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Role of biogeochemical processes in metal cycling in remote lakes from the Huntsville and Clyde Forks areas, Ontario, and Kejimkujik Park, Nova Scotia, Canada.

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To My Parents

Abstract

The study of metal speciation and the role of biogeochemical processes in metal distribution and cycling in lake sediments was carried out in remote lakes from the Huntsville and the Clyde Forks areas, Ontario and Kejimkujik Park, Nova Scotia, Canada. The main objectives were to determine; a) the role of the organic matter, oxides (amorphous and crystalline), sulfides, and silicates in trace metal distribution in lake sediments, b) the importance of trace metal atmospheric and geological fluxes in remote lakes, c) the role of humic substances (HS) transformation in trace metal distribution in lake sediments, and d) the role of biogeochemical processes controlling metal cycling in lakes.

Based on geochemical data and sequential extraction results of trace elements from sediment cores of 20 lakes from the Huntsville region, Ontario, Canada, it was demonstrated that relative affinities to organic matter and mineral fractions (silicates) played an important role in the distribution of total metal values and hence in the shape of the metal concentration profiles. Therefore, the enrichment of trace metals such as Hg, As, Sb, Pb, Cd, and Zn in surface sediment from these lakes was attributed to their affinity to organic matter and their distribution in the oxide fractions, rather than to the increase of their loading to the lakes.

The importance of atmospheric and geological trace metal fluxes was studied by using sediment traps in two circum-neutral remote lakes, Lavant Long Lake and Perch Lake, in Lanark County, southeastern Ontario, Canada, to measure sedimentation rates, to quantify trace element fluxes from watershed and atmospheric sources, and to investigate the distribution of elements amongst component phases of the trapped sediments. The results of this study showed that local watershed sources were the dominant source of Hg, Cu, Al, Fe, Mn, Sb, in both lakes with ratio sometimes exceeding 9:1 (geogenic to atmospheric). This was consistent with previous observations of pyrite (Fe_2S), chalcopyrite ($CuFeS_2$), tetrahedrite ($Cu_{12}Sb_4S_{13}$), and cinnabar (HgS) mineralization in the bedrock of the study area and the occurrence of these elements in elevated concentrations in glacial and postglacial deposits of the study area.

The study of the effect of humic substances (HS) content and their transformation on their interaction with metals was carried out in three remote lakes: Lavant Long Lake,

Perch Lake; and Big Dam Lake. HS transformation was demonstrated by the increase of HA aromaticity and the decrease of the E4/E6 ratio in Lavant Long Lake, by the increase of ^{13}C resonance signal in the aromatic-C region (105-150 ppm) in Perch Lake, and by the gradual decrease of the HS content with depth in Big Dam Lake. It was concluded that HS transformation, which is characterized by a decrease in COOH and OH functional groups abundance, may result in a release of metals originally associated with these functional groups to pore waters and/or a redistribution amongst other binding fractions within sediments.

A quantitative study of trace metal cycling between pore waters and sediments using the most comprehensive diagenetic models was carried out using a two-layer diagenesis model to account for the bioturbation zone and the zone below the bioturbation zone. Sulfate reducing bacteria (SRB) populations were determined in the three lakes using the most probable number (MPN) method. In the zone of bioturbation of Perch Lake, Co, Cu, and Hg predicted and observed concentrations in the pore waters were close. In Lavant Long Lake and for the rest of the elements in Perch Lake, trace metal concentrations predicted by the model were generally lower than the observed. This suggested that a release of trace elements to the pore waters occurred, consistent with the findings from Manuscripts 3. In the zone below the zone of bioturbation, comparison of the predicted and the observed trace element concentrations in the pore waters showed no significant difference for Cu, Ni and Pb (in Perch Lake). In the case of Zn and Hg, however, the difference between the predicted and the observed concentrations was significant suggesting that there were a number of processes controlling the release and the mobilization of trace element that the model did not account for. In Big Dam Lake, the low SRB was in favour of Hg availability for other Hg methylating Bacteria.

Résumé

L'étude de la speciation et des processus biogéochimiques impliqués dans la distribution et le recyclage des métaux traces a été effectuée dans des lacs isolés des régions de Huntsville et de Clyde Forks, Ontario et du Parc Kejimkujik, Nouvelle Ecosse, Canada. Les objectifs de cette étude étaient de déterminer a) le rôle de la matière organique, des oxides (amorphes et crystallins), des sulfures et des silicates dans la distribution des métaux traces dans les sédiments, b) l'importance des apports atmosphériques et géogéniques dans les lacs isolés, c) le rôle de la transformation des substances humiques (SH) dans la distribution des métaux trace dans les sédiments de lac et d) le rôle des processus biogéochimiques dans le recyclage des métaux dans les lacs.

En se basant sur les résultats des extractions séquentielles à partir de carottes de sédiments provenant de 20 lacs de la région de Huntsville. Il a été démontré que l'affinité à la matière organique et à la fraction minérale (silicates) a joué un rôle important dans la concentration totale des métaux traces et la nature de leurs profils verticaux. Par conséquent, l'enrichissement de certains métaux comme le Hg, As, Sb, Pb, Cd et Zn dans les sédiments de surface a été relié à leur affinité pour la matière organique et à leur association avec les oxides et non à l'augmentation de leurs apports vers les lacs.

L'importance des flux atmosphériques et géologiques a été examinée en utilisant des trappes à sédiments dans deux lacs isolés et à pH neutre. Il s'agit des lacs Lavant Long et Perch de Clyde Forks. Durant cette étude, les flux de métaux ont été mesurés en se basant sur les taux de déposition et la distribution des métaux dans différentes phases des sédiments collectés a été aussi examinée. Les résultats ont montré que dans les deux lacs, la contribution géologique locale en Hg, Cu, Al, Fe, Mn, Sb et Zn dépasse hautement la contribution atmosphérique avec un rapport des fois supérieur à 9:1 (géologique: atmosphérique). Ces résultats sont consistents avec la présence de ces métaux en forme de sulfures comme la pyrite (Fe_2S), la chalcopyrite ($CuFeS_2$), la tetrahedrite ($Cu_{12}Sb_4S_{13}$) et le cinabre (HgS) dans le socle et à des concentrations élevées dans les dépôts glaciaires et postglaciaires dans les bassins versant des deux lacs.

L'étude de l'effet de la teneur en substances humiques (SH) et de leur transformation sur leur interaction avec les éléments traces a été effectuée dans les lacs Lavant Long, Perch et Big Dam. La transformation des SH a été démontrée par l'augmentation de

l'aromaticité de l'acid humique en fonction de la profondeur et la diminution du rapport E4/E6 indiquant dans le lac Lavant Long, pare l'augmentation du signal de la resonance magnétique du C^{13} dans la région du carbon aromatique (105-150 ppm) dans le lac Perch et par la diminution de la teneur en acid fulvique et humique en fonction de la profondeur Dans le lac Big Dam. Il a été conclu que la transformation des SH qui se fait par la l'élimination des groupes fonctionnels COOH et OH peut aboutir à une libération des métaux originellement associés à ces groupes dans les eaux interstitielles ou à leur redistribution dans les sédiments.

L'étude quantitative du recyclage des métaux trace entre les sédiments et les eaux interstitielles a été effectuée en utilisant des modèles diagénétiques. Ces derniers ont été établis pour la zone de bioturbation et la zone au-dessous de celle-ci. Pendant cette étude, une énumération des bactéries sulfato-reductrices (BSR) a été aussi effectuée en utilisant la méthode MPN. Dans le lac Perch, les concentrations prévues par le modèle et celles observées n'ont pas montré de différence dans le cas du Co, Cu et Hg . Alors que dans le lac Lavant Long et pour le reste des éléments dans le lac Pech, les résultats ont montré que les concentrations prévues par le modèle ont été inférieures à celles observées. Ceci a suggéré qu'une libération des métaux des sédiments est responsable des concentrations élevées de ces derniers dans les eaux interstitielles. Ces résultats sont consistents avec les conclusions du manuscript 3.

Dans la zone au-dessous de la zone de bioturbation, la comparaison entre les concentrations prévues par le modèle et celle observées n'ont pas montré une grande différence dans le cas de Cu, Ni et Pb (dans le lac Perch). Dans le cas du Zn et du Hg, la différence était importante. Ceci a suggéré, dans le cas du Zn et Hg, que d'autres processus, que le modèle n'a pas pris en considération, sont responsables de cette différence. Dans le lac Big Dam, les populations faibles des BSR ont favoris la disponibilité du Hg pour la methylation par d'autres microorganismes.

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Table of Contents

Abstract i

Résumé iii

Acknowledgments v

Table of Contents vi

List of Figures xi

List of Tables xx

General Introduction 1

Manuscript 1

Role of sediment geochemistry in trace metal distribution in lake sediments: A case study of twenty lakes from the Huntsville region, Ontario, Canada.

Abstract 14

1. Introduction 15

2. Geological Setting 17

3. Methodology 17

3.1. Lake Sediment Sampling 17

3.2. Soil Sampling 18

3.3. Total Trace Element Analysis 19

3.4. Sequential Extraction 19

4. Results 24

4.1. Analytical Parameters 24

4.2. Metal Enrichment in Surface Sediments 24

4.3 Sequential Extraction of Soils and Sediments 25

4.3.1. Lake Sediments 26

a) Elements with high affinity for organic matter 26

b) Elements with high distribution in the mineral fraction 28

4. 3.2. Soils 29

5. Discussion 30

6. Conclusion 34

Summary of Manuscript 1 36

Acknowledgements 37

Manuscript 2

Sedimentation rates and metal fluxes in two remote lakes of Clyde Forks, Lanark County, Ontario. Canada: The role of local geology.

Abstract 57

1. Introduction 58

2. Study Area 61

3. Geology 61

4. Hydrology 62

5. Material and methods 62

5.1. Watershed area and lake area calculation 62

5.2. Sediment trap description 62

5.3. Sediment trap deployment 63

5.4. Sediment trap recovery and processing 63

6. Sequential Extraction 64

7. Results and discussion 65

7.1. Rate of sedimentation in Lavant Long and Perch Lakes 65

7.2. Total metal fluxes 65

7.3. Loading calculations and results 66

7.4. Metal distribution 71

8. Conclusion 72

Summary of Manuscript 2 73

Acknowledgments 74

Manuscript 3

Humic substances from three remote lakes in Canada: Transformation with depth and interaction with trace metals

Abstract 87

1. Introduction 88

2. Definition of humic substances 89

3. Methodology 90

3.1. Sampling 90

3.2. Organic carbon and nitrogen analysis 90

3.3. Humic substances extraction 91

3.4. HA Purification 92

3.5. FA Purification 92

3.6. Optical density ratio (E4/E6) 93

3.7. Solid ^{13}C-NMRS 93

3. 8. Trace element extraction 94

4. Results and discussion 94

4.1. HS transformation 94

4.2. Effects on trace metal distribution 97

5. Conclusions 99

Summary of Manuscript 3 100

Acknowledgements 101

Manuscript 4

Trace metal distribution in lake sediments and pore waters: Adequacy of predictive models

Abstract 113

1. Introduction 114

2. Methodology 116

2.1. Sample collection 116

2.2. Preparation and analysis 117

2.2.1. Sediments 117

2.2.2. Metal analysis 118

2.2.3. Sulfate-reducing bacteria enumeration 118

3. Results 119

3.1. Sediments 119

3.2. Pore waters 121

3.3. Sulfate-Reducing bacteria 122

4. Discussion 123

4.1. The predictive models 123

4.1.1. Zone of bioturbation 123

a) Model 123

4.1.2. Below the zone of bioturbation 127

a) Model 127

5. Conclusion 134

Summary of Manuscript 4 135

Acknowledgements 136

General conclusions 150

References 156

Appendices 179

List of Figures

Manuscript 1

Fig. 1. (a) Study area location; (b) Lake samples in this study (•). TI= soil transect I, TII= soil transect II, and TIII=soil transect III. 40

Fig. 2. Average metal enrichment factor in the 20 lakes (n=20). Bars represent the variability (STD) of metal enrichment from one lake to another. The enrichment factor corresponds to the average ratio of metal concentration in surface sediments (top 10 cm) to its concentration in deep sediments (average 70- 100 cm) for a total of twenty lakes. 41

Fig. 3. Graph summarizing relationships between trace metals, Hg and organic carbon in the sediment cores from the 20 lakes (n=20). Average concentrations were calculated for each lake from the 0-10 cm intervals. Positive correlations are indicated by the positive axis, and negative correlations are indicated by the negative axis. 42

Fig. 4. Graph summarizing relationships between trace metals, Cd and organic carbon in the sediment cores from the 20 lakes (n=20). Average concentrations were calculated for each lake from the 0-10 cm intervals. Positive correlations are indicated by the positive axis, and negative correlations are indicated by the negative axis. 43

Fig. 5. Graph summarizing relationships between trace metals, Al and organic carbon in the sediment cores from the 20 lakes (n=20). Average concentrations were calculated for each lake from the 0-10 cm intervals. Positive correlations are indicated by the positive axis, and negative correlations are indicated by the negative axis. 44

Fig. 6. Variation of total Cd concentration with depth, and partitioning of Cd amongst five sediment fractions at various depths in lake sediment cores as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. Note the high % of Cd associated with soluble organics at all depths. 45

Fig. 7. Variation of total Cu concentration with depth, and partitioning of Cu amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 46

Fig. 8. Variation of total Pb concentration with depth, and partitioning of Pb amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 47

Fig. 9. Variation of total Hg concentration with depth, and partitioning of Hg amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential

extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 48

Fig. 10. Variation of total Zn concentration with depth, and partitioning of Zn amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 49

Fig. 11. Variation of total Fe concentration with depth Partitioning of Fe amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 50

Fig. 12. Variation of total Al concentration with depth, and partitioning of Al amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 51

Fig. 13. Variation of total Cr concentration with depth, and partitioning of Cr amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef= enrichment factor. 52

Fig. 14. Variation of total Mn concentration with depth, and Partitioning of Mn amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 53

Fig. 15. Variation of total Ni concentration with depth, and partitioning of Ni amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor. 54

Manuscript 2

Fig. 1. Study area location in Ontario (a). The hydrology of the study area showing the watershed areas for both Lavant Long and Perch Lakes (b). 75

Fig. 2. Trap sediment structure, planar view (a); side view of trap sediment deployment in a lake environment (b). 76

Fig. 3. Schematic representation of the major fluxes to the lakes, their components and the factors defining them. 77

Manuscript 3

Fig 1: ^{13}C-NMR spectra for HA from 0, 10, 25, and 35 cm in Big Dam Lake, from 0, 10, and 20 cm in Perch Lake and from 0, 10 and 50 cm from Lavant Long Lake. 103

Fig 2. Relationship between E4/E6 ratios and aromaticity (%) 104

Fig. 3. Variation of the FA and HA content (%) with depth in Lavant Long Lake, Perch Lake, and Big Dam Lake 105

Fig. 4. Model for metal-HS (HA and/or FA) interaction 106

Manuscript 4

Fig. 1. Organic matter content expressed as LOI (%) in lake sediments from Lavant Long Lake, Perch Lake, and Big Dam Lake. 137

Fig. 2. Sulfate concentration profile in pore waters from Lavant long and Perch Lake. 138

Fig. 3. Redox potential and SRB populations in lake sediments from Lavant Long Lake, Perch Lake, and Big Dam Lake. 139

Fig. 4. a. Modeling of Al, Fe, Mn, Mg, Ba, Co, and Cu concentration profiles in the pore waters in the bioturbation zone from Lavant Long Lake. 140

Fig. 4. b. Modeling of Pb, Sb, Zn and Hg concentration profiles in the pore waters in the bioturbation zone from Lavant Long Lake. 141

Fig. 5. a. Modeling of Al, Fe, Mn, Mg, Ba, Co, and Cu concentration profiles in the pore waters in the bioturbation zone from Perch Lake. 142

Fig. 5. b. Modeling of Pb, Sb, Zn, and Hg concentration profiles in the pore waters in the bioturbation zone from Perch Lake. 143

Fig. 6. Results of modeling Ni, Cu, Zn, Pb, and Hg distribution in pore waters below the zone of bioturbation in Perch Lake (km is the metal sulphide precipitation rate). 144

Fig. 7. Results of modeling Cu, Ni, Zn, and Hg distribution in pore waters below the zone of bioturbation in Lavant Long Lake(km is the metal sulphide precipitation rate). 145

List of Tables

Manuscript 1

Table 1. Analytical precision tests, A and B. N represents the proportion of samples for which certain elements were found below the detection limit (DL) and were assigned the value of ½ DL. 38

Table 2. Trace metal distribution in the soil samples from the three transects shown in Figure 1 (b), expressed as percentages of total* element concentrations (average, standard deviation and RSDs are based on 24 samples). 39

Manuscript 2

Table 1. Sequential extraction scheme. 78

Table 2. Measured average sediment deposition (g) based on sediment weights in the six tubes of each sediment trap, and the calculated sedimentation rate (g m^{-2} day^{-1}). 79

Table 3. Total metal fluxes (F_t) in mg m^{-2} y^{-1}, in both Lavant Long Lake and Perch Lake. 80

Table 4. Summary of F_{gw} calculations and sources of F_{dir} and k. 81

Table 5. Trace element proportions (%) of atmospheric (F_{dir} and F_{ind}) and geological fluxes (F_{gw}) relatively to the total flux (F_t). 82

Table 6. Comparison of F_{dir} and F_{gw} (as F_{gw}') assuming F_{dir} is constant with time, F_{ind} =0, and $F_{gw}' = F_{gw}/12$. See text for more detail. 83

Table 7. Sequential extraction results presented as concentration (ppm or ppb) and as % of the total concentration. 84

Manuscript 3

Table 1. Ratios of the optical densities at 445 and 665 nm of HA from different depths in the three lakes. 107

Table 2. Results of the integration of HA ^{13}C-NMR spectra showing the six main regions of the spectra and the importance of each one and the variation of the aromaticity (%) with depth. 108

Table 3. Organic carbon, organic N content, and C/N ratios of the first 10 cm surface sediments from depositional basins of Lavant Long Lake, Perch Lake and Big Dam Lake. 109

Table 4. Metal content in the soluble organic fraction (extraction using 0.1 M $Na_4P_2O_7$) and COOH and OH content (in %) in HA and FA. 110

Manuscript 4

Table 1. Sequential extraction scheme. 146

Table 2. Precision based on 33 pairs of replicates. 147

Table 3. Organic carbon and total sulfur content in the sediments from Lavant Long Lake, Perch Lake and Big Dam Lake. 148

Table 3. Model parameters, their values and their sources 149

General Introduction

The following work is a paper format thesis aimed at investigating a) the role of the organic matter, oxides (amorphous and crystalline), sulphides, and silicates in trace metal distribution in lake sediments, b) the importance of trace metal atmospheric and geological fluxes in remote lakes, c) the role of organic matter transformation in trace metal distribution in lake sediments, and d) the role of biogeochemical processes controlling metal cycling in lakes. Four papers are the product of this work and are in their order of appearance as follows:

1) Role of sediment geochemistry in trace metal distribution in lake sediments: A case study of twenty lakes from the Huntsville region, Ontario, Canada.

2) Geochemistry and rate of sediment fluxes in Lavant Long and Perch Lakes, Clyde Forks, Lanark County, Ontario. Canada.

3) Humic substances in Sediments of Three Remote Lakes in Canada: Transformation with Depth and Interactions with Metals

4) Trace metal distribution in Lake Sediments and Pore Waters: Adequacy of Predictive Models.

All papers are answers to questions raised in the first manuscript. First, the sequential extraction results from the soil B-horizon and lake sediments from the Huntsville area showed that there was a similarity between trace metal distribution in both environments. This raised the question regarding the importance of trace metal burdens from geological and atmospheric sources to lakes in remote areas. The Manuscript 2 treats this question based on a study carried out in two remote lakes. During this study, trace metal geogenic fluxes were measured based on a balance model approach and on the use of sediment

traps. Second, following the finding of a strong relationship between some trace metals enrichment in lake sediments and the content of organic matter (originally Rasmussen *et al.*, 1998 in the case of Hg), it was important to investigate how this relationship was affected by the abundance of COOH and OH functional groups and consequently by HS transformation (Manuscript 3). This study was conducted based on a characterization study of HS (humic and fulvic acids). Finally, since metal cycling also involves processes such as diffusion (biomixing, irrigation, molecular diffusion), adsorption, mineral salt formation, organic matter decay by bacteria, and other processes, the last part of this work was to quantitatively study, based on both field observations and theoretical assumptions, trace metal diagenesis using diagenetic modeling approaches (Manuscript 4).

This thesis is a result of combination of field and laboratory experimental approaches. Field experiments consisted mainly of sampling pore waters using peepers, lake sediments for trace element analyses and sulfate reducing bacteria (SRB) enumeration, and measuring, *in situ* using a field glove box, the E*h* and the pH of the pore waters under N_2 atmosphere. Field experiments, also included the deployment and the recovery of sediment traps in order to measure trace metal deposition rates. Laboratory experimental approaches consisted of carrying out sequential extractions to determine trace elements distribution in different phases, and developing a new technique of humic substance extraction and purification resulting in representative and non-altered HS extracts. Laboratory experiments also included the use of different approaches to characterize HS such as the spectrophotometry and ^{13}C NMR (carbon 13 nuclear magnetic resonance)

techniques, besides the use of special software to treat the magnetic resonance data. Statistical analyses of existing core data were carried out to reach conclusions regarding trace metal relationships with different fraction from the sequential extraction. During this work, a mass balance model for trace metal fluxes calculation based on the geochemical data from sediment traps, and numerical models to predict trace metal distribution in pore waters in the zone of bioturbation and below the zone of bioturbation in lake sediments were developed.

Although there is a big debate about the efficiency of sequential extraction procedures to achieve quantitative and qualitative representative results, many studies (Tessier *et al.*, 1979; Hall *et al.*, 1996) have shown that these procedures represent a successful tool to reach conclusions regarding metal distribution in different fractions of a given sample. However, the order (the scheme) of extractions is important to carrying out a successful sequential extraction. The scheme used in this study has been proven to be very successful (Tessier *et al.*, 1979; Hall *et al.*, 1996).

The sequential extraction scheme used in our study allows extractions of trace metals from i) carbonates, ii) soluble organics, iii) amorphous oxides, iv) crystalline oxides, v) insoluble organics/sulfides, vi) silicates (residual fraction). Trace metals were extracted from the carbonate fraction using a weakly acidic reagent consisting of 1 M CH_3COONa adjusted to pH = 5.0 using CH_3COOH (Tessier *et al.*, 1979). Metals bound to the soluble organic fraction, were extracted using 0.1 M $Na_4P_2O_7$ at pH = 10 (Hall and Pelchat, 1997). Metals bound to amorphous oxides were extracted by reduction reaction involving 0.25 M $NH_2OH.HCl$/0.25 M HCl (Chao and Zhou, 1983), whereas metals bound to

crystalline oxides were removed using 1 M $NH_2OH.HCl$/25% CH_3COOH (Chester and Hughes, 1983). Metals bound to insoluble organics/sulfides were extracted using $KClO_3$-HCl-HNO_3 (Chao and Sanzalone, 1977). Finally, metals from silicates were extracted using a multi-acid digestion HCl-HF-$HCLO_4$-HNO_3 (Tessier *et al.*, 1979). (See Appendix 1-3 for the detail of the procedure).

The comparison of trace element distribution and their concentration in the soil B-horizon and lake sediments from the Huntsville region showed a close relationship between both environments. This observation, plus other studies in the region (Rasmussen, 1993), raised the question about the importance of trace element fluxes from geological sources in remote lakes. Thus, a study of trace metal fluxes was carried out in two remote lakes from Lanark County, Ontario, and is presented in the Manuscript entitled *Geochemistry and rate of sediment fluxes in Lavant Long and Perch Lakes, Clyde Forks, Lanark County, Ontario, Canada.* In this study sediment traps were used to collect sediments and geological fluxes were measured and compared to the atmospheric flux. Sequential extractions were carried out on the sediments collected from the traps to study the forms under which they occur.

The strong relationship between soluble organic matter and trace metal enrichment in surface sediments had been shown from the correlation tests and confirmed by the sequential extraction results from the first manuscript. It was then important to investigate how this relationship changed with depth, i.e., how HS content, transformation, and the abundance of the COOH and OH sites affect trace metal-organic matter interactions with depth. To carry out this study we had to develop an extraction

procedure of humic and fulvic acids, under which the extracted humic substances were not altered and remained representative of the sediments. The extraction study used a sequence of 0.1 M NaOH, 0.5 M $Na_4P_2O_7$, and H_2O, because all three solvents complete each others efficiency (See Manuscript 3). This study was conducted by carrying solid state ^{13}C NMR (CP/MAS) (Carbon 13 nuclear magnetic resonance cross polarization magic angle spinning) analysis technique. The ^{13}C NMR CP/MAS was carried out on both HA and FA extracted from the sediments from different depths (see Manuscript 3) to determine how the abundance of hydroxylic (OH) and carboxylic (COOH) groups is affected by the organic matter transformation and consequently how the latter affects their interaction with trace elements.

Below the sediment-water interface, properties of sediments may change upon burial due to physical and biogeochemical processes, therefore, quantitative modeling provides reliable estimates of these processes. If *P* represents any property of a sediment, for example, concentration of a chemical compound, grain size, color etc. *P* will vary laterally at the time of deposition, due to a variation in the environment of deposition. Vertically variations in *P* also arise upon burial either by historical changes at the site of deposition or by post-depositional processes (diagenesis). A complete variation of *P* will entail knowledge of both lateral and vertical variations and how they change with time. However, on the scale of a few meters, especially in a flat organic-rich lake basin such as the case of our lakes, vertical changes in sediment properties are more important than lateral changes. Following is a literature synthesis for the mathematical meanings (equations **1-10**) of the vertical changes of a sediment property *P*. In our study

(Manuscript 4) we were interested by vertical changes because they are more sensitive to time and depth than lateral changes (above argument). Therefore, the sediment property P will be treated in one spatial dimension in that it will be function of only depth (x) and time (t) as the case in most of diagenetic modeling

$$P = f(x,t) \tag{1}$$

Where x = depth in sediment and

t = time

Depth can be calculated from two coordinates:

1- a given layer (an infinitely thin layer)

2- sediment water interface

For a given layer, transformation from one origin to the other is expressed by

$$\frac{\partial P}{\partial t}\Big)_x = \frac{\partial P}{\partial t}\Big)_{fixedlayer} - \omega \frac{\partial P}{\partial x}\Big)_t \tag{2}$$

Where ω represents the rate of burial of the layer below the sediment-water interface, which, in the absence of complicating factors, such as compaction and non-steady sedimentation, is simply the rate of deposition.

If we choose the sediment-water interface as origin, depth will be measured positively downward from this interface. If also we are using a total derivative to denote changes "following the motion" of the layer, the above equation will be simplified to:

$$\left.\frac{\partial P}{\partial t}\right)_x = \frac{dP}{dt} - \omega \left.\frac{\partial P}{\partial x}\right)_t \qquad (3)$$

In this study if we choose the sediment-water interface as origin and assumed that ω (see Manuscript 4 table 3) is constant with time or depth and that there is no compaction, we will face three situations i.e., 1) when there is no diagenesis, 2) steady state and diagenesis, 3) steady state and no diagenesis

1- No diagenesis

P at a layer is constant at deposition time t_o and at $t_o+\Delta t$ ($P_{to} = P_{to+\Delta t}$). In this situation $\frac{dP}{dt} = 0$, substituting in equation (3)

$$\left.\frac{\partial P}{\partial t}\right)_x = -\omega \left.\frac{\partial P}{\partial x}\right)_t \qquad (4)$$

Since ω is assumed to be constant, measuring $\frac{\partial P}{\partial x}$ and the elapsed time represented by the thickness of the layer, enables us to calculate the original rate of change at the time of sedimentation.

2- Diagenesis

In this case, all changes of P with depth are due to diagenesis, meaning that there was no important historical variation of P at the time of deposition. i.e. for a layer at depth x (whose property P has changed), at the time it was deposited, had the same value of P as the layer currently being deposited (a steady state diagenesis).

Under steady state conditions $$\left.\frac{\partial P}{\partial t}\right)_x = 0 \quad (5)$$

By substituting (5) in (3)

$$\frac{dP}{dt} = \omega \left.\frac{\partial P}{\partial x}\right)_t \quad (6)$$

3- There is a steady state at all depths but no diagenesis

$$\left.\frac{\partial P}{\partial t}\right)_x = 0 \quad (7)$$

$$\frac{dP}{dt} = 0 \quad (8)$$

and $$\left.\frac{\partial P}{\partial x}\right)_t = 0 \quad (9)$$

In our study, both Perch and Lavant Long Lakes are remote lakes, with no roads, cottages or homes within 3.5 km. They are isolated from any point sources of metals, such as domestic and/or local industrial inputs. Therefore we assume that trace metal input to the lake did not undergo historical changes and hence we propose steady state diagenetic model (situation 2).

The general diagenetic equation is then:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial F_i}{\partial x} + \Sigma R_i \quad (10)$$

Where: C_i = concentration of the solid or liquid component i in mass per unit volume of total sediment (solid and pore water)

F_i = flux of a component i in terms of mass per unit area of total sediment per unit time

R_i = rate of each diagenetic chemical, biochemical, and radiogenic reaction affecting i,

Σ = summation sign

Fluxes can be divided into two types, diffusive and advective. Diffusive fluxes arise as the result of random motion of individual particles, ions, and they follow Fick's laws of diffusion, whereas, advective fluxes are unidirectional to an impressed force (compaction):

$$F_i = -D\frac{\partial C_i}{\partial x} + \vartheta C_i \quad \text{(Berner, 1980)} \tag{11}$$

Where: D= diffusion coefficient in area of total sediment per unit time

ϑ = velocity of flow relative to the sediment-water interface.

For solids $\vartheta = \omega$ (rate of burial):

$$\frac{\partial C_i}{\partial t} = \frac{\partial\left[\left(\frac{\partial C_i}{\partial x}\right)\right]}{\partial x} - \frac{\partial(\omega C_i)}{\partial x} + \Sigma R_i \quad \text{(Berner, 1980)} \tag{12}$$

For pore waters ϑ is different:

$$\frac{\partial C_i}{\partial t} = \frac{\partial\left[D\left(\frac{\partial C_i}{\partial x}\right)\right]}{\partial x} - \frac{\partial(\vartheta C_i)}{\partial x} + \Sigma R_i \quad \text{(Berner, 1980)} \qquad \textbf{(13)}$$

The above equations are function of the three major processes affecting the concentration of a component in sediments during an interval of time and at a certain depth. These are diffusion, advection/or burial, and diagenetic reaction. The above equations (12-13) represent the general diagenetic equations (Berner, 1980).

These equations provided the conceptual ground for the last part of this work. In Manuscript 4, we examined the effect of adsorption, and the formation of metal sulfides as a result of sulfate reduction by sulfate-reducing bacteria. In this study, sediments were divided into two layers, based on differences between the surface sediments and deep sediments. In surface sediments, biological mixing resulting from biological activity of benthic organisms is important, compaction is low, whereas porosity is high. In deep sediments, compaction increases, and no biomixing is present. These differences, result in chemical and mechanical differences between the two layers and hence lead to different diagenetic equations when modeling trace metal distribution in pore waters in both zones.

Manuscript 1

Role of sediment geochemistry in trace metal distribution in lake sediments: A case study of twenty lakes from the Huntsville region, Ontario, Canada.

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Abstract

Sediment cores were collected from 20 lakes from the Huntsville region, Ontario, Canada, to study the change in metal concentration profiles with depth as a function of their distribution within soluble organics, hydrous and crystalline oxides, insoluble organics/sulphides, and silicates. Results from the speciation study revealed that relative affinities to organic and mineral fractions played an important role in the distribution of total metal values and hence in the shape of vertical metal concentration profiles. Metals were divided into two groups based on their relationship with organic carbon and Al contents of the sediments. The first group, composed of Hg, As, Sb, Pb, Cd, and Zn, showed enrichment in the total metal concentration at the surface by a factor ranging from 2.02 to 24.24 (average n=20 lakes), a positive correlation with organic carbon, and a negative correlation with Al. In surface sediments, a high proportion of these elements was associated with particulate organic carbon and crystalline Fe and Mn oxides and/or amorphous Fe oxides. The second group, composed of Al, Cr, Co, Fe, Ni and Mn, showed no consistent enrichment in the total metal concentration at the surface (range: 1.03-1.45, n=20 lakes), a negative correlation with organic carbon, and a positive correlation with Al. Metals of the latter group were typically associated with the oxide (Fe, Mn) fractions at the surface of the sediment column and with the residual silicate fraction in deep sediments. A study of metal speciation in B-horizon samples representative of well-drained soils from the same watersheds showed a close relationship between the geochemistry of lake sediments and the soils of the contributing drainage basin.

1. Introduction

Vertical concentration profiles in lake sediments have been used for many years as a tool to monitor levels of trace elements in the environment, especially metals and metalloids which may accumulate to concentrations that exceed established sediment quality guidelines. Chemical speciation studies have shown that trace metals display different degrees of affinity to either organic or inorganic compounds and this is an important factor that influences metal transport and retention. In fact, many studies have shown that in lake sediments, metals can be scavenged from surface waters to surface sediments by oxides (Suarez and Langmuir, 1976; Murray, 1975) and organic ligands with which they form stable complexes (Ali and Dzomback, 1996; Davis, 1984; Tessier *et al.*, 1996).

