GEOCHEMISTRY OF THE RECENT SEDIMENTS FROM A LAKE IN THE VICINITY OF THE COAL-FIRED POWER PLANTS IN CENTRAL ALBERTA, CANADA

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ABSTRACT
This study investigates the geochemical characteristics of recent sediments and their porewaters from the Wabamun Lake in central Alberta (Canada) to elucidate the possible impact from coal utilization in this region. A multi-elemental analysis of recent sediments in conjunction with other inorganic and organic geochemical approaches are applied to determine the sources, quantity, and processes involved in the distribution of trace elements in the sediments. Concentration versus depth profiles in the sediments and the associated porewaters suggest that geochemical processes impact the mobility and vertical distribution of trace elements in these sediments. Although inputs of trace elements to ecosystems have clearly been elevated by emissions from the coal-fired power plants, diagenetic processes and natural inputs cannot be ignored in the distribution of lake sediments. A combination of various biogeochemical processes may control the distribution of elements in sediment and porewater. However, because of the alkalinity and eutrophic conditions of the studied lake, the Ca-OM fraction plays the most important role as substrate for trace elements. The higher input of calcareous fly ash in the Wabamun Lake, adjacent to the power plants, may cause scavenging of trace metals. The size of fly ash particles tends to decrease towards the more recent part of the sediment profile indicating the effect of particle emission control measures adopted by the power plants. There is no evidence of fly ash particles in the sediments deposited prior to the commencement of coal-fired power plants in the study area (before 1956).

INTRODUCTION
The main pathways of trace elements to lake ecosystems are from surface runoff, groundwater, waste outlets, and atmospheric deposition. Trace elements can then be scavenged from lake water to surface sediments during various geochemical processes. Therefore, the geochemical study of recent lacustrine sediments can be used as a tool to monitor levels of trace elements in the environment.

The temporal variation of trace elements in a vertical profile of recent lacustrine sediments offers a key to the pollution history of the lake. Several coal-fired power plants are located in the Wabamun area in central Alberta (Canada), which have been in operation for more than half a century (Figure 1). Emissions from these facilities can be a significant source of elements deposited in the local environment, and as a result are a subject of environmental concern. Lake basins cover large portions of land in the Wabamun region, and may act as sinks for emitted particles/elements from the coal-fired power plants. Therefore, this study utilizes the geochemical approaches to characterize the recent sediments as related to the possible impact from coal-utilization in the study area.

STUDY AREA
The Wabamun region in Central Alberta is located in the focal point of four major power plants; the Wabamun, Sundance, Keephills and Genesee power plants (Fig. 1). The Wabamun Lake is a freshwater, eutrophic, shallow lake (mean depth: 6 m) located in proximity to the coal-utilization installations in the Wabamun region (Fig. 1). Most of the lakes in the Wabamun region are essential for domestic, municipal and industrial water sources, and are often used for recreation and urban development. Therefore, a variety of anthropogenic as well as geogenic and natural activities may influence these lakes. In this study, more attention was given to Wabamun Lake since it hosts the Sundance and Wabamun generating stations upon its shore (Fig. 1), so it will likely show the strongest influence of the stations within its sediments.

METHODOLOGY
Coring, sample preparations
The coring project was conducted in October 2002. Two representative undisturbed cores were taken from the deepest part of Wabamun Lake using a modified Kajak-Brinkhurst (KB) core sampler. The sediment cores were sub-sampled to 1-cm sediment intervals using an extrusion device. The entire sub-sampling and sample preparation was carried out under anoxic conditions (N₂-filled glove bag). The porewater samples were retrieved by centrifuging the wet sediment samples at 5000 rpm inside the sealed centrifuge tube filled with N₂ headspace. The supernatant water in each centrifuge tube was filtered using a < 0.45 µm Millipore® syringe filter. The porewater samples were treated using 0.5% Bromine monochloride (BrCl) solution for preserving bivalent mercury and 1% HNO₃ to preserve the remaining metals in the solution. The porewater and sediment samples were subjected to various geochemical analyses, which are discussed further in this paper. In all analytical methods, duplicate samples and laboratory standards were used to monitor analytical accuracy and precision. For porewater samples, both the laboratory and field blanks were tested to insure the quality of the analyses.

