the Ottawa River Valley.

Mer Bleue's almost 33 km^2 (roughly 5,000 acre) wetland represents a throwback to the eras of the Wisconsin Ice Sheet and the Champlain Sea. Over 9,000 years ago, a southern branch to the Ottawa River ran through this area. Approximately eight thousand years ago, the southern branch to the estuary had disappeared, replaced by a wetland created because underlying clay prevented the water from escaping. Meanwhile, just north of the Mer Bleue wetland, the channel of the Ottawa River watershed was narrowing as the land rebounded from the weight of the ice sheet.

Approximately 50% of Mer Bleue is a raised boreal peat dome *Sphagnum* bog, an ecological community usually found much further north in Canada (in the northern boreal forest). Peat deposits in the bog proper are up to six metres thick.

Drainage in the bog is poor due to underlying clay deposits as well as numerous beaver dams surrounding the bog. Water eventually drains slowly via adjacent creeks. In the Mer Bleue, water levels remain at or near the surface of the bog for most of the year.

The porewater at Mer Bleue is highly acidic, rich in dissolved organic carbon and poor in nutrients. The surface is slightly domed. Vegetation on the surface is composed of ericaceous shrubs (dominantly *Chamaedaphne calyculata*, *Kalmia angustifolia*, and *Ledum groenlandicum*) and grasses. The hummocks are covered by Sphagnum moss (dominantly *Sphagnum capillifolium* and *Sphagnum fuscum*) while the hollows are covered by *Smilacina trifolia*, *Eriophorum vaginatum*, *Sphagnum magellannicum* and *Sphagnum angustifolium*.

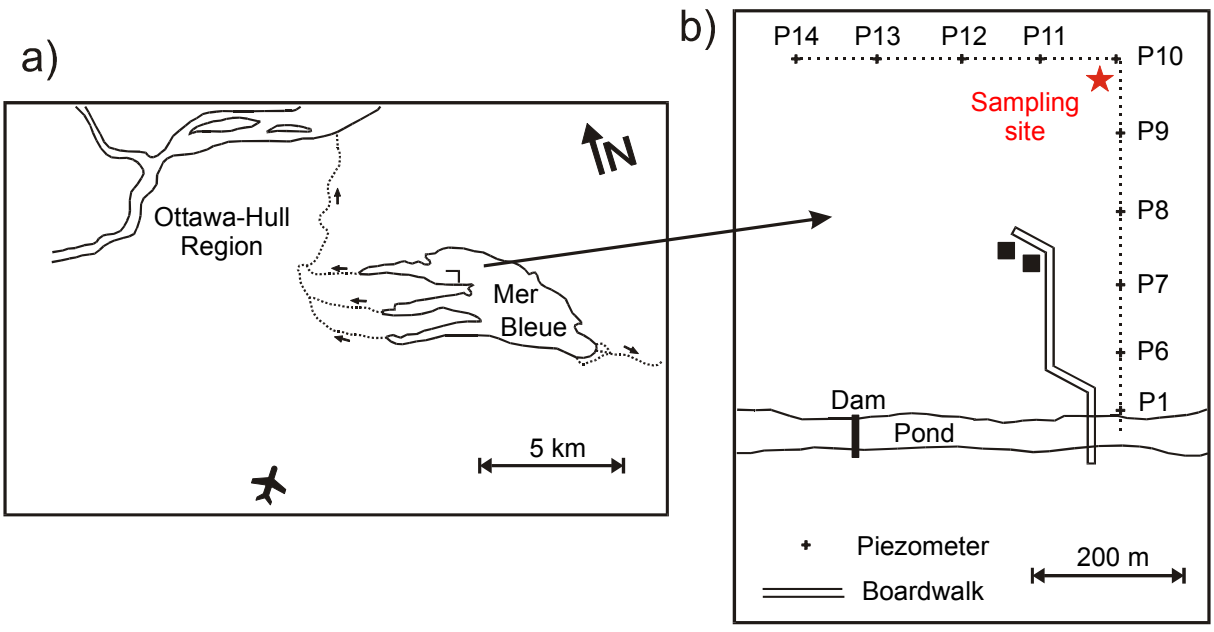


Figure 4. (a) Map of the Mer Bleue Bog showing the three western-draining basins and the eastern-draining basin with respect to Ottawa, Ontario. (b) Schematic of the field instrumentation at Mer Bleue Bog and location of the peat cores sampling site in the northeastern arm of the bog. (Figure adapted from (Fraser *et al.*, 2001)

Selection criteria of the sampling location within the Mer Bleue Bog (figure 4a) were ombrotrophic status, the maximum of peat accumulation spanning the longest time period in order to obtain a record with the highest resolution possible. Regarding the literature, the north-eastern arm has been actively studied and information such as thickness of peat accumulation, age of the basal layer, dated peat profiles and basic geochemical data describing the trophic status of the peat accumulation along those profiles (Richard, personal communication) as well as groundwater geochemistry (Fraser *et al.*, 2001) were available.

At the centre of the northeastern arm, about 5 to 6 meters of peat accumulated during the last 8,500 years and the peatland has been a bog for the last 6,500 years (representing up to 3 meters). The sampling site was selected along the piezometer transect near piezometer P10 (figure 4b) were the peat accumulation is known to be maximum.



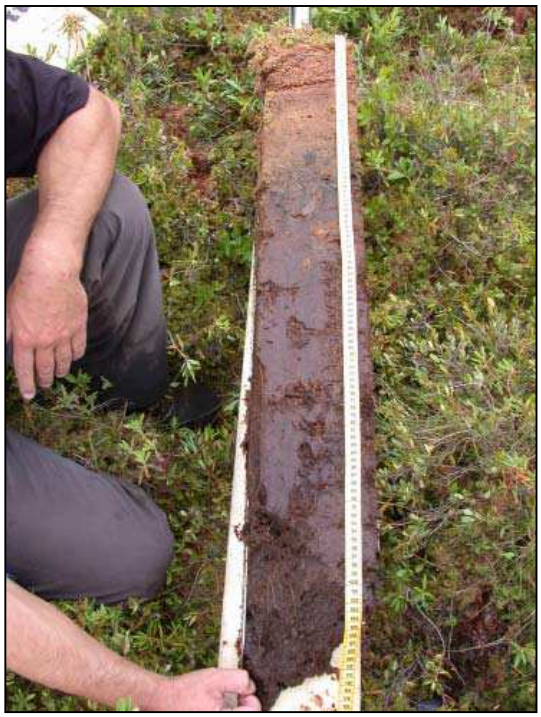
Photo 17. The norteastern arm of Mer Bleue Bog. Roger McNeely (left) and Tommy Nørnberg (right) waiting to start work…

3.2.1 Day by day chronology

July 22, 2003

During this day, complete profiles were collected from the northeastern arm of the bog (photo 17), about 10 meters apart. The top most layers of peat were collected using a 1-meter Wardenaar corer as a 15×15 cm peat monolith. In addition to three short peat cores, two complete profiles were taken in 50 cm sections using a stainless steel Belarus corer (photo 20).