Metals can be remobilized from deep to surface sediments by diffusion (Carignan and Tessier; 1985; Tzur, 1971; Manheim, 1970), a process which commonly involves organic matter ((Miller *et al*, 1975; Schnitzer, 1991; Nissenbaum and Swain, 1976; Krom, 1978; Nissenbaum *et al.*, 1972; Bender and Heggie, 1984; Krom and Sholkovitz, 1977; Tills and Alloway, 1983; Jonasson, 1977; Hart and Davies, 1977; Douglas *et al.*, 1986). However, few studies have considered the role of chemical speciation of trace metals and their affinity to organic or inorganic fractions when interpreting vertical metal concentration profiles in lake sediments. In fact, most commonly an increase or a decrease in metal concentration in modern sediments is regarded as an increase or a decrease in human activities or as a failure or a success of the measures adopted to reduce emission of these metals to the environment. In a recent geochemical study in the Huntsville area, Ontario, Canada, however, Rasmussen *et al.* (1998) found that decreases in Hg concentration with sediment depth paralleled decreases in organic matter content

(expressed as % loss-on-ignition (LOI)). The authors concluded that the vertical changes in sediment lithology and geochemistry (especially the proportion of organic matter versus mineral fraction) strongly influenced the shape of total Hg concentration profiles. In the same study, two groups of trace metals were discriminated depending on their correlation with either organic or inorganic (mineral) fractions. In the first group, which was represented by K, Fe, Ba, Sr, Na, Mn, and Ti, all elements showed a positive correlation with Al (representing the inorganic fraction) and a negative correlation with organic matter. In contrast, the second group formed by Hg, As, Sb, Pb, Ni, Cr, Cu, Cd, and Zn showed a positive correlation with organic matter. A correlation test of As, Sb, Cu, Ni, Cu, Cd and Zn vis -à-vis Hg and LOI showed that these metals exhibited a stronger correlation with Hg than with LOI, suggesting that additional factors influenced their distribution.

The present work is a follow-up study to that by Rasmussen *et al.* (1998). Its main objectives are:

1) To determine if the relationships between trace metals and organic/inorganic fractions observed in the previous study (Rasmussen *et al.*, 1998) are maintained for a larger set of lakes in the same region.
2) To determine, using sequential extractions, the distribution of metals amongst the following sediment fractions: i) soluble organics, ii) amorphous iron/crystalline manganese oxides iii) crystalline iron oxides, iv) insoluble organic/sulphides, and v) silicates.

3) To determine the partitioning of metals in mineral soil samples (B horizon) collected from the contributing watershed, using the same sequential extraction scheme as (2) for sediments
4) Finally, to compare metal distribution and partitioning behaviour in both sediment and soil samples.

2. Geological Setting

The 20 lakes sampled in this survey are located east of the town of Huntsville (longitude 79°12', latitude 45°20'), about 250 km north of Toronto (Fig. 1a, 1b). The lakes are: Arrowhead, Axe, Bella, Rebecca, Fairy, Fawn, Peninsula (Pen), Waseosa, Cecebee, Mary, Bear, Bay, Sugar, Skeleton, Diamond (Dia), Heney, Brandy, Pickerel, Doe, and Rainy. The study area is part of the Grenville structural province near the southern margin of Ontario's Precambrian Shield. Bedrock geology consists of metamorphosed igneous and sedimentary units that have been grouped into lithotectonic domains (Davidson, 1984). These prominent structural features have influenced the hydrology of the region resulting in the elongated forms of some of the lakes, and the geometric patterns of the tributaries (Rasmussen, 1993). Quaternary deposits are mainly outwash sand, tills and glaciolacustrine clays.

3. Methodology

3.1. Lake Sediment Sampling

Sediments were collected manually using a modified piston core sampler and clear plastic core barrels, with the assistance and guidance of Dr. J. McAndrews from the Department of Botany, Royal Ontario Museum (ROM) during the winter of 1994. At least 2 cores, 1 meter each, have been sampled from each lake. The sampling of more than one core allowed an examination of chemical and lithological variability within lakes, and provided more material for chemical analysis. Cores from the 20 lakes were immediately sectioned every 10 cm and submitted to Acme Analytical Laboratories in Vancouver, British Columbia for the determination of total trace elements and total carbon and sulphur (described below). The sequential extraction procedure was conducted on samples from Fairy, Peninsula and Diamond lakes in the Analytical Method Development Laboratories (AMD) of the Geological Survey of Canada, Ottawa. The choice of these three lakes was based on the fact that amongst all the 20 lakes, Diamond Lake sediments represented the highest content in organic C (mean org.C=20.1%), Peninsula contained the most clay material and Fairy was typical of lake sediments of the large lakes.

3.2. Soil Sampling

Samples of the mineral horizon of Podzolic soils (B-horizon) were collected every 1000 m along three transects (Transects I, II, III located in Fig. 1b). All sampling sites were located on high, dry ground in undisturbed forested areas remote from any human sources of contamination. The soil was sampled within a depth interval of 5-10 cm below the litter horizon by horizontally inserting a plastic cylinder into the soil face of a freshly dug pit, and then ejecting the contents into a double-sealed plastic bag to prevent the sample

from contamination during transportation to the laboratory. A total of 21 samples were submitted for sequential extractions to the Geological Survey of Canada, Ottawa.

3.3. Total Trace Element Analysis

Lake sediment samples were digested with 30 mL of $HCl:HNO_3:H_2O$ mixture (3:1:2 volume to volume) at 95°C for one hour and were diluted to 100 mL with DDI H_2O. Solutions from this digestion were analyzed for Mn, Fe, Sr, Ca, P, La, Cr, Mg, Ba, Ti, B, W, Na, K, and Al directly by ultrasonic nebulization (USN) ICP-AES, and for Hg by cold vapour atomic absorption spectrometry. Solutions for Mo, Cu, Pb, Zn, Ag, As, Au, Cd, Sb, Bi, Tl, Se, Te, and Ga determination were extracted using methylbutylisoketone (MIBK) which was then analysed by USN ICP-AES.

Total carbon and total sulphur were determined directly on solid samples using a LECO analyzer. Total organic carbon and insoluble sulphur were determined by LECO after a 15% HCl digestion for one hour at 70°C.

Standards and replicates were used as controls to monitor the precision. Four lake sediment standards were used during this study; LKSD1-4 (Lynch, 1990).

3.3. Sequential Extraction

The principle of trace metal sequential selective extraction is based on dissolving a specific component and bringing into solution metals associated with the targeted component using reagents which leave intact the same metals associated with other components. Five operationally defined fractions (phases) were targeted by the extraction

because of the role they play in trace metal cycling in lake sediments i) humic material (humic and fulvic acids), ii) amorphous Fe and crystalline Mn oxides, iii) crystalline oxides Fe oxides, iv) insoluble organics/sulfides, and v) silicates/residuals. The following review explains why certain reagents were selected instead of others and why the five fractions were targeted in this study.

Trace metals were extracted from the humic and fulvic acids because of the role played by their carboxylic and hydroxylic functional groups in forming organometallic complexes and chelates as observed in soils and sediments. Iron and manganese oxides have high adsorption capacities compared to other oxides such as Al and Si oxides. They precipitate under oxic conditions and dissolve under anoxic conditions (Jenne, 1977). Oxides are also strong scavengers of metals (Chao and Theobald, 1976; Stumm and Morgan, 1997) and hence play an important role in metal distribution especially in surface sediments where they are commonly present due to the prevailing oxic conditions. In lake sediments, under anoxic conditions the reduction of SO_4^{2-} to H_2S/HS^- caused by, among other processes, organic matter breakdown by bacteria favors the formation of metal sulfides such as ZnS, Fe_2S, CdS, HgS, etc. It is thus important to know the amount of these metals associated with sulfides in general although it is difficult to separate between primary or secondary (diagenetic) mineral sulfides. Silicates and resistant mineral phases (residuals) from the overall extraction represent the last fraction to be decomposed since they are more resistant and require a strong acid attack.

Removing trace metals from soil and sediment humic material requires a solution containing anions able to remove these metals by precipitation or by the formation of chelates or coordinate complexes (Bremner and Lees, 1949). Pyrophosphate represents

one of these anions. Pyrophosphate was initially used by soil scientists to extract organic-chelated metals from soils (McKeague, 1967; Bascomb, 1968; Ball and Beaumont, 1972; Tan, 1978) and from sediments (Wihelm *et al.*, 1979). Pyrophosphate anion effectiveness is however influenced by the pH and by the concentration of the pyrophospahte solution. At pH = 7, pyrophosphate favours aged Fe amorphous oxides extraction instead of organic matter (Bascomb 1968). McKeague (1967) however demonstrated that at pH=10, 0.1 M $Na_4P_2O_7$ does not attack amorphous or crystalline oxides. H_2O_2 and NaOCl were also used to extract metals associated with organic matter, however in both cases the treatment was revealed not effective because an appreciable amount of organic matter remains after peroxidation (Farmer and Mitchell, 1963), because H_2O_2 attacks sulphide minerals present in soils and sediments (Chao and Sanzalone, 1977) and because oxalate forms as a result of H_2O_2 treatment (Martin, 1954; Farmer and Mitchell., 1963) which may dissolve oxides of iron and manganese (Williams *et al.*, 1958). NaOCl was used to study the scavenging of metals by organic matter in soils and sediments (Hoffman and Fletcher, 1979; 1981), however the treatment of soils and sediments by NaOCl was observed to attack of sulfides present in the sample (Rose, 1975). In this study, the extraction of amorphous iron oxides and Mn oxides was performed using 0.25 M $NH_2OH.HCl$ in 0.25 M HCl at 60°C. It is the same extraction used by Chao and Zhou (1983). Unlike the acid ammonium oxalate 0.175 M $(NH_4)_2C_2O_4$-0.1M H_2CO_4 (McKeague and Day, 1966; Blum and Schwertmann, 1969) which results in a significant dissolution of crystalline iron oxides such as magnetite (Rhoton et al. 1981; Chao and

Zhou, 1983) and lepidoccrosite (Schwetmann, 1973), this extraction does not affect crystalline iron oxides.

Chester and Hughes (1967) used 1M NH_2.OH.HCl in 25% acetic acid (HOAc) to study partitioning of trace metals in crystalline oxides from pelagic sediments and this is the extractant used in our scheme. HCl and oxalic acids have been also used to extract trace metals associated with crystalline oxides (Bradshaw *et al.*, 1974; Malo, 1977), but unlike 1M NH_2.OH.HCl under the above conditions, they tend to dissolve iron oxides of varying degrees of crystallinity (Chao and Zhou, 1983; Ball and Beaumont, 1972). At high temperature, HCl tends also to dissolve silicates and carbonates as well as clay minerals. On the other hand, the problems related to the oxalic acid treatment rose from its ability to dissolve sulfide minerals and the lack of specificity such as differentiating between the different iron oxide minerals.

To release trace metals from the insoluble inorganics/sulphides phases, a highly oxidizing attack should be performed at this stage. The treatment used in our study is the one suggested by Chao and Sanzalone (1977) which consists of using $KClO_3$-HCl (12 M) (750 mg/5mL (weight/volume)) and 4 M HNO_3. Olade and Fletcher (1974) found that potassium chlorate-hydrochloric acid does not damage silicates and was most selective for sulphides and therefore was a suited extractant for our sequential selective leach. Other reagents including peroxide-ascorbic acid were also used to extract trace metals from sulphides (Lynch, 1971). However, peroxide-ascorbic acid treatment allows precipitation of $PbSO_4$ as reported by Peachy and Allen (1977) and attacks only partially (43 to 66 %) sulphide minerals (galena, chalcopyrite, cinnabar, molybdenite, pyrite,

sphalerite, and tehtrahedrite) as reported by Chao and Sanzalone (1977). Thus sediment treatment with peroxide-ascorbic acid was discarded from our scheme.

A final strong acid attack was performed to dissolve the silicates and the resistant fractions. We used an acid mixture attack HF:$HClO_4$:HNO_3 as suggested by Tessier *et al.* (1979).

In summary, the hierarchical order of extractants used in the sequential leach in this study is the following (see appendix 1-3 for the detail of the extraction protocol):

1- Soluble organics using 0.1 M $Na_4P_2O_7$ at pH 10 (Hall and Pelchat, 1997)

2- Amorphous Fe oxides and crystalline Mn oxides using 0.25 M $NH_2OH.HCl$/0.25 M HCl at 60°C. (Chao and Zhou, 1983)

3- Crystalline Fe oxides using 1.0 M $NH_2OH.HCl$ in 25% CH_3COOH at 90°C (Chester and Hughes, 1967)

4- Insoluble organic and sulphides using $KClO_3$ - HCl, and HNO_3 (Chao and Sanzalone, 1977)

5- Silicates/residuals using an acid mixture of HF:$HClO_4$:HNO_3 (in a ratio of 5:3:2) (Tessier *et al.*, 1979).

The above extractions were performed at the Analytical Method Development Laboratory of the Geological Survey of Canada, Ottawa, as described by Hall *et al.* (1996). The leachates from the 5 fractions were analyzed for Al, Cr, Ni, and Mo by ICP-AES; for Pb and Cd using ICP-MS; for Zn, Cu, Mn and Fe using FAAS, and for Hg using hydride generation ICP-MS.

4. Results

4.1. Analytical Parameters

An assessment of the reproducibility of the total element determinations is summarized in Table 1. "Test A" refers to the determination of precision expressed as the average relative standard deviation (RSD) using 19 pairs (n2=19) of replicates (split from same sample) for Hg, total C, total S, organic C, and insoluble S, and 12 pairs (n1=12) of replicates for the remainder of the elements. "Test B" refers to the determination of precision in six replicates of a homogenized blind control sample (homogenized mixture of lake sediments from the same study area). Results were determined to be quantitative based on a total of 37 analyses of the Canadian Certified Reference Material Program (CCRMP) lake sediment standards (LKSD1-4) (Appendix 1). Reproducibility was found to be acceptable for all elements with the exception of those present at concentrations near the detection limits. Thus, high RSDs (average RSDs) resulted for As, U, Sb, Bi, B, Tl, Te in test A, and Bi, Tl and Ga for test B. Values of half the detection limit were assigned to samples below the detection limit.

Results of accuracy and precision tests on sequential extraction results from both soil and sediment samples are illustrated in the Appendix 2.

4.2. Metal Enrichment in Surface Sediments

To compare the relative enrichment of different elements in surface sediments, we calculated the average enrichment factor for each element across the 20 lakes (Fig. 2). This factor corresponds to the average ratio of total metal concentration in surface

sediments (top 10 cm) to its concentration in deep sediments (average 70-100 cm). Surface sediments (0-10 cm) refer to modern *Ambrosia* horizon based on C-14 dates and deep sediments (70-100 cm) refer to pre-colonial sediments (840 years before present) (Rasmussen *et al.*, 1998). As indicated in Figure 2, Pb, Sb, As, Hg, Ag, Zn, Cd, and Se, are significantly enriched (average factor 2.02 or greater) whereas Cu, Ni, Mn, Fe, Co, Cr, Mg, Al, are only slightly enriched in surface sediments. The remaining elements show no enrichment.

Relationships between trace metals, organic C, Hg, Cd, Al were also examined. Trace metals with high affinity for organic matter, such as Cd and Hg, would be expected to show a positive correlation with organic carbon. Trace metals that tend to partition into the silicate fraction, in contrast, would be expected to show a positive correlation with Al, due to the presence of aluminosilicates.

Based on Pearson's correlation coefficients, results from the 20 lakes (n=20) showed that the elements fell into two groups. The first group (Pb, Sb, Cd, Zn, Se, Hg, Cu, Sr As, Mo) showed a positive correlation with organic C and Hg in the surface sediments, while the second group (Mg, Ti, K, Cr, Al, Mn, Na, Ba, V, Fe, Ag, Ca) showed a negative correlation with organic C and Hg (Fig. 3). Similar results were observed when comparing trace metal relationships with organic C and Cd (Fig. 4).

Comparisons of metal relationships with Al and organic C also displayed the above relationships (Fig. 5). In fact, most of the elements of the second group exhibited a positive correlation with Al and a negative correlation with organic C.

4.3 Sequential Extraction of Soils and Sediments

The results of the sequential extraction of soil samples from the Huntsville area are tabulated as average values in Table 2. In this table the variability data (STD and RSDs) indicate the natural heterogeneity of the soils over an area of about 150 km^2. In addition, the sequential extraction data and the vertical lake sediment profiles are summarized in the form of pie diagrams showing percentages of metal in each fraction and in the form of binary diagrams showing the variation of total concentration of each element with depth (Fig. 6-15), to reduce the large volume of data that is generated by the analytical scheme.

4.3.1. Lake Sediments

a) Elements with high affinity for organic matter

Cadmium

Cadmium showed an enrichment factor of 3.02, 1.57, and 1.43 in Peninsula, Fairy and Diamond Lakes respectively. Results from the sequential extractions indicate that most of the Cd is associated with soluble organics in surface sediments. This distribution is also maintained in deeper sediments (Fig. 6).

Copper

Only Peninsula and Fairy lakes exhibited Cu enrichment in surface sediments of 1.4, 1.2 respectively, whereas Diamond displayed an enrichment factor of 0.8. Results from the sequential extraction showed that in the three lakes, most Cu was associated with the soluble organic and oxides in surface sediments (Fig. 7).

Lead

Among all elements, Pb showed a dramatic change of its total concentration with depth and exhibited the highest enrichment factor. Pb enrichment factors were 25.57, 15.25 and 12.10 in Diamond, Fairy and Peninsula Lakes respectively. In terms of its relation with the 5 fractions, most of Pb was associated with the soluble organics and crystalline oxide fractions in the surface sediments in the three lakes (Fig. 8). In deeper sediments, however, Pb was mainly associated with the silicate fraction (Fig. 8).

Mercury

For all three lakes, Hg showed enrichment in surface sediments relative to deep sediments. The enrichment factors for Hg were of 3.28, 2.77, and 2.38 in Peninsula, Fairy, and Diamond respectively. In terms of Hg partitioning amongst the 5 fractions, results from the sequential extractions showed that, in the three lakes, Hg was mainly associated with three fractions, i.e., soluble organics, crystalline Fe, Mn oxides and insoluble organics/sulphides (Fig. 9).

Zinc

Zinc showed a slight enrichment in the surface sediments in the three lakes, and a high proportion was associated with the soluble organics. Zn increased in the surface layer by a factor of 1.70, 1.60, and 1.38 in Fairy, Peninsula and Diamond Lakes respectively. In terms of Zn partitioning amongst the 5 fractions, most Zn was associated with soluble organics at the surface (10 cm) in all the three lakes (Fig. 10). However, Zn showed a different behaviour in the deeper portion of the sediments in Fairy and Peninsula

compared to Diamond. In the former, Zn is associated with both soluble organics and amorphous and crystalline oxides at all depths, whereas, in Diamond Lake, most Zn in deep sediments is associated with the soluble organics fraction. (Fig. 10).

b) Elements with high affinity for the mineral fraction

Iron

Surface-to-deep enrichment factors for iron were 1.10, 0.87 and 1.24 in Peninsula, Fairy and Diamond lakes respectively. Results from the sequential extraction indicate that most Fe was distributed between the residuals and the crystalline oxide fractions in Peninsula and Fairy lakes, whereas in Diamond Lake, Fe was associated with the soluble organics, residuals and crystalline oxide fractions (Fig. 11).

Aluminum

In general, Al showed no enrichment in the surface sediments with enrichment factors of 0.94, 0.97, and 0.88 in Peninsula, Fairy and Diamond lakes respectively. In both Peninsula and Fairy lakes, most Al (73% in Peninsula and 82% in Fairy) was associated with the residual fraction at all depths (Fig. 12). In Diamond Lake however, most Al was associated with the soluble organic fraction and to less extent, with residuals (Fig. 12).

Chromium

Enrichment factors for chromium were 0.95, 1.02 and 0.89 for Peninsula, Fairy and Diamond Lakes respectively. In terms of Cr distribution in surface sediments, results

from the sequential extraction indicated that a large portion of Cr was associated with the residual fraction in all the three lakes (Fig. 13).

Manganese

Manganese was slightly enriched in the surface sediments relative to the deep sediments. Enrichment factors were 1.30, 1.24, and 1.15 in Peninsula, Fairy and Diamond Lakes respectively. Like Fe, most Mn in surface sediments was associated with the silicates, soluble organics and oxides fractions in Peninsula and Fairy and Diamond Lakes. In deep sediments (> 30 cm), most Mn was associated with the soluble organic and oxide fractions in Diamond Lake, whereas in Peninsula and Fairy Lakes, most Mn was associated with the silicate and oxide fractions (Fig. 14).

Nickel

Nickel showed enrichment factors of 1.28, 0.97, and 0.70 in Peninsula, Fairy and Diamond Lakes. According to the sequential extraction results, Ni is distributed mainly in the silicate fraction (and soluble organics to lower extent) in Diamond Lake, and with oxides and silicates in Peninsula and Fairy Lakes in surface and deep sediments (Fig. 15).

4.3.2. Soils

Results from the sequential extraction (Table 2) carried out on 24 soil samples from the 3 transects showed that on average, Al occurs in the silicate fraction (90%, total average = 4.56%, n=24), Cr occurs mainly in the silicate fraction (92%, total average. = 18 ppm; n=24), and Fe occurs in the silicates (68%) and in the crystalline Fe oxides (22%) with a

total average of 2.2%. Pb presented a total average of 24 ppm from the 24 soil samples with 60% distributed in the silicate fraction, 20 % associated with the soluble organics and 14% associated with the amorphous oxides. Total average Mn content was 504 ppm with 84% distributed in the silicate fraction. 80% of Ni was distributed in the silicate fraction with a total average (n=24) content of 8 ppm. Cd, Hg, Mo, Zn, and Cu were mainly associated with soluble organics (42% for Hg, 61% for Cd, 22% for Zn, 35% for Mo, and 22% for Cu). High proportion of Hg was also associated with the insoluble organic/sulphides fraction (40%), whereas only 14% was associated with crystalline oxides fraction (Table 2).

5. Discussion

Sequential extraction results presented here show a strong geochemical relationship between organic matter, oxides and the group of elements formed by Pb, Hg, Cd, Cu, and Zn in the surface sediments. These results also indicate a strong geochemical relationship between the silicate (residual) fraction and the group formed by Cr, Mn, Fe, Al, Co, and Ni.

As demonstrated experimentally and in natural systems, the affinity of Hg, Cd, Cu, Pb, and Zn for organic matter is related to both the high adsorptive capacity of humic substances and the stability of their organometallic species (Strohal and Huljev, 1970; Siegel, 1971, Stumm and Brauner, 1975; Schnitzer, 1971; Lu *et al.*, 1983). Moreover, Lu *et al.* (1983) compared the adsorptive capacity of Hg by humic acids (HA) organic matter, MnO_2, illite, kaolinite, montmorillonite, Fe_2O_3, SiO_2 and found that HA had the highest adsorptive capacity among all the tested compounds. The adsorption of Hg occurs

in the order HA > MnO_2 > illite > kaolinite > montmorillonite > Fe_2O_3>SiO_2. In addition, Jonasson (1977), established a probable order of binding strength of a number of metal ions onto humic and fulvic acids as follows: Hg^{2+}>Cu^{2+}>Pb^{2+}>Zn^{2+}>Ni^{2+}>Co^{2+}.

Such relationships raise questions regarding the influence of the high affinity of Hg, Pb, Cd, Cu and Zn for organic matter on the enrichment behaviour of these elements in surface sediments. The answer to this question relies on determining whether the surface enrichment in the studied area is historical (anthropogenic) or simply controlled by chemical speciation during diagenesis. Recently Gobeil *et al.* (1999) concluded that diagenetic processes, not contamination, is the likely cause of near-surface Hg enrichment observed in widely distributed sediment cores from the major Arctic basins. In fact, based on strong similarities between Hg and reactive Fe profiles, on Mn and Fe enrichment in the surface sediments, and on the very low sedimentation (< 1cm ka^{-1}) and biomixing (<0.03 cm^2 yr^{-1}) rates, Gobeil *et al.* (1999) suggested that Hg enrichment at the surface was due to a redistribution of Hg caused by a recycling mechanism involving reactive Fe during redox changes. Similarly, Matty and Long (1995) demonstrated the important influence of diagenesis on vertical concentration profiles in sediment cores from the Great Lakes. In interpreting the present results, if we were to assume that the surface enrichment of Hg, Pb, Cd, Cu, and Zn observed in the studied lakes is a record of increased metal loading (Barrie, 1988), we might expect elements such as Ni and Cr, which are smelted near Sudbury located 200 km north of our study area, also to be enriched in modern sediments. However, Cr does not show a significant, consistent enrichment in modern sediments (mean enrichment factor of 1.04 with an RSD of 15.2% for 20 lakes). Similarly, there is no consistent, regionally significant enrichment in total

Ni (Figure 2). The mean enrichment factor for Ni is 1.46 for the 20 lakes, a value that is strongly influenced by remote Axe Lake, an outlier wherein an enrichment factor of 3.08 was observed. This is a small lake in a large, low-lying basin, which raises the question of the degree to which watershed morphology influences the Ni enrichment factor. Our results show that there is no relationship (R^2=0.11) between the watershed area to lake area ratios and the Ni enrichment factor in the 20 lakes included in this study.
Moreover, our extraction results showed that Ni and Cr presented a positive correlation with Al (Fig. 6) and are both distributed in the silicate (residual) fraction, similar to the remainder of the elements forming the second group (Al, Mn, Fe, Cr, Co, Ni).

Soluble organics have an important influence on the mobility of trace metals, as reported by Nissenbaum *et al.* (1972), Bender and Heggie (1984), Krom and Scholkovitz (1977), Hart and Davies (1977) and many others. It has been argued that the high enrichment factors of metals such as Pb, Cd, Hg, Cu, and Zn, in combination with their association with soluble organic matter (0.1M $Na_4P_2O_7$ fraction) is evidence of their anthropogenic mobilization. In a case where partitioning behaviour indicates an anthropogenic source, we would expect this relationship to be restricted to the post-colonial surface sediments. However, the present study shows that, although a high proportion of Cd and Cu is found in the soluble organic fraction in modern sediments, this relationship is preserved in the deep pre-colonial sediments. Thus, the partitioning of a metal in the organic fraction does not necessarily imply an anthropogenic (historical) mobilization, but simply an affinity between organic matter and trace metals that exists regardless of the source (Mantoura *et al.*, 1978).

The results of the Diamond Lake extractions, in particular, show that changes in speciation from top to deep sediments are strongly controlled by the high content of organic matter. In this case, most of the metals were associated with the organic fraction because Diamond Lake is highly organic (mean org.C = 20.11 wt %, n=10, min = 11.26 wt % and max = 24.61 wt %) when compared to Peninsula Lake (mean org. C = 3.95 wt %, n=10, min = 3.43 wt % and max = 4.70 wt %) and Fairy Lake (mean org. C = 3.28 wt %, n=10, min = 2.24 wt % and max = 5.07%) lakes.

The sequential extraction results indicate a close association between certain metals and the oxide fractions of the surface sediments. In Fairy Lake, about 49% of Pb was indeed associated with the oxide fractions (35% amorphous and 14% crystalline oxides) in surface sediments.

The influence of oxides on trace metal distribution in lake sediments has been discussed extensively by Carignan and Nriagu (1985), and Tessier *et al.* (1985, 1989), with a chief mechanism being the flux of Fe and Mn near the sediment-water interface (Davison *et al.*, 1991; Belzile and Tessier, 1990; Davison,1993, Fortin *et al.*, 1993). In surface oxic sediments, oxyhydroxides (amorphous oxides) and Fe-Mn oxides (crystalline oxides) have been shown to play an important role in metal adsorption (Lion *et al.*, 1982; Tessier *et al.*, 1985). Thus, surface enrichment may not be solely attributed to an anthropogenic remobilization but also or instead to the fact that oxides precipitate close to the sediment-water interface.

Results of the sequential extraction study on soils (Table 2) shed light on the terrestrial contribution to lake sediment composition. On average, 60% of total Pb occurs in the

silicate (residual) fraction, 20% in the soluble organic fraction, and 14% in amorphous oxide fraction. Most Hg occurs in the soluble organics (42 %), insoluble organic/sulphide (40 %) , and oxides (16%), whereas Cd occurs mostly in soluble organics (60%). In contrast, most of the elements from the second group including Al, Cr, Mn, and Fe are distributed in the silicate fraction (Table 2).

The occurrence of significant portions of certain elements such as Hg (total average = 59 ppb, n=24, Pb (total average = 24 ppm, n=24), and Cd (total average = 272 ppb, n=24) as oxides, soluble organics, insoluble organics/sulphides complexes in the soil horizon B indicates the importance of the mineral soil contribution to the geochemistry of the lake sediments. These metal complexes are highly stable and can be transported from soils to the lakes by rainwater or snowmelt (Dreever and Clow, 1995).

6. Conclusion

Total element correlations for the 20 lakes show that trace metals behave differently vis-à-vis the organic C and mineral fractions, in agreement with previous work (Rasmussen *et al.*, 1998). To explore the meaning of that behaviour in terms of chemical relationships, we examined the metal distribution in different fractions of sediment samples (soluble organic, amorphous oxides and crystalline oxides, insoluble organics/sulphides, and silicates). The extractions clarified the elemental associations indicated earlier by the total element correlations and enabled us to evaluate the involvement of these fractions in metal distribution. Correlations between total trace elements, organic C, and Al in surface sediment, combined with partitioning behaviour revealed by sequential extractions and evidence from the low enrichment factor of Cr and Ni and their high distribution in the

silicate fraction, show that the affinity to organic fraction and the role of oxides, and not necessarily the increased loading, are the chief processes controlling the enrichment of Hg, Pb, Cd, Cu, and Zn in surface sediments. This study also raises the importance of considering metal speciation when interpreting vertical trace metal concentration profiles in lake sediments.

Similarities in metal speciation between soils and sediments in the same watershed indicate the importance of the terrestrial contribution, but do not explain the shape of the vertical sediment concentration profiles.

The similarities between trace metal distribution and concentrations in the lake sediments and the soil B-horizon raise the question with regard to the importance of the geological contribution from the watersheds to the lakes trace metal budget in remote areas. The answer to this question will be the task of the following manuscript (2).

Summary of Manuscript 1

1- Statistical tests showed a positive correlation between Hg, Pb, Cd, Cu, Zn and the organic C contents and a negative correlation between Cr, Mn, Fe, Al, Co, Ni and organic C contents. These tests also showed a positive correlation between Cr, Mn, Fe, Co, Ni and Al contents and negative correlation between Hg, Pb, Cd, Cu, Zn ans Al contents.

2- Sequential extraction results confirmed the statistical relationships by showing a strong geochemical relationship between the soluble organic and the oxide fractions and the group of elements formed by Pb, Hg, Cd, Cu, and Zn on one hand, and between the silicate fraction and the group of elements formed by Cr, Mn, Fe, Al, and Ni on the other.

3- The enrichment of Hg, Pb, Cd, Cu, Zn in the surface sediments from the 20 lakes is due to their affinity to organic matter and oxides and not to an increased metal loading to the lakes.

4-Similariry between trace metal contents and their distribution in the soil B-horizon and in lake sediments suggests the importance of geological contributions to the gechemical composition of the lake sediments.

Acknowledgements

We thank Roxanne Beer and Judy Vaive of Analytical Methods Laboratory, Mineral Resources Division, GSC, NRCan for their assistance with the sequential extractions, and David Gardner, GIT Inc., for his assistance with the design of the ACCESS database. We would like to thank the Geological Survey of Canada Metals in the Environment Program, NSERC (grant to D. Fortin), and the University of Ottawa for financial support.

Table 1

Analytical precision tests, A and B. N represents the proportion of samples for which certain elements were found below the limit of detection (DL) and were assigned the value of 1/2 DL.

