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Climatic and anthropogenic effects on atmospheric mercury accumulation rates in ombrotrophic bogs from Southern Ontario

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Abstract. To quantify the effects of human activities on atmospheric deposition of mercury in eastern Canada, an improved understanding of the natural variations of the concentrations, fluxes and sources of Hg over a long period of time is required. Peat cores from 3 sites in southern Ontario were used to reconstruct changes in atmospheric mercury accumulation rates for the past 10,000 years. The net mercury accumulation rates and excess mercury (mainly anthropogenic) were calculated using the long-term average Hg/Br and Hg/Se. The average background mercury accumulation rate during the pre-anthropogenic period was 1.4 ± 1.0 μg m^{-2} yr^{-1}. An excess of Hg was observed only once during that period, probably reflecting a change in climate. Mercury contamination from anthropogenic sources began about AD 1475 at the Luther Bog, corresponding to extensive 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. Hg pollution increased again at the beginning of the 19^{th} century. The maximum increase (up to 30 times) compared to "background" occurred during the 1950s, when the anthropogenic component represented up to 85% of the total atmospheric mercury deposition.

1. INTRODUCTION

Peat cores were collected from three ombrotrophic peat deposits in southern Ontario: Sifton Bog in the city of London, Luther bog which is in a rural location, and Spruce Bog which is comparatively remote, in Algonquin Park. The main goal of the 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 profile from Luther Bog (representing ca. 10,000 years of peat accumulation) has been studied in detail to quantify the long term, natural variation in atmospheric Hg accumulation rates. Several dating methods have been combined to allow reliable age-depth models to be reconstructed for each peat profiles. In an effort to distinguish between natural and anthropogenic sources of Hg, the natural variation in Hg to bromine (Br) and selenium (Se) in ancient samples is used to calculate the amount of natural mercury in modern samples

2. MATERIAL AND METHODS

The top most layers of peat were collected as a single 15×15cm monolith using a 1-meter titatinium Wardenaar cores. In addition to short peat cores collected at all sites, a complete peat profile was taken at Luther Bog (ca. 600cm) in 50cm sections using a stainless steel Belarus corer. A 50cm section was lost during the coring session. All samples were frozen at –18°C for storage and transport to Berne. The Wardenaar and Belarus cores were sectioned into 1 and 2cm slices respectively and the Hg concentration

measured in solid peat samples using the LECO AMA 254 Hg analyser as described by [1]. A dried, milled subsample for each slice was measured for 19 major and trace elements using EMMA XRF such as Br and Se. Selected powdered bulk samples and plant material of the cores were age dated by ^{14}C using decay counting at the University of Heidelberg, Germany and Acceleration Mass Spectrometry (AMS) at the University of Århus, Denmark and at the ETH Zurich, Switzerland. An age-depth relationship was reconstructed for each of the profiles from dated points using polynomial regressions.

3. RESULTS

3.1. Ash contents and Hg concentrations

The ash content of the peat profiles average 4%, which is typical of ombrotrophic bogs. The variations in ash content reflect organic matter loss during humification, change in atmospheric soil dust deposition rates, or both. Analysis of the peat core from Luther Bog shows law and quite stable Hg concentrations, with values in the range 14 to 32 ng g^{-1} from 150cm to 490cm. Above 60cm; however, the concentrations of Hg increase to values as great as 188, 250 and 333 ng g^{-1} in Spruce Bog, Luther Bog and Sifton Bog respectively. While the concentrations of conservative, lithogenic elements such as Ti in the Luther core indicate some change in the soil dust fluxes, these have no impact on the Hg concentrations. Assuming that the Hg concentrations between 490 and 150cm at Luther (14 to 32 ng g^{-1}) reflect the range in natural concentrations, the maximum Hg concentrations at Spruce, Luther and Sifton Bogs exceed this range by factors 6-13, 8-18 and 10-23 respectively.