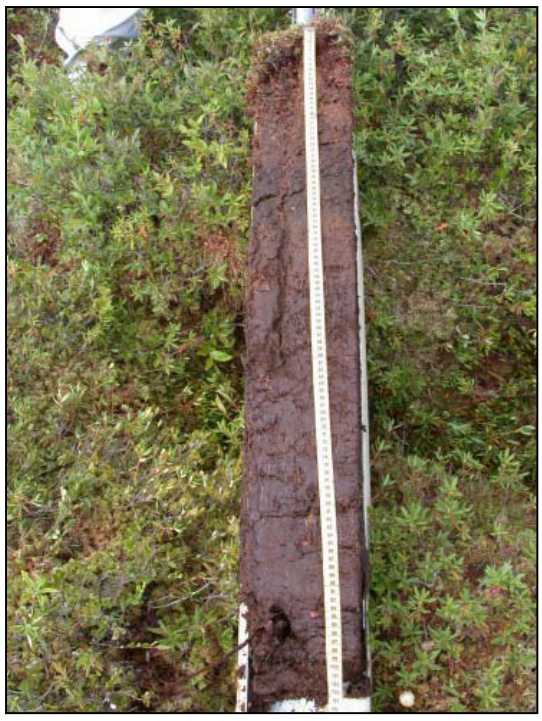
Two-Wardenaar peat cores were collected approximately 20 cm apart and labelled MBB 01 (photo 18) and MBB 02 (photo 19). A wood sample located at 87 cm depth was sampled by Dr. Roger McNeely on MBB 01 for ^{14}C age dating. At this site, the watertable was measured 26 cm below the bog surface.



MBB 01

Coordinates:	45°24'41.4" N
	75°31'01.6" W
Elevation:	~70 m asl
Length:	102 cm
Compression:	6 cm

Photo 18. MBB 01 peat core



MBB 02

Coordinates:	45°24'41.4" N
	75°31'01.6" W
Elevation:	~70 m asl
Length:	97 cm
Compression:	9 cm

Photo 19. MBB 02 peat core

At this site, the deeper peat layers (100-500 cm depth) were sampled using a stainless steel Belarus corer (Belokopytov *et al.*, 1955) (photo 20). Cores were removed from two holes approximately 30 cm apart: one at depths of 100-150, 200-250, etc and the second at depths of 150-200, 250-300, etc until the interface between the underlying sediment was reach at 477 cm depth. Peat cores are carefully packed into plastic semi tubes, which were lined with polyethylene film, and wrapped with polyethylene. Section 450-500 cm was sampled twice and one was provided to Roger McNeely for ^{14}C age dating (MBB 04, 450-500 cm).



Photo 20. The Belarus corer is pushed into the bog by hand

At about 10 meters apart the two first Wardenaar cores, a third core was collected and labelled MBB 03 (photo 21). At this second site, the deeper layers (100-550 cm) were collected using the Belarus corer and labelled MBB 05. A darker layer was easily visible by eye at 132 cm depth (photo 22). The transition between the peat and the gyttja was reached at 489 cm depth and the transition gyttja/marine silt well visible (photo 23). Section MBB 05, 450-500 cm was collected twice and one provided to Roger McNeely for ^{14}C age dating.

MBB 03

Coordinates:	45°24'41.4" N
	75°31'02.1" W
Elevation:	~70 m asl
Length:	111 cm
Compression:	5 cm

109-111 cm depth sampled by Roger McNeely for ^{14}C age dating



Photo 21. MBB 03 peat core



Photo 22. Section of MBB 05, 100-150 cm. Visual inspection of the section indicated a darker layer at 132 cm depth.



Photo 23. Section of MBB 05, 500-550 cm. Transition between the gyttja and the marine silt.

3.2.2 Summary of collected samples

All samples were frozen just after collection at the Geological Survey of Canada in Ottawa for storage and transport to Heidelberg.

45°24'41.4 N, 75°31'01.6 W

MBB 01, 0-102 cm, Wardenaar core
MBB 02, 0-97 cm, Wardenaar core

MBB 04, 100-150 cm, Belarus core
MBB 04, 150-200 cm, Belarus core
MBB 04, 200-250 cm, Belarus core
MBB 04, 250-300 cm, Belarus core
MBB 04, 300-350 cm, Belarus core
MBB 04, 350-400 cm, Belarus core
MBB 04, 400-450 cm, Belarus core

45°24'41.4 N, 75°31'02.1 W

MBB 0, 450-500 cm, Belarus core

MBB 03, 0-111 cm, Wardenaar core

MBB 05, 100-150 cm, Belarus core
MBB 05, 150-200 cm, Belarus core
MBB 05, 200-250 cm, Belarus core
MBB 05, 250-300 cm, Belarus core
MBB 05, 300-350 cm, Belarus core
MBB 05, 350-400 cm, Belarus core
MBB 05, 400-450 cm, Belarus core
MBB 05, 450-500 cm, Belarus core

Status of the study

The present status of the study as of October 24, 2003 is briefly as follow:

All samples are stored and archived at the University of Heidelberg in Germany. None of the samples have been yet prepared.

Samples will be prepared and analysed at the Institute of Environmental Geochemistry of the University of Heidelberg by N. Givelet as part of a postdoctoral fellowship as described in the elsewhere protocol (Givelet *et al.*).