		Test A using 12 (n1=12) and 19 (n2=19) pairs of replicates						Test B, using 6 (n=6), replicates of the homogenized blind control sample					
Compound (ppm)	DL	Mean	Min	Max	STD	RSD	N	Mean	Min	Max	STD	RSD	N
Mo	0.1	2.1	0.5	7.6	0.10	4.0%		0.6	0.5	0.7	0.08	13.6%	
Cu	0.1	18.9	8.6	47.6	0.75	4.1%		16.2	13.1	18.6	1.99	12.3%	
Pb	0.1	13.5	1.6	75.6	0.85	9.2%		4.4	3.8	6.6	1.02	23.0%	
Zn	0.1	115.9	32.4	328.3	4.93	4.9%		117.5	110.4	126.3	5.22	4.4%	
Ag	0.02	0.12	0.03	0.58	0.01	10.5%	2 of 24	0.05	0.02	0.07	0.02	30.0%	
Ni	1	14	7	20	0.71	5.7%		16	14	17	1.07	6.7%	
Co	1	10	5	16	0.25	2.3%		7	7	7	0.00	0.0%	
Mn	1	440	152	786	11.25	3.3%		263	253	267	4.46	1.7%	
Fe(%)	0.01	2.67	1.55	4.25	0.05	2.1%		1.82	1.77	1.85	0.03	1.4%	
As	0.3	4.6	0.2	36.2	0.62	15.6%	4 of 24	0.4	0.4	0.5	0.04	8.9%	
U	5	3	2.5	7	0.04	0.6%	22 of 24	2.50	2.50	2.50	0.00	0.0%	6 of 6
Au	0.02	0.04	0.01	0.70	0.03	8.1%	23 of 24	0.01	0.01	0.01	0.00	0.0%	6 of 6
Th	1	3	0.50	6	0.15	7.4%	5 of 24	0.50	0.50	0.50	0.00	0.0%	6 of 6
Sr	1	27	15	70	0.42	1.6%		33	31	33	0.76	2.4%	
Cd	0.02	0.65	0.09	1.25	0.03	5.1%		1.13	0.99	1.31	0.10	8.6%	
Sb	0.1	0.2	0.05	1.3	0.05	8.5%	12 of 24	0.05	0.05	0.05	0.00	0.0%	6 of 6
Bi	0.1	0.2	0.05	0.8	0.04	15.0%	14 of 24	0.08	0.05	0.20	0.06	74.5%	5 of 6
V	2	36	16	53	0.79	2.3%		25	24	25	0.50	2.0%	
Ca(%)	0.01	0.89	0.28	5.88	0.02	1.9%		0.45	0.43	0.45	0.01	1.7%	
P(%)	0.001	0.084	0.052	0.133	0.00	1.8%		0.081	0.078	0.082	0.00	1.8%	
La	2	51	10	124	1.29	2.3%		52	50	53	1.11	2.1%	
Cr	1	25	11	42	0.63	2.7%		23	22	24	0.69	3.0%	
Mg(%)	0.01	0.45	0.12	0.78	0.01	1.7%		0.41	0.39	0.41	0.01	1.9%	
Ba	2	128	78	201	2.92	2.3%		122	118	126	2.77	2.3%	
Ti(%)	0.01	0.12	0.03	0.18	0.00	3.2%		0.09	0.09	0.09	0.00	0.0%	
B	2	4	1	10	1.00	27.0%	4 of 24	5	3	6	1.07	22.1%	
Al(%)	0.01	1.33	0.43	2.11	0.03	2.0%		1.84	1.82	1.85	0.01	0.6%	
Na(%)	0.01	0.04	0.01	0.07	0.00	0.9%		0.04	0.03	0.04	0.00	12.9%	
K(%)	0.01	0.18	0.04	0.34	0.00	2.0%		0.17	0.17	0.18	0.00	2.2%	
W	2	1	1	1	0.00	0.0%	24 of 24	1	1	1	0.00	0.0%	6 of 6
Tl	0.1	0.2	0.1	0.5	0.05	19.8%	10 of 24	0.2	0.05	0.8	0.28	159.7%	5 of 6
Se	0.1	0.7	0.1	3.7	0.16	26.6%		0.6	0.4	0.8	0.13	21.5%	
Te	0.1	0.2	0.1	1.6	0.08	18.3%	18 of 24	0.1	0.1	0.4	0.13	120.4%	5 of 6
Ga	0.1	4.4	1.6	7.5	0.26	5.7%		4.0	3.3	4.6	0.49	12.4%	
Hg (ppb)	5	74	10	225	57.82	4.9%		73	65	80	4.79	6.6%	
TOT-C(%)	0.01	8.74	1.83	18.20	5.42	6.4%		11.64	10.93	11.95	0.34	2.9%	
TOT-S(%)	0.01	0.19	0.03	0.79	0.16	8.6%		0.16	0.13	0.17	0.01	8.8%	
ORG-C(%)	0.01	7.44	2.18	17.08	4.83	6.8%		10.71	10.19	10.96	0.25	2.3%	
INS-S(%)	0.01	0.15	0.03	0.43	0.11	11.4%		0.13	0.10	0.15	0.02	11.9%	

Concentrations are in ppm unless, otherwise indicated.

RSDs refers here to relative standard deviations over n1=12, n2=19 pairs of replicates, and n=6 replicates.

n1= Number of pairs of replicates used to determine the precision for all the elements except for Hg, Tot-C, Tot-S, Org-C, and Ins-S.

n2= Number of pairs of replicates used to determine precision for Hg, Tot-C, Tot-S, Org-C, and Ins-S.

Minimum (Min) and maximum (Max) values are from the analyses of n1=12, n2=19 pairs of replicates, and n=6 replicates from the blind control sample.

Table 2
Trace metal distribution in the soil samples from the three transects shown in Figure 1 (b), expressed as percentages of total* element concentrations (averages, standard deviations and RSDs are based on 24 samples).

Element	Average soluble Organics (%)	STD	RSD (%)	Average amorphous Oxides (%)	STD	RSD (%)
Al	7	5	74	1	1	64
Cd	61	15	25	10	5	56
Cr	6	10	172	0	1	490
Cu	22	10	44	14	3	22
Fe	20	9	44	3	1	34
Pb	20	9	44	14	4	30
Mn	8	8	102	5	8	156
Hg	42	12	28	2	1	67
Mo	35	4	12	11	1	12
Ni	4	2	47	4	5	149
Si	10	6	63	5	3	60
Zn	22	9	41	10	3	33

Element	Average crystalline Fe-Mn Oxides (%)	STD	RSD (%)	Average insoluble Organic/Sulphides (%)	STD	RSD (%)
Al	0	0	106	1	1	90
Cd	4	3	87	3	2	70
Cr	0	0	0	2	4	186
Cu	14	3	19	18	6	30
Fe	6	4	71	4	3	92
Pb	4	2	44	1	1	98
Mn	1	1	56	1	1	94
Hg	14	11	82	40	11	28
Mo	18	2	12	18	2	12
Ni	2	1	49	2	3	109
Si	2	1	61	3	1	31
Zn	6	3	51	11	3	32

Element	Average Residuals (%)	STD	RSD (%)	Totals* Average (ppm)
Al	90	6	7	4.56 (%)
Cd	22	13	57	272 (ppb)
Cr	92	12	13	18
Cu	31	6	19	4
Fe	68	12	18	2.20 (%)
Pb	60	12	20	24
Mn	84	16	19	504
Hg	2	1	63	59 (ppb)
Mo	18	10	53	0.2
Ni	87	8	9	8
Si	80	8	10	0.86 (%)
Zn	51	10	20	43

* Total average is ,here, the averaged (n=24) sum of metal concentration from the five fractions .

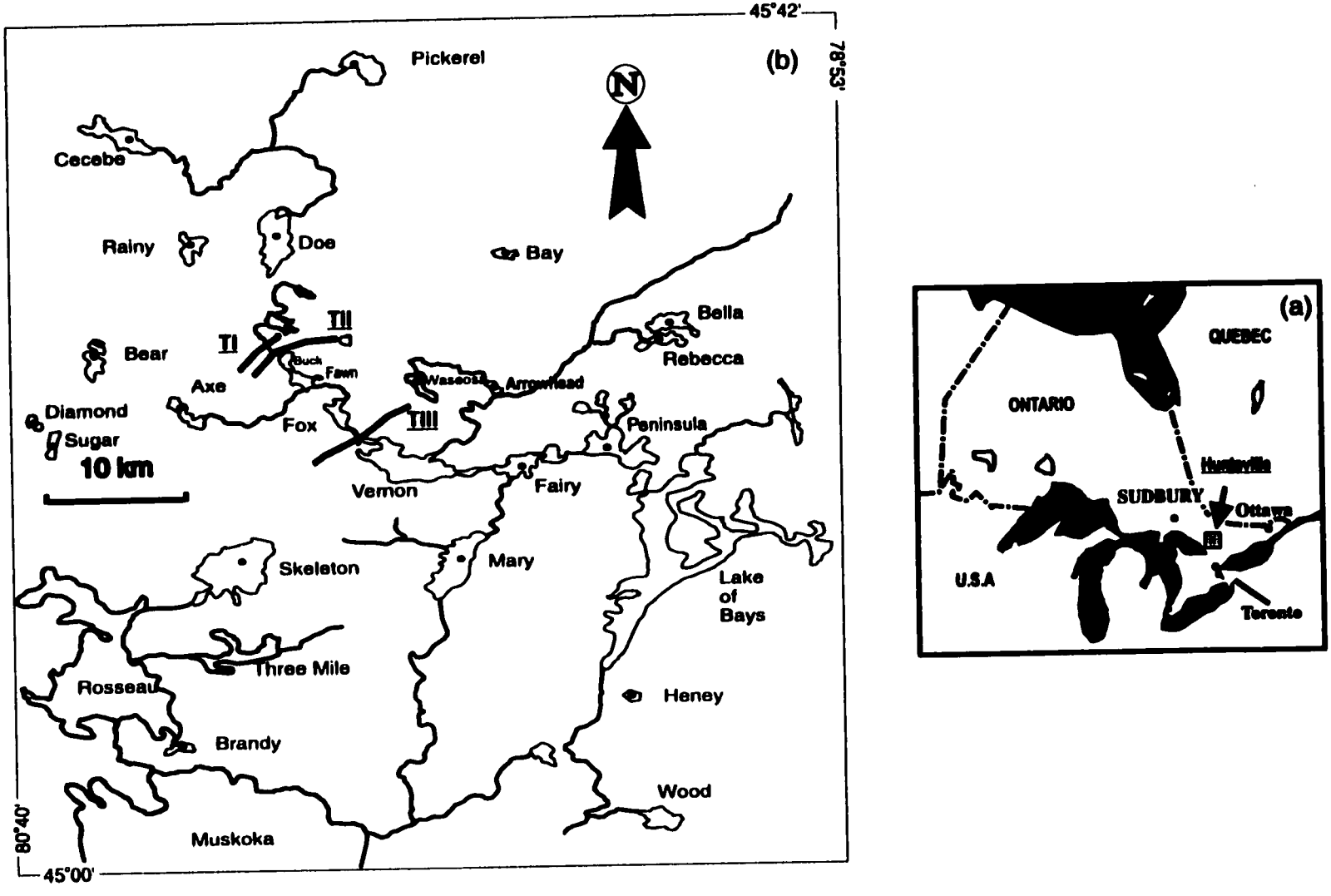

Fig. 1. (a) Study area location; (b) Lake samples in this study (•). TI= soil transect I, TII= soil transect II, and TIII=soil transect III.

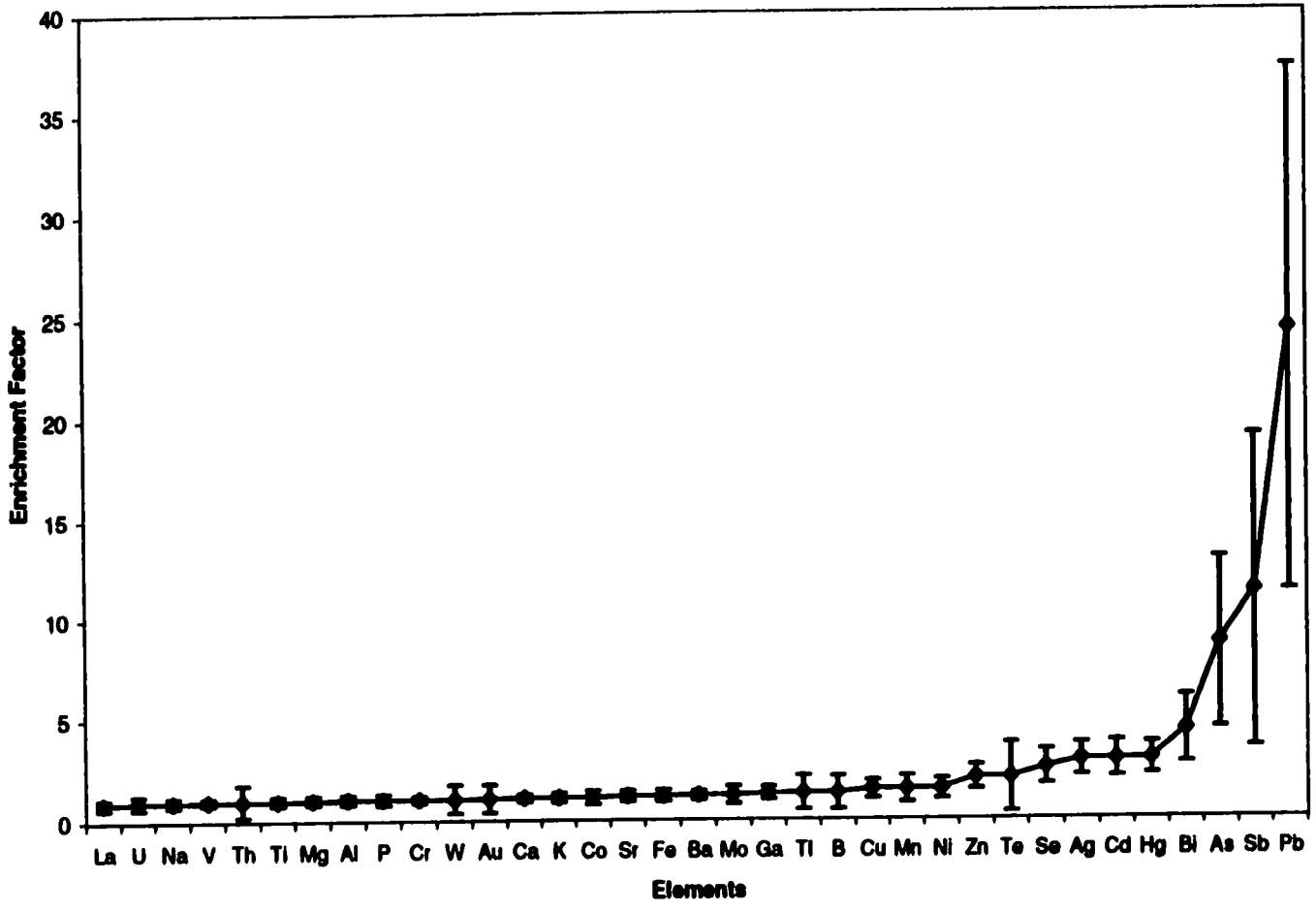

Fig. 2. Average metal enrichment factor in the 20 lakes (n=20). Bars represent the variability (STD) of metal enrichment from one lake to another. The enrichment factor corresponds to the average ratio of metal concentration in surface sediments (top 10 cm) to its concentration in deep sediments (average 70- 100 cm) for a total of twenty lakes.

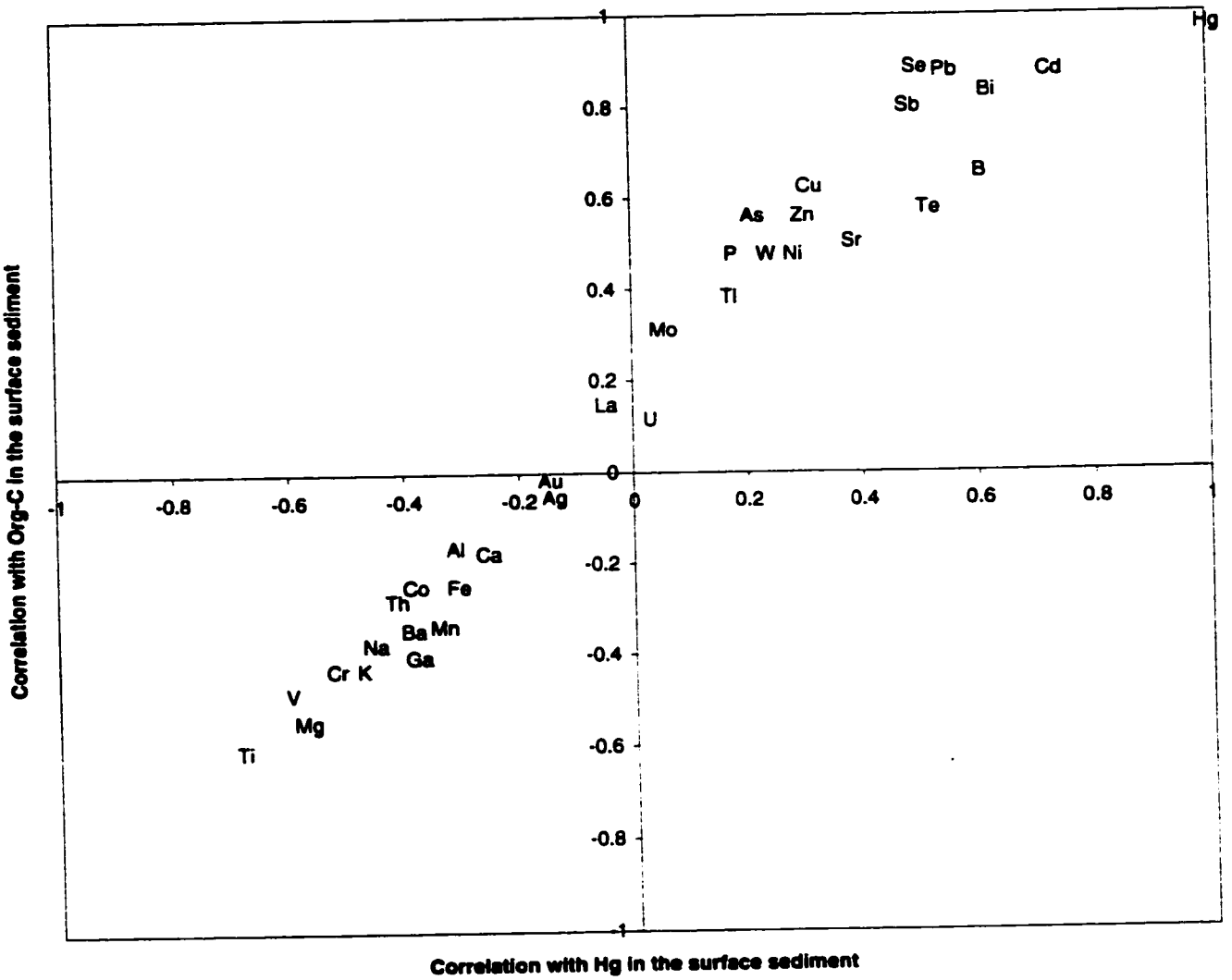

Fig. 3. Graph summarizing relationships between trace metals, Hg and organic carbon in the sediment cores from the 20 lakes (n=20). Average concentrations were calculated for each lake from the 0-10 cm intervals. Positive correlations are indicated by the positive axis, and negative correlations are indicated by the negative axis.

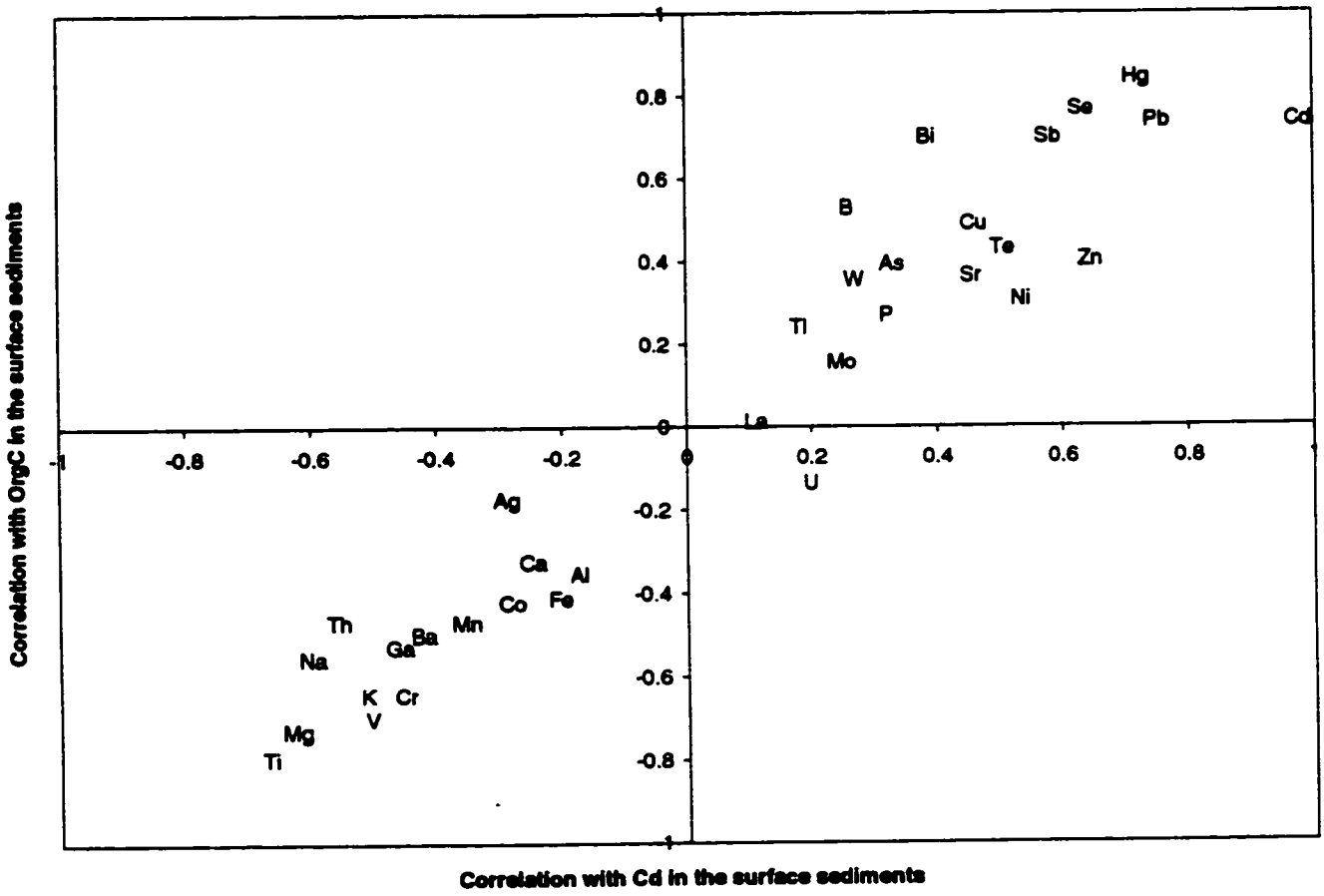

Fig. 4. Graph summarizing relationships between trace metals, Cd and organic carbon in the sediment cores from the 20 lakes (n=20). Average concentrations were calculated for each lake from the 0-10 cm intervals. Positive correlations are indicated by the positive axis, and negative correlations are indicated by the negative axis

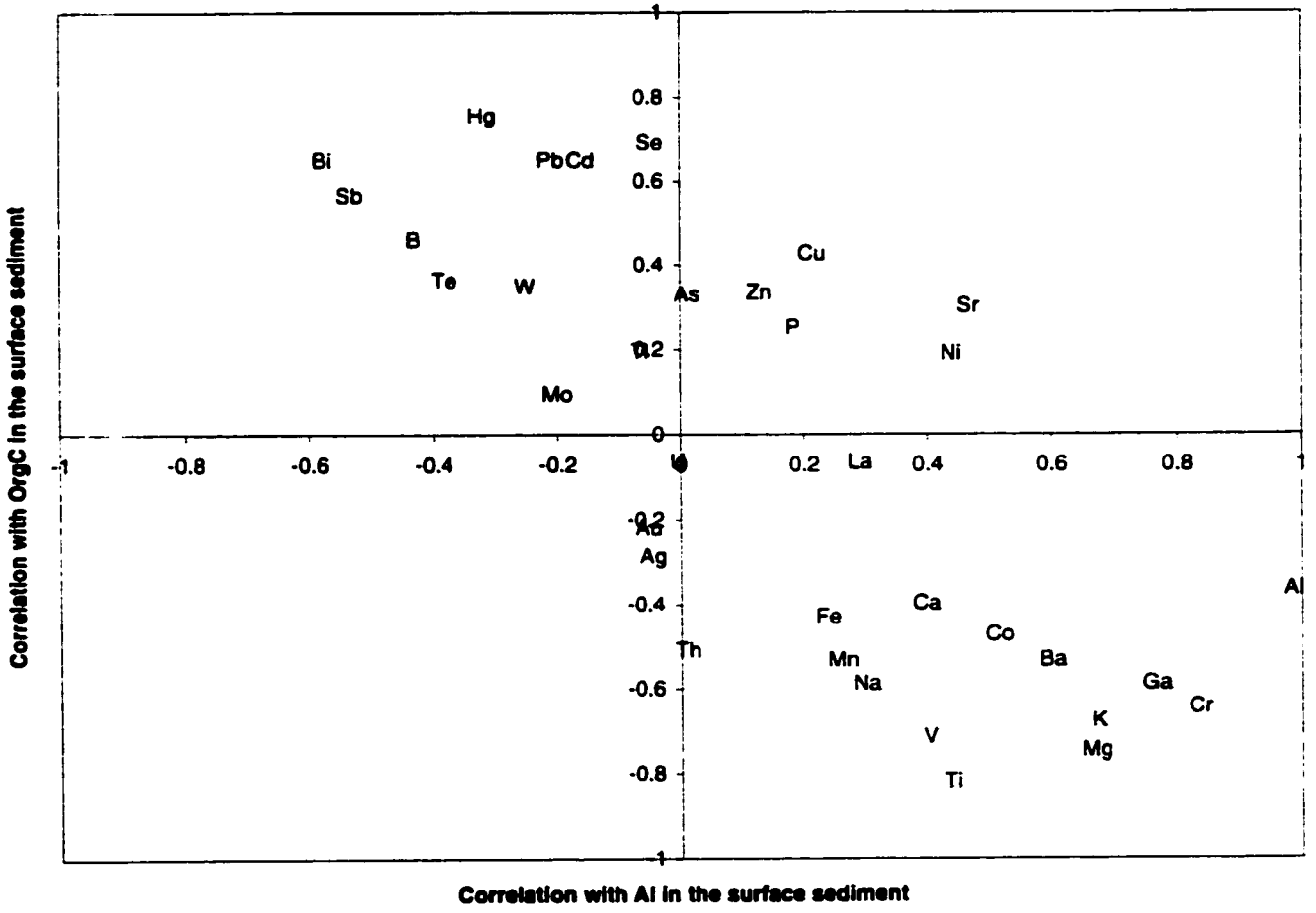

Fig. 5. Graph summarizing relationships between trace metals, Al and organic carbon in the sediment cores from the 20 lakes (n=20). Average concentrations were calculated for each lake from the 0-10 cm intervals. Positive correlations are indicated by the positive axis, and negative correlations are indicated by the negative axis.

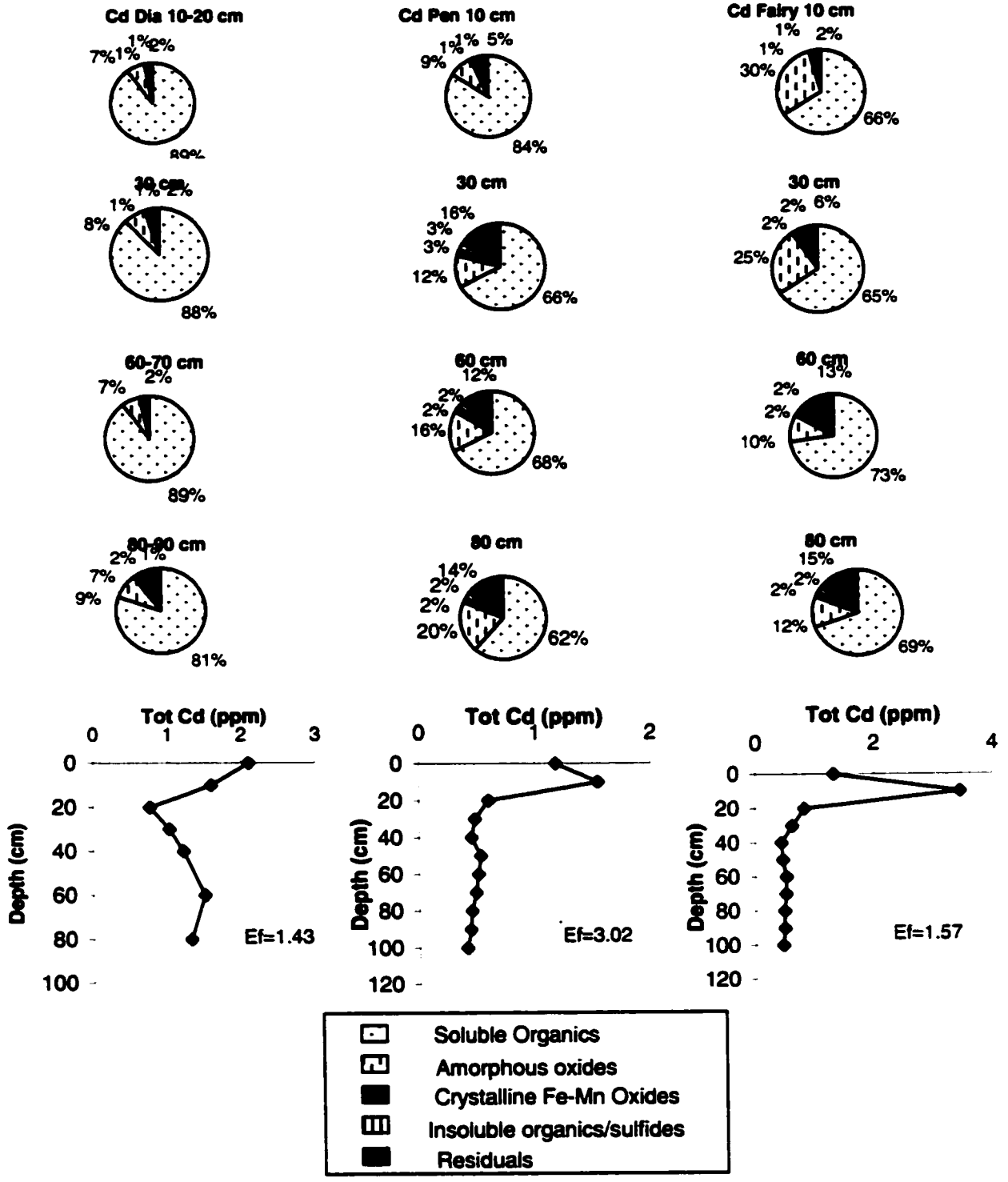

Fig. 6. Variation of total Cd concentration with depth, and partioning of Cd amongst five fractions at various depths in Lakesediments cores as revealed bysequential extra results. Dia= Diamond Lake, Pen= Peninsula Lake, Fairy =FairyLake. Ef= enrichment factor. Note the high % of Cd associated with soluble organics at all depths

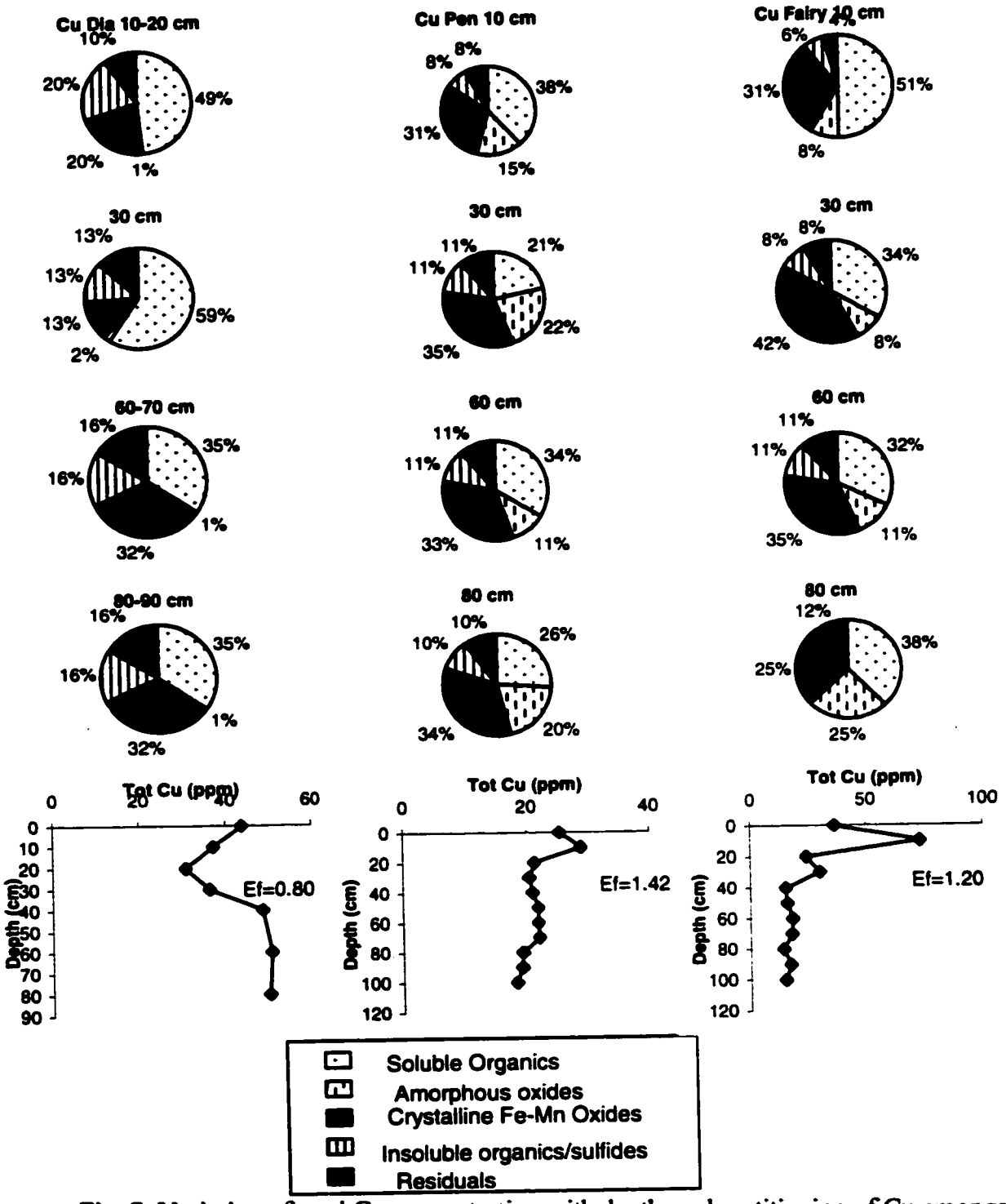

Fig. 7. Variation of total Cu concentration with depth, and partitioning of Cu amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor.