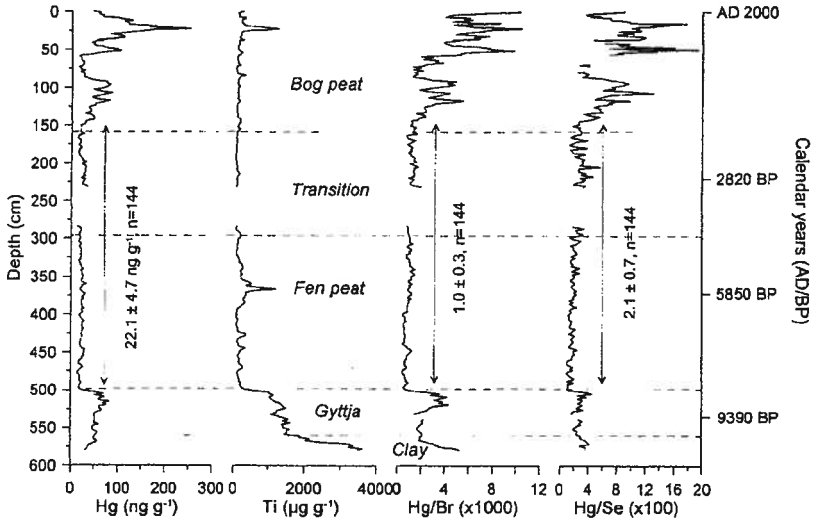

Figure 1. Hg and Ti concentrations, Hg/Br and Hg/Se ratios profiles in the Luther bog.

To estimate the atmospheric Hg fluxes, Hg accumulation rates (AR) expressed in µg m^{-2} yr^{-1} were calculated using: AR = 10 × {Hg} × BD × GR 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}).

3.2. Bromine and Selenium relationship to mercury

A correlation of mercury to Br and Se concentrations is observed throughout most of the profile, from 490 to 150cm and from 85 to 70cm depth. Assuming that Br and Se are supplied exclusively by

natural atmospheric sources, are effectively in the peat column, we used the Hg/Se and Hg/Br ratios to try to distinguish between natural and anthropogenic Hg. Natural mercury concentration was calculated from those relationship. "Excess Hg" is defined as the difference between the natural component and the total Hg concentration.

4. DISCUSSION

4.1. Pre-anthropogenic Hg accumulation rates

From the Hg AR profile, it is clear that total Hg deposition varied throughout the last 10,000 years. The Luther Bog record of Hg accumulation shows that Hg AR varied between 0.4 to 7.7 $\mu g\ m^{-2}\ yr^{-1}$ (average $1.4 \pm 1.0\ \mu g\ m^{-2}\ yr^{-1}$) during the Holocene. Those values are consistent with natural Hg AR measured in bogs from Spain, Switzerland [2], Greenland, and Maine. This variation is thought to be primarily due to climate change.

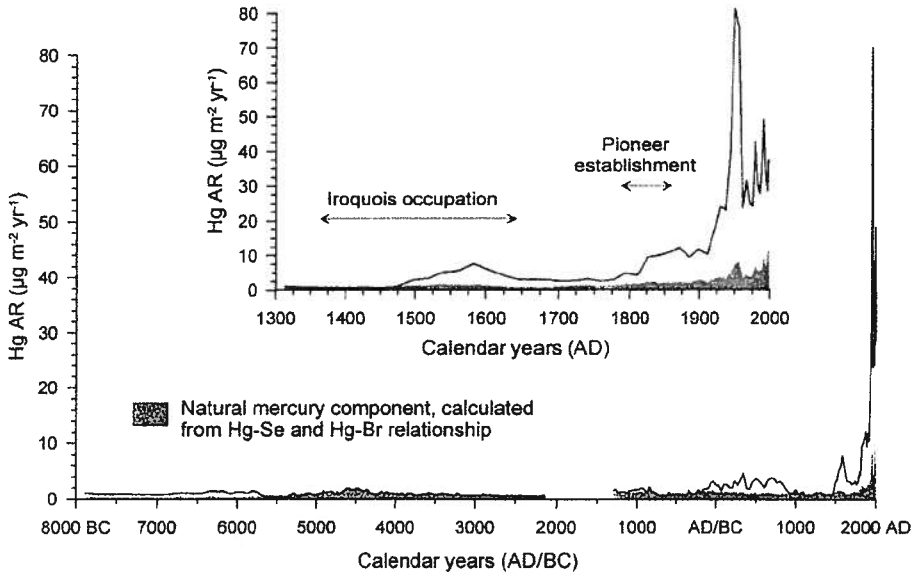

Figure 2. Total and natural mercury accumulation rate profile for Luther Bog.