The peat cores will be precisely cut while frozen into 1 cm slices using a stainless steel band saw with stainless blades. The outside edges of each slide will be removed using a titanium knife in order to avoid any possible contamination occurred during the sampling and handling stage. A subsample will be dried overnight at 105°C in a drying oven and milled in a centrifugal mill with titanium sieve. The resulting powder samples, after manual homogenization, will be measured in more than 20 major and trace elements by XRF. Three sub-samples from the middle of each slice will be used for Hg analysis. These will be air-dried at room temperature under a Class 100 laminar flow clean air cabinet. Mercury concentrations will be measured in solid peat samples by Atomic Absorption Spectrometry (AAS) using a Leco AMA 254 as described in detail elsewhere (Roos-Barraclough *et al.*, 2002).

Radiocarbon dating methods (the carbon bomb pulse of ^{14}C, ^{210}Pb and conventional ^{14}C dating) will be combined to allow reliable age-depth models to be reconstructed for each peat profiles.

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Appendix I. List of field equipment

Specific equipment

North Quebec

- Nørnberg corer
- Engine for Nørnberg corer
- Ti Wardenaar corer
- Ti pry bar and Ti lifting rod
- Rope
- Piece of wood
- Large nylon Sledgehammer
- 10 tubes for Nørnberg cores
- Inside film for Nørnberg cores
- 4 wooden boxes for Wardenaar cores
- 1 backpack for carrying equipment

Contained in one large aluminum box

Mer Bleue Bog

- Stainless Belarus corer
- Stainless extension for Belarus corer
- Backpack for stainless Belarus Corer
- 30 Peat core tubes with plastic dividers between layers
- Ti Wardenaar corer
- Ti pry bar and Ti lifting rod
- Rope
- Piece of wood
- Large nylon Sledgehammer
- Small nylon sledgehammer
- 3 wooden boxes for Wardenaar cores

Contained in one medium size aluminum box and one specific aluminum box for Belarus core sections.

Packing equipment (used at both location)

- 1 blue packing equipment backpack
- 1 field orange bag
- Brush
- Bicycle pump
- Extra transport strap
- Hatchet, shovel
- 50 ml plastic containers
- 5 l red plastic container
- Polyethylene film
- Zip-loc sample bags (large and small)
- Tool kit (wrenches, screwdrivers, knifes, screws)
- Set of Knifes
- One-way latex gloves
- Blue plastic ground sheet
- 1 meter depth probing rod
- Non-slip rubber gloves for coring
- Permanent marker
- Measuring tape
- Spatula
- Tape
- Rags
- Digital camera
- Regular camera
- GPS
- Black garbage bags
- First aid kit
- pH meter and standard solution
- Compass
- Field notebook

Appendix A

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An analytical protocol for the determination of total mercury concentrations in solid peat samples

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Abstract

Traditional peat sample preparation methods such as drying at high temperatures and milling may be unsuitable for Hg concentration determination in peats due to the possible presence of volatile Hg species, which could be lost during drying. Here, the effects of sample preparation and natural variation on measured Hg concentrations are investigated. Slight increases in mercury concentrations were observed in samples dried at room temperature and at 30 °C (6.7 and 2.48 ng kg^{-1} h^{-1}, respectively), and slight decreases were observed in samples dried at 60, 90 and 105 °C (2.36, 3.12 and 8.52 ng kg^{-1} h^{-1}, respectively). Fertilising the peat slightly increased Hg loss (3.08 ng kg^{-1} h^{-1} in NPK-fertilised peat compared to 0.28 ng kg^{-1} h^{-1} in unfertilised peat, when averaged over all temperatures used). Homogenising samples by grinding in a machine also caused a loss of Hg. A comparison of two Hg profiles from an Arctic peat core, measured in frozen samples and in air-dried samples, revealed that no Hg losses occurred upon air-drying. A comparison of Hg concentrations in several plant species that make up peat, showed that some species (*Pinus mugo, Sphagnum recurvum* and *Pseudevernia furfuracea*) are particularly efficient Hg retainers. The disproportionally high Hg concentrations in these species can cause considerable variation in Hg concentrations within a peat slice. The variation of water content (1.6% throughout 17-cm core, 0.97% in a 10×10 cm slice), bulk density (40% throughout 17-cm core, 15.6% in a 10×10 cm slice) and Hg concentration (20% in a 10×10 cm slice) in ombrotrophic peat were quantified in order to determine their relative importance as sources of analytical error. Experiments were carried out to determine a suitable peat analysis program using the Leco AMA 254, capable of determining mercury concentrations in solid samples. Finally, an analytical protocol for the determination of Hg concentrations in solid peat samples is proposed. This method allows correction for variation in factors such as vegetation type, bulk density, water content and Hg concentration in individual peat slices. Several subsamples from

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each peat slice are air dried, combined and measured for Hg using the AMA254, using a program of 30 s (drying), 125 s (decomposition) and 45 s (waiting). Bulk density and water content measurements are performed on every slice using separate subsamples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mercury; Peat bog archives; Atmospheric pollution

1. Introduction

Records of net accumulation of atmospheric Hg are well-preserved in peat cores from ombrotrophic bogs (Madsen, 1981; Jensen and Jensen, 1991; Benoit et al., 1998; Burgess et al., 1998; Martinez-Cortizas et al., 1999; Shotyk et al., 2001). By measuring the concentrations of Hg in peat extending back in time to pre-anthropogenic periods, natural 'background values' and their climate- (Martinez-Cortizas et al., 1999) and volcanism-related variations can be quantified and used to identify the effects of recent increases due to human activities. During traditional acid digestion of peat samples, various sources of contamination must be considered and clean techniques such as those employed by Weiss et al. (1999a) used. Analysis of solid samples by combustion and subsequent trapping of Hg on gold before analysis by AAS (Salvato and Pirola, 1996) using the Leco AMA 254 (Martinez-Cortizas et al., 1999) not only avoids several possible sources of contamination (acids, digestion vessels) but is also safer and less expensive (no acids required) and allows a high sample throughput. The ash from the combusted samples can be recovered and used for further analysis, for example determination of refractory trace metals such as Ti and Zr by X-ray fluorescence spectrometry (XRF). However, the volatility of Hg (0) combined with the natural variability of peat structural components (water content, bulk density, ash content) mean that care must also be taken to achieve accurate results when analysing solid samples.

2. Methods

All tests were carried out in the trace metals laboratory of the Geological Institute of the University of Berne. Mercury concentrations were determined by AAS using the Leco AMA 254.