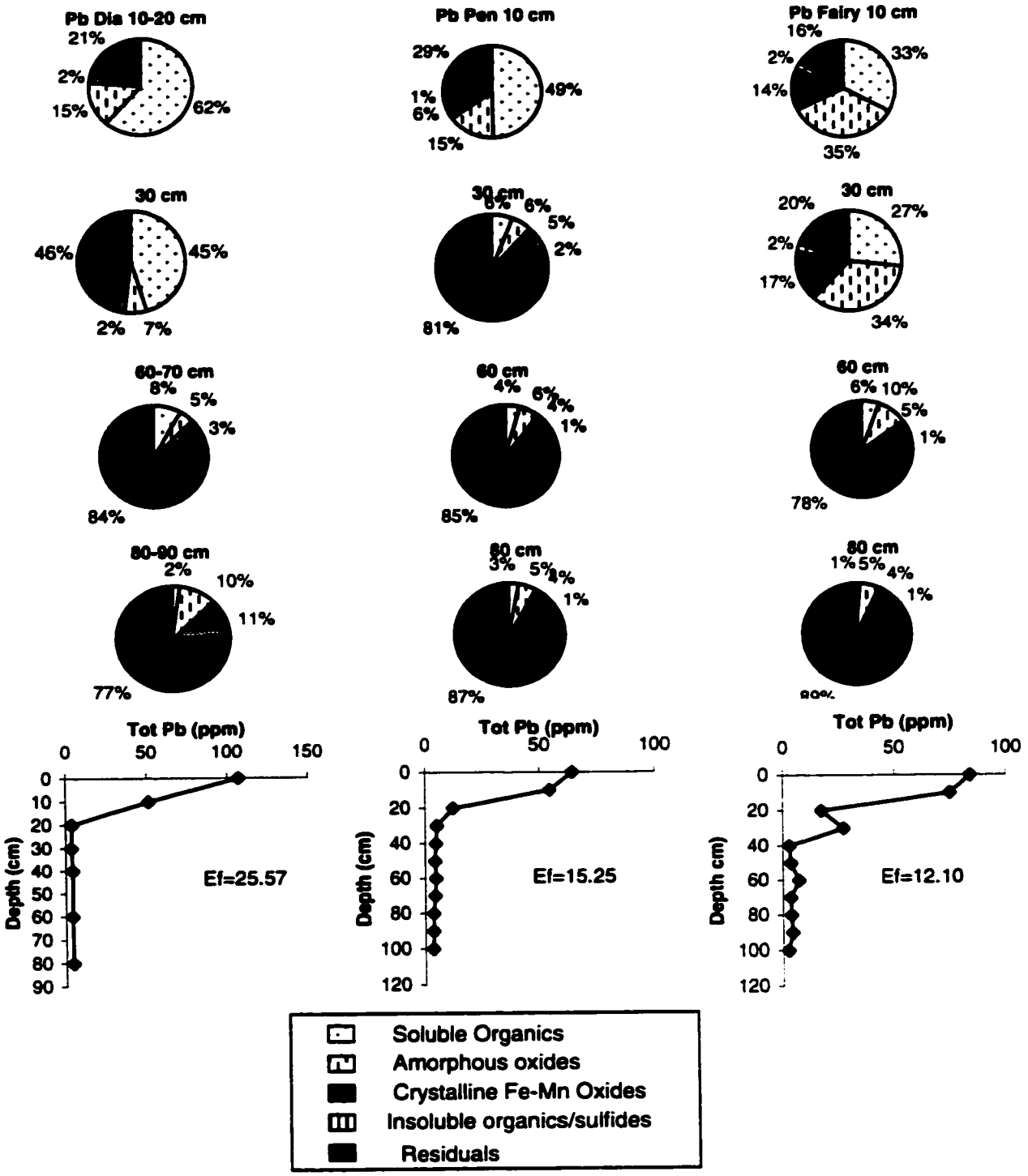

Fig. 8. Variation of total Pb concentration with depth, and partitioning of Pb amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor.

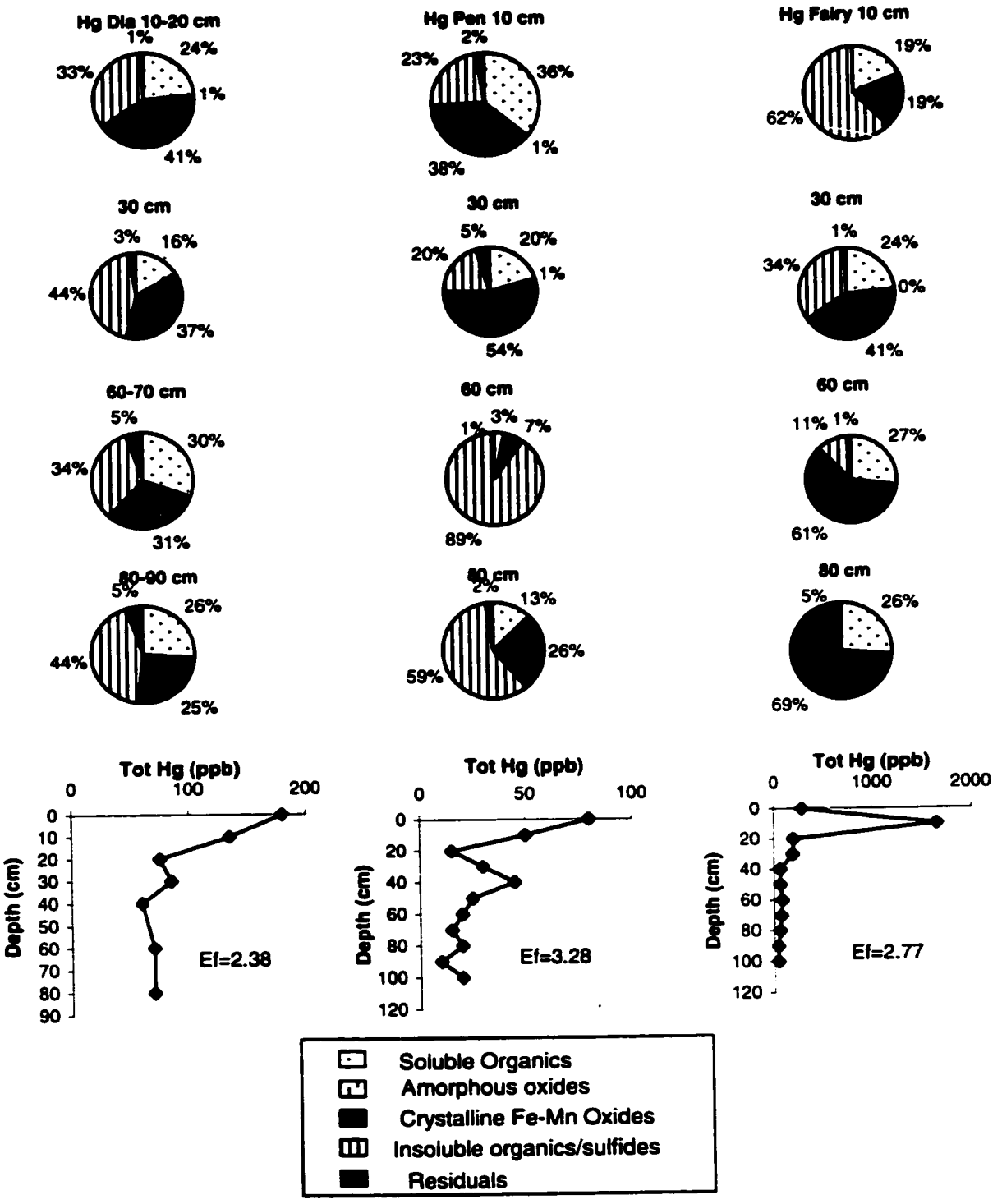

Fig. 9. Variation of total Hg concentration with depth, and partitioning of Hg amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor.

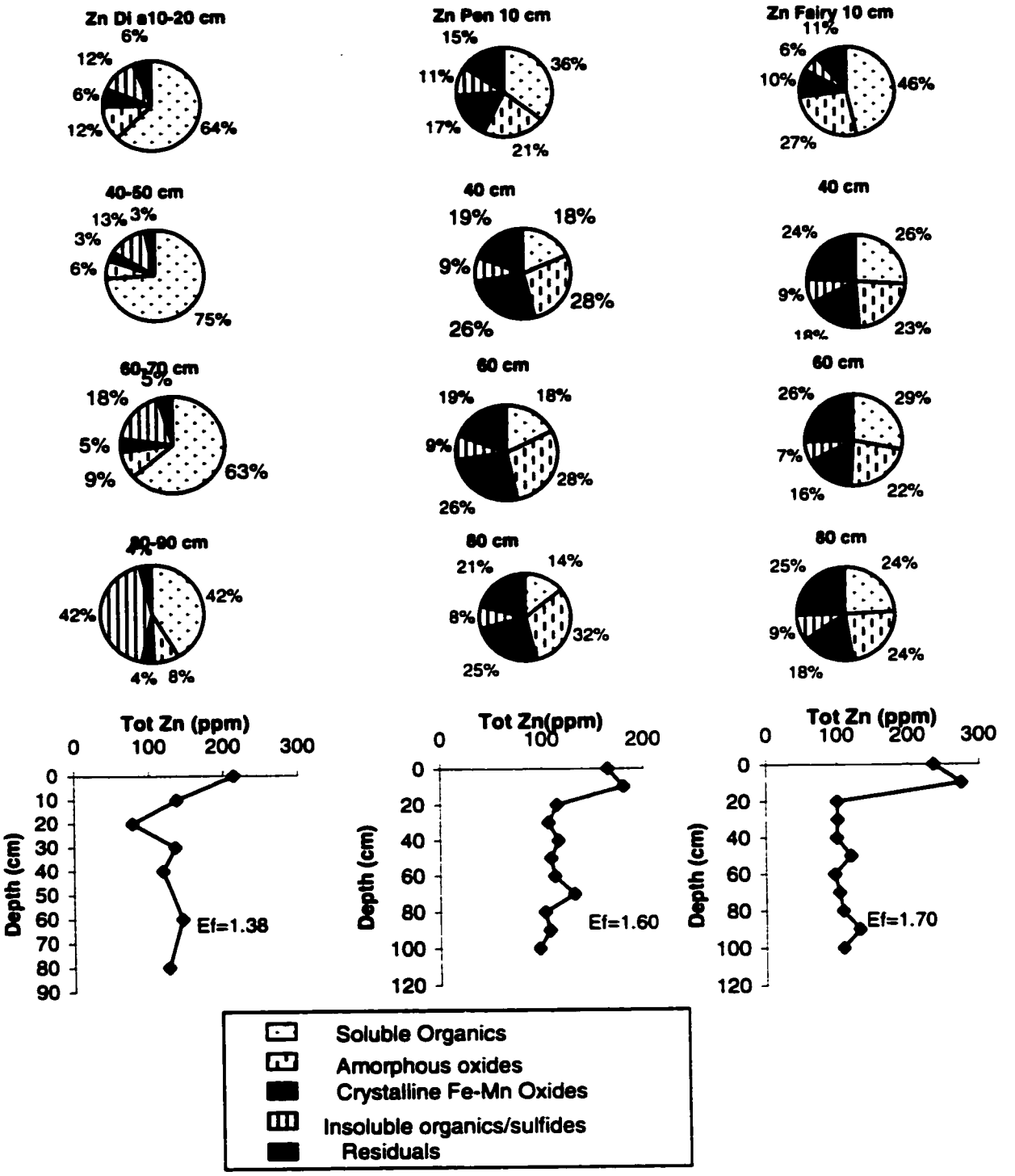

Fig. 10. Variation of total Zn concentration with depth, and partitioning of Zn amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor.

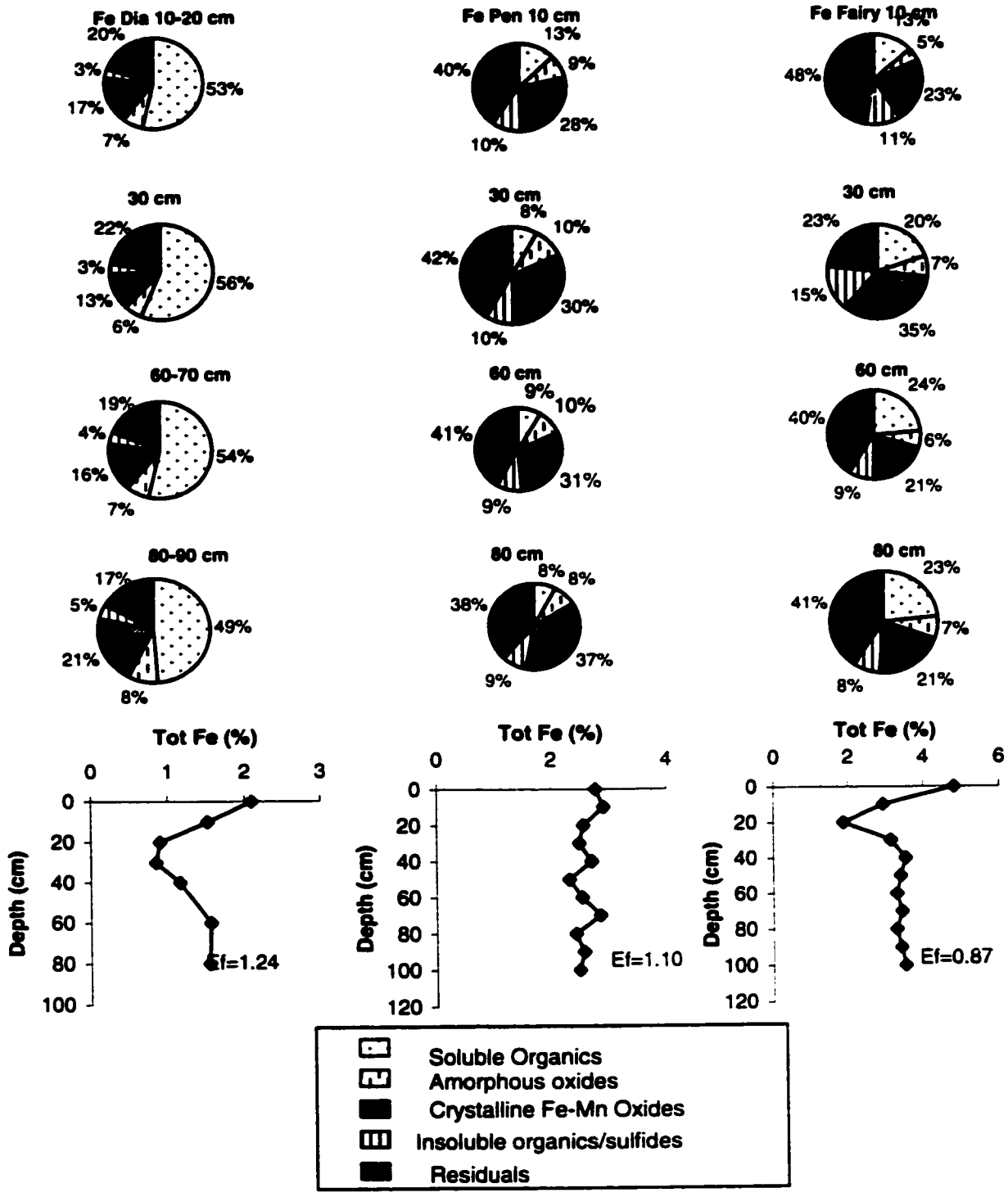

Fig. 11. Variation of total Fe concentration with depth Partitioning of Fe amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor

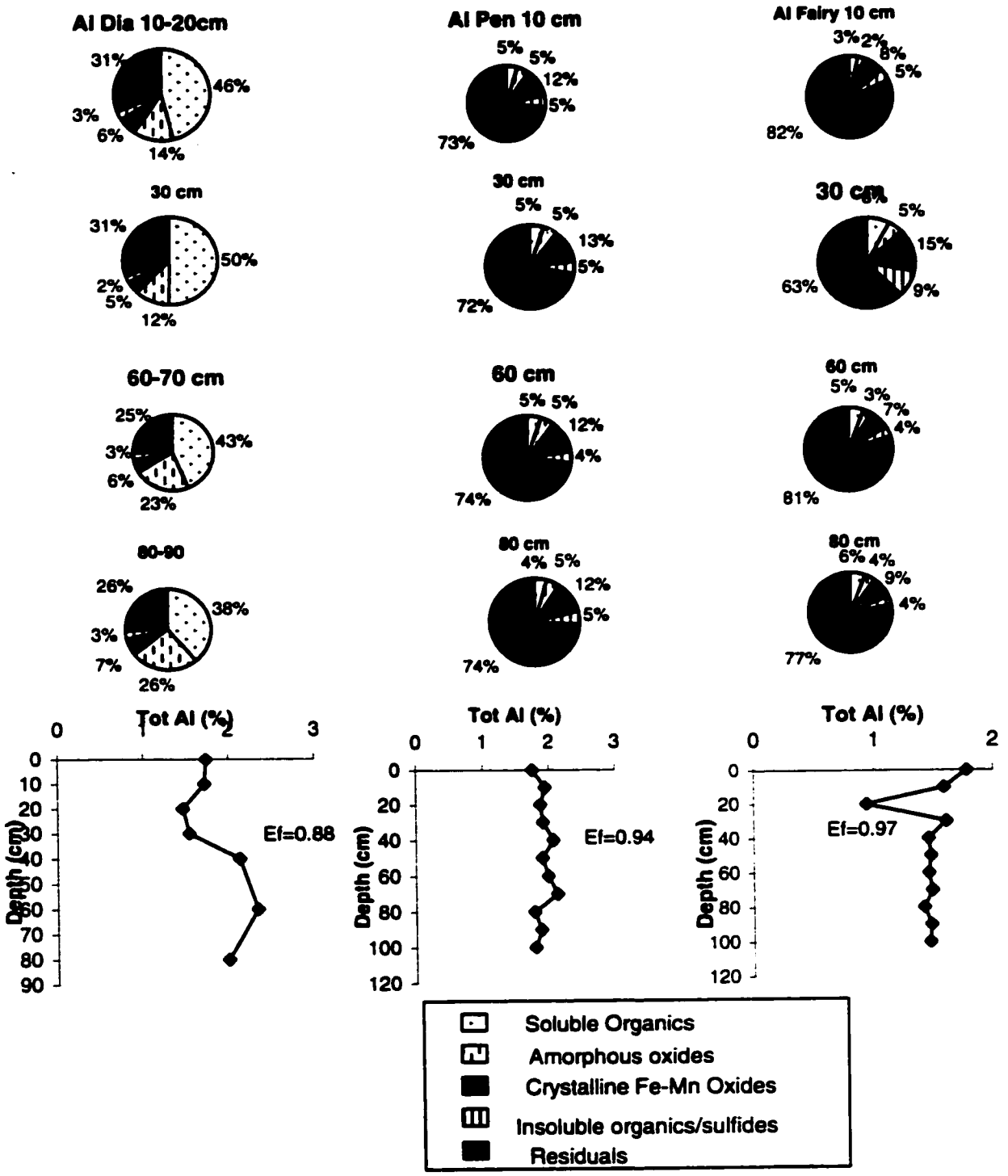

Fig. 12. Variation of total Al concentration with depth, and partitioning of Al amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor

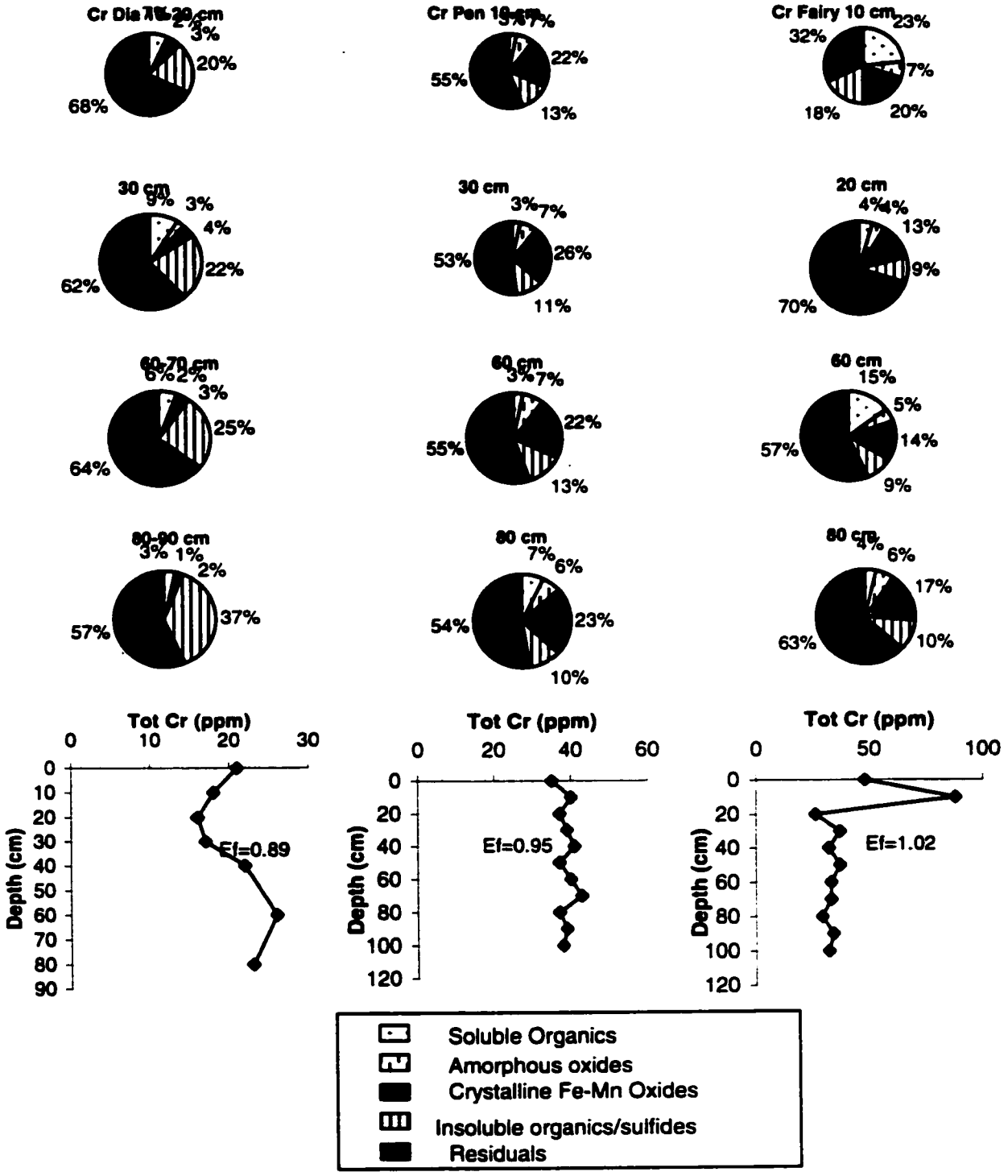

Fig. 13. Variation of total Cr concentration with depth, and partitioning of Cr amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef= enrichment factor.

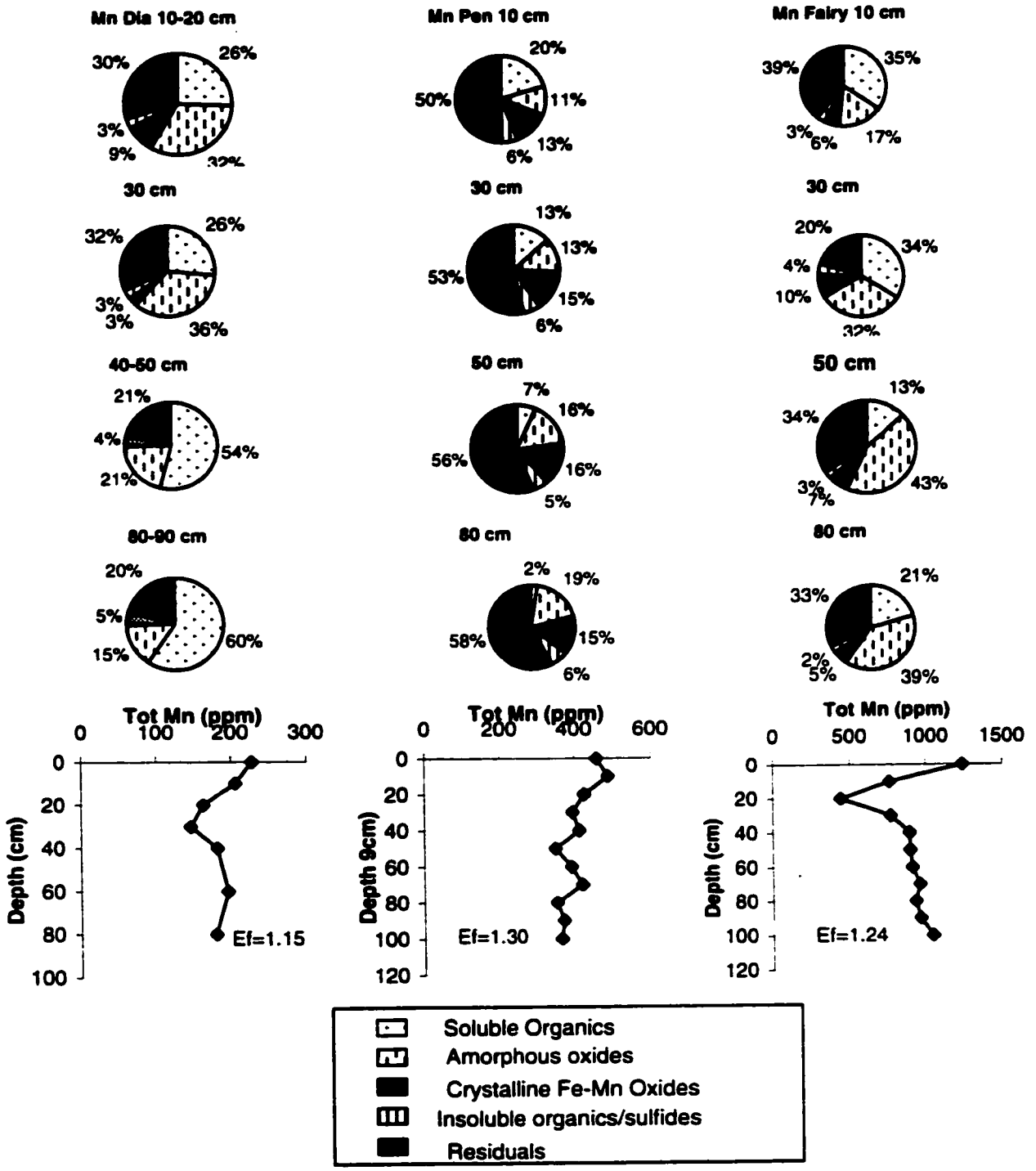

Fig. 14. Variation of total Mn concentration with depth, and Partitioning of Mn amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor.

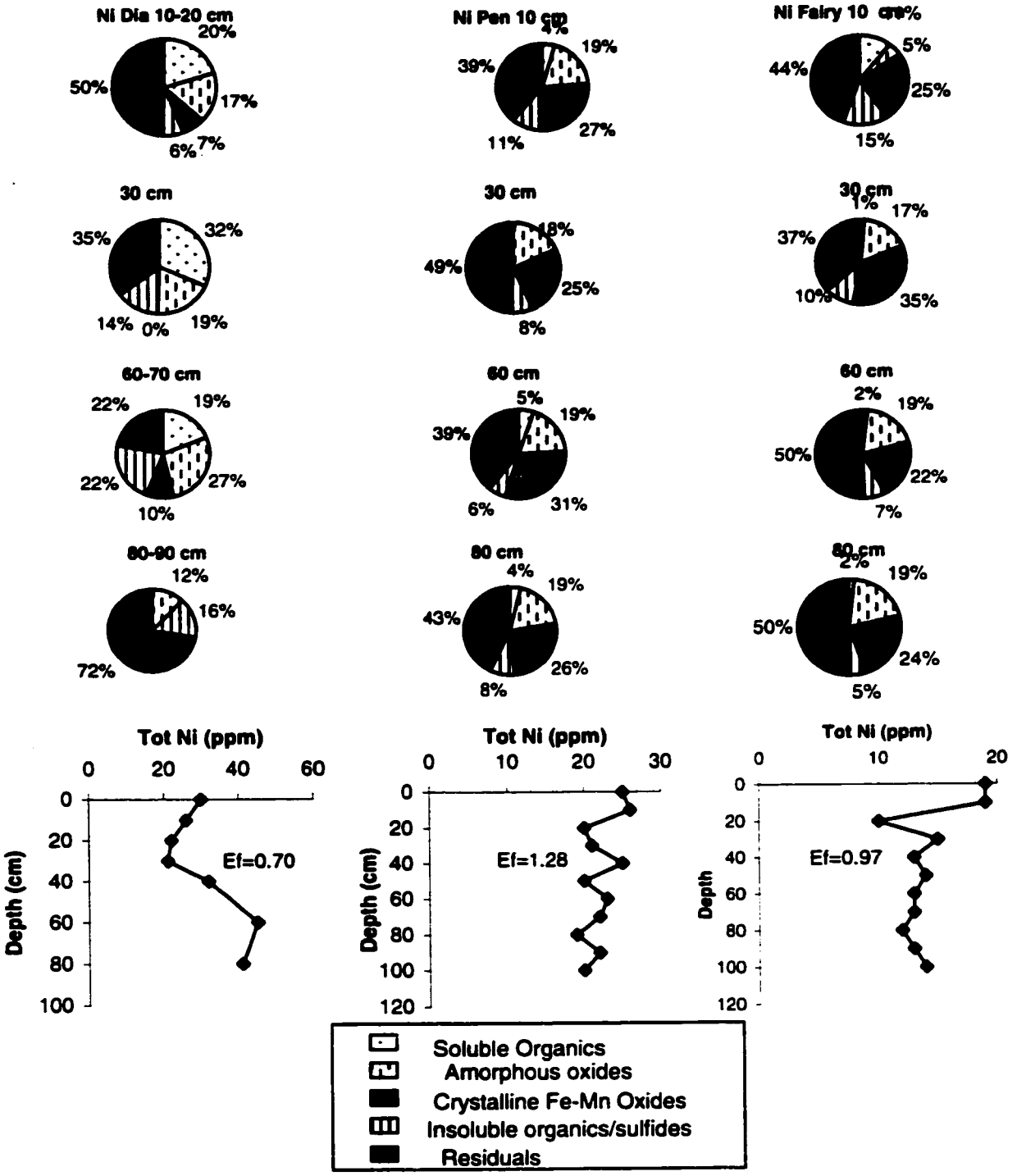

Fig. 15. Variation of total Ni concentration with depth, and partitioning of Ni amongst five sediment fractions at various depths in lake sediment cores, as revealed by sequential extraction results. Dia = Diamond Lake, Pen = Peninsula Lake, Fairy = Fairy Lake. Ef = enrichment factor.

Manuscript 2

Sedimentation rates and metal fluxes in two remote lakes of Clyde Forks, Lanark County, Ontario. Canada: The role of local geology.

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Abstract

Sediment traps were deployed in two circum-neutral remote lakes, Lavant Long Lake and Perch Lake, in Lanark County, southeastern Ontario, Canada, to measure sedimentation rates, to quantify trace element fluxes from watershed and atmospheric sources, and to investigate the distribution of elements amongst component phases of the trapped sediments. Average sedimentation rates were in the order of 4.8 g m^{-2} day^{-1} for Lavant Long Lake and 5.6 g m^{-2} day^{-1} for Perch Lake. Total element fluxes were calculated on the basis of the sedimentation rates and on concentration values in the trapped sediments determined using ICP-MS for As, Cd, Pb, Cu, Sb, Zr, Mo; ICP-OES for Fe, Al, Mn, Ni, Co, Cr, Cu, Zn; and cold vapour AAS for Hg. A comparison of the measured elemental fluxes with published mean atmospheric deposition rates for rural southern Ontario indicates that local watershed sources are the dominant source of Hg, Cu, Al, Fe, Mn, and Sb, in both lakes. This is consistent with previous observations of pyrite (Fe_2S), chalcopyrite ($CuFeS_2$), tetrahedrite ($Cu_{12}Sb_4S_{13}$), and cinnabar (HgS) mineralization in the bedrock of the study area and the occurrence of these elements in elevated concentrations in glacial and postglacial deposits of the study area. In the case of Ni and Cd, inputs from local watersheds are in the same range as atmospheric deposition rates. Sequential extractions indicate that a significant proportion of the elements Hg, Cu, Fe, and Sb occurs in the sulphide/insoluble organic fraction of the trapped sediments.