Analytical
The age of the sediment profiles and sedimentation rate was determined using ²¹⁰Pb (and ¹³⁷Cs) isotope dating. For this purpose, the sediments were subjected to Gamma-ray
spectrometry analyses to determine the activity of radionuclides in the studied sediments. The concentrations of elements in sediment samples were analyzed using both Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Instrumental Neutron Activation Analysis (INAA). The two sets of data were compared against analytical standards, and the elemental results with the best detection limit/precision were chosen. The concentration of mercury in sediments was determined using Cold Vapor Atomic Absorption (CVAA) following the Aqua Regia digestion. The quantitative measurements of all elements (except Hg) in porewater samples were carried out using ICP-MS. An analysis of the total mercury in porewater was conducted using an atomic fluorescence mercury analyzer following the U.S. EPA method 1631\textsuperscript{[15]}. The analyses of total bulk concentrations of carbon and sulphur in the sediment samples were conducted using LECO®-SC42 sulphur-carbon analyzer. The quantity of total organic carbon was measured using Rock-Eval pyrolysis\textsuperscript{16}. The morphological and mineralogical/chemical composition of the sediments were studied using the Scanning Electron Microscope equipped with Energy Dispersive X-ray in back-scattered mode (SEM/EDX) on gold-coated, surface polished, sediment pellets.

RESULTS AND DISCUSSION
The temporal distributions of trace elements As, Sb, U, V, Cr, Cu, Mo, Pb, Se, Hg, and Zn in the Wabamun Lake sediment cores show different concentrations between the younger sediment layers and the older sediment layers, as characterized by an episode of high concentrations in the upper section of the sediment profiles (Fig. 2). There are several scenarios for enrichment of trace elements in surficial sediments from Wabamun Lake:

**Anthropogenic input**
The depth profiles of As, Sb, Cu, Cr, Mo, Pb, Se, Hg, and Zn in the Wabamun Lake sediment cores show significant correlation with those of Ca, U, V, and W, which are known to be enriched in power plant fly ash (Table 1). This suggests that the concentrations of metals in the sediment profile from Wabamun Lake are likely controlled by the input of calcareous fly ash emitted from the power plants in the study area. Moreover, the correlation of the elemental profiles with the \textsuperscript{210}Pb data (Fig. 1) confirms the link between the sudden increase in concentration of trace elements in the Wabamun sediment profile and commencement of the Wabamun coal-fired power plant in 1956 in the lake’s watershed (Fig. 2). The concentrations of trace elements reach their maximum levels at a depth (~10-12 cm) coinciding with the historical peak emission in the 1970’s caused by the simultaneous operation of the Wabamun and Sundance power plants in the study area (Fig. 2). Subsequently, the elemental contents tend to return to low concentrations towards the sediment-water-interface (SWI) (Fig. 2), possibly due to the more recent decreases in emissions of the power plants or the dissolution of elements near the SWI. Elemental output by the power plants has gradually declined in recent years due to the introduction of emission control systems.

The mineralogy and morphology of the post-industrial sediments (SEM/EDX) from Wabamun Lake confirms the abundance of spherical particles of fly ash in post-industrialized sediments deposited after 1956 intervals (determined using \textsuperscript{210}Pb dating) (Fig. 3a). The size of fly ash particles tend to decrease (PM2.5; Fig. 3b) towards the more recent part of the sediment profile indicating the effect of particle emission control measures adopted by the power plants (e.g., ESP technology), which filters the emission of larger particles. There is no evidence of fly ash particles in the sediments deposited prior to the commencement of coal-fired power plants in Wabamun Lake (before 1956).
Early diagenesis processes

Without taking the elemental mobility and porewater-sediment interactions into account, the variations of elements throughout the sediments can be well explained by the emission history of the coal-fired power plants in the study area. However, the study of porewater suggests that complex geochemical processes may also have a role in the observed elemental distributions in the studied sediment profiles. The results of the porewater analyses indicate the increased concentrations of dissolved As, Sb, Cu, Mo, Pb, and Zn at deeper sections of porewater profile (Fig. 4). This suggests that diagenetic dissolution/diffusion of these elements may have occurred at depth, thus acting as a conveyor of elements to the upper part of the sediment profile. This can partly contribute to the elevated concentrations of trace elements near the surface sediments (Fig. 4), which are often attributed solely to the activities of power plants in this region. The strong positive correlation between trace elements, Ca and organic matter (OM) in sediments from Wabamun Lake (Fig. 5) suggest that the Ca-OM fraction, combined together, play a major role as substrate for trace elements and nutrient (P) in Wabamun Lake. This positive correlations between Ca and trace metals (As, Cu, Cr, Hg, Mo, Pb, Sb, Se, and Zn) in Wabamun Lake sediment are partly due to their association with power plant fly ash, but also may be due to diagenetic processes within the sediment column.