The bog at Etang de la Gruere (EGR) in the Swiss Jura mountains is ombrotrophic, with 6.5 m of peat dating from 12 370 ^{14}C yr BP (Shotyk et al., 1998). Peat from the ombrotrophic, pre-anthropogenic part of the EGR2A core was homogenised and used to determine losses upon drying at different times and temperatures, in both unfertilised and artificially fertilised peat. Twenty-three different plant species were collected over a period of 4 years from the surface of the bog at Etang de la Gruère and their mercury concentrations were determined using the Leco AMA 254. The range in water content in air-dried peat subsamples (cylindrical 'plugs', 16-mm diameter) was also determined using samples from this core.

The Hg concentration profile was measured twice in a peat core from the High Arctic of Canada, using (1) frozen samples and (2) samples which had been air-dried in a clean-air cabinet overnight at room temperature (RT) to determine whether Hg losses occurred upon drying.

A peat monolith from Schoepfenwaldmoor (SWM), Switzerland (Weiss et al., 1999b), was used to investigate the variation of water content, bulk density and Hg concentration in a typical ombrotrophic peat. Water content and bulk density were studied both in a short core (17 cm) and within an individual peat slice ($10\times10\times1$ cm). Variation of Hg concentrations within a single slice was also recorded. The investigation of the effect of air drying at room temperature was also carried out using samples from this core.

The effect of grinding dry samples and of alterations to the Leco AMA 254 analysis program were studied using an in-house peat standard (OGS 1878P), which had previously been dried at 105 °C and homogenised.

2.1. Determination of a suitable peat analysis program for Hg analysis using the Leco AMA 254

The Leco AMA 254 is fully compliant with EPA (1998) method 7473. Samples contained in nickel sample holders enter a sealed drying and combustion furnace, where they are dried in a stream of oxygen before being thermally decomposed. Gases from the thermally decomposed sample are swept in the stream of oxygen through a catalyst furnace at 750 °C, which fully decomposes the gases and traps NO_2, SO_2 and halogens. Mercury is trapped on a gold amalgamator situated at the end of the furnace. Waste gases are removed from the system by the gas stream. The amalgamator is then heated to 500 °C to release the mercury, which is measured by atomic absorption spectrometry. The detection limit of the instrument is 0.01 ng Hg and the working range is 0.05–600 ng Hg, with repeatability being $<1.5\%$.

The instrument was calibrated using liquid standards prepared from Merck mercury standard solution, 1000 mg l^{-1}. Solutions of concentration 10 and 1000 ng ml^{-1} were used to dose the instrument. A 10-point calibration was made from 0.00 to 29 ng Hg. The equation used to calculate the calibration curve is:

$$\kappa(\mathrm{NST}) = \frac{1}{n}\sum_{\mathrm{ji}}\{A_{\mathrm{ji}}(\mathrm{NST})/m_{\mathrm{ji}}\}$$

Where κ is the constant of proportionality, NST is the relative non-absorbable radiation flux, A is the corrected absorbance and m is the quantity of mercury in the cell. For the calibration obtained, slope $(\kappa) = 42.64 \pm 0.62$ ng.

To test the effect of increased drying time (and therefore increased Hg passing through the apparatus from oxygen supply), blanks were run on the Leco AMA 254 using drying times of 9 and 500 s (other parameters being kept constant: decomposition time 150 s, waiting time 45 s).

The validity of the recommended drying time was also tested [0.7×vol. water (μl)] s. Ten samples of the in-house peat standard OGS 1878 P were moistened (made up to 95% water, $R_{\mathrm{H_2O}} \geq 18\ \Omega$) and analysed using the recommended drying time. Ten dry samples were also analysed using a drying time of 20 s.

A suitable decomposition time was established by measuring Hg in nine samples of OGS 1878 P at 100, 125, 150 and 175 s decomposition time (drying and waiting time being constant at 30 and 45 s, respectively). One coal and five plant-derived certified standard reference materials (SRMs) were analysed using this program.

2.2. Effects of sample preparation: drying times and temperatures

Homogenisation of the sample is difficult if the peat is wet but can easily be carried out by hand using dry peat. However, drying peat, particularly samples from cold regions, could results in a loss of Hg by volatilisation. For this reason, tests of the effect of air-drying peat at room temperature on Hg content were carried out. The Hg profile of an Arctic peat core was measured twice; once using samples which had been kept frozen since collection and once using samples which had been air-dried overnight in a class 100 clean-air cabinet. All samples were measured in duplicate using the Leco AMA 254 program recommended here. Bulk density was determined for each sample as described below and from this, the volumetric concentrations (ng cm^{-3}) were calculated.

To investigate the effect of prolonged drying at high temperatures and the effect of fertilisation upon Hg losses upon drying, bulk samples of peat from the ombrotrophic, pre-anthropogenic section (88–234 cm) of the EGR2A core was homogenised using a food mixer. The mixture was divided into five sections of 150 g each. Three sections were artificially fertilised with NH_4NO_3 (1 mM), $Ca_3(PO_4)_2$ (1 mM), K_2CO_3 (1 mM), respectively, and a fourth was fertilised with a mixture of the three above additives (1 mM each). The fifth section was left unfertilised. These sections were then subsampled into five parts, which were dried at the following temperatures; RT, 30, 60, 90 and 105 °C for the following times; 0, 19, 24, 48, 120, 168 and 336 h. The drying was carried out in acid-cleaned, Teflon bowls, each containing 3.5 g of peat slurry. After drying, the samples were stored frozen, sealed in air-tight plastic bags until AAS Hg analysis using the Leco AMA 254.

2.3. Effects of sample preparation: grinding samples

Five samples of an in-house peat reference material were ground using a coffee mill. These samples were analysed for Hg using the Leco AMA-254 and the values obtained were compared to those obtained using five unground samples of the same material.

2.4. Effects of sample preparation: water content in air-dried plugs

The EGR2A core (co-ordinates CH 570.525, 232.150) was collected on 26 August 1991. The core was taken using a Livingston corer (Aaby and Digerfeldt, 1986). The cylindrical core was initially taken in 1-m sections (total length 692 cm, $d=8$ cm). The core was then sliced, frozen, into 2-cm slices. The slices were stored in individual airtight plastic bags at -18 °C until analysis. Slices from 46 to 592 cm were thawed before plugs were taken. Four plugs were taken from each slice. One plug from each slice was weighed wet. All the plugs were allowed to air dry in a class 100 clean air cabinet for 20 h. The air-dried plugs, which had been weighed wet, were re-weighed after 20 h and then placed in an oven at 105 °C until constant weight was obtained. The percentage water remaining in the air-dried plugs was then calculated from the air-dried weight and the constant dry weight of the plugs. This value for water content of air-dried samples was used to calculate the theoretical dry weight of the remaining air-dried plugs, which were subsequently analysed for Hg.