1. Introduction

Trace metal increases in the environment have been the focus of many studies in the last three decades (Nriagu 1979; Nriagu *et al.*, 1982; Wong *et al.*, 1984; Patterson and Settle, 1987). Most agree that human activities such as fossil fuel combustion (containing additives such as lead in gasoline), ore roasting for refining metals, and the processing of crustal materials for manufacturing cement, result in high levels of trace metals in the environment. Attention focused on atmospheric pollution, because the latter was considered the main pathway for trace metal transport and dispersion into ecosystems such as lakes, forests, and oceans (Lantzy and Mackenzie, 1978; Galloway and Lickens, 1979; Siccama *et al.*, 1980).

Several approaches have been used to establish the magnitude of trace metal atmospheric deposition fluxes versus their natural background. For example, ice cores have been used to establish historical trends of Pb fluxes (Boutron and Patterson, 1987; Wolff and Peel, 1985). Lake and marine sediments have also been used to establish historical trends of metals (Shirahata *et al.*, 1980; Veron *et al.*, 1987). However, data on natural background fluxes of metals to freshwater lakes are still scarce, due in part to the variability of factors controlling aqueous metal inputs, and in part to the confounding influence that post-depositional processes may play in the vertical re-distribution of metals in lake sediments. Examples of these processes include 1) the role of the geochemical composition of the lake sediments in metal distribution (Rasmussen *et al.*, 1998); 2) diagenetic processes such as the relocation of trace metals within the sediment (Engstrom and Wright, 1984), 3) the deposition of metals, by diffusion, in sediments not of the same age as the sedimentation processes (Carignan and Tessier, 1985), and 4) the

loss of trace metals from the sediments due to a change of the chemical conditions of the water column (Kahl and Norton, 1983). Moreover, converting measured concentration profiles into accurate time scales that correspond to atmospheric fluxes was and still is a challenge. One issue is the dating of lake and marine sediments using the ^{210}Pb or ^{137}Cs method. The distribution of ^{210}Pb and ^{137}Cs in sediments may be subject to post-depositional changes because element migration and the frequent physical resuspension, due to storm activity or bioturbation, tend to modify their original distribution (Lerman and Leitzke, 1975). In addition, it has been demonstrated that sediment focusing (movement of fine sediments from shallow to deep zones (Likens and Davis 1975; Lehman 1975) can result, in case of irregular basins, in different sedimentation rates in one lake basin (Nriagu *et al.*, 1982; Evans and Rigler, 1980). As a consequence, sedimentation and trace metal deposition rates calculated using these methods are subject to questioning.

In order to overcome the difficulties outlined above, sediment traps can be used as a tool to measure sedimentation rates and to study the geochemistry of the trapped sediments before they reach the bottom sediments and undergo post-depositional biogeochemical transformation and redistribution. Sediment traps have often been used to measure the rate of sedimentation and to quantify and characterize settling and suspended particulate matter, (Molonski and Klug., 1980; Eadie *et al.*, 1984; Sigleo and Schultz, 1993; Baker *et al.*, 1991). However, problems related to sediment trap design and bacterial growth have been reported to affect their collection efficiency and the integrity of the collected sediments, respectively (Gardner, 1980; Ducklow *et al.*, 1985; Hargrave and Burns, 1979; Bloesch, 1995). The collection efficiency of sediment traps can be

affected by vertical or horizontal currents (Oviatt and Nixon, 1975). However, traps with an open frame design exhibit a collection efficiency higher than 90% (Gardner, 1980; Bloesch and Burns, 1980), since this design reduces the resuspension effect of already settled sediments. On the other hand, the decomposition of collected particles, especially particulate organic carbon, by bacterial growth on the traps can be a problem (Ducklow *et al.*, 1985). Ducklow *et al.* (1985) examined the effect of bacterial abundance and productivity on samples from sediment traps and showed that decomposition rates depended on water depth, temperature, and on the time of deployment. They attributed this to their observation that bacterial growth was slower and decomposition rates were lower in colder, deeper layers compared to surface layers where bacteria were more abundant and decomposition was higher.

In this study, total metal fluxes to two neighbouring lakes are calculated on the basis of sediment fluxes measured using open frame structure sediment traps. The contribution from atmospheric deposition is estimated using accepted literature values applied to watersheds and lake areas calculated using a Geographic Information System. The two study lakes, Perch Lake and Lavant Long Lake, are isolated from roads and human activity. Therefore, based on the absence of local anthropogenic inputs, the local geogenic contribution from weathering of till and bedrock and release to surface and subsurface water may be derived by subtraction. In this way, we are avoiding the confounding factors inherent in the use of historical records to estimate natural background inputs. The distribution of metal distribution (Al, Fe, Mn, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Hg, Zn, and Zr) was investigated by conducting sequential chemical extractions on the trapped sediments from both lakes.

2. Study Area

Perch and Lavant Long Lakes are located 3 km west of the small village of Clyde Forks, Lanark County, Ontario, which is 100 km southwest of Ottawa (Fig. 1).

This area was chosen because both Perch and Lavant Long Lakes are remote lakes, with no roads, cottages or homes within 3.5 km. They are therefore isolated from any point sources of metals, such as domestic and/or local industrial inputs.

While the bedrock geology is characterized by the natural occurrences of sulphide mineralization (Jonasson, 1976), there are no present or historical mining or smelting activities within the watershed boundaries. The nearest smelters are located 550 and 700 km away, in Sudbury and Rouyn-Noranda respectively.

3. Geology:

The bedrock geology of the study area, as described by Kettles (1992), is characterized by Precambrian outcrops north of Lavant Long Lake and south of Perch Lake. These outcrops consist mainly of medium to high-grade gneiss, carbonate metasediments, metavolcanics, felsic and mafic intrusive rocks, and non-calcareous metasediments. Most of the study area is covered by discontinuous glacial deposits cover (till) less than 1m thick. The till consists of small deposits of sand and gravel or silty clay. Post glacial deposits are also present in the study area surrounding both Lavant Long and Perch Lakes and consist of muck and peat; their thickness varies from 1 to 5 meters and they occur in bogs, fens, swamps and poorly drained areas (Kettles, 1992).

Early work by Jonasson (1976) in the study area showed the presence of pyrite-magnetite mineralization in the gneiss in the vicinity of both lakes and tetrahedrite in the marbles at the east of Lavant Long Lake.

South of Lavant Long Lake and east of Perch Lake, mineralization consists of pyrite-chalcopyrite, tetrahedrite, and cinnabar in carbonate rich skarns and marbles, and barite.

4. Hydrology:

Perch Lake is located southwest of Lavant Long Lake (Figure 1). Water in Perch Lake originates from Robinson Lake in the south, via a chain of swamps and marshes (Figure 1). Water flows north from Perch Lake to join Middle Branch Creek, which connects to Lavant Long Lake. In Lavant Long Lake, surface water originates from Middle Branch Creek that connects waters from both Perch and Govan Lakes. Water from Lavant Long Lake flows northwest into Clyde Creek, which joins the Clyde River to the east of Clyde Forks village. Well developed forest floor and dense vegetation consisting mainly of white pine, white cedar and white birch surrounds both lakes.

5. Material and methods:

5.1. Watershed area and lake area calculation:

Perch and Lavant Long Lakes surface and watershed areas (Figure 1) were calculated using a GIS (geographic information system) (SPANS Explorer by TYDAC Technologies Inc.). The lake and watershed areas were: 1.01 km^2 and 24.65 km^2 for Lavant Long Lake and 0.21 km^2 and 5.13 km^2 for Perch Lake respectively.

5.2. Sediment trap description:

Each sediment trap consisted of a frame holding 7 identical polycarbonate cylinders. Each cylinder was 61 cm long with an internal diameter of 4.8 cm (Figures 2a). The frame had an open structure that reduced the amount of turbulence. It was also equipped with a fin that allowed it to swivel into the direction of the current (Figure 2b). Sediment traps with the above design are reported to have a collection efficiency of more than 90 % (Bloesh and Burns 1980; Gardner, 1980)

5.3. Sediment trap deployment:

Capped and acid- washed (10% HNO_3) tubes were loaded into the trap frame. Tubes were secured to the trap frame using plastic wire ties. The tubes were then filled by immersion in surface water and one tube was recapped at 3 feet for use as a field blank. The field blank was used to correct for the suspended sediment introduced during the initial filling. Subsurface buoys and an anchor beneath the trap provided vertical stability (Figure 2b). Traps were positioned at 4.5 m above the sediment-water interface to minimize sediment resuspension. Depth selection and the overall deployment procedure were done by scuba diving to ensure that the traps were maintained vertically, that the tubes were vertical, and that there was no contact with the sediments at the bottom of the lake.

5.4. Sediment trap recovery and processing:

Traps were recovered from the water column by securing them with safety line from the boat and gently bringing them up to the surface with the help of divers. Sediment trap

tubes were then all capped before bringing them on board, and stored in upright position in the trap frame in opaque plastic bags.

In the laboratory, the sediments were allowed to settle for several hours at room temperature. After settling, the overlying water was removed from each tube using a peristaltic pump until less than 45 mL of water remained at the bottom of the tube. The remaining material was re-suspended and poured quickly through a 215 μm Nytex zooplankton screen and funnelled into a labeled pre-weighed centrifuge tube. Each sediment trap tube was rinsed twice with distilled de-ionized water (DDI water), and the rinse water was also screened into the same tube. The screen and the funnel were also rinsed. An air space was left in the centrifuge tubes to allow for water expansion during freezing. Centrifuge tubes were sealed, frozen, and freeze-dried and weighed thereafter.

6. Sequential Extraction:

Metals from the freeze-dried sediments were sequentially extracted from six fractions using the scheme summarized in Table 1. The fractions included in this scheme are carbonates, amorphous iron and crystalline Mn oxides, sulphide/insoluble organics, and finally silicates. Solutions from each extraction were analyzed for As, Cd, Pb, Cu, Sb, Zr, and Mo using an inductively coupled plasma mass spectrometer *(ICP-MS)* and for Fe, Al, Mn, Ni, Co, Cr, Cu, Zn using an inductively coupled plasma optical emission spectrometer *(ICP-OES)*. Hg was analyzed using a cold vapour atomic absorption spectrometry technique. Sample replicates, and replicates of the CCRMPP lake sediment standard LKSD-4, and operational blanks were used for quality assessment and control.

7. Results and discussion

7.1. Rate of sedimentation in Lavant Long and Perch Lakes:

The mean sediment mass per tube deposited in the Lavant Long Lake trap over the period of deployment (July to August) was 0.30 ± 0.04 g (RSD = 12.3%, n = 6 tubes) (Table 2). In Perch Lake the mean sediment mass deposited per tube during the deployment period was 0.36 ± 0.05 g (RSD = 13.7%, n = 6 tubes). On average, the sediment flux corresponded to 4.83 g m^{-2} day^{-1} or to an annual average of 1.76 kg $m^{-2}year^{-1}$ for Lavant Long Lake, and 5.60 g m^{-2} day^{-1}or 2.04 kg $m^{-2}year^{-1}$for Perch Lake (Table 2).

Sediment fluxes were calculated as the weight of the freeze-dried sediments divided by the area of collection and the time of deployment (Table 2). These results were calculated based on the assumption that the measured sedimentation and trace metal deposition rates were constant with time and were representative for other periods of the year. The validity of these results was tested using another set of calculations based on the assumption that there was no trace metal deposition from the watershed for other times of the year (See below for results and discussion of the second set of calculations).

7.2. Total Metal Fluxes:

The total metal fluxes (F_t) to Perch and Lavant Long Lakes during the period of trap deployment were calculated as the sum of metal concentrations found in the six fractions of the sequential extraction (Table 3). In order to determine their equivalent rate in mg m^{-2} $year^{-1}$, the totals were calculated relatively to the yearly sedimentation rate per square meter in both lakes (2.04 kg m^{-2} $year^{-1}$ in Perch Lake and 1.76 kg m^{-2} $year^{-1}$ in Lavant Long Lake) (Table 4). In general, the results showed that total trace metal fluxes were

higher in Perch Lake than in Lavant Long Lake, with the exception of Mn and Hg which fluxes were higher in Lavant Long Lake than in Perch Lake (Table 4).

It has been shown that trace element loss from the trapped sediments and/or trace metal input from the underlying sediments into the traps could influence the measured total metal flux (F_t) (Charlton, 1983). Both Perch Lake and Lavant Long Lake are circum-neutral (pH = 7.37 in Lavant Long Lake and pH = 7.22 in Perch Lake) and have an oxygenated water column. In such lakes, the amount of trace metals regenerated from the particulate fractions (suspended and sediments) to the water column can be expected to be negligible (Nriagu *et al.*, 1982; Wong *et al.*, 1984; Kramer 1976; Kahl and Norton 1983; Young and Harvey, 1992). Consequently, since the chemistry of the study lakes does not favour regeneration of metals from the sediments to the waters column, it is likely that the total flux measured from the trapped sediments is representative of the two main contributing fluxes (atmospheric and aqueous). Moreover, at the sedimentation rate measured in both lakes the amount of suspended sediment is ~ 1% (Charlton, 1983).

7.3. Loading calculations and results:

In order to evaluate the importance of the local geological and the atmospheric contributions to the total flux in both lakes, we first evaluated the importance of the watershed loading to each lake, by resolving the following equation (Figure 3):

$$F_t = F_{ws} + F_{dir} \qquad (1)$$

where F_t is the measured total deposition of a trace metal expressed in mg $year^{-1}$ m^{-2} (Table 4), F_{dir} is the atmospheric deposition directly to the lake surface based on the

published values from Jeffries and Snyder (1981) for the net atmospheric deposition for Pb, Cd, Cu, Ni, Zn, Al, Mn and Fe in rural North America and Mierle (1990) for mercury, and where F_{ws} corresponds to the contribution of the watersheds. The F_{dir} values used in this study (from the published work by Jeffries and Snyder, 1981) may be higher than the present day values, due to a decrease in the emission of some metals to the atmosphere as consequence of recent environmental guidelines as reported in the case of Pb (Eisenreich *et al.*, 1986; Vile *et al.*, 2000) and Hg in Canada, as reported by the National Pollutant Release Inventory (Environment Canada, 1997). However, they allow us to compare, to a certain extent, the importance of the geological and atmospheric fluxes.

F_{ws} was then calculated by subtracting F_{dir} from F_t (equation 1). The contribution from the watersheds (F_{ws}) depends on two fluxes, i.e., on the metal flux from geological weathering, which includes trace elements from surface and groundwater (F_{gw}) and on the metal flux from the indirect contribution of the atmosphere (F_{ind}) (equation. 2).

$$F_{ws} = F_{gw} + F_{ind} \qquad (2)$$

The latter (F_{ind}) is influenced by the watershed area to the lake area ratio (r), and also by the fraction of trace metals released to the water run-off after atmospheric deposition (k) (equation 3).

$$F_{ws} = F_{gw} + k F_{dir} r \qquad (3)$$

F_{gw} is unknown; however, it can be estimated if F_{ind} (k F_{dir} r) is determined from equation 3. By determining F_{gw}, we can evaluate the importance of the geological and the atmospheric flux contributions to the total metal flux in a lake.

Many studies (Mierle. 1990; LaZerte et al, 1989; Arden *et al.*, 1975; Smith and Siccama, 1981; Friedland *et al.*, 1986; Siccama *et al.*, 1980; Troutman and Peters, 1980) have shown that a high proportion of trace metals from atmospheric deposition can be retained within the watersheds, with only a small fraction (k) supplied to the watershed flux (F_{ws}) as an indirect atmospheric contribution. In this study, we have used k values from the literature to carry out our calculations (see Table 4 for k values and their sources). Values for k were chosen from case studies, which considered parameters such as the abundance of organic matter on the forest floor, presence of poorly drained soils etc. An early study by Schnitzer (1978) demonstrated that the forest floor (the organic horizon of soil comprised of decomposing needles, leaves, twigs, that overlies the mineral soil) is an effective accumulator of metals. Friedland (1990) also showed that humic substances interact strongly with metals in soils. In our study area, the watersheds of both lakes contain a well developed forest floor and the lakes are surrounded by poorly drained postglacial deposits (1-5 m thick) consisting of muck and peat (Kettles, 1992). These observations suggest that high amounts of trace metals from the direct deposition should be retained in the watersheds. However, an arbitrary value of k=1 (100%), was used to calculate fluxes for Mn, Fe, and Al, because they were not available in the literature. Thus, these calculations will result in maximum values for atmospheric input of Mn, Fe,

and Al. In our calculation of F_{ws}, the role of the watershed area to the lake area ratio had to be taken into account. Technically, F_{ws} should be proportional to the size of the catchment, although in reality, many studies have reported no relationships between metal concentration in lake sediments and the watershed area to lake area ratios (Dillon and Evans, 1982; Arden *et al.*, 1975; Mierle, 1990). Based on the results from the watershed and lake area calculations using GIS, the ratio *r* (watershed area to lake area ratio) was 24.36 for Lavant Long and 24.83 for Perch Lake.

Results for F_{ind}, F_{gw}, and F_{ws}, calculations (Tables 5, and 6) showed that in Lavant Long Lake, all the trace metals, except Cd and Ni, presented high F_{ws} values. The latter were mainly influenced by the high F_{gw} values and the low atmospheric flux ($F_{dir} + F_{ind}$). In Lavant Long Lake, the F_{gw} and atmospheric fluxes of Cd and Ni were similar (Tables 5 and 6). Our calculations also showed that F_{gw} for Hg represented the highest contribution to the total (99.67% of F_t) when compared to F_{gw} of other metals (Table 6). Several studies (Kemp *et al.*, 1978; Lindqvist *et al.*, 1991; Swain *et al.*, 1992) related Hg enrichment in surface sediments from remote lakes to the increase in atmospheric loading caused by human activity regardless of potential post-depositional processes and suggested a standard ratio of Hg from anthropogenic to natural sources of 3/1 for Hg. Our results showed, based on flux calculation using sediment traps, that the aqueous pathway dominated over the atmospheric pathway because of the high flux from geochemical weathering (F_{gw}). When F_{gw} (considered natural flux obtained by subtraction) was compared to Hg flux from atmospheric deposition (both direct and indirect) the ratio was ~9:1.

In both lakes, the results showed that even if 100% of Al, Fe, and Mn deposited from the atmosphere onto the terrestrial portion were released to the run-off, the geological contribution of these metals would exceed their atmospheric contribution.

In Perch Lake in general, F_{gw} values generally exceeded the atmospheric values ($\Sigma F_{dir} + F_{ind}$) for most of the elements. Similar to Lavant Long Lake, F_{gw} values calculated for Cd and Ni were low comparatively to F_{gw} values calculated for the rest of the elements (Tables 5, and 6). Hg flux from geochemical weathering was lower in Perch Lake (13.97 mg $year^{-1}$ m^{-2}) than in Lavant Long Lake (15.20 mg m^{-2} $year^{-1}$) but its contribution to F_t was higher (99.64%) than $\Sigma F_{dir} + F_{ind}$ (0.36%).

These results can be explained by the fact that Cd and Ni naturally occur at low levels in the watershed areas of the two lakes. In fact, the geochemical survey carried out at the Clyde Forks-Westport area of Ontario, (Kettles, 1992) showed that Cd and Ni occurred at very low levels in the postglacial deposits in the watersheds of both lakes. The same survey showed that the Ni content of the glacial sediments ranged from 4 to 45 ppm, whereas Cd presented concentrations below 0.05 ppm.

A limitation of the above flux calculations is that they are based on an extrapolation from daily to annual sedimentation rate, assuming that the deposition rates were constant with time. It is possible that during other periods of the year, both sedimentation and trace metal fluxes, especially F_{ws}, may be low and hence the above results may be affected. To account for this possibility, we have made a separate set of calculations (as mentioned

earlier) assuming that F_{ws} = 0 for all other times of the year, and that F_{dir} remains constant with time throughout the whole year. This way, we are assuming that there was no contribution from the watersheds (F_{ws} =0) out of the period of deployment. F_{gw} becomes F_{gw}' (= F_{gw} /12 months) (Table 6). The results showed that Hg, Cu, Al, Fe, Mn, fluxes from the geological source were still higher than the deposition rate from the atmosphere even though our new assumptions result in a minimum (probably unrealistically low) geological flux calculation. The above result is consistent with their abundance at high levels in the bedrock and the postglacial deposit as mentioned earlier, although our latest assumption is unrealistically low as metal fluxes from the watershed to lakes only decrease not disappear during the winter periods (Mierle, 1990).

7.4. Metal distribution.

In Lavant Long Lake, As, Pb, Mn, and Ba were predominantely associated with carbonates, while Cd and Zn were predominately associated with amorphous oxides (Table 7). In Perch Lake, only Mn and Ba were usually associated with carbonates, while As, Cd, Pb, and Zn were predominately associated with amorphous oxides (Table 7). In both lakes Al and Zr were mainly associated with silicates, while Cu, Fe, Ni, Hg, and Sb were predominately associated with the sulphide/insoluble organic fraction (Table 7). These observations are consistent with the high F_{gw} calculated values for these elements (Tables 4-5), since they occur as $CuFeS_2$ (chalcopyrite), FeS_2 (pyrite), HgS (cinnabar), $Cu_{12}Sb_4S_{13}$ (tetrahedrite) in the bedrock of the study area (Jonasson, 1976; Kettles 1992). Moreover, elements such as Al and Zr which predominately occur in the silicate fraction in lake sediments (Table 7), are contributed by weathering of siliceous gneiss and

aluminosilicates minerals in bedrock and glacial overburden may indicate, to some extent, the geological contribution, since both elements occurred mostly in the silicate fraction in the bedrock of the study area.

8. Conclusion:

Our results indicate that trace metal fluxes from geochemical weathering in watersheds of both Perch Lake and Lavant Long Lake significantly exceed the direct and indirect atmospheric deposition rates for most elements. This strongly suggests that geological materials are the main source of trace metal in surface waters of these remote lakes basins. Our findings are in agreement with other studies whereby the local geological contribution is typically not negligible and should be carefully considered in the studies of global geochemical cycles of trace elements.

Whether in soils, in bottom lake sediments or in the trapped sediments, sequential extractions from manuscripts 1 and 2 demonstrated the strong interaction between organic matter and trace metals. On the other hand, organic matter undergoes transformation and decay once buried and metal-organic matter compounds can be remobilized from one depth to another. Thus, it will be important to investigate how these transformations and remobilization influence the trace metals-organic matter relationship in lake sediments and therefore trace metal distribution in lake sediments. The Manuscript 3 will investigate the importance of these processes in trace metal distribution in lake sediments.

Summary of Manusript 2

1- In Perch Lake and Lavant Long Lake, trace metal deposition rates showed, based on mass balance model that geogenic metal flux exceeded the atmospheric flux.

2- There was consistency between the trace metals with a high geogenic component and their occurrence at high levels in the bedrock and in the postglacial deposits in the watersheds of both study lakes.

3- The association of high amounts of Cu, Ni, Fe, Hg, Sb with the sulphide fraction in the sediments collected in the traps was consistent with their occurrences as sulphide minerals in the watersheds of the study area and hence supports the high geogenic metal flux.

Acknowledgments

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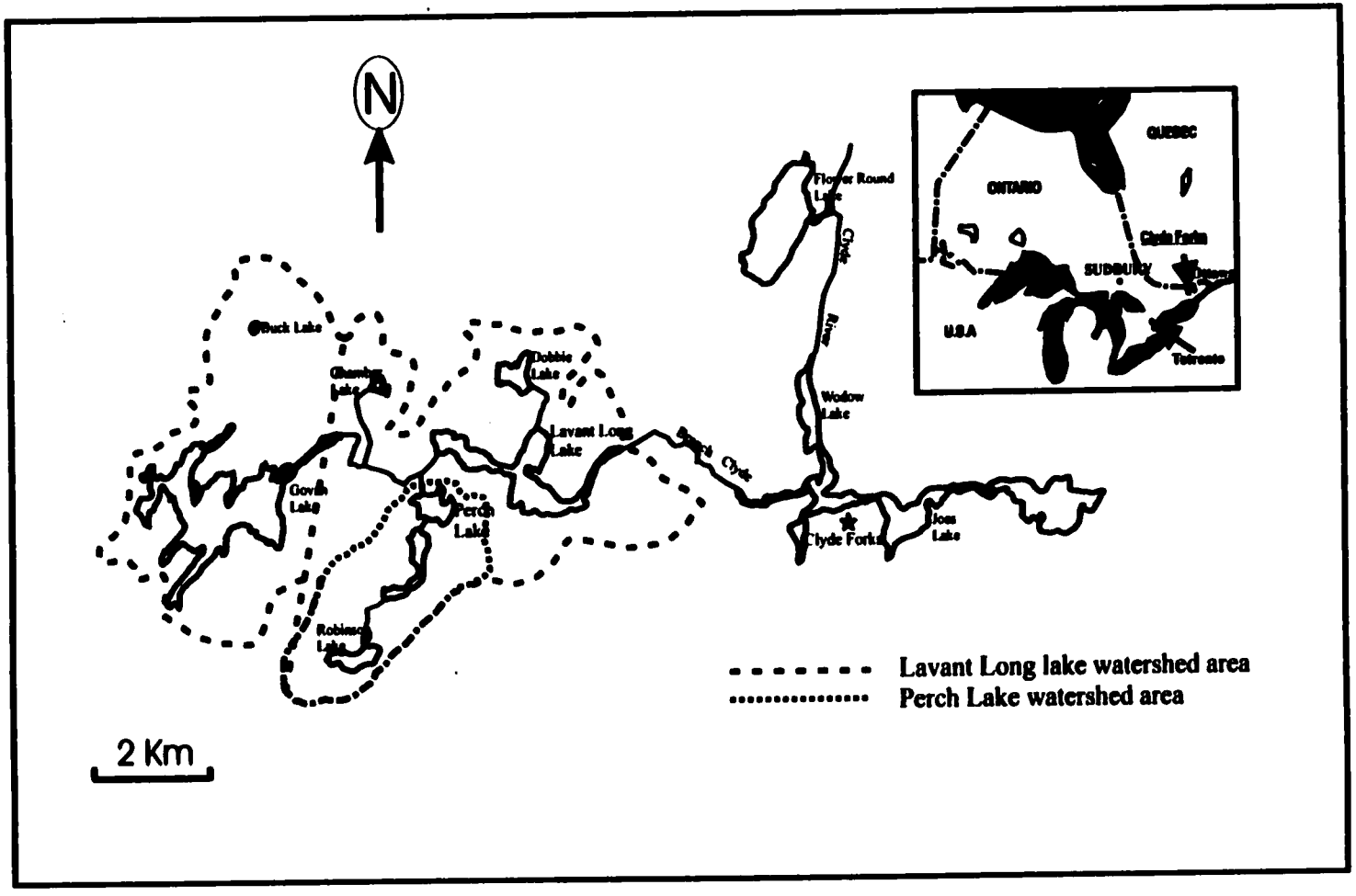

Fig. 1: Study area location in Ontario (a). Hdrology of the study area showing the watershed areas for both Lavant Long anf Perch Lakes (b).

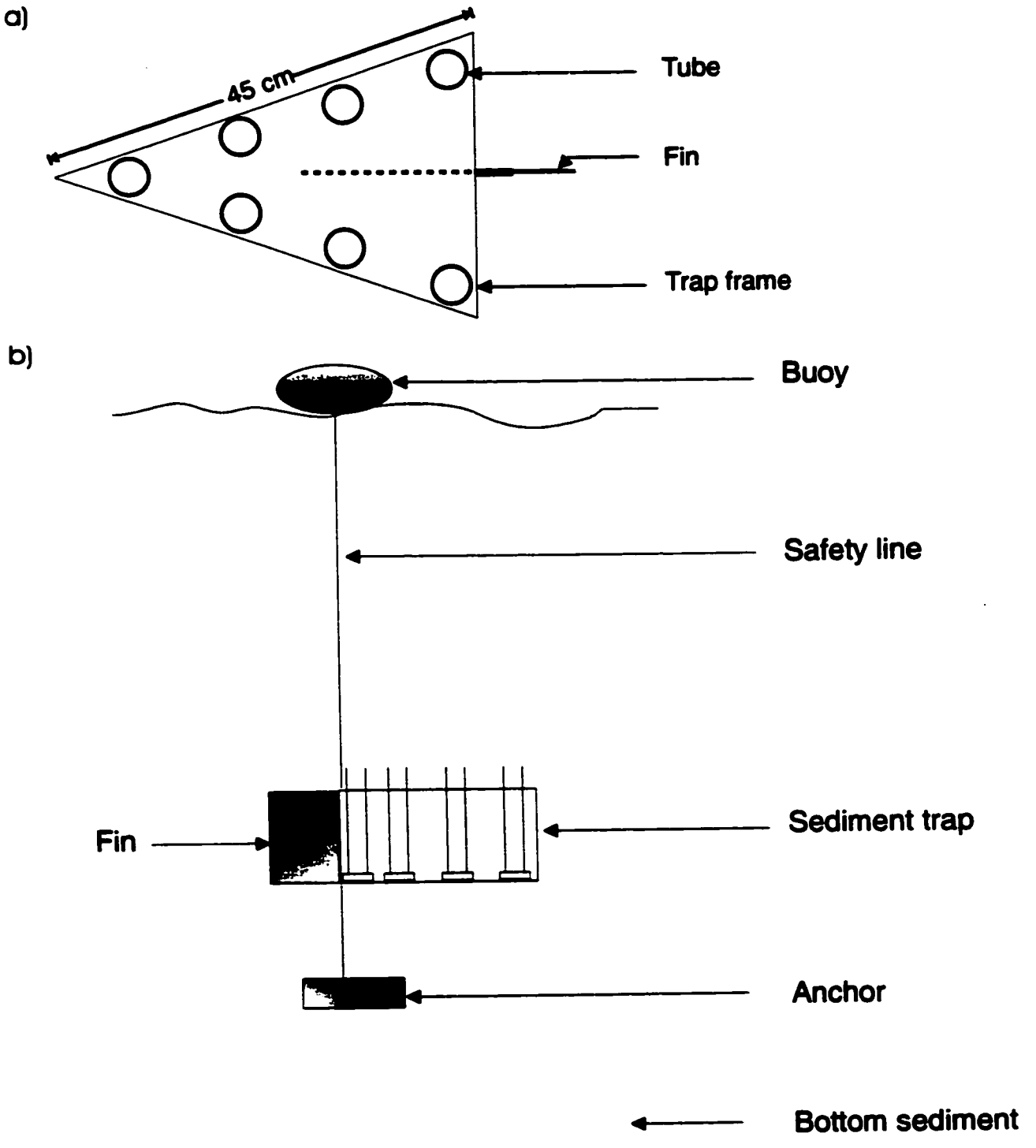

Fig. 2. a) Planar view of sediment trap structure. b)Side view of sediment trap deployment in lake environment.

$$F_t = F_{dir} + F_{ws}$$
$$F_{ws} = F_{ind} + F_{gw}$$
$$F_{ind} = krF_{dir}$$

F_t= total measured Flux
F_{dir}=direct atmospheric deposition Flux (literatur
F_{ws}=watershed Flux
F_{ind}=indirect atmospheric Flux
F_{gw}=geochemical weathering Flux
k=Fraction released to run-off (literature)
r=watershed area to lake area ratio(measured)

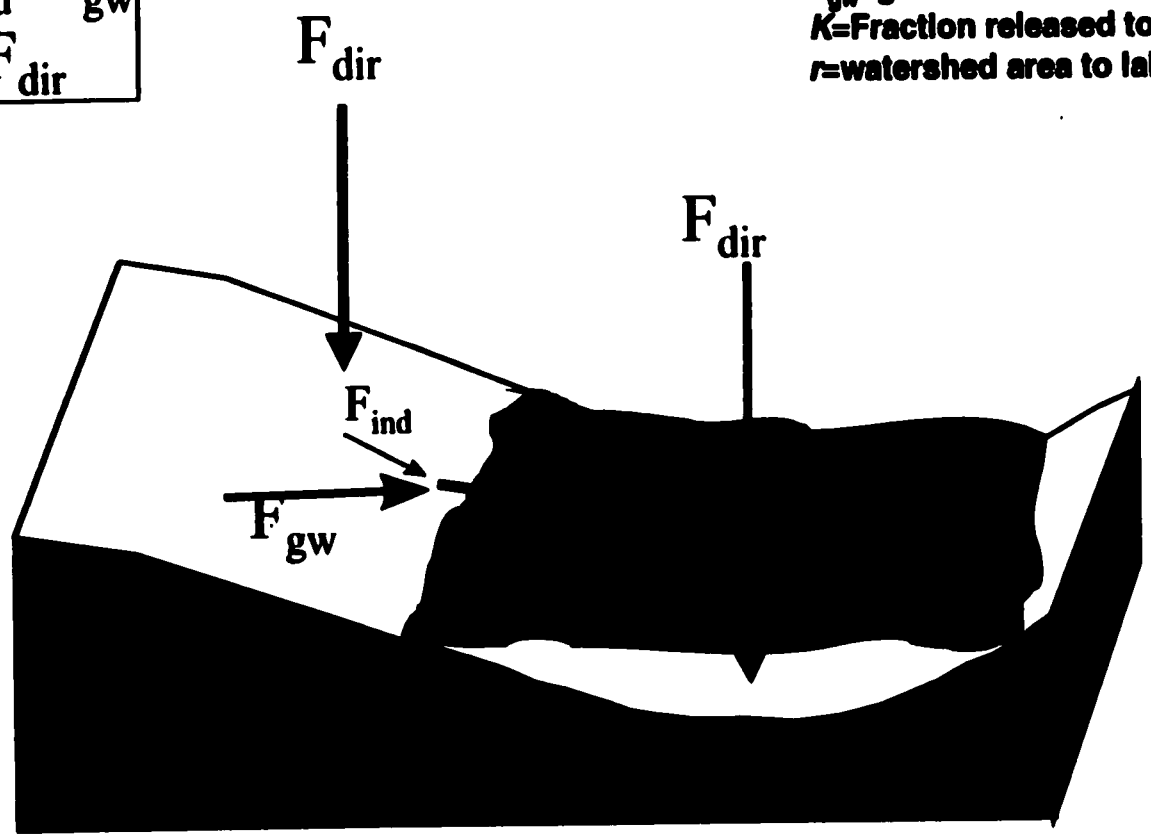

Fig. 3. Schematic representation of the major fluxes to the lakes, their components and the factors defining them.