Calcium in the form of lime (CaO, CaCO\textsubscript{3}, Ca(OH)\textsubscript{2}) is known to be an important substrate for trace elements, specifically in a hard water lake with a neutral pH such as Wabamun Lake\textsuperscript{17-22}. The cycle of calcium is also interrelated with the diagenesis of organic matter in sediments and porewater. Sholkowitz\textsuperscript{17} and Sholkowitz and Copland\textsuperscript{18} showed that the increased salinity (especially Ca\textsuperscript{2+}) increases the trace metal removal by flocculation of trace metal-DOM (dissolved organic matter) complexes. Calcium may bind to the DOM and hence prevent the formation of dissolved organic colloids, resulting instead in the formation of larger calcium induced particles, which readily precipitate\textsuperscript{22}. Degradation of organic matter in the deeper part of the sediment profile may result in the formation of highly soluble metal-organic complexes, which is responsible for the mobilization of trace elements during early diagenesis. The organic decomposition in deeper sediments may also cause dissolution of Ca-compounds and release trace elements attached to Ca-minerals into the porewater. The dissolved metals may migrate upward in the column and become immobilized due to the re-precipitation of calcium minerals in the upper section of the sediment profiles. The addition of carbonates through the emission of calcareous fly ash into Wabamun Lake may serve as liming treatment for precipitation of sparingly soluble trace metal compounds and dissolved nutrients\textsuperscript{19-28}.

CONCLUSIONS

This study investigates the temporal distribution of trace elements in the sediment cores from Wabamun Lake in central Alberta in relation to activities of the coal-fired power plants in the study region. The relative enrichment of trace elements (As, Sb, U, V, Cr, Cu, Mo, Pb, Se, Hg, and Zn) in the younger sediment layers of Wabamun Lake can be partly due to the emissions from the coal-fired power plants in the study area (as suggested by isotope dating data). However, the study of porewater suggests that diagenetic dissolution/diffusion of some of the trace elements may have occurred at depth, acting as a conveyor of elements to the upper part of the sediment profile. This can also contribute to the elevated concentrations of trace elements near the surface sediments, which are often attributed solely to the activities of power plants in this region. This study indicates that a combination of various biogeochemical processes may control the temporal distribution of elements in sediment and
porewater from the Wabamun Lake. However, the Ca-OM fraction appears to play the most important role as a substrate for trace elements. Deposition of Ca-rich fly ash in the Wabamun Lake may be beneficial partly because of the effect it has on raising the pH levels. Furthermore, the input of calcium in Wabamun Lake may increase the scavenging of trace metals and nutrients. This effect is evident as more trace metals are correlated with the carbonate-organic fraction in Wabamun Lake.
REFERENCE


(15) EPA. Method 1631: Mercury in Water by Oxidation Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry, EPA number: 821R96012, 1996, 39


Figure 1: Map of the lakes in Central Alberta, locations of the sediment cores in the Wabamun Lake, and locations of the coal-fired power plants in Wabamun area.
Figure 2: The temporal distribution of elements and organic matter throughout the WAB1 sediment profile in relation to the $^{210}$Pb-dates of the sediments.
Figure 3a-b: The morphology and mineralogy (back-scattered SEM/EDX) of the sediment sample from (a) surficial sediments (depth 1 cm) showing the finer particles of ferrocalsialic fly ash; (b) sediment intervals 9-10 cm, corresponding to the peak power plant emission period in 1970 in the region indicates the abundance of larger spherical particles of fly ash (PM10).
Figure 4: The distribution of trace metals and calcium between sediments and porewater throughout the WABI core.
Figure 5: The calculated correlation coefficients (Spearman) of elements with respect to Ca and S1-OM (labile organic matter) in the sediments from Wabamun core.
Table 1: The Spearman correlation matrix for the elements and organic content of the sediments in WAB1 core.