2.5. Effects of peat properties: Hg concentrations in different bog plant species

Twenty-three plant species were collected from the surface of the ombrotrophic bog at Etang de la Gruère in the Swiss Jura Mountains (1005 m) between July 1997 and September 2000. The samples were stored in air-tight plastic bags immediately after collection and were kept frozen until analysis. Samples were then air dried in a class 100 laminar flow cabinet overnight and analysed for Hg content by AAS, using the Leco AMA 254.

2.6. Bulk density and water content in a peat monolith

A peat monolith was collected at SWM (co-ordinates CH 631.250, 177.000) on 28 August, 1991, using a Wardenaar corer (Wardenaar, 1987). The monolith obtained ($10\times10\times100$ cm) was stored at -18 °C after collection. It was then cut (frozen) into 1-cm slices, using a stainless steel band saw and the individual slices were again stored at -18 °C until analysis. The top 17 slices were used in the following analyses. A stainless steel tube with a sharpened end, of diameter 16-mm was used to remove three plugs of known volume from each 1-cm slice. The wet weight of each plug was recorded and the plugs were then dried to constant weight in an oven at 105 °C. The dry weights were recorded and the plugs were then stored in air-tight plastic boxes, which had been soaked for 1 h in 10% HNO_3 and rinsed six times with water ($R_{H_2O}\geq 18\ \Omega$).

2.7. Effects of peat properties: variation in Hg concentrations within one $10\times10\times1$ cm slice

The slice 15 cm from the surface of SWM core was used to investigate the diversity of Hg concentrations within a single $10\times10\times1$ cm slice of peat. The slice appeared to be homogenous in terms of composition of plant material. However, wood was removed from the samples before analysis. Sixteen plugs (four rows of four) were extracted as described above, at even distance from one another. The samples were analysed for Hg using the Leco AMA 254. The theoretical dry weight of the samples was calculated using their wet weights and the average water content of slice 15, previously determined to be $93.0\pm0.4\%$. The Hg concentration was calculated and expressed as ng g^{-1} in dry weight of peat.

3. Results

3.1. Suitable peat analysis program using the Leco AMA 254

Increasing the drying time from 9 to 500 s only increased the blank value from 0.020 Hg ($n=2$)

Table 1
Results of the analysis of six certified standard reference materials using the suggested program on the Leco AMA 254

SRM	Measured [Hg] (ng/g)	*n*	Certified [Hg] (ng/g)
NIST 1515	45.1 ± 0.8	13	44 ± 4
NIST 1547	32.3 ± 1.4	17	31 ± 7
NIST 1575	118.9 ± 0.9	2	150 ± 50
NIST 1630a	99.2 ± 2.7	2	93.8 ± 3.7
BCR 281	16.6 ± 0.5	2	21 ± 2
IAEA 336	170.2 ± 0.1	2	200 ± 40

to 0.025 ng Hg ($n=2$). It was therefore concluded that the effect of the length of program was negligible with respect to increased blank values due to increased Hg from the oxygen supply during longer programs.

The result of 10 analyses of in-house peat standard OGS 1878 P, which were made up to 95% water ($R_{H_2O} \geq 18\ \Omega$), using the recommended drying times, was 84.0 ± 18.0 ng g^{-1} Hg: a relative standard deviation of 22%. The result of 10 analyses of the dry material was 76.6 ± 2 ng g^{-1} Hg: a relative standard deviation of 8%. Thus, analysis of dried samples appears to reduce the standard deviation of the results.

Analysis using a decomposition time of 125 s resulted in the lowest standard deviation among 10 analyses of OGS 1878P (1.9% compared to 5.15, 8.87 and 9.68% at 100, 150 and 175 s, respectively). Six SRMs analysed using this program gave the results shown in Table 1.

3.2. Effect of prolonged drying at high temperatures in unfertilised and artificially fertilised peat

The results (Fig. 1) show overall trends in changes in Hg concentration at a rate of 6.7 ng kg^{-1} h^{-1} at RT, 2.48 ng kg^{-1} h^{-1} at 30 °C, −2.36 ng kg^{-1} h^{-1} at 60 °C, −3.12 ng kg^{-1} h^{-1} at 90 °C and −8.52 ng kg^{-1} h^{-1} at 105 °C for these samples (Table 2). Therefore, it appears that there is an increase over time in [Hg] in peat, which is left to air dry at low temperatures, probably due to absorbance of Hg from the lab air. In contrast, there is a decrease in Hg concentrations in samples dried at higher temperatures, probably due to loss of Hg by volatilisation. This loss is so gradual that drying at low temperatures for a few hours should not measurably affect the Hg concentrations. However, prolonged drying at higher temperatures could result in a significant loss of Hg and extensive drying at room temperature could give rise to significant Hg contamination.

Artificial fertilisation of the peat was carried out to stimulate microbial activity. Artificial fertilisation has been found in the past to increase Hg loss by volatilisation (Lodenius et al., 1983). Average changes in Hg concentrations over the whole temperature range were −0.26 ng kg^{-1} h^{-1} for N-fertilised peat, −2.38 ng kg^{-1} h^{-1} for P-fertilised peat, 1.18 ng kg^{-1} h^{-1} for K-fertilised peat, −3.08 ng kg^{-1} h^{-1} for N, P and K-fertilised peat and −0.28 ng kg^{-1} h^{-1} for unfertilised peat. These results indicate that the addition of phosphorus in particular increases mercury losses, probably due to increased microbial activity. The addition of potassium, however, appeared to decrease Hg loss.