Table 1. Sequential extraction scheme.

Fraction	Reageant	Source
F1: Carbonates	1 M CH3COONa	Tessier *et al*., 1979
F2: Soluble Organics	0.1 M Na4P2O7 (pH 10)	Hall and Pelchat, 1997
F3: Amorphous oxides	0.25 M NH2OH.HCl	Chao and Zhou, 1983
F4: Crystalline oxides	1 M NH2OH.HCl in 25% CH3COOH	Chester and Hughes, 1967
F5: Sulphide/insoluble organics	KClO3-HCl-HNO3	Chao and Sanzalone, 1977
F6: Silicates	HF-HClO4-HNO3	Tessier *et al*., 1979

Table 2. Measured average sediment deposition (g) based on sediment weights in the six tubes of each sediment trap, and the calculated sedimentation rate (g $m^2 day^{-1}$).

Lavant Long Lake		*Perch Lake*	
Tubes	weight (g)	Tubes	weight (g)
LLT1	0.33	TPL1	0.35
LLT2	0.27	TPL2	0.28
LLT3	0.35	TPL3	0.31
LLT4	0.32	TPL4	0.41
LLT5	0.26	TPL5	0.39
LLT6	0.27	TPL61	0.40
Mean	*0.30*	*Mean*	*0.36*
STDEV	*0.04*	*STDEV*	*0.05*
RSD	*12%*	*RSD*	*13.7%*
Rate of sedimentation	4.84	Rate of sedimentation	5.60
Deployment date/time	Jul 4/2:15	Deployment date/time	Jul 25/2:30
Recovery date/time	Aug 8/12:30	Recovery date/time	Aug 29/2:45

Table3. Total metal fluxes (F_t) in mg m^{-2} day^{-1} and in mg m^{-2} y^{-1}, in both Lavant Long Lake (LL) and Perch Lake (PL).

	Lavant Long Lake		
	LL (µg/kg)	LL mg m^{-2} day^{-1}	LL mg m^{-2} y^{-1}
As	2855.81	0.01	5.04
Ba	117843.77	0.57	208.11
Cd	1112.89	0.01	1.97
Co	7223.11	0.03	12.76
Cr	6420.55	0.03	11.34
Cu	38055.11	0.18	67.21
Mo	1926.83	0.01	3.40
Ni	7958.80	0.04	14.06
Pb	72070.63	0.35	127.28
Sb	700.91	0.00	1.24
Zn	101658.64	0.49	179.53
Zr	7276.62	0.04	12.85
Hg	8636.54	0.04	15.25
Al	5343766.72	25.86	9437.09
Fe	11116238.63	53.80	19631.28
Mn	1798421.62	8.70	3176.01

	Perch Lake		
	PL (µg/kg)	PL mg m^{-2} day^{-1}	PL mg m^{-2} y^{-1}
As	4541.38	0.03	9.28
Ba	119261.03	0.67	243.77
Cd	1491.88	0.01	3.05
Co	9262.03	0.05	18.93
Cr	11054.68	0.06	22.60
Cu	114331.24	0.64	233.69
Mo	3784.48	0.02	7.74
Ni	13893.04	0.08	28.40
Pb	84872.02	0.48	173.48
Sb	771.34	0.00	1.58
Zn	156558.11	0.88	320.00
Zr	8012.15	0.04	16.38
Hg	6861.57	0.04	14.03
Al	7405138.93	41.47	15136.10
Fe	18387112.84	102.97	37583.26
Mn	858480.23	4.81	1754.73

Table 4. Summary of F_{gw} calculations and sources of F_{dir} and k.

Lavant Long Lake

Elements	F_t	F_{dir}	K(%)	F_{int}	F_{wp}	F_{gw}	Source of F_{dir}	Source of K
Cd	1.97	0.67	2%	0.33	1.30	0.97	Jeffries and Snyder (1981)	KCd=KPb (Siccama et al., 1980)
Cu	67.21	3.70	2%	1.80	63.51	61.70	Jeffries and Snyder (1981)	LaZerte et al, 1989 (kCu=kPb)
Ni	14.06	4.70	2%	2.29	9.36	7.07	Jeffries and Snyder (1981)	Assumed
Pb	127.28	16.80	2%	8.18	110.48	102.29	Jeffries and Snyder (1981)	Arden et al 1975 (Dillon and Evans)
Zn	179.53	47.20	2%	22.99	132.33	109.34	Jeffries and Snyder (1981)	kZn=kCu (Friedland et al., 1986)
Hg	15.25	0.01	16%	0.04	15.24	15.20	Mierle (1992)	Mierle 1991
Al	9437.09	46.00	100%	1120.40	9391.09	8270.69	Jeffries and Snyder (1981)	K=1 Assumed
Fe	19631.28	219.00	100%	5334.06	19412.28	14078.21	Jeffries and Snyder (1981)	K=1 Assumed
Mn	3176.01	3.00	100%	73.07	3173.01	3099.94	Jeffries and Snyder (1981)	K=1 Assumed

Perch Lake

Elements	F_t	F_{dir}	K(%)	F_{int}	F_{wp}	F_{gw}	Source of F_{dir}	Source of K
Cd	3.05	0.67	2%	0.33	2.38	2.05	Jeffries and Snyder (1981)	KCd=KPb (Siccama et al., 1980)
Cu	233.69	3.70	2%	1.84	229.99	228.16	Jeffries and Snyder (1981)	LaZerte et al, 1989 (kCu=kPb)
Ni	28.40	4.70	2%	2.33	23.70	21.36	Jeffries and Snyder (1981)	Assumed
Pb	173.48	16.80	2%	8.34	156.68	148.34	Jeffries and Snyder (1981)	Arden et al 1975 (Dillon and Evans)
Zn	320.00	47.20	2%	23.43	272.80	249.37	Jeffries and Snyder (1981)	kZn=kCu (Friedland et al., 1986)
Hg	14.03	0.01	16%	0.04	14.01	13.97	Mierle (1992)	Mierle 1991
Al	15136.10	46.00	100%	1141.96	15090.10	13948.15	Jeffries and Snyder (1981)	K=1 Assumed
Fe	37583.26	219.00	100%	5436.71	37364.26	31927.54	Jeffries and Snyder (1981)	K=1 Assumed
Mn	1754.73	3.00	100%	74.48	1751.73	1677.26	Jeffries and Snyder (1981)	K=1 Assumed

All fluxes are in mg m^{-2} $year^{-1}$
F_{dir} are for rural North America

Table 5. Trace element proportions (%) of atmospheric (F_{dir} and F_{ind}) and geological fluxes (F_{gw}) relatively to the total flux (F_t) .

Lavant Long	Elements	F_{dir}(%)	F_{ind}(%)	F_{gw}(%)
	Cd	34.09	16.61	49.30
	Cu	5.51	2.68	91.81
	Ni	33.44	16.29	50.27
	Pb	13.20	6.43	80.37
	Zn	26.29	12.81	60.90
	Hg	0.07	0.26	99.67
	Al	0.49	11.87	87.64
	Fe	1.12	27.17	71.71
	Mn	0.09	2.30	97.60
Perch	Elements	F_{dir}(%)	F_{ind}(%)	F_{gw}(%)
	Cd	21.97	10.91	67.12
	Cu	1.58	0.79	97.63
	Ni	16.55	8.22	75.23
	Pb	9.68	4.81	85.51
	Zn	14.75	7.32	77.93
	Hg	0.07	0.29	99.64
	Al	0.30	7.54	92.15
	Fe	0.58	14.47	84.95
	Mn	0.17	4.24	95.58

Table 6. Comparison of F_{dir} and F_{gw} (as $F_{gw'}$) assuming F_{dir} is constant with time, $F_{ind} = 0$, and $F_{gw'}=F_{gw}/12$. See text for more detail.

Lavant Long Lake

Elements	Fdir	Fgw'
Cd	0.67	0.08
Cu	3.70	5.14
Ni	4.70	0.59
Pb	16.80	8.52
Zn	47.20	9.11
Hg	0.01	1.27
Al	46.00	689.22
Fe	219.00	1173.18
Mn	3.00	258.33

Perch Lake

Elements	Fdir	Fgw'
Cd	0.67	0.17
Cu	3.70	19.01
Ni	4.70	1.78
Pb	16.80	12.36
Zn	47.20	20.78
Hg	0.01	1.16
Al	46.00	1162.35
Fe	219.00	2660.63
Mn	3.00	139.77

TABLE 7. Sequential extraction results presented as concentration (ppm or ppb) and as % of the total concentration.
Car=carbonates, SO= soluble organic, Am=amorphous oxides, Cryst=crystalline oxides, sulp=insoluble organic/sulphide, Sili= silicates.

Lavant Long Lake

Compund	Carb	*Carb (%)*	SO	*SO (%)*	Am	*Am (%)*	Cryst	*Cryst (%)*	Sulp	*Sulp (%)*	Sili	*Sili(%)*	TOTAL
Al (ppm)	0.00	*0%*	0.00	*0%*	1946.23	*36%*	0.00	*0%*	708.94	*13%*	2688.60	*50%*	5343.77
Fe (ppm)	32.77	*0%*	514.98	*5%*	1518.19	*14%*	187.27	*2%*	8132.69	*73%*	730.34	*7%*	11116.24
Mn (ppm)	1338.95	*74%*	307.65	*17%*	76.91	*4%*	0.00	*0%*	53.50	*3%*	21.40	*1%*	1798.42
As (ppb)	1732.21	*61%*	100.32	*4%*	421.35	*15%*	0.00	*0%*	307.65	*11%*	294.28	*10%*	2855.81
Ba (ppb)	67883.90	*58%*	0.00	*0%*	17723.38	*15%*	0.00	*0%*	2006.42	*2%*	30230.07	*26%*	117843.77
Cd (ppb)	0.00	*0%*	113.70	*10%*	595.24	*53%*	37.45	*3%*	0.00	*0%*	366.51	*33%*	1112.89
Co (ppb)	936.33	*13%*	1337.61	*19%*	2006.42	*28%*	1070.09	*15%*	1337.61	*19%*	535.05	*7%*	7223.11
Cr (ppb)	0.00	*0%*	0.00	*0%*	2675.23	*42%*	0.00	*0%*	2675.23	*42%*	1070.09	*17%*	6420.55
Cu (ppb)	468.16	*1%*	3344.03	*9%*	11369.72	*30%*	5885.50	*15%*	16720.17	*44%*	267.52	*1%*	38055.11
Mo (ppb)	0.00	*0%*	735.69	*38%*	284.24	*15%*	197.97	*10%*	508.29	*26%*	200.64	*10%*	1926.83
Ni (ppb)	468.16	*6%*	1337.61	*17%*	0.00	*0%*	0.00	*0%*	5350.45	*67%*	802.57	*10%*	7958.80
Pb (ppb)	30524.34	*42%*	27421.08	*38%*	11637.24	*16%*	1284.11	*2%*	401.28	*1%*	802.57	*1%*	72070.63
Sb (ppb)	196.63	*28%*	53.50	*8%*	20.06	*3%*	16.05	*2%*	334.40	*48%*	80.26	*11%*	700.91
Zn (ppb)	32771.54	*32%*	0.00	*0%*	56848.58	*56%*	2140.18	*2%*	4012.84	*4%*	5885.50	*6%*	101658.64
Zr (ppb)	0.00	*0%*	1036.65	*14%*	46.82	*1%*	0.00	*0%*	93.63	*1%*	6099.52	*84%*	7276.62
Hg (ppb)	100.94	*1%*	2306.71	*27%*	96.07	*1%*	2090.70	*24%*	3952.67	*46%*	89.45	*1%*	8636.54

Perch Lake

Compound	Carb	*Cab (%)*	SO	*SO(%)*	Am	*Am(%)*	Cryst	*Cry (%)*	Sulp	*Sulp (%)*	Sili	*Sili (%)*	TOTAL
Al (ppm)	0.00	*0%*	263.92	*4%*	2502.24	*34%*	422.27	*6%*	1055.67	*14%*	3161.04	*43%*	7405.14
Fe (ppm)	488.00	*3%*	557.71	*3%*	1705.51	*9%*	557.71	*3%*	13574.35	*74%*	1503.83	*8%*	18387.11
Mn (ppm)	592.57	*69%*	154.37	*18%*	39.84	*5%*	0.00	*0%*	39.84	*5%*	31.87	*4%*	858.48
As (ppb)	871.43	*19%*	343.59	*8%*	1459.02	*32%*	1075.59	*24%*	353.55	*8%*	438.20	*10%*	4541.38
Ba (ppb)	59605.62	*50%*	2489.79	*2%*	20416.29	*17%*	1593.47	*1%*	3485.71	*3%*	31670.15	*27%*	119261.03
Cd (ppb)	0.00	*0%*	14.94	*1%*	1190.12	*80%*	239.02	*16%*	19.92	*1%*	27.89	*2%*	1491.88
Co (ppb)	697.14	*8%*	0.00	*0%*	1493.88	*16%*	1593.47	*17%*	4481.63	*48%*	995.92	*11%*	9262.03
Cr (ppb)	0.00	*0%*	0.00	*0%*	2987.75	*27%*	0.00	*0%*	5477.54	*50%*	2589.38	*23%*	11054.68
Cu (ppb)	2788.57	*2%*	3983.67	*3%*	19420.38	*17%*	21113.43	*18%*	65232.55	*57%*	1792.65	*2%*	114331.24
Mo (ppb)	0.00	*0%*	388.41	*10%*	219.10	*6%*	677.22	*18%*	2290.61	*61%*	209.14	*6%*	3784.48
Ni (ppb)	1045.71	*8%*	0.00	*0%*	1493.88	*11%*	0.00	*0%*	9959.17	*72%*	1394.28	*10%*	13893.04
Pb (ppb)	11223.98	*13%*	16432.63	*19%*	43272.58	*51%*	10755.90	*13%*	2091.43	*2%*	1095.51	*1%*	84872.02
Sb (ppb)	13.94	*2%*	9.96	*1%*	12.45	*2%*	7.97	*1%*	597.55	*77%*	129.47	*17%*	771.34
Zn (ppb)	8017.13	*5%*	0.00	*0%*	113285.53	*72%*	23902.00	*15%*	7967.33	*5%*	3386.12	*2%*	156558.11
Zr (ppb)	0.00	*0%*	1269.79	*16%*	19.92	*0%*	0.00	*0%*	189.22	*2%*	6533.21	*82%*	8012.15
Hg (ppb)	79.19	*1%*	1760.54	*26%*	74.04	*1%*	1336.32	*19%*	3500.96	*51%*	110.52	*2%*	6861.57

Manuscript 3

Humic Substances in Sediments of Three Remote Lakes in Canada: Transformation with Depth and Interaction with Metals

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Abstract

The study of the effect of humic substances content and transformation on their interaction with metals was carried out in three remote lakes: Lavant Long Lake and Perch Lake, located in southeastern Ontario, and Big Dam Lake located in Kejimkujik Park, Nova Scotia, Canada. The lake sediments were subjected to a sequence of chemical extractions consisting of 0.1 M $Na_4P_2O_7$, 0.5 M NaOH, and H_2O in order to extract Humic and Fulvic acids (HA and FA respectively), and to determine their content with depth. FA and HA were characterized using the E4/E6 ratios of their optical densities at 465 and 665 nm and ^{13}C-NMR. Transformation of humic substances was evidenced by: an increase in aromaticity and decrease of E4/E6 ratios in Lavant Long Lake; an increase of ^{13}C-NMR signal in the aromatic-C region (105-150 ppm) in Perch Lake; and a decrease of humic and fulvic acid contents in Big Dam Lake. It was concluded that humic substances transformation, which is characterized by a decrease in COOH and OH functional groups abundance and by an increase in aromaticity, may result in a release of metals originally associated with these functional groups to pore waters and /or a redistribution amongst other binding fractions within sediments.

1. Introduction

Research focus on toxic metals in the environment during the last four decades has demonstrated the importance of humic substances (HS) in trace metal cycling. Humic substances play a key role in organic matter-trace metal interactions, and are involved in both trace metal immobilization and transport mechanisms in natural environments (Breault *et al.*, 1996; Meili, 1991; Lindqvist *et al.*, 1991; Mierele and Ingram, 1991). Under natural conditions, the stability of trace metal-HS complexes is attributed to the humic acid (HA) and fulvic acid (FA) carboxylic (COOH) and phenolic (OH) functional groups and their abundance (Schnitzer and Khan, 1972; Stevenson, 1982).

The close relationship between trace metals and HS was confirmed by selective extractions carried out on lake sediments and soils using 0.1 M $Na_4P_2O_7$ (Hall and Pelchat, 1997; McKeague, 1967). However, it has never been shown how changes in HS chemical characteristics due to their diagenetic transformation influence their relationship with trace elements.

In marine sediments, organic matter transformation has been shown to take place by condensation (mechanism that condenses soluble organic monomers to insoluble humic polymers) in the following order: degraded cellular material → water-soluble complexes containing amino acids and carbohydrates → FA → HA → humin (Nissenbaum and Kaplan, 1972). Ishiwatari *et al.* (1977), have concluded, based on their experimental results, that organic matter transformation evolves towards increasing aromaticity. Moreover, Huc and Durand (1973), and Chen *et al.* (1977) have shown that this transformation takes place by the elimination of COOH and OH functional groups.

Therefore, organic matter transformation may have direct implications on the distribution of metals with high affinity for HS.

The characterization of HS using their optical density ratios has been shown to be a useful tool to distinguish between their sources (McNight *et al.*, 2001) and to evaluate their degree of transformation (Campbell *et al.*, 1967). By studying their optical density ratios, Campbell *et al.* (1967) found that HS mean residence time was inversely proportional to their E4/E6 ratio (ratio of optical densities at 465 and 665 nm). This ratio was influenced by the degree of condensation of the aromatic carbon network (*Konova*, 1966). During this study, our main objective was to determine how HS transformation could affect trace metal distribution in lake sediments based on results from a characterization of HS extracted from sediments of three remote lakes: Perch Lake and Lavant Long Lake located in Clyde Forks, Lanark County, Ontario, Canada, and Big Dam Lake West of Kejimkujik Park, Nova Scotia, Canada. Lavant Long Lake and Perch Lake are both remote lakes surrounded by dense forest. There are no signs and/or record of logging activities in the past or in the present. Big Dam Lake West, however underwent changes in the 1800s because of the logging activity by the first settlers and by the fact that it was dammed. Both activities may have changed the original limnological context in Big Dam Lake West.

2. Definition of Humic Substances

One of the difficulties faced by researchers studying HS relates to the definition of HS. HS do not correspond to a specific chemical compound and therefore are not defined based on their chemical structure. They also cannot be defined in functional terms since

they are not biologically assigned a specific biochemical role. Therefore, they are defined operationally. HS are defined as a general category of naturally occurring, biogenic and heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight, and refractory. HS comprise three major fractions operationally defined in terms of their solubilities, i) humin, ii) Humic acid, and iii) Fulvic acid. Humin is the fraction of HS that is not soluble in water at any pH. Humic acid (HA) is the fraction of HS that is not soluble in water under acidic conditions (below pH 2). Fulvic acid (FA) is the fraction of HS that is soluble under all pH conditions. Water solubility is an effective criterion since it relates to important chemical characteristics, such as acidic functional group content, molecular weight, and aromaticity.

3. Methodology:

3.1. Sampling:

Sediment cores were recovered from the depositional basins of Lavant Long Lake, Perch Lake, and Big Dam Lake at a water depth of 17, 20, and 15 m respectively. Sediment cores from Lavant Long Lake, Perch Lake, and Big Dam Lake were 55, 40, and 35 cm long respectively. They were sectioned upon retrieval in the field, into 2-cm intervals for the first 20-cm, and into 5 cm intervals for the rest of the core and stored in a field cooler. Once at the laboratory, sediment samples were stored in the cooler at 4°C.

3.2. Organic Carbon and Nitrogen Analysis:

Air-dried sediments were pre-weighed (7-8 mg) in thin micro-containers, and analyzed for total organic carbon and N using an elemental analyzer, EA-1110 by CE Instruments,

at the G.G. Hatch Isotope Laboratory of the University of Ottawa. Blanks, sample replicates, L-cystine, sulphilamide, and urea standard reference materials (Fison Istrumental) were used as controls.

3.3. Humic Substances Extraction:

HS extraction has always involved either 0.1 M $Na_4P_2O_7$ or 0.5 M NaOH. However, the use of one or the other has shown profound implications on the amount of the extracted HS and also on their chemical nature. The extraction with 0.1 M $Na_4P_2O_7$ removes organic matter that is complexed to metals and clays and more organic matter from finer particles than from coarser ones. This can lead to an underestimation of the organic matter content when compared to the extraction with 0.5 M NaOH (Schnitzer and Schppli 1989 a, b). Moreover, the extraction with 0.5 M NaOH removes free organics, including less decomposed materials, and removes more organic matter from coarser particles than from finer ones (Schnitzer and Schppli 1989 a, b). In order to avoid the problems listed above, we used a sequence of solvent attacks, involving 0.1 M $Na_4P_2O_7$, 0.5 M NaOH, and H_2O (Schnitzer and Schppli 1989 a, b), followed by HA and FA purification (Thurman and Malcolm, 1981; Ephraim *et al.*, 1989). During the extraction, 10 g of air-dried sediments were mixed with 100 mL of 0.1 M $Na_4P_2O_7$ under N_2 atmosphere and shaken on a reciprocal shaker at room temperature for 24 hours. The mixture was then centrifuged for 10 min at a rate of 10,000 rpm (step 1). The extract was filtered, concentrated to a small volume on a rotary evaporator, and freeze-dried. The residual fraction from step 1 was shaken for 24 h with 100 mL of 0.5 M NaOH under N_2 atmosphere and then centrifuged for 10 min at a rate of 10,000 rpm (step 2). The extract

was then filtered and concentrated to a small volume on a rotary evaporator and freeze-dried. The residual material from step 2 was shaken for 24 h with 100 mL of DDI H_2O and the mixture was centrifuged for 10 min at a rate of 10,000 rpm (step 3). The extract was filtered and concentrated to a small volume on a rotary evaporator and freeze-dried. Dried extracts obtained from steps 1 to 3 were then dissolved in 100 mL DDI H_2O and the dark colored extracts were separated from insoluble residues by centrifugation at 10,000 rpm for 10 minutes. The samples were then passed through a 0.45 μm filter to remove the suspended material and the clear supernatants were acidified with 6 M HCl to pH 1 and allowed to stand at room temperature for 24 hours. After acidification, soluble fulvic acid (FA) was separated from coagulate (HA) by centrifugation at a rate of 10,000 rpm for 10 minutes.

3.4. HA Purification:

Suspended clays were removed from the HA by dissolving HA in a minimum volume of 0.1 M KOH and adding KCl to obtain a final concentration of K of 0.3 M. The mixture was let stand for 4 hours and the suspended solids were then removed by centrifugation at 10,000 rpm for 10 minutes. The clear HA solution was acidified to pH 1 with 6M HCl and allowed to coagulate. The HA was separated by centrifugation at 10,000 rpm for 10 minutes and washed with DDI H_2O. The purified HA was freeze-dried and weighed.

3.5. FA Purification:

Soluble FA was adsorbed onto a clean Amberlite XAD-8 resin (Halltech Environmental Inc.) to remove the excess of NaCl from the use of the extractants (NaOH, $Na_4P_2O_7$) and KCl. Before use, the XAD-8 resin was cleaned following the method proposed by

Thurman and Malcolm (1981). After FA adsorption, the resin was rinsed with one bed of H_2O. The FA was desorbed with 0.1 M NaOH and the eluate was passed through a cation-exchange resin (H^+-form, Amberlite IR 120-H, Mallinkrodt). One bed volume of DDI H_2O was then used for further rinsing and the sample was freeze-dried and weighed.

3.6. Optical Density Ratio (E4/E6):

2 to 4 mg of the extracted humic material (HA) from different depths of LL, PL, and Big Dam Lake sediments were dissolved in 10 ml of 0.05 M $NaHCO_3$ and adjusted to pH~8 (Schnitzer, 1982). The 0.05 M $NaHCO_3$ solution was used in the reference cell for calibration. The absorbances at 465 nm (E4) and at 665 nm (E6) were measured on a Beckman DU-65 Spectrophotometer with a 1cm-path quartz cell.

3.7. Solid ^{13}C-NMR:

Solid ^{13}C-NMR analyses were conducted on freeze-dried HA and FA using a Bruker ASX-200 spectrometer. Spectra were recorded as ^{13}C cross polarization magic angle resonance (^{13}CCP/MAR) at the NMR laboratory of the University of Ottawa. FA spectra were recorded at a frequency of 50.32 MHz with a magic angle spinning rate of 4 kHz, whereas, HA spectra were recorded at the same frequency but with a magic angle spinning rate of 5 kHz. ^{13}C-NMR spectra were obtained for HA and FA extracted at different depths from the three lakes. Spectra were divided into 6 regions; 0-40 ppm (paraffinic C), 40-60 ppm (C in OCH_3 groups and amino acids, peptides, proteins), 60-105 ppm (C in carbohydrates), 105-150 ppm (aromatic C), 150-170 ppm (phenolic C), and finally, 170-190 ppm (C in COOH). Baseline correction and integration by regions were performed using the MestRe-C 2.1.1 program (Cobas *et al.*, 1999). After spectral

integration, aromaticities were calculated using the following expression (Schnitzer, 1991).

$$Aromaticty(\%) = \frac{[AromC(150-170ppm) + PhenolC(105-150ppm)]}{[AromC(150-170ppm) + PhenolC(105-150ppm) + AliphC(0-105ppm)]} \times 100 \quad (1)$$

3.8. Trace Element Extraction:

Trace elements associated with humic material were selectively extracted using 0.1 M $Na_4P_2O_7$ (McKeague, 1967). The samples were analyzed for Hg using cold vapour atomic fluorescence spectrometry (M-6000A by Varian) at the University of Ottawa. Al, Ni, Fe, Mn, Co, Ba, Cu, and Zn were analyzed using an inductively coupled plasma-optical emission spectrometry *(ICP-OES)*, whereas Pb, Cd, Mo, Sb, As, Zr were analyzed using inductively coupled plasma-mass spectrometry *(ICP-MS)* at the Analytical Chemistry Laboratory, Mineral Resources Division of the Geological Survey of Canada.

4. Results and Discussion:

4.1. HS Transformation:

Optical density measurements (Table 1) showed that the E4/E6 ratio of HA from Lavant Long Lake, Perch Lake and Big Dam Lake presented different trends with depth. In Big Dam Lake, the E4/E6 ratio of HA showed a progressive increase with depth. In Lavant Long Lake Lake, the E4/E6 was higher in surface sediments (0 and 10 cm) and lower in deep sediments (50 cm), whereas in Perch Lake the E4/E6 ratio of HA showed no significant change with depth (Table 1).

Characterization studies of HS have involved, among other techniques, the absorption in the UV, visible, and IR regions. In the visible region, soil scientists were mainly interested by the E4/E6 ratios. The latter varies with the amount of carbon nuclei in the aromatic network of HS molecules. In fact, Kononova (1966) showed that in soils, progressive transformation of HS and increasing condensation were indicated by a decrease in E4/E6 ratio. In addition, Campbell *et al.* (1967) showed an inverse relationship between the E4/E6 ratio and HS residence time. The E4/E6 changes with depth in Lavant Long Lake suggest that HS transformation increased with depth, whereas in Perch Lake it is difficult to assess the degree of transformation of the HA because the E4/E6 ratio is invariant (Table 1). In Big Dam Lake, the results suggest that significantly transformed HS occurred at the surface sediments, whereas less transformed HS were present in deeper sediments consistent with different sources of organic matter after damming.

The interpretation of the above observations mainly depends on the information provided by ^{13}C-NMR spectra for HA (Figure 1). In fact, we should expect HA with a high E4/E6 ratio to present a low degree of transformation and hence, a low aromaticity and vise versa.

In Lavant Long Lake, results showed that aromaticity increased with depth (Table 2). These observations are consistent with the E4/E6 measurements, which suggest that less transformed (low aromaticity) HA occurred at the surface, whereas transformed HA (high aromaticity) occurred in deep sediments. In Perch Lake, HA showed an overall increase in aromaticity with depth (Table 2) but no relationship between their E4/E6 ratio and their aromaticity could be established, since no real variation of the E4/E6 ratio was

observed. However, the fact that their aromaticity showed an increase with depth as indicated by the increasing signal intensity in the aromatic–C region (105-150 ppm) (Figure 1), suggests a progressive transformation of HA with depth.

In Big Dam sediments, aromaticity showed an opposite trend. In fact, HS with high aromaticity occurred in the surface sediments, whereas HS with low aromaticity occurred in the deeper sediments (Table 2). These observations are consistent with the earlier results from the E4/E6 values of HA from Big Dam Lake. Moreover the comparison of E4/E6 values to the aromaticity (Figure 2) shows a stronger inverse relationship between both parameters in Lavant Long Lake and Big Dam Lake than in Perch Lake, consistent with the results from Campbell *et al.* (1967). However, in Big Dam Lake the only evidence of HS transformation with depth is the progressive decrease of HA and FA contents with depth when compared to Lavant Long Lake and Perch Lake (Figure 3). This decrease of HA and FA with depth can be interpreted as an increase of soluble organic matter (HA and FA) transformation into insoluble organic compounds (humin) (Ishiwatari and Kawamura, 1981). Moreover, the occurrence of HA with high aromaticity at the surface in Big Dam Lake could be explained by a terrestrial flux of organic material with high aromaticity deposited at this shallow depth. Leenheer *et al.* (1989) showed that terrestrially derived HS presented higher aromaticity than HS originating from the water column. Another supporting evidence of the terrestrial origin of organic material in Big Dam Lake is the C/N ratio in surface sediments. Based on the fact that organic matter loses a large part of its nitrogen content by degradation in soil environments, a high C/N ratio in surface sediments is an indicator of organic matter derived from surrounding soils and higher plants (allochthonous) (Wetzel, 1975). In

contrast, in lake environments (remote and unpolluted) where organic N is mainly derived from the primary productivity in the water column (autochthonous), organic matter is characterized by a low C/N ratio (Kemp *et al.*, 1977; Nriagu *et al.*, 1982). The same authors (Kemp *et al.*, 1977; Nriagu *et al.*, 1982), pointed out that dilution (mixing of organic matter from both environments) might play an important role on the values of the C/N ratio and hence should be taken into account. C and N results (Table 3) showed that the average C/N ratio from the surface sediments (0-10 cm) in Lavant Long and Perch L Lakes presented similar values, i.e., 11.17 ± 0.01 and 11.14 ± 0.05 respectively. In contrast, in Big Dam Lake, the C/N ratio presented an average value of 13.52 ± 0.07. These observations imply that the dilution of autochthonous organic matter with low C/N ratio (7-9) (Nriagu *et al.*, 1982) by allochtonous organic matter with high C/N ratio (15-20) (Kemp *et al.*, 1977; Nriagu *et al.*, 1982) is likely responsible for the C/N ratio values in Perch Lake and Lavant Long Lake. In Big Dam Lake, the higher C/N ratio (13.52) indicates a possible allochthonous origin for the organic matter (Kemp *et al.*, 1977; Nriagu *et al.*, 1982; Kaushik and Hynes, 1970; Glooshenko *et al., 1981*), which may explain the observed low values of E4/E6 in the surface sediments of Big Dam Lake.

4.2. Effects on Trace Metal Distribution

The ability of humic substances, HA and FA, to form metal complexes is well established (Davis, 1982,1984; Stumm and Morgan, 1997; Sigg *et al.*, 1992; Schnitzer, 1969; Gamble *et al.*, 1970; Mantoura *et al.*, 1978). HS binding capacity of metals was attributed mainly to the high content of carboxylic and phenolic functional groups (Schnitzer, 1969; Gamble *et al.*, 1970).