|     | As | Ca  | Cd  | Co  | Cr  | Cu  | Fe  | Hg  | Mn  | Mo  | Ni  | P   | Pb  | Sb  | Se  | U   | V   | W   | Zn  | Zr  | S   | TOC | Si  |
|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Al  |    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| As  | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ca  | 0.6 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cd  | -0.7 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Co  | -0.6 | -0.8 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cr  | 0.4 |     | -0.5 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Cu  | 0.9 | 0.6 |     | 0.5 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Fe  | -0.7 | -0.9 | 0.6 | 0.8 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Hg  | 0.7 | 0.7 | -0.5 | -0.6 | 0.4 | 0.9 | -0.8 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Mn  | -0.5 |     |     |     | 0.5 | -0.4 | 0.5 |     | 0.4 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Mo  | 0.9 | 0.7 | -0.7 | 0.4 | 0.9 | -0.8 | 0.8 | -0.5 | ***|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Ni  | -0.7 | -0.8 | 0.5 | 0.9 |     | -0.7 | 1.0 | -0.8 | 0.5 | -0.8 | ***|     |     |     |     |     |     |     |     |     |     |     |     |
| P   | 0.7 | 0.9 | -0.5 | -0.8 | 0.8 | -1.0 | 0.8 | -0.5 | 0.8 | -1.0 | ***|     |     |     |     |     |     |     |     |     |     |     |     |
| Pb  | 0.9 | 0.6 |     | 0.4 | 0.9 | -0.7 | 0.8 | -0.5 | 0.9 | -0.6 | 0.7 | ***|     |     |     |     |     |     |     |     |     |     |     |
| Sb  | 1.0 | 0.6 |     | 0.5 | 0.9 | -0.7 | 0.8 | -0.4 | 1.0 | -0.7 | 0.8 | 0.9 | ***|     |     |     |     |     |     |     |     |
| Se  | 0.8 | 0.7 | -0.5 | -0.5 | 0.7 | 0.9 | -0.7 | 0.8 |     | 0.9 | -0.6 | 0.7 | 0.8 | 0.9 | ***|     |     |     |     |     |     |     |
| U   | 0.7 |     |     |     | 0.6 | 0.7 |     | 0.5 | 0.7 |     | 0.6 | 0.7 | 0.6 | ***|     |     |     |     |     |     |     |     |
| V   | 0.4 |     |     |     |     |     |     | 0.4 |     |     | 0.5 | 0.5 | 0.7 | 0.7 | ***|     |     |     |     |     |     |     |     |
| W   | 0.7 | 0.7 | -0.4 | -0.5 | 0.5 | 0.7 | -0.7 | 0.8 |     | 0.7 | -0.7 | 0.8 | 0.8 | 0.8 | 0.8 | 0.5 | 0.4 | ***|     |     |     |     |
| Zn  | 0.8 | 0.6 | -0.5 | 0.5 | 0.7 | -0.7 | 0.7 | 0.8 |     | 0.6 | 0.7 | 0.8 | 0.8 | 0.8 | 0.6 | 0.4 | 0.7 | ***|     |     |     |     |
| Zr  | -0.5 | -0.7 |     | 0.9 |     | -0.4 | 0.8 | -0.6 | 0.7 | -0.5 | 0.9 | -0.8 | -0.4 | -0.5 |     |     |     |     |     |     |     |     |
| S   | -0.8 | -0.6 | 0.5 | -0.5 | -0.7 | 0.7 | -0.6 | 0.4 | -0.8 | 0.6 | -0.7 | -0.7 | -0.8 | -0.6 | -0.4 | -0.7 | -0.8 | ***|     |     |     |     |
| TOC |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Si  | 0.6 | 0.6 |     | 0.5 | -0.7 | 0.6 |     |     | 0.5 | -0.7 | 0.7 | 0.6 | 0.6 | 0.5 |     | 0.7 | 0.5 | -0.6 | -0.5 | 0.7 | ***|     |

* Only correlation coefficients significant at 95% confidence limit (p<0.05 at 0.39; n=24) are shown.
** Negative correlations are shown in italic.