3.3. Effect of air-drying at room temperature on Hg content of peat

The Hg concentration profile in the Arctic peat core was measured once using samples which had remained frozen since collection and once using samples which had been air-dried at RT in a clean-air cabinet overnight. Both sets of samples were corrected for bulk density and the results are displayed as volumetric concentrations (ng cm^{-3}, Fig. 2). The average difference in Hg concentration between Hg content of the samples was 0.3 ± 0.9 ng cm^{-3}, $n=63$, with the wet samples being on average slightly lower in Hg than the air-dried samples. This difference can be accounted for by a combination of the error involved in the bulk density determination and uptake of Hg from the lab air during air-drying. However, the previous experiment suggested a rate of increase in Hg concentration of 6.7 pg g^{-1} h^{-1} during air drying

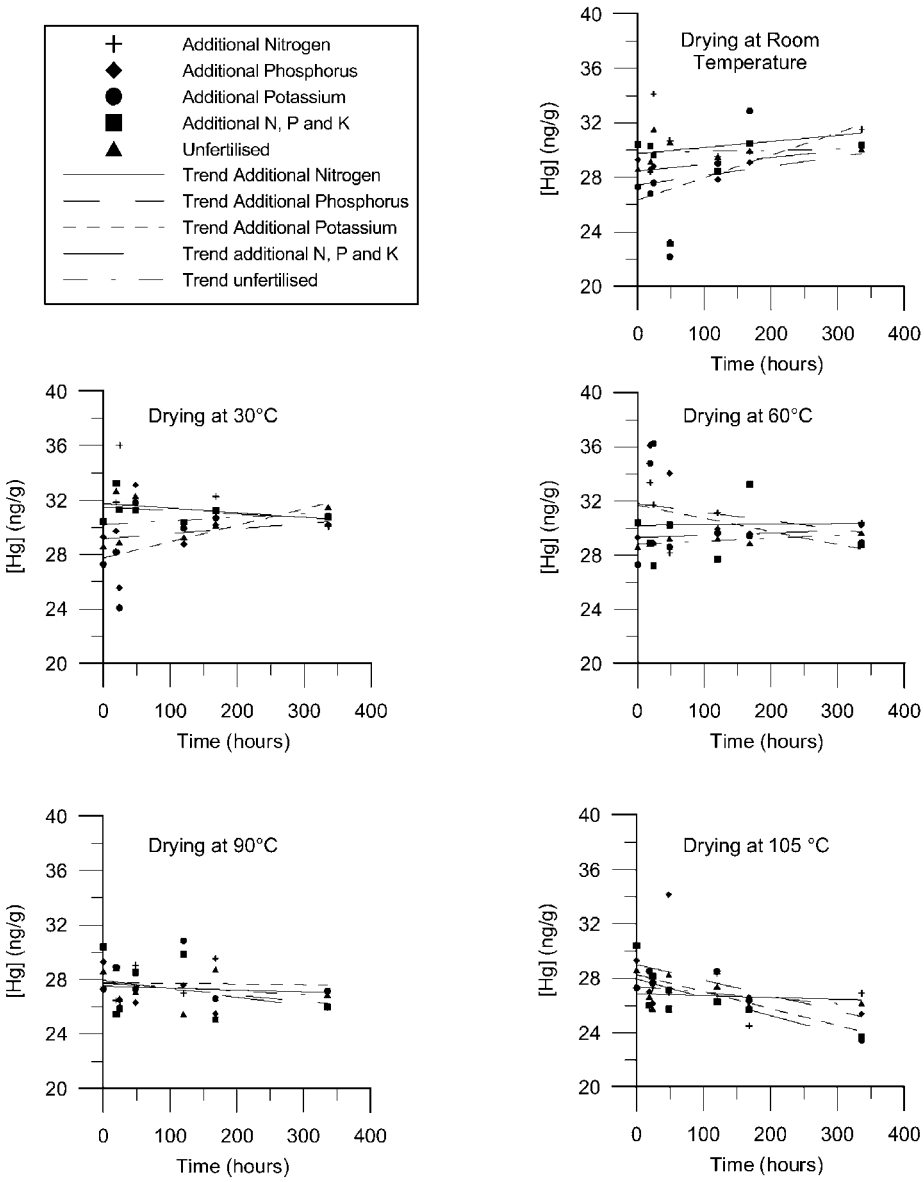


Fig. 1. Hg concentrations measured in both unfertilised and artificially fertilised peat dried at RT, 30, 60, 90 and 105 °C for up to 2 weeks.

at RT and would therefore account for an increase of only 0.9 ng g^{-1}, or 2%, during 14 h of air drying. It is therefore likely that most of the observed increase stems from error in the bulk density determination, which was high in this case due to the presence of ice in the peat.

3.4. Effect of grinding samples

Grinding promotes homogenisation of the sample by reducing particle size and by mixing. It also allows a greater mass of sample to be analysed at one time, as more material can be placed into each sample vessel. Therefore grinding allows a more representative value to be obtained.

The average Hg concentration for unground samples was 47.9 ± 1.2 ng g^{-1} ($n=5$) and the average for ground samples was 45.2 ± 1.2 ng g^{-1} ($n=5$). It is therefore possible that a slight loss of Hg occurs on grinding, possibly due to elevated temperature, coupled with smaller particle

Table 2
Trends of Hg loss/gain during drying in both unfertilised and artificially fertilised peat samples over time (up to 2 weeks) at various temperatures

Trendline gradients							
Temperature	N	P	K	NPK	Unfertilised	Average gradient	Av. loss/gain in ng/kg per h
22	0.0045	0.0068	0.0165	0.005	0.0007	0.0067	6.7
30	−0.0034	0.0036	0.012	−0.0025	0.0027	0.00248	2.48
60	0.0004	−0.0063	−0.0097	0.0016	0.0022	−0.00236	−2.36
90	−0.0014	−0.0047	−0.0005	−0.0062	−0.0028	−0.00312	−3.12
105	−0.0014	−0.0113	−0.0124	−0.0133	−0.0042	−0.00852	−8.52
av. gradient	−0.00026	−0.00238	0.00118	−0.00308	−0.00028		
av. loss/gain in ng/kg per h	−0.26	−2.38	1.18	−3.08	−0.28		

size within the grinder. To achieve a homogenised sample without loss of Hg, dried samples can be crushed by hand in a sealed plastic sample bag. In this way, a fine-grained powder can be obtained from the mossy part of the sample, although fibres from grass and wood remain intact. This facilitates the selection of the mossy part of the samples for Hg analysis, reducing the amount of grassy and woody material in the samples and therefore also reducing the variation in Hg concentration values caused by variation in peat type. The relative standard deviation in Hg concentration results, using samples homogenised in this way, measured in duplicate was 4.0% ($n=265$ duplicate pairs).