Generally, the affinity of humic and fulvic acids for metals was reported to follow the Irving-Williams series: $Hg^{2+}>Cu^{2+}>Ni^{2+}=Zn^{2+}>Co^{2+}>Mn^{2+}=Cd^{2+}>Ca^{2+}>Mg^{2+}$. In natural environments however, this affinity is influenced by the presence of other competing ligands such as OH^-, CO_3^{2-}, Cl^-, and the oxides presenting hydroxyl functional groups.

In the three lakes, the relationships between the trace metals and COOH/OH functional groups in HA and FA show the role played by these groups in the binding of the trace metals. However, the difference in trace metal behaviour vis-à-vis COOH and OH in the three lakes can be related to other factors such as, the chemical structure of the HS, the abundance of the binding sites, the ionic strength, and the composition of the pore waters (*Mantoura et al., 1978*). Based on the results from trace metal content associated with HS as shown in Table 4, and on the assumption that carboxylic and phenolic groups are the only sites binding trace metals, the association of trace metals with HA and FA from the three lakes is likely to occur as illustrated in Figure 4. According to this model, trace metal binding may involve 2 COOH molecules (reaction I), 1 COOH and 1 OH molecules (reaction II), or 2 OH molecules (reaction III).

During organic matter diagenesis, HS form intermediate products, which are also subject to diagenetic transformation. In lakes, the transformation of HS occurs during diagenesis to achieve a thermodynamic stabilization (Stumm and Morgan, 1997). This process takes place through the elimination of the least stable and the most reactive components, mainly the oxygen containing functional groups (Chen *et al.*, 1977; Ishiwatari, 1975b) by generating CO_2 and H_2O (Ishiwatari *et al.*, 1977), and by the transformation of open chain structures into aromatic networks. The question that arises from this is how does HS transformation affect trace metal distribution in the three lakes?

In the three lakes, HS transformation is evident from the increasing aromaticity and decreasing E4/E6 ratios in Lavant Long Lake, the increasing resonance signal in the aromatic-C (105-150 ppm) region in Perch Lake, and the progressive decrease in HA and FA content with depth in Big Dam Lake.

In aquatic environments, the transformation of HS into more stable organic compounds occurs through the condensation mechanism. According to this process, organic substances are degraded microbially (carbohydrates are transformed into sugars and proteins into amino acids) to form soluble monomers (FA and HA) and finally the soluble monomers condense to form insoluble organic compounds (humin). Moreover, Huc and Durand (1973) and Stach (1975), have shown that HS condensation takes place by a chemical change involving the loss of oxygen functional groups in soluble organic compound (FA, HA) resulting, hence, in more stable and insoluble organic compounds. In relation to this study, transformation of HS may have an impact on the HS-trace metal interaction and hence, on the fate of the metals. In fact, trace metals associated with these functional groups will be either released to the pore waters and/or redistributed amongst other binding fraction in the sediment column.

5. Conclusions

This study has shown how changes in HS chemical characteristics due to their diagenetic transformation influence their relationship with trace elements. It was the first time that a combination of different characterization tools of HS was used to demonstrate HS transformation with depth in lake sediments. These findings showed the impact that HS transformation may have on the distribution of trace metal with high affinity to HS in lake sediments and pore waters.

Until now we have been dealing with observed data and interpreting their variations based on field measurements and on our understanding of biogeochemical processes affecting trace elements behaviour. However it is important to predict, by using quantitative modeling the importance of these processes, especially when certain parameters are difficult to measure. Since in the three lakes, sediments present high organic matter content, bacterial activity will be expected to be high. Consequently, HS transformation (as demonstrated in Manuscript 3) will take place resulting in the release and adsorption of trace elements by organic matter and oxides (under oxic conditions), and the formation of metal sulphides, etc. The next manuscript (4), deals with modeling trace metal cycling between lake sediments and pore waters based on field and experimental observations.

Summary of Manuscript 3

1- Organic matter presents an autochthonous origin in Lavant Long and Perch Lakes, whereas in Big Dam Lake organic matter presents an allochthonous origin.

2- In Lavant Long Lake, the increase of the HA aromaticity and the decrease of the E4/E6 ratio indicate HS transformation with depth.

3- In Perch Lake, the increase of the ^{13}C resonance signal in the Aromatic-C (105-150 ppm) region indicates HS transformation with depth.

4- In Big Dam Lake, the gradual decrease of the HS content with depth suggests HS transformation.

Acknowledgments

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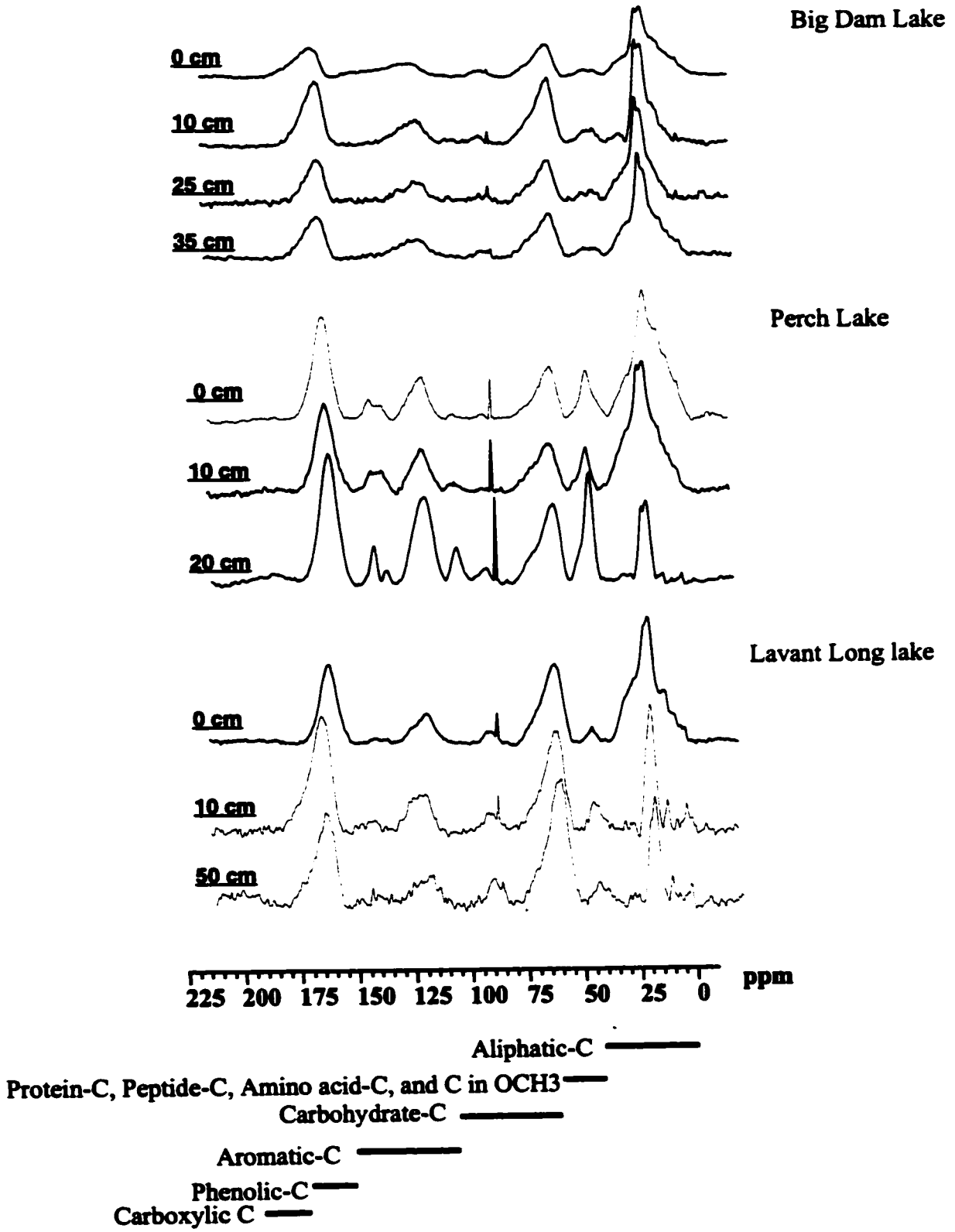


Fig. 1. ^{13}C-NMR spectra for HA from 0, 10, 25, and 35 cm in Big Dam Lake West, from 0, 10, and 20 cm in Perch Lake, and from 0, 10 and 50 cm from L avant Long Lake.

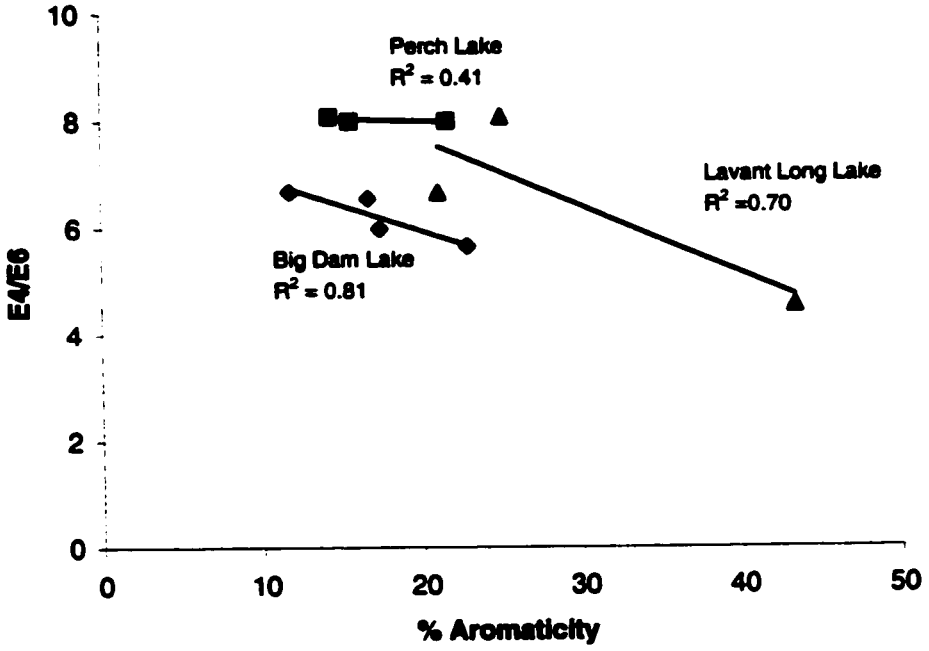


Fig. 2. Relationship between E4/E6 ratios and aromaticity (%).

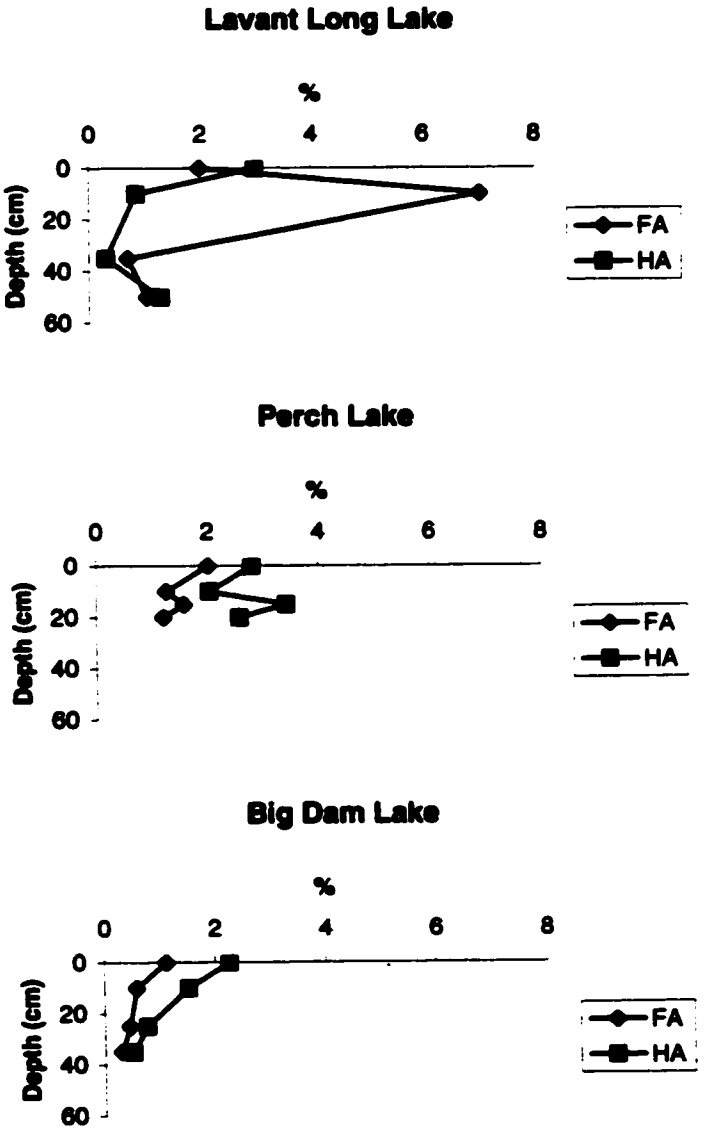
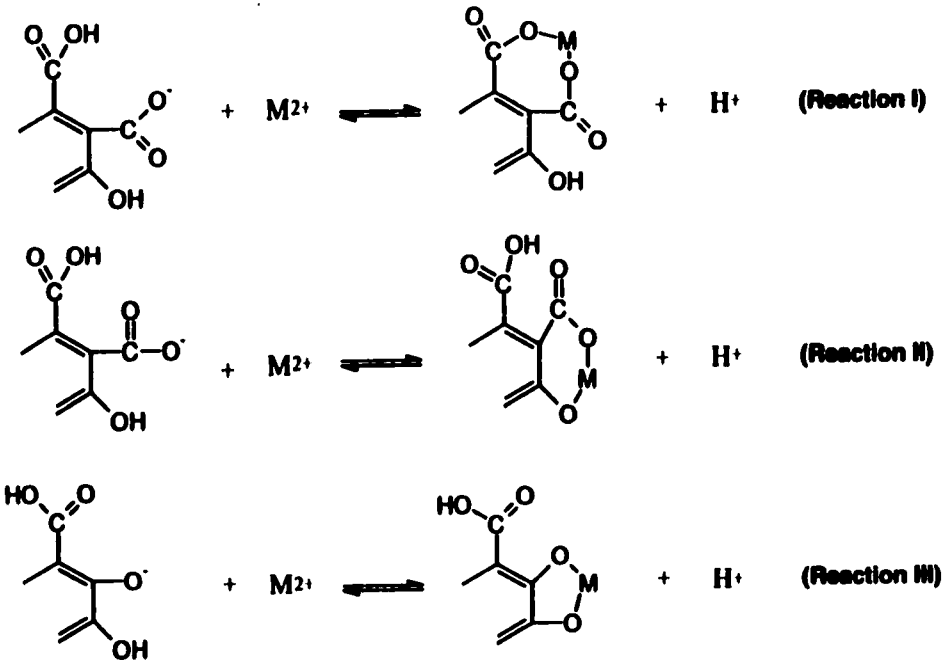


Fig. 3. Variation of the FA and HA content (%) with depth in Lavant Lon Lake, Perch Lake, and Big Dam Lake.



	Lavant Long Lake	
	HA	FA
I	Cd, Zr, Hg	Zr, Hg, Cd
II	Hg, Mo, Zr	Cd, Hg, Mo, Zr
III	Hg, Zr, Co	Cd, Zr, Hg, Cu
	Perch Lake	
	HA	FA
I	As, Sb, Cu	Zr, Cu, Mn, Mo, Pb, Hg, Sb
II	As, Sb, Cu	Pb, Mn, Hg, Mo, Zr
III	As, Sb, Cu	Pb, Mn, Hg, Mo, Zr
	Big Dam Lake	
	HA	FA
I	Mn, Al, Fe, Hg, Zr, As, Sb	Mn, Al, Fe, Hg, Zr, As
II	As, Sb, Mn, Hg, Zr, Fe, Al	Mn, Al, Fe, Hg, Zr, As
III	Sb, Pb, As, Zr, Fe, Hg, Al, Mn	Mn, Al, Fe,Hg, Zr, As

Fig. 4. Model for metal-HS (HA and/or FA) interaction in Lavant Long Lake, Perch Lake, and Big Dam Lake, Based on qualitative examination of data in Table 4. Interaction with COOH (Reaction I), with OH and COOH (Reaction II), and with OH (Reaction III).

TABLE 1. Ratios of the optical densities at 465 nm and 665 nm of HA from different depths in the three lakes.

Sample	E4/E6	RSD*	pH	Depth (cm)
LL1H	6.66	0.19	8.2	0
LL2H	8.08	0.19	8.3	10
LL4H	4.55	0.23	8.3	50
PL1H	8.08	0.16	8.3	0
PL2H	8.00	0.09	8.5	10
PL4H	8.00	0.26	8.3	20
BD1H	5.65	0.10	8.5	0
BD2H	5.99	0.11	8.3	10
BD3H	6.55	0.14	8.3	25
BD4H	6.68	0.08	8.2	35

*RSDs were calculated based on measurements done on triplicates from each sample. pHs ~ 8.
BD: Big Dam Lake
LL: Lavant Long Lake
PL: Perch Lake

TABLE 2. Results of the integration of HA ^{13}C-NMR spectra showing the six main regions of the spectra and the importance of each one and the variation of the aromaticity (%) with depth.

	HA Chemical Shifts							
HA	0-40 ppm	40-60 ppm	60-105 ppm	105-150 ppm	150-170 ppm	170-190 ppm	Aromaticity(%)	Depth (cm)
LL1H	43.48	8.70	13.04	13.04	4.35	17.39	21.05	0
LL2H	41.67	8.33	12.50	12.50	8.33	16.67	25.00	10
LL3H	-	-	-	-	-	-	-	35
LL4H	9.43	12.26	22.64	24.53	9.43	21.70	43.37	50
PI1H	40.00	8.00	24.00	8.00	4.00	16.00	14.29	0
PI2H	18.18	3.64	30.91	10.91	3.64	32.73	21.62	10
PI3H	-	-	-	-	-	-	-	15
PI4H	16.39	3.28	42.62	9.84	1.64	26.23	15.56	20
BD1	21.28	2.13	34.04	14.89	2.13	25.53	22.86	0
BD2	33.33	3.33	26.67	13.33	0.00	23.33	17.39	10
BD3	45.45	4.55	18.18	13.64	0.00	18.18	16.67	25
BD4	47.62	4.76	19.05	9.52	0.00	19.05	11.76	35

BD: Big Dam Lake
LL: Lavant Long Lake
PL: Perch Lake

TABLE 3. Organic carbon, organic N content, and C/N ratios of the first 10 cm surface sediments of Lavant Long Lake, Perch Lake and Big Dam Lake. Error (average RSD) based on sample replicates and on standard reference material; urea, sulphilamide, and L-cystine.

LL	Depth (cm)	N (+/-0.24) (%)	C (+/- 0.26)(%)	C/N
	0	1.07	12.17	11.35
	2	1.07	11.89	11.14
	4	1.77	19.28	10.91
	6	1.27	14.33	11.27
	8	1.42	15.88	11.17
Average		**1.32**	**14.71**	**11.17**
STDEV		**0.26**	**2.71**	**0.15**
RSD		**0.20**	**0.18**	**0.01**
Range		**1.07-1.42**	**11.89-19.28**	**10.91-11.35**

PL	Depth (cm)	N (+/-0.24) (%)	C (+/- 0.26)(%)	C/N
	0	1.02	10.91	10.69
	2	0.74	7.95	10.81
	4	0.93	10.20	10.99
	6	1.30	14.06	10.78
	8	1.02	11.70	11.43
	10	0.93	11.27	12.16
Average		**0.99**	**11.02**	**11.14**
STDEV		**0.17**	**1.82**	**0.51**
RSD		**0.17**	**0.17**	**0.05**
Range		**0.74-1.30**	**7.95-14.06**	**10.69-12.16**

BD	Depth (cm)	N (+/-0.24) (%)	C (+/- 0.26)(%)	C/N
	0	0.88	11.48	12.98
	2	0.47	6.71	14.15
	4	0.80	10.46	13.12
	6	0.80	10.27	12.89
	8	0.88	11.56	13.12
	10	0.76	11.29	14.88
Average		**0.77**	**10.29**	**13.52**
STDEV		**0.14**	**1.68**	**0.74**
RSD		**0.18**	**0.16**	**0.07**
Range		**0.47-0.88**	**6.71-11.48**	**12.89-14.88**

BD: Big Dam Lake
LL: Lavant Long Lake
PL: Perch Lake

TABLE 4. Trace metal contents in the humic material fraction (extraction using 0.1 M $Na_4P_2O_7$) and COOH and OH contents (%) in HA and FA. Numbers between brackets refer to depths in cm. Values under the detection limit (DL) are reported as 1/2 DL.

Compound	DL	PL1 (0)	PL2 (10)	PL3 (15)	PL4 (20)	LL1 (0)	LL2 (10)	LL3 (35)	LL4 (50)	BD (0)	BD (10)	BD (25)	BD (35)
COOH-FA (%)	-	26.09	23.81	23.94	-	27.27	30.56	37.10	-	20.93	31.76	27.27	32.73
COOH-HA (%)	-	16.00	32.73	-	26.23	17.39	16.67	-	21.70	17.39	23.33	18.18	19.01
OH-FA (%)	-	108.76	19.05	28.17	-	6.06	5.56	9.68	-	6.98	12.94	6.06	14.55
OH-HA (%)	-	8.00	10.91	-	9.84	13.04	12.50	-	24.53	14.89	13.33	13.64	9.52
Al (ppm)	16.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	30820.75	201311.73	7131.30	7189.16
Fe (ppm)	3.00	131.40	1.5	1.5	1.5	1.5	1.5	1.5	1.5	8888.33	43415.61	1916.45	1698.99
Mn (ppm)	0.20	920.89	779.09	518.08	976.18	0.1	514.36	0.1	985.66	818.94	5980.33	221.50	223.30
As (ppb)	0.02	4861.28	5533.57	7091.23	6040.09	2234.51	13437.55	1102.37	0.10	9406.63	24775.63	861.92	1063.08
Ba (ppb)	1.00	1158.64	0.5	29142.04	0.5	0.5	0.5	0.5	0.5	31980.13	170866.44	0.5	0.5
Cd (ppb)	0.20	3343.72	1418.35	0.10	0.10	4901.64	128.59	11338.68	1232.33	2102.26	0.10	0.10	0.10
Co (ppb)	1.00	1026.23	17979.10	0.50	97617.59	47653.29	0.00	7874.09	73939.66	0.5	0.5	0.5	0.5
Cu (ppb)	1.00	6036.57	7990.71	16190.02	18303.30	3243.86	12858.90	15748.17	0.5	11338.11	23299.97	0.5	0.5
Mo (ppb)	0.20	6317.10	2976.54	5472.23	7260.31	3220.11	1414.48	8582.75	0.10	2167.52	1941.66	0.10	101.94
Ni (ppb)	3.00	1423.01	1.5	1.5	1.5	1.5	51435.60	1.5	1.5	17638.87	93199.88	1.5	1.5
Pb (ppb)	0.10	124037.38	107774.73	30275.34	54604.84	58189.58	243997.64	5118.16	0.50	162697.06	26406.63	1589.01	2572.76
Sb (ppb)	0.20	453.40	659.23	194.28	488.09	289.66	1285.89	236.22	246.47	1041.90	1009.67	24.08	19.42
Zn (ppb)	1.00	12420.01	155818.88	0.5	0.5	0.5	237889.66	0.5	0.5	30031.52	0.5	0.5	0.5
Zr (ppb)	0.50	3752.12	2517.07	2849.44	4758.86	5955.87	8872.64	15590.69	14787.93	4898.73	14756.65	481.52	582.51
Hg (ppb)	0.00	108.76	68.85	110.18	241.72	166.23	236.12	266.43	452.85	64.77	287.86	17.23	17.70

BD: Big Dam Lake
LL: Lavant Long Lake
PL: Perch Lake

Manuscript 4

Trace Metal Distribution in Lake sediment and Pore waters: Adequacy of Predictive Models

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Abstract

Lake sediment cores and pore waters were sampled from three remote lakes, Lavant long Lake, Perch Lake, and Big Dam Lake to quantitatively study trace metal cycling between pore waters and sediments using diagenetic modeling. The latter was carried out using a two-layer diagenesis model to account for the bioturbation zone and the zone below the bioturbation zone. Trace elements were sequentially extracted to determine their distribution amongst soluble organics, amorphous oxides, crystalline oxides, insoluble organics and sulfides, and silicates. Sulfate-reducing bacteria (SRB) populations were also determined in the sediments from the three lakes using the most probable number (MPN) method. In the bioturbation zone, the model accounted for the role of biodiffusion and adsorption onto soluble organic matter, amorphous and crystalline oxides. However, in the zone below the zone of bioturbation, the diagenetic model accounted for the role of molecular diffusion, adsorption onto soluble organic, amorphous and crystalline oxide fractions and also the formation of metal sulphides. In Lavant Long and Perch Lakes, modeling results in the zone of bioturbation showed an exponential decrease of trace metal concentration with depth. The difference between the modeled and the observed trace element concentration was not significant for Hg, Cu and Co in Perch Lake. In Lavant Long Lake and for the rest of the elements in Perch Lake, concentration output from the model were lower than the observed data, suggesting that other processes such as a release of trace elements from the sediments was involved in the observed high concentrations. In Lavant Long and Perch Lakes, modeling results in the zone below the zone of bioturbation showed no significant difference between the predicted and the observed concentrations for Ni, Cu and Pb (in Perch Lake). On the other hand, in both lakes the difference between the predicted and the observed concentrations for Zn and Hg

was significant. In Big Dam Lake, the low SRB populations and the low total S in the sediments are in favour of the availability of Hg for other (than SRB) Hg-methylating bacteria and is a key to the understanding of the high Hg content in common loons in the Kejimkujik Park.

1. Introduction

The role of sediments as sources or sinks for contaminants, including metals, in aquatic environments was recognized in early sixties following the work of Sayre et al. (1963) in the Columbia and the Clinch Rivers and by De Groot (1966) in the Rhine River. However, it was only after the catastrophic Cd and Hg poisoning incidents in Japan and the contamination of aquatic ecosystems in the Wabigoon River, Laurentian Great Lakes, and Swedish lakes and terrestrial ecosystems near mining areas, that the threat of metal contamination attracted public and scientific attention.

During the last decade, metal pollution in surface waters attracted a lot of interest, because of the importance of water quality in human health, in food quality, and in maintaining and preserving aquatic resources and populations. The relationship between sediment chemistry and water chemistry has led to an increasing interest in understanding the physical, chemical and biogeochemical processes controlling the mobility, accumulation, and bioavailabilty of different metal species.

Metal distribution in fresh water lake sediments and pore waters is influenced by a number of processes (rate of sedimentation, diffusion, convection, bioturbation, and adsorption-desorption reactions etc.) which are in turn influenced by a variety of intrinsic parameters, notably organic matter content, anions, porosity, bacteria, redox conditions, pH, and temperature. Metal distribution in lake sediments and pore waters can also be understood in terms of theoretical models that take into account post-depositional processes affecting metal behaviour below the sediment-water interface (Berner, 1971, 1974, 1976, 1980); Lasaga, 1979, Lasaga and Holland; 1976, Lasaga, 1998, Lerman, 1979). These authors have successfully been able, based on qualitative chemical,

physical, biological, and mechanical data, to show using numerical models the importance of post-depositional changes in metal distribution in lake sediments and pore waters using the general diagenetic equation as proposed by Berner (1971, 1980). The latter includes the role played by molecular diffusion, advection, burial, and adsorption-desorption reactions in metal distribution in lake sediments and pore waters.

In this study, our objective is to prdict trace element distribution, using the general diagenetic equation including the role of sulfate-reducing bacteria in the formation of metal sulfides and also the role played by organic matter and oxides in trace metal adsorption. The study lakes are Lavant Long and Perch Lakes, Clyde Forks, Lanark County, Ontario, Canada, and Big Dam Lake, Kejimkujik Park, Nova Scotia, Canada.

2. Methodology

2.1. Sample collection

Sediments were sampled from Lavant Long Lake, Perch Lake and Big Dam Lakes in the summer of 1999 using a Plexiglas cylinder core sampler. Sediment cores were collected by scuba diving by vertically inserting an acid-washed cylinder without disturbing the bottom sediment. After retrieval, the sediments were sliced and preserved in acid-washed plastic containers and stored at a cool temperature (4°C). Their pH and E*h* were measured *in situ*.

Sediments from the same locations were collected for sulfate-reducing bacteria (SRB) enumeration. Pore waters (only Lavant Long Lake and Perch Lake) were sampled in Lavant Long and Perch Lakes using peeper techniques (Hesselin, 1976; Carignan, 1984; Carignan and Lean, 1991). This technique allows the peepers filled with de-ionized

deoxygenated water to reach equilibrium with the surrounding water through a dialysis membrane. Each peeper comprises 38 x 4-mL cells. Before sampling, peepers were prepared by filling the compartments with DDI-H_2O and by covering them with a dialysis membrane (Gelman 0.2 μm) which itself is covered by a thinner acrylic sheet which is screwed down to the thicker layer (containing the compartments). The whole sampler is then placed in DDI-H_2O bubbling with nitrogen for 24 to 48 hours to remove most of its dissolved gases (Carignan, 1984). In the lake, peepers were inserted in the sediments by scuba diving next to where the sediment cores were collected and were left for 20 days to equilibrate with the sediment pore waters before retrieval. After 20 days, peepers were retrieved and their pH and E*h* were measured under N_2 atmosphere inside a field glove box. Upon collection pore waters were preserved in 0.4 % HNO_3 at 4°C for cation analysis. Another fraction was put aside for SO_4^{2-} analysis.

2.2. Preparation and analysis

2.2.1. Sediments

Sediment organic matter content was determined by measuring their loss on ignition (LOI %) i.e., combustion at 450°C for 7 hours (Jackson, 1958). Air-dried sediments were pre-weighed (7-8 mg) in thin micro-containers, and analyzed for total organic carbon and total S using an CNHS EA 1110 elemental analyzer by CE Instruments at the G.G. Hatch Isotope Laboratory of the University of Ottawa. Standard reference materials BBOT, sulphilamide, urea, (by Fission Instrumental), sample replicates were used as controls. Sediment relative densities were determined by drying them at 100°C for 24 hours. Metals from sediments were sequentially extracted from 5 fractions (Manuscript 1)

(Table 1, Appendix 1-3 for the detail of the procedure). After their extraction, solutions were analyzed for their metal content.

2.2.2. Metal analysis

Pore water samples and leachates from the chemical extraction were analyzed for Al, Ni, Fe, Mn, Co, Ba, Cu, and Zn using an inductively coupled plasma-optical emission spectrometer (ICP-OES) and for Pb, Cd, Mo, Sb, As, Zr using an inductively coupled plasma-mass spectrometer (ICP-MS) at the Analytical Chemistry Laboratory, Mineral Resources Division of the Geological Survey of Canada, Ottawa. Hg was analyzed using cold vapour atomic fluorescence spectrometry (M-6000A by Varian) at the University of Ottawa. Sulfate was determined using a turbidity method as described by Rodier (1975). Sample replicates, lake sediment standard LKSD-4 from the Canadian Certified Reference Material Program (CCRMP), and operational blanks were used as controls.

2.2.3. Sulfate-reducing bacteria enumeration

Bacterial enumeration was carried out using the Most Probable Number technique (MPN) (Fortin *et al.*, 2000). The growth medium contained tryptone (10 g/L), Na-Lactate (60%) (5.9 mL/L), $MgSO_4.7H_2O$ (2g/L), Na_2SO_3 (0.5 g/L, and $FeSO_4.7H_2O$ (0.5g/L) adjusted to pH 7.5 using NaOH. The reducing agent supplement (RAS) consisted of ascorbic acid (7.5 g/L) and thioglycollic acid (7.5 mL/L) and adjusted to pH 7.5 with NaOH. The dilution water was composed of NaCl (2.1 g/L), RAS (100 mL/L) and the solution was adjusted to pH 7.5 using NaOH. All solutions were autoclaved for 20 minutes at 121°C. Ranges of dilution were chosen depending on the sediment redox potentials. To perform

dilution, 1g of wet sediments was added to 9 mL of dilution water (x 10^{-1}). 1mL of this same solution (x 10^{-1}) was added to 9 ml of dilution water to perform a x10^{-2} dilution and so on till reaching the desired dilution. 1mL of each dilution series was then used to inoculate 5 tubes of growth medium and RAS. Tubes were stored in the dark for at least 2 weeks before counting the number of positive, i.e., the ones with an Fe sulfide precipitate. A statistical table (Cochran, 1950) was then used to determine the population in Colony Forming Units per gram of dry weight sediment (CFU/g dry wt sed.).

3. Results:

The results are used only to build the models and to determine the values of some variable. They ate not discussed in this work.

3.1. Sediments

The quality of the data was assessed based on thirty pairs of replicates. On average the precision was 12% (n = 60). Precision for Hg was less 4 % (n=60)(Table 2). Trace metal concentrations in lake sediments were calculated as a function of sediment relative densities (Appendix 4. 1-6). Results showed that in Lavant Long Lake, all metals, except Pb, presented a total concentration peaks at 20 cm (Appendix 4.1. a-c). Below 20 cm, the total metal concentration decreased to minimum values. Sequential extraction results showed that Al, Ba, and Zr occurred in the silicate fraction at all depths (Appendix 4.2. a, 2c), whereas, most of Fe, Cu, Ni, Sb, and Mo occurred in the sulphide/insoluble organic fraction. Most Mn, As, Cd, Pb, and Zn were associated with the soluble organic and the

amorphous Fe and crystalline Mn oxide fractions (Appendix 4. 2. a-c). Hg was associated with the soluble organic and crystalline Fe oxide fraction.