During the pre-anthropogenic period, an excess of Hg occurred only once, from ca. 200 cal years BC to AD 1200. A decrease in the degree of peat decomposition was measured during that period, which follows a period of low effective precipitation during the late middle Holocene warm and dry period in Ontario [3]. These changes reflect increased atmospheric humidity at that time, which must have led to a corresponding increase in wet deposition of atmospheric Hg. Two others explanations are possible, which may be the indirect result of climate change. A change in relative abundance of plant species or greater tree cover, may have led to a change in the efficiency by which Hg was deposited, captured and/or retained by the bog.

4.2. Anthropogenic effects on the environment

A notable peak of Hg AR (up to 5 time relative to "background") occurs from AD 1475 to AD 1650 reaching 7.7 $\mu g\ m^{-2}\ yr^{-1}$. Since AD 1475, Hg AR have been elevated and the Hg/Br and Hg/Se ratios have

continuously been outside of their long-term average range. It is known from archaeological evidence that Iroquoians settled in the Grand River watershed of southern Ontario from AD 1370 to AD 1650. Forest fires have been found to be significant sources of Hg emissions in Manitoba and Amazon. It is most likely that the increase in Hg AR seen in the Luther profile bog reflects extensive biomass burning by Native North Americans for agriculture.

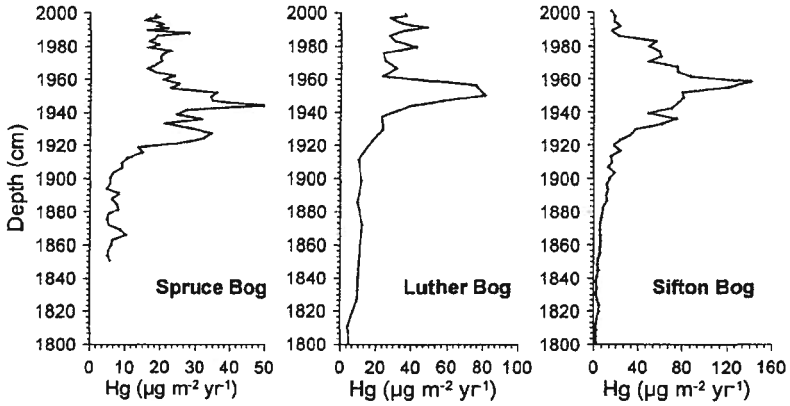

Figure 3. Net Hg accumulation rates profiles calculated for Spruce, Luther, and Sifton Bogs. Inset: focus on the anthropogenic effects on the mercury accumulation for the last 700 years.

Moving to the modern period, Hg AR signals from Sifton, Luther and Sifton bogs reflect closely the economic and industrial development of Ontario. During the late 17^{th} and 18^{th} centuries, deposition of anthropogenic Hg was at least as great as that of Hg from natural sources. Mercury contamination increased again at the beginning of the 19^{th} century and peaked during the 1950's. At that time, anthropogenic mercury contributed at least to 85% of the total Hg AR reaching 49.5, 81.0 and 128.5 0 µg m^{-2} yr^{-1} for Spruce, Luther, and Sifton bogs respectively, which are up to 11 to 27 times greater than the natural background rates. Today, the Hg AR are at the same level as those reached during the 1960's at all sites, these values, however are approximately 20 to 30 times the natural background values for remote, and urban and rural sites respectively.

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REFERENCES

1. Roos-Barraclough, F., N. Givelet, A. Martínez-Cortizas, M.E. Goodsite, H. Biester, and W. Shotyk, Sci. Tot. Environ., 2002. **292**: p. 129-139.
2. Roos-Barraclough, F., A. Martínez-Cortizas, E. Garcia-Rodeja, and W. Shotyk, Earth Planet. Sci. Lett., 2002. **202**: p. 435-451.
3. Yu, Z., J.H. McAndrews, and U. Eicher, Geology, 1997. **25**(3): p. 251-254.