3.5. Variation of water content in air dried plugs

After drying overnight at RT in the clean air cabinet, the average water content of the plugs extracted from the EGR core was $9.1\pm2.0\%$ ($n=296$). Water content of samples to be analysed can thus be calculated by comparison with a similarly sized and shaped sample, which has been allowed to dry for the same length of time and is subsequently dried to constant weight.

3.6. Comparison of Hg concentrations in bog plant species

The comparison of Hg concentrations in a collection of 23 plant species all collected from the surface of the one bog over a period of 4 years (Fig. 3) shows an overall agreement among most species in each year of collection (1997: 207 ± 44 ng g^{-1}, $n=5$; 1999: 47 ± 29 ng g^{-1}, $n=10$; 2000: 50 ± 45 ng g^{-1}, $n=20$). Species which showed unusually high Hg concentrations are the mosses *Sphagnum recurvum* and *Pseudivernia furfuracea* and the needles and twigs, but not cones or bark, of the tree *Pinus mugo*. Omission of these from the data results in average concentrations of 36 ± 19 ng g^{-1}, $n=8$ for 1999 and 32 ± 14 ng g^{-1}, $n=17$ for 2000, i.e. reducing the standard deviation from 62 to 53% and 90 to 44%, respectively.

3.7. Inconsistency in Hg concentration in a lateral peat slice

Mercury concentrations of the 16 samples taken from one SWM peat slice were found to vary by over 20%: 69.2 ± 14.7 ng g^{-1}, min. 41.4 ng g^{-1}, max. 98.7 ng g^{-1} Hg. These results indicate the importance of homogenising the peat moss prior to analysis and/or analysing several samples from each slice and averaging the results in order to obtain values representative of the whole slice.

3.8. Bulk density and water content

The average water content of the 17 slices of the SWM core analysed was $94.0\pm1.6\%$. The average relative standard deviation of the percentage of water in a single slice was 0.97%. These results indicate that water content fluctuation is negligible in the part of the core studied.

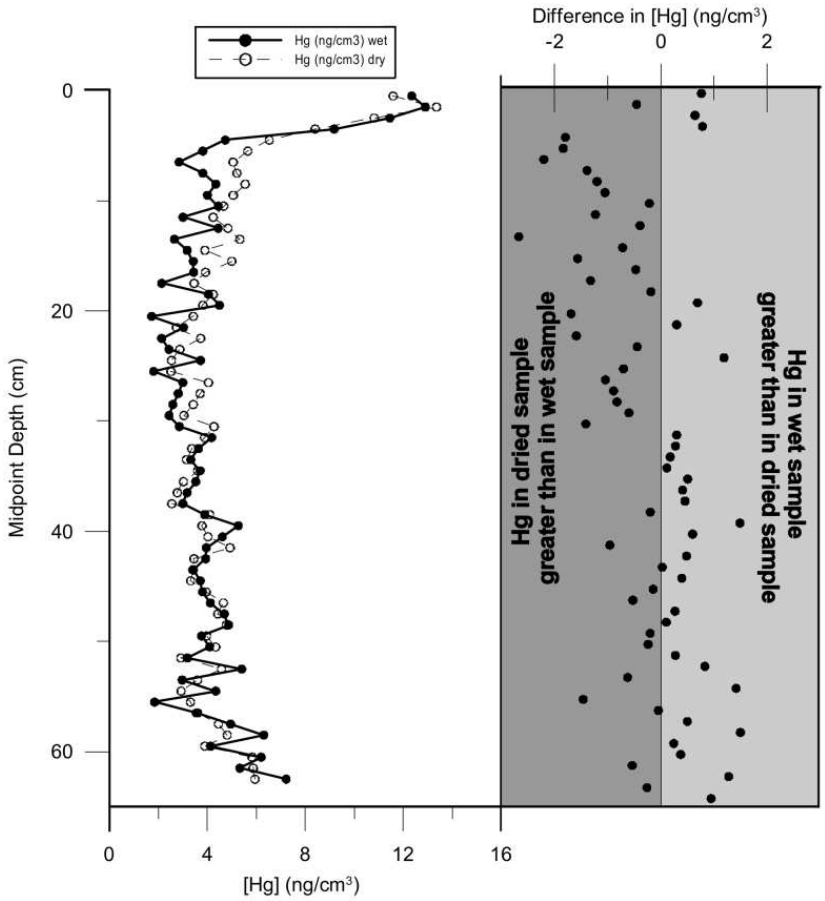


Fig. 2. Comparison of Hg concentration profiles measured in (a) frozen and (b) air-dried samples from a peat core from the High Arctic of Canada.

However, the average bulk density for all the samples studied was 0.05 ± 0.02 g cm^{-3} and the average relative standard deviation of bulk density within a slice was 15.6% ($n = 16$). This is a significant fluctuation, indicating that bulk density variation should be taken into account when comparing Hg values from different parts of a core and should be determined throughout the whole core if its values are to be used to calculate Hg flux data.

4. Discussion

The results of the experiments above indicate that great care must be taken during peat sample preparation and Hg analysis in order to obtain accurate and representative results.

Although the Leco AMA 254 is a suitable instrument for Hg analysis in both wet and dry peat samples, drying facilitates homogenisation of the peat and also allows a greater amount of sample to be analysed and therefore a more representative value to be obtained. Analysis of dry samples also resulted in a lower standard deviation than analysis of wet samples. Air drying at room temperature overnight appeared, in this set of experiments, not to result in a significant loss or gain of Hg in the samples, even in peat from the High Arctic. However, prolonged drying was shown to lead to significant increases in Hg concentrations, due to uptake of Hg from the lab air. Prolonged drying at higher temperatures lead to an overall decrease in Hg concentrations and should therefore be avoided in total Hg studies. This is in