In Perch Lake, a total metal concentration peak was observed at 16 cm below the sediment-water interface (Appendix 4. 3. a-c). Elements such as Al, Fe, Mg, Cd, Cu, Ni, Pb, Zn, Zr, and Hg also showed high concentrations in surface sediments. Sequential extraction results (Appendix 4. 4. a-c) showed that most Al, Cr, and Zr occurred in the silicate fraction, along with Mg, and Ba, but to a lesser extent since they were also associated with the amorphous oxide fraction. Fe, Ni, Cu, and Sb were associated with the sulfide/insoluble organic fraction. Mn, As, Cd, Co (in deeper sediment 16 cm and below), Mo, Pb, and to a lesser extent Zn, were found associated with the soluble organic fraction. Sequential extraction results also showed that both the crystalline oxide and the soluble organic fractions controlled Hg distribution.

Total metal concentration in Big Dam Lake (Appendix 4. 5. a-c) showed high total concentration peaks at 12 cm with the exception of Cd, Pb and Sb, which also showed a high concentration in the surface sediments. Below 12 cm, the total metal content decreased sharply reaching lower concentrations. In Big Dam, sequential extraction results (Appendix 4. 6. a-c) showed that most Al, Mn, As, and Cd and Pb (in the surface sediments) were associated with the soluble organic and the amorphous Fe and crystalline Mn oxides fraction. Fe, Mg, Co, Cu, Ni and Sb were found associated with the soluble organic and the sulfide/insoluble organic fractions. These results also showed that the Zr and Ba were associated with the amorphous oxides and the silicate fractions, whereas Hg, was associated with the soluble organics and the crystalline oxide fractions.

Organic carbon analyses of lake sediments showed a higher organic carbon content in Lavant Long Lake than in Perch and Big Dam Lakes. In fact, in Lavant Long Lake, the organic carbon concentration averaged around 15.5 (± 0.2) (wt %), whereas in Perch and Big Dam Lakes, the average organic carbon content was 12.5 (± 0.2) (wt %) and 10.1 (± 0.2) (wt %) respectively (Table 3). Total sulfur content varied in the sediments from the three lakes. In Big Dam Lake, all the sediments contained less than 0.01 (wt %) sulfur (<100 ppm) the detection limit for the method, whereas, the average sulfur values for sediments in Lavant Long and Perch Lakes were 0.7 (± 0.2) (wt %) and 1 (± 0.2) (wt %) respectively (Table 3).

Organic matter content (% LOI) also varied with depth (Fig. 1) in the three lakes. The sediments from both Perch Lake and Lavant Long Lake presented high organic matter content than the sediments from Big Dam Lake. In Lavant Long Lake and Perch Lake the average organic matter content was 60 and 53 (wt%) respectively, whereas in Big Dam lake the average organic matter content was 36 (wt%).

3.2. Pore waters

As mentioned earlier, pore water data were only available for Lavant Long and Perch Lakes. The metal content in pore waters was generally lower than in the sediments. Exceptions were Mn and Mg concentrations, which were similar to and sometimes higher in pore waters compared to sediments (Appendix 4. 7-8). Pore waters from both lakes presented a neutral pH.

In both Lavant Long and Perch Lakes As, Cd, Cr, Mo, and Zr in pore waters were below the detection limits. In Lavant Long Lake Al, Mn, Fe, Mg, Co, Cu, Pb, and Zn showed

high concentrations in the pore waters within the first 10 cm (Appendix 4. 7. a-b), whereas Hg concentration showed no clear trend but a slight increase with depth (Appendix 4. 7. b). For both lakes the Fe enrichment below the sediment-water interface corresponds to the reduction of solid iron oxides at this level. Other metals such as, Mg and Ba did not show a strong variation of their concentration with depth (Appendix 4. 7. a). In Perch Lake, Al, Fe, Co, Cu, Zn, Hg and to certain extent Sb, showed high concentrations in the pore waters from the surface (Appendix 4- 8 a-b). However, Mn showed an opposite behaviour than in Lavant Long Lake, since relatively high Mn concentrations were found in pore waters from the deeper sediments.

Sulfate concentration in the pore waters showed no real trend (Fig. 2) and varied in both Lavant Long Lake and Perch Lake with higher concentration in Lavant Long Lake. However, a decrease in sulfate content was observed in between 6 to 10 cm (sometimes in deeper sediments) in both lakes. This decrease (at 6-10 cm) is typical for sulfate reduction.

3.3. Sulfate-Reducing Bacteria

The SRB enumeration results showed that in Lavant Long and Perch Lake sediments, SRB populations were higher in number compared to Big Dam Lake sediments (Fig. 3). In Lavant Long Lake, SRB populations ranged from a minimum of 6×10^3 to a maximum of 1.30×10^8 CFU/g sed at 30 cm. This depth corresponded to more reducing conditions (Fig. 3). In Perch Lake, the highest SRB populations were observed at 3 cm, which corresponded to slightly reducing conditions. SRB populations in Perch Lake ranged from a minimum of 6.92×10^4 to a maximum of 9.85×10^5 CFU/g sed. In Big Dam sediments, SRB populations ranged from 1×10^3 to a maximum of 4.18×10^4 CFU/g sed.

High SRB peaks were observed at 1, 5 and 15 cm but did not seem to be linked to the E*h* variations, especially at 10 cm where more reducing conditions were observed.

4. Discussion:

As suggested by Berner (1980) and Vanderborght et al. (1977a, b), the theoretical modeling of metal cycling in pore water-sediment system can be done via a two-layer modeling using two different diagenetic models ruled by the physical and chemical differences prevailing in both zones (deep and surface sediments). Based on physical and chemical differences, sediments were divided into two different zones, the zone of bioturbation and the zone below the zone of bioturbation (Vanderborght *et al.*, 1977a). The zone of bioturbation refers to the zone where sediments mix with the overlaying waters (0-9 cm for our study, based on field observations of the sediment cores) and where solute and particle transport and migration are affected by burrowing organisms and turbulence resulting from currents. In this zone, oxides are abundant and along with humic substances play a major role in the adsorption reactions affecting trace elements. On the other hand, in the zone below the zone of bioturbation where sediments are anoxic, molecular diffusion, burial, adsorption reactions, and the formation of diagenetic minerals such as metal sulphides are the main processes controlling solute and particle migration.

4.1. The predictive models

4.1.1. Zone of bioturbation:

a) Model

In the zone of bioturbation, oxic conditions prevail, biodiffusion (D_B) controls atomic and molecular transport, and sulfur occurs as sulfate. Therefore, mineral sulfide formation does not occur and metal adsorption by oxides and organic molecules is important and represents the process by which solutes are removed from the pore waters.

In our model we assume that in the bioturbation zone, biodiffusion is the only process controlling solute and molecular migration (i.e. $D_B \neq 0$, $D_I = 0$, $D_S = 0$). The model for metal cycling in this zone is then represented by the following diagenetic equation (Berner, 1980):

$$\frac{\partial C}{\partial t} = D_B \frac{\partial^2 C}{\partial x^2} - \omega \frac{\partial C}{\partial x} + \Sigma R_s \qquad (1)$$

where C: concentration of a dissolved element in mass per volume unit

D_B: biodiffusion coefficient

ω: rate sedimentation

ΣRs: the sum of all biological and chemical processes affecting a trace element concentration in the pore water. In the bioturbation zone, we assume that metal adsorption onto oxides and soluble organics to form metal oxides and/or organo-metallic complexes dominates and follows a first order kinetic equation:

$$\Sigma Rs = (-KC) \qquad (2)$$

Where K: first order adsorption constant

We also assume that at the sediment-water interface, C_0 is constant and that the system is in a steady state, i.e. there is no accumulation ($\partial C/\partial t = 0$). As a result, equation (1) becomes:

$$D_B \frac{\partial^2 C}{\partial x} - \omega \frac{\partial C}{\partial x} - KC = 0 \qquad (3)$$

The solution for the above equation under the following boundary conditions

$$x = 0 \qquad C = Co$$

$$x \rightarrow \infty \qquad C = 0$$

is:

$$C = C_0 \exp\left[\frac{\omega - \left(\omega^2 + 4KD_B\right)^{1/2}}{2D_B} x\right] \qquad (4)$$

The sequential extraction results support this model, due to the association of trace metals with both oxides (amorphous and crystalline) and soluble organic fractions in the bioturbation zone. The adsorption constant (K) was determined from trace metal repartitioning between pore waters and sediments (soluble organic and oxides fractions). Modeling results using equation 4, (see Table 4 for the values and the sources of the parameters) predicted an exponential decrease of trace metal concentration in pore waters with depth (Fig. 4, 5). In Perch Lake, the difference between the observed and the predicted concentrations in the pore waters was not significant in the case of Hg,

whereas, in the case of Cu and Co the predicted concentration and the observed concentration showed the same trends. However, for the other results (in Lavant Long Lake and the rest of the elements in Perch Lake) the comparison between the predicted and the observed trace element concentrations showed the difference was significant. In fact, the observed concentrations are higher than those predicted by the model, suggesting that other processes, not included in the model, are involved in the high concentrations these elements in the pore waters. The high concentrations in the pore waters can be explained by the release of metals from the sediments to the pore waters by a process that the equation (5) did not account for. In the previous manuscript (3), we have demonstrated humic substance diagenesis in both Lavant Long and Perch Lakes. In fact, based on the increase of both the C/N ratio and organic C content and on the increasing aromaticity with depth we demonstrated humic substance transformation via a decrease in COOH and OH functional group and consequently, trace metal release to the pore waters. This observation may explain the difference between the observed and the modeled trace metal concentrations. Another possibility is the abiotic reduction by humic substances (Allard and Arsenie, 1991; Goodman and Cheshire, 1975; Wilson and Weber 1979; Skogerboe and Wilson, 1981; Alberts *et al.*, 1974; Miller *et al.*, 1975). In fact, it has been demonstrated that under oxidizing conditions and pH similar to those occurring in natural environment, fulvic acid can be oxidized by a decay of the semiquinones radical to quinones (Senesi et al., 1977) and hence act as an electron donor. Turner *et al.* (1989) pointed out, in the case of Hg, that reduction of Hg by humic substances may account for 10 to 70% of reduced Hg. Allard and Arsenie (1991) have demonstrated

experimentally, the reduction of Hg by fulvic acid, whereas Skogerboe and Wilson (1981) have shown reduction of Fe and V.

Since both Lavant Long Lake and Perch Lake are highly organic (Fig. 1), we expect a reduction of trace elements by humic substances and their subsequent release to pore waters from the sediments to take place and may explain, to certain extent, the observed concentrations.

4.1.2. Below the zone of bioturbation:

a) Model

In this zone, molecular diffusion is assumed to be the main process controlling solute and particle transport because in this zone irrigation (D_I) and biomixing (D_B) were assumed to be non existent ($Ds \neq 0$, $D_I = 0$, $D_B = 0$). The general diagenetic equation in this zone is represented by the following expression (Berner, 1980);

$$\frac{\partial C}{\partial t} = \frac{1}{1+K_{Me}} D_s \frac{\partial^2 C}{\partial x^2} - \omega \frac{\partial C}{\partial x} + \frac{1}{1+K_{Me}} (\Sigma R_s) \qquad (5)$$

C = concentration of dissolved element in mass per unit volume of pore water

t = time

x = depth

D_s = molecular diffusion

ω = rate of sedimentation

K_{Me} = first order adsorption constant (identical to K in zone of bioturbation)

In the zone below the zone of bioturbation the model was based on the following considerations:

1- Metals are released to the pore waters from organic matter decay which follows a first order kinectics following the equation

$$\frac{dCorg}{dt} = -kCorg \qquad (6)$$

Metal sulphide compounds are formed by bacterial reduction of SO_4^{2-} in the pore waters in conjunction with organic matter decay by bacteria (SRB).

2- Equilibrium adsorption followed a simple linear relation ($Cs=K'Ci$)

3- Precipitation of metal sulfide (Rppx)to form sulfide minerals took place following a linear rate kinetics Rppx = k_m (C-Ceq) (Ceq = concentration at saturation with authigenic minerals)

4- Compaction, water flow, porosity gradient, were ignored

5- Diffusion occurred via molecular processes only.

6- Steady state diagenesis was present ($\frac{\partial C}{\partial t} = 0$)

Based on the assumptions above, equations 6 and 5 respectively become

$$-\omega\frac{\partial(Corg)}{\partial x} - k(Corg) = 0 \qquad (7)$$

$$\left(\frac{D_s}{1+K_{Me}}\right)\frac{\partial^2 C}{\partial^2 x} - \omega\frac{\partial C}{\partial x} + \frac{FkCorg}{1+K_{Me}} - \frac{k_m(C-Ceq)}{1+K_{Me}} = 0 \qquad (8)$$

Where C: Concentration of a dissolved metal species.

Ceq: Concentration at saturation with authigenic mineral.

$Corg$: Concentration of trace metal produced as a result of organic matter decay.

k: rate constant for organic C decomposition.

km: metal sulphides precipitation rate constant.

K_{Me}: equilibrium adsorption constant.

Under the following boundary conditions

$$x = 0 \qquad Corg = Corg_o \qquad C = C_0$$

$$x \rightarrow \infty \qquad Corg = 0 \qquad C = C_{eq}$$

Solutions for the diagenetic equations are (Berner, 1980)

$$Corg = C_{org_0} Exp\left(-\frac{k}{\omega}\right)x \tag{9}$$

$$C = \left[\left(\frac{FkC_{org_0}\omega^2}{D_s + (1+K_{Me})\omega^2 k - k_m}\right) - (C_{eq} - C_0)\right] Exp\left\{\frac{(1+K_{Me})\omega - \left[(1+K_{Me})^2\omega^2 + 4K_m D_s\right]^{1/2}}{2D_s}x\right\} \tag{10}$$

$$-\left[\frac{FkC_{org_0}\omega^2}{D_s k^2 + (1+K_{Me})\omega^2 k - K_m\omega^2}\right] Exp\left[\left(-\frac{k}{\omega}\right)x\right] + Ceq$$

There are two cases where the above equation and solution can apply. The first case is where $C_{org_0} = 0$ and $K_m \neq 0$ and the second case is where $K_m = 0$ *and* $C_{org_0} \neq 0$. We

assume that diffusion of trace metal to pore waters from organic matter decay ($C_{org_0} \neq 0$) and their participation in the formation of authigenic mineral ($K_m \neq 0$) do not coexist at least for Lavant Long and Perch Lakes, which have high populations of SRB and high sulfate concentrations in their porewaters. In those lakes, metals released from organic matter decay in this anoxic layer should be consumed by sulfides to form metal sulphides.

In the situation where $C_{org_0} = 0$, $K \neq 0$, the equation (8) becomes

$$C = (C - Ceq)\exp\left[\frac{(1+K_{Me})\omega - \left[(1+K_{Me})^2\omega^2 + 4K_m D_s\right]^{1/2}}{2D_s}\, x\right] + Ceq \quad (11)$$

In the situation where $K_m = 0$ the equation (8) becomes

$$C = \left(\frac{FC_{org_0}\omega^2}{D_s K_{Me} + (1+K_{Me})\omega^2}\right)\left(1 - \exp\left[\left(-\frac{K}{\omega}\right)x\right]\right) + C_0 \quad (12)$$

Modeling trace metal distribution in the pore waters from Lavant Long Lake and Perch Lake depends on the assumption that trace metals released to the pore waters from bacterial decomposition of organic matter are consumed by H_2S/HS^- to form metal sulfides. Therefore, based on the information provided by the MPN results and the SO_4^{2-} reduction as shown in figure 10, it seems likely that the situation where $C_{org_0} = 0$ and

$K_m \neq 0$ fits best the data from both lakes. Also, since 0.2 μm membrane has been used to sample pore water, the observed concentrations are for dissolved species.

During our modeling, different metal sulphide precipitation rates (K_m) are used and K_m = 0 was used only for reference, C_0 is the concentration immediately below the zone of bioturbation and *Ceq* is the lowest concentration of the same trace metal in the pore waters. K_{Me} is calculated from trace metal distribution between pore waters and the soluble organic, amorphous and crystalline oxides fractions assuming metals are adsorbed onto these fractions using the following relationship (see Table. 4 for the values and sources of the parameters):

$$K_{Me} = K'[\rho_s(1-\phi)/\phi] \text{ where } K' = Cs/Ci \qquad (13)$$

Where ρ_s = sediment density,

ϕ = porosity

Cs = metal concentration in the solid sediments

Ci = metal concentration in the pore waters

In Perch Lake, the comparison of the observed and the predicted concentrations (Fig. 6) showed generally no significant difference for Cu, Ni and Pb, whereas for Zn and Hg the difference was significant. The model predicted that Cu and Ni occur as metal sulphides whereas Pb does not occur as metal sulphide. These predictions are confirmed by the sequential extraction results which showed that significant amount of Cu and Ni occurred

in the sulphide fraction whereas Pb was associated with the soluble organic and the oxide fractions (Appendix 4. 4d).

Hg and Zn observed and predicted concentrations were different (Fig. 6). The model also predicted their occurrence as metal sulphide whereas sequential extraction results showed that most Hg and Zn occurred as oxides (Appendix 4. 4. d, 4. e).

These observations suggest that processes other than those the model accounted for were involved in trace metal cycling, for example when adsorption predominates over metal sulphide formation (Hg and Zn in Perch Lake and Lavant Long Lake).

In Lavant Long Lake, the comparison of the observed and the predicted (by the model) trace metal concentrations in the pore waters below the zone of bioturbation was carried out for Cu, Ni, Zn and Hg (Fig. 7). Results showed that the observed concentrations of Cu and Ni in the pore waters were generally close to those predicted by the model (Fig. 7). Moreover, their occurrence as metal sulphide as predicted by the model was confirmed by the sequential extraction results as shown in Figure 2b and by the sulfate concentration profile in Lavant Long Lake (Fig. 2), which shows a decrease of sulfate concentration caused by the reduction of sulfate to sulphide. For Zn and Hg, the difference between the predicted and the observed concentrations were significant as the model was unable to predict Zn, and Hg distribution in Lavant Long Lake. In fact, although Hg concentration paralleled sulfate reduction (Appedix 4. 8. b and Fig. 2 respectively) the sequential extraction results (Appendix 4. 2. c) showed that most Hg and Zn occurred in the soluble organic and the oxide fractions.

It is significant that in Big Dam Lake SRB populations were observed to be lower than in Lavant Long Lake and Perch Lake and that the total sulfur content was lower than 100 ppm (Fig. 3, Table 3), given the importance of methylmercury production and bioaccumulation in loons in Kejimkujik Park and the effect it has shown on their rate of reproductivity and behaviour as demonstrated by Nocera and Taylor (1998). The low SRB populations will have profound impact on the cycling of elements such as Hg, Fe, Cu, Pb, Cu, Cd, Zn, and As. These elements are expected to behave differently in Big Dam Lake than in Lavant Long and Perch Lakes. In fact, in Big Dam Lake the low SRB populations (Figure 3) should directly affect the H_2S/HS^- production. Therefore, metal sulphide precipitation rate *(K_m)* would be very low since only a small amount of free cations from the pore waters will form metal sulphides. Another factor is that the low pH (~4) will favour H_2S formation over HS^- and hence over metal sulphide formation. Besides their adsorption onto humic substances, metals whose cycling is influenced by SO_4^{2-} reduction by SRB, Hg in particular, would be available for methylation by other bacteria to form methylmercury, which at pH 4 will be predominantly under $CH_3\text{-}Hg^+$ form. This interpretation is consistent with the observation of high level of Hg in the blood of common loons in Kejimkujik Park.

In a recent study, King *et al.* (2000) confirmed the role played by SRB as principal methylators of Hg in sediments joining therefore early work by Compeau and Bartha (1985). In fact, under ideal conditions (where sulfur content is high and where SRB population is important), Hg reacts with H_2S (produced during SO_4^{2-} reduction by SRB) to form HgS. In Kejimkujik, however, both SRB population and sulfur content are low, it

seems likely that Hg is methylated by other bacterial communities which need to be identified in further work.

5. Conclusion

This study showed significant difference between the predicted and the observed trace metal concentrations in pore waters from Lavant Long and Perch Lakes. Although a number of processes were used to predict trace metal concentration in the pore waters, the above differences are related to the fact that there is number of processes involved in metal cycling and that adequate predictive models are still lacking. This translates how little we know about these processes and how important is the need for further work to develop adequate predictive models.

Summary of Manuscript 4

1- In Perch Lake in the zone of bioturbation the predicted concentrations for Co, Cu, and Hg were close to their observed concentration in the pore waters. In Lavant Long Lake and in Perch Lake (for the rest of the elements), trace metal concentrations predicted by the model are generally lower than the observed. This suggested that a release of trace elements to the pore waters occurred, consistent with the findings from Manuscripts 3.

2- In the zone below the zone of bioturbation, comparison of the predicted and the observed trace element concentrations in the pore waters showed no significant difference for Cu, Ni and Pb (in Perch Lake). In the case of Zn and Hg, however, the difference between the predicted and the observed concentrations was significant suggesting that there were a number of processes controlling the release and the mobilization of trace element that the model did not account for.

3- In Big Dam Lake, the low SRB is in favour of Hg availability for other Hg methylating Bacteria. This observation is a key to understanding the high Hg in common loons in Kejimkujik Park.

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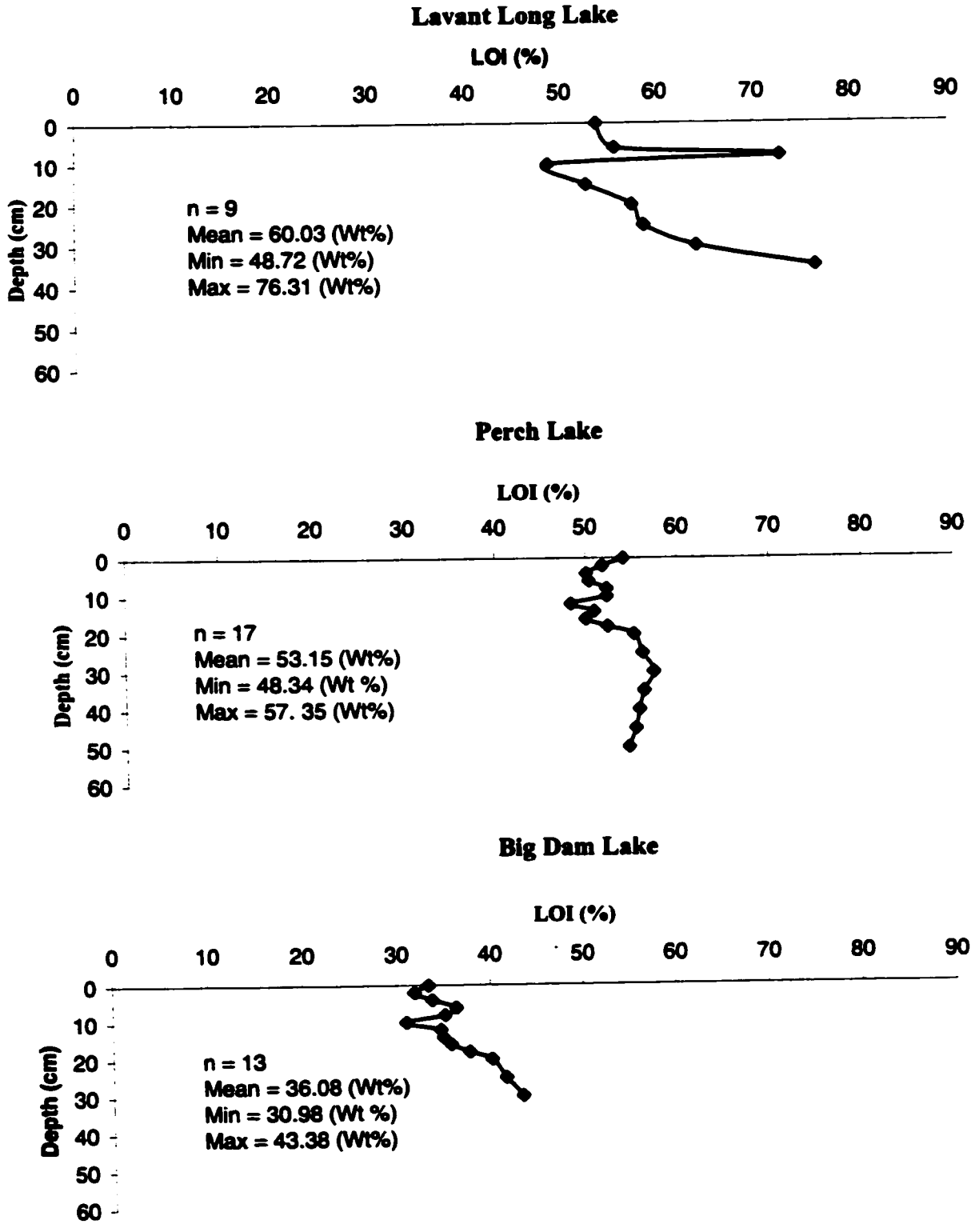

Fig. 1. Organic matter content expressed as LOI (%) in lake sediments from Lavant Long Lake, Perch Lake, and Big Dam Lake.

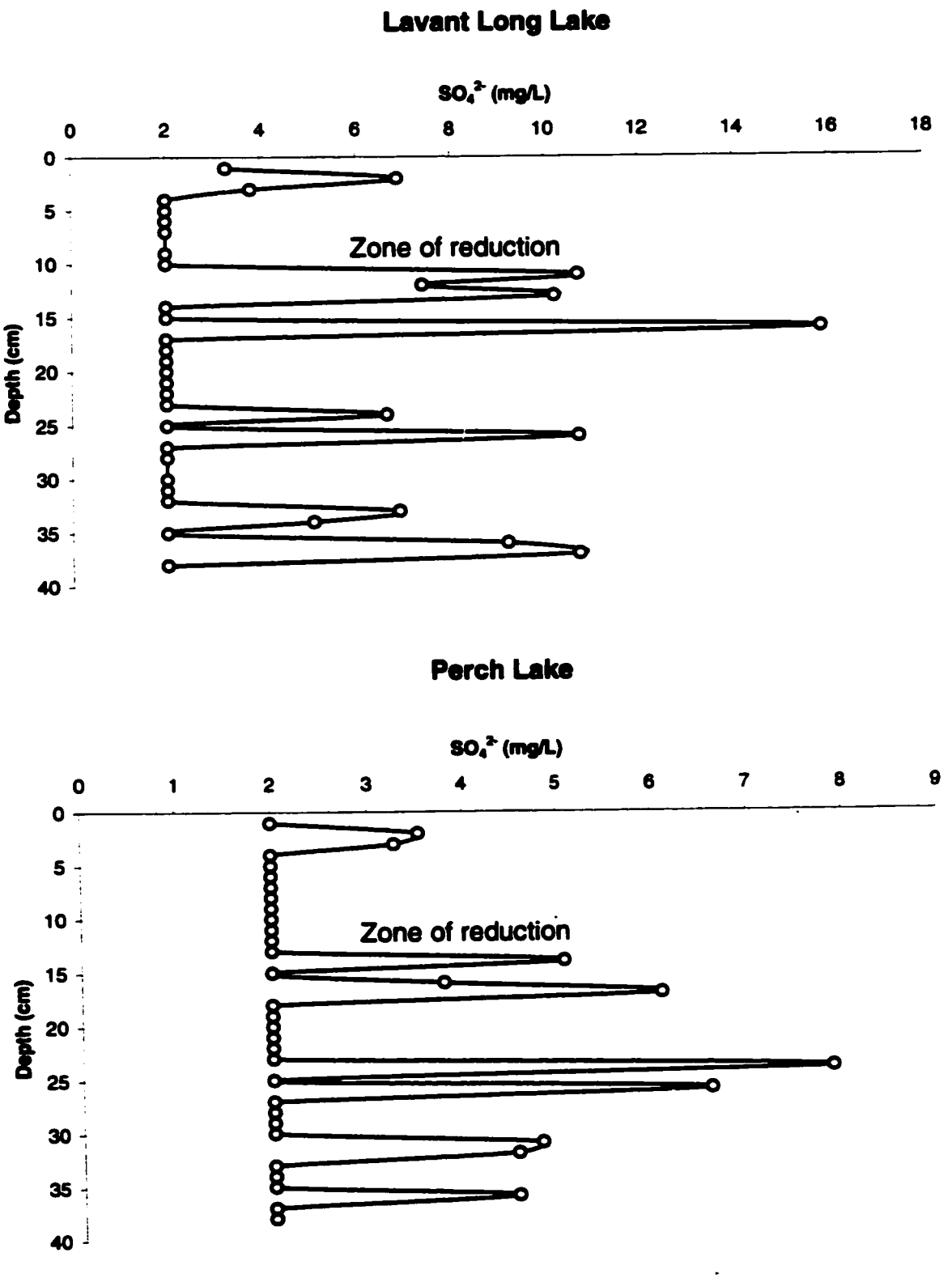

Fig. 2. Sulfate concentration in pore waters from Lavant long Lake and Perch Lake.

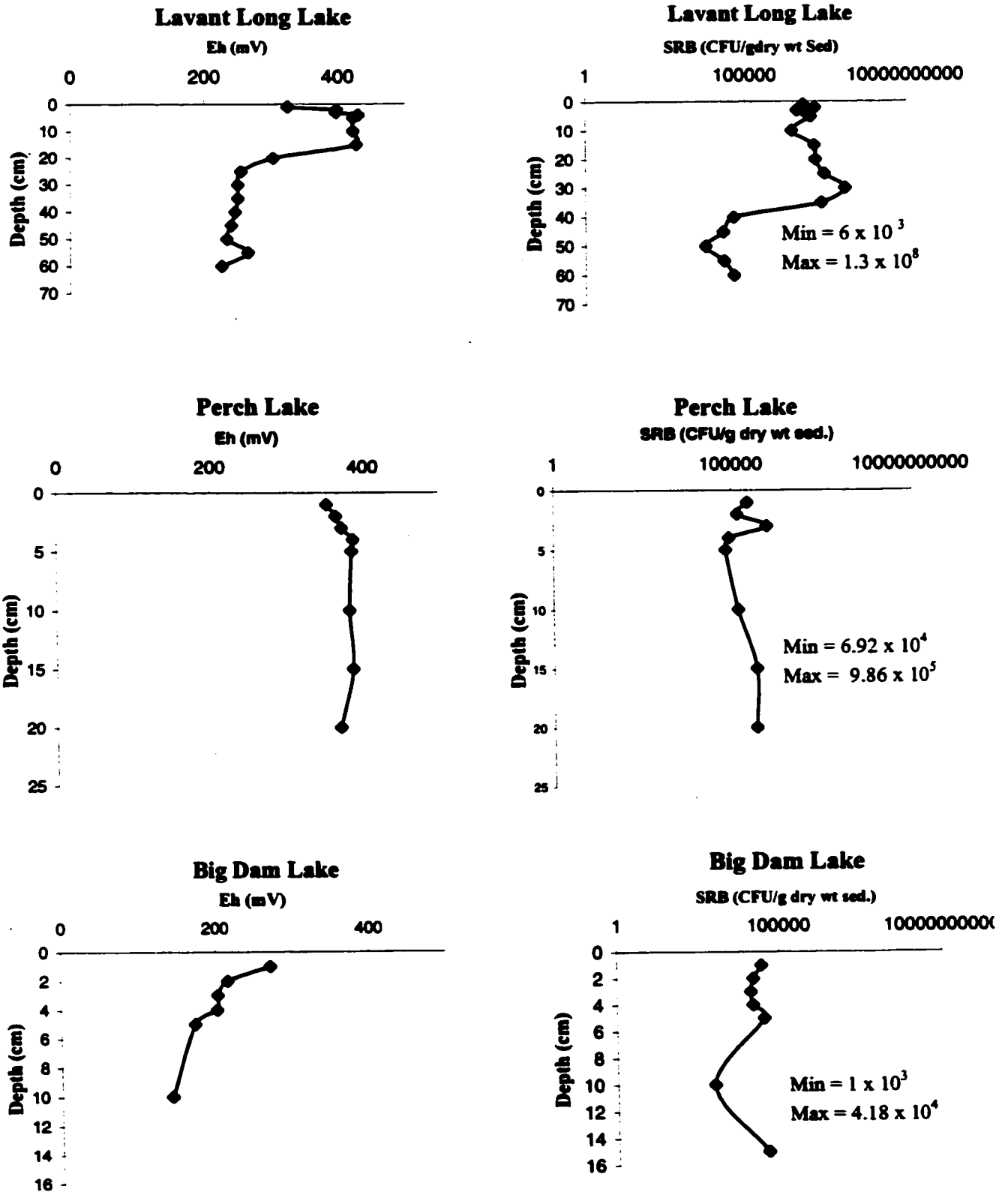

Fig. 3. Redox potential and SRB populations in lake sediments from Lavant Long Lake, Perch Lake, and Big Dam Lake.