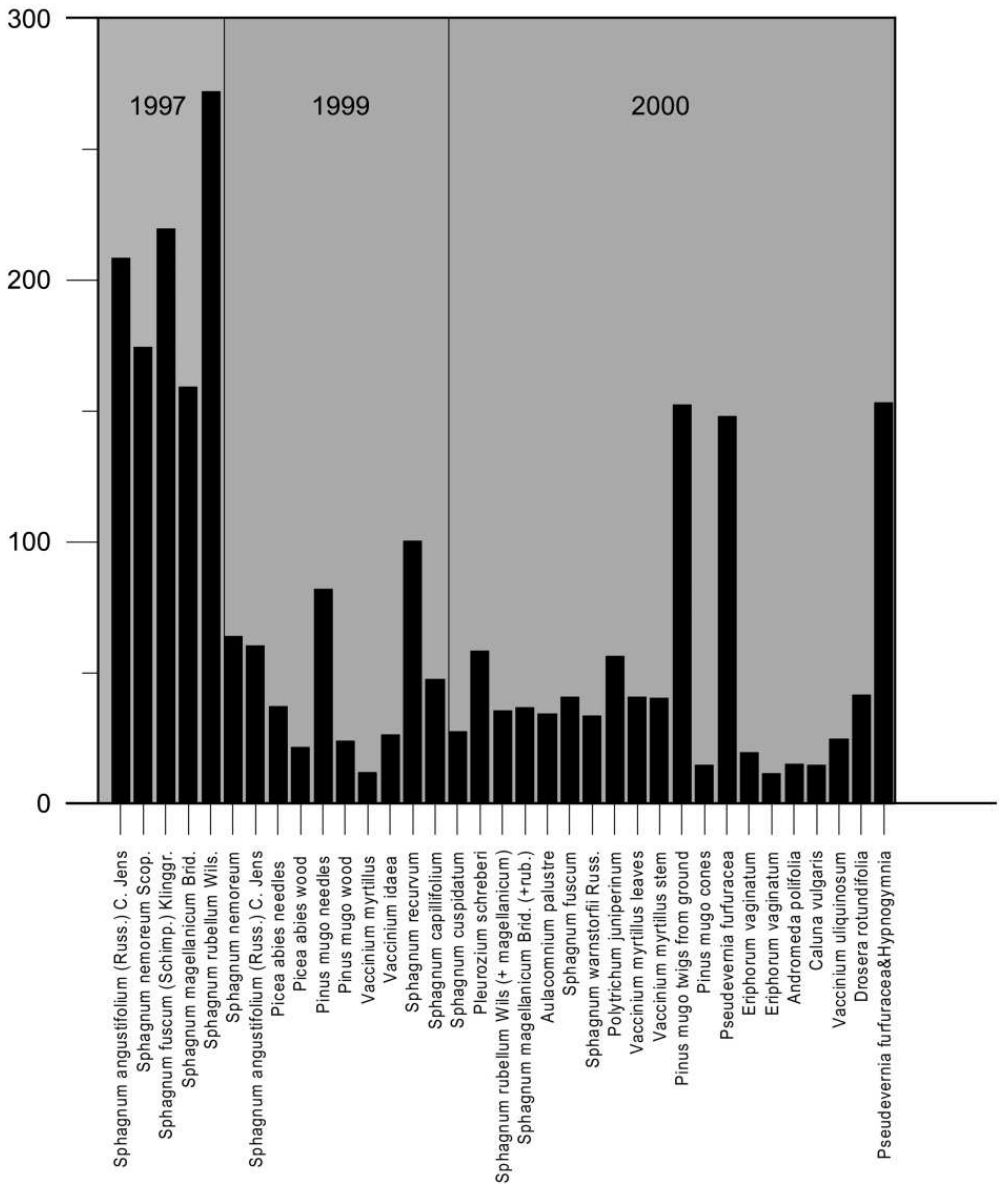


Fig. 3. Hg concentrations measured in 23 peat-forming plant species collected from the surface of one bog over a period of 4 years. N.B. Only *Sphagnum* collected in 1997.

agreement with the findings of Norton et al. (1997) and Martinez-Cortizas et al. (1999). Fertilisation with phosphorus increased Hg losses, probably due to increased microbial activity. Variation in the water content of air-dried plugs is small and can be corrected by measuring a comparable plug from the same slice, which has been dried in the same manner.

Mercury concentrations vary greatly between different bog plants and even between different parts of the same plant species, with certain mosses and trees having Hg concentrations much higher than average. Differences in vegetation composition can exist between bogs or even within the same bog at different times. This could potentially affect the Hg record and also the comparability of records from different bogs. It is therefore suggested that leaves, grass and wood be removed from the samples before Hg analysis. However, even Hg concentrations between different moss

species or between mosses growing within different microclimates on the surface of a bog could be inconsistent (Norton et al., 1997). Mercury concentrations within one small horizontal section of peat may be uneven. Several subsamples should be taken from each peat slice in order to obtain a representative Hg concentration for the whole slice. Because large fluctuations in bulk density values can occur throughout a peat core, bulk density should be determined in each slice to allow Hg flux rates to be calculated accurately.

Finally, mixing together the moss component of the subsamples increases the homogeneity of the material to be analysed. Here, grinding in a coffee mill resulted in a slight loss of Hg. However, simple hand mixing of the dried samples held in a plastic bag resulted in low standard deviation of duplicate pairs.

5. Conclusions

The following protocol is proposed for the determination of mercury concentrations in solid peat samples:

Cores should be transported frozen from the field to the laboratory, if possible, to avoid unnecessary compaction and losses of water or Hg. The peat should be kept in clean (wrapped airtight in plastic), cool conditions until analysis. The edge of the core should be removed prior to analysis in case of contamination (by smearing) during core collection. Several subsamples should be analysed from each peat slice in order to obtain a representative value. These subsamples can be air-dried at room temperature in a clean environment, such as a Class 100 laminar flow cabinet, without significant loss of mercury. During this period, the cabinet should be darkened to avoid light-enhanced evasion of mercury from the samples (Gustin and Maxey, 1998). Dried subsamples can be homogenised by crushing air-dried plugs of peat together into a powder and mixing; this can be done by hand, with the samples in a sealed plastic bag.

One or more subsamples from each slice should be used for bulk density determination, which is required to allow mercury deposition fluxes to be calculated. Bulk density can be determined from the dry weight of a peat subsample of known volume. Air drying this subsample with the subsamples to be used for mercury analysis (of the same shape and volume) before drying it in a drying oven to constant weight allows the water content of the air-dry samples to be accurately estimated; this information can be used to correct the masses of the samples analysed for Hg to their true dry weights.

Suggested times for a Leco AMA 254 air-dry peat analysis program are: 30 s (drying), 125 s (decomposition) and 45 s (waiting for emission of waste gases before Hg content determination by AAS).

Acknowledgments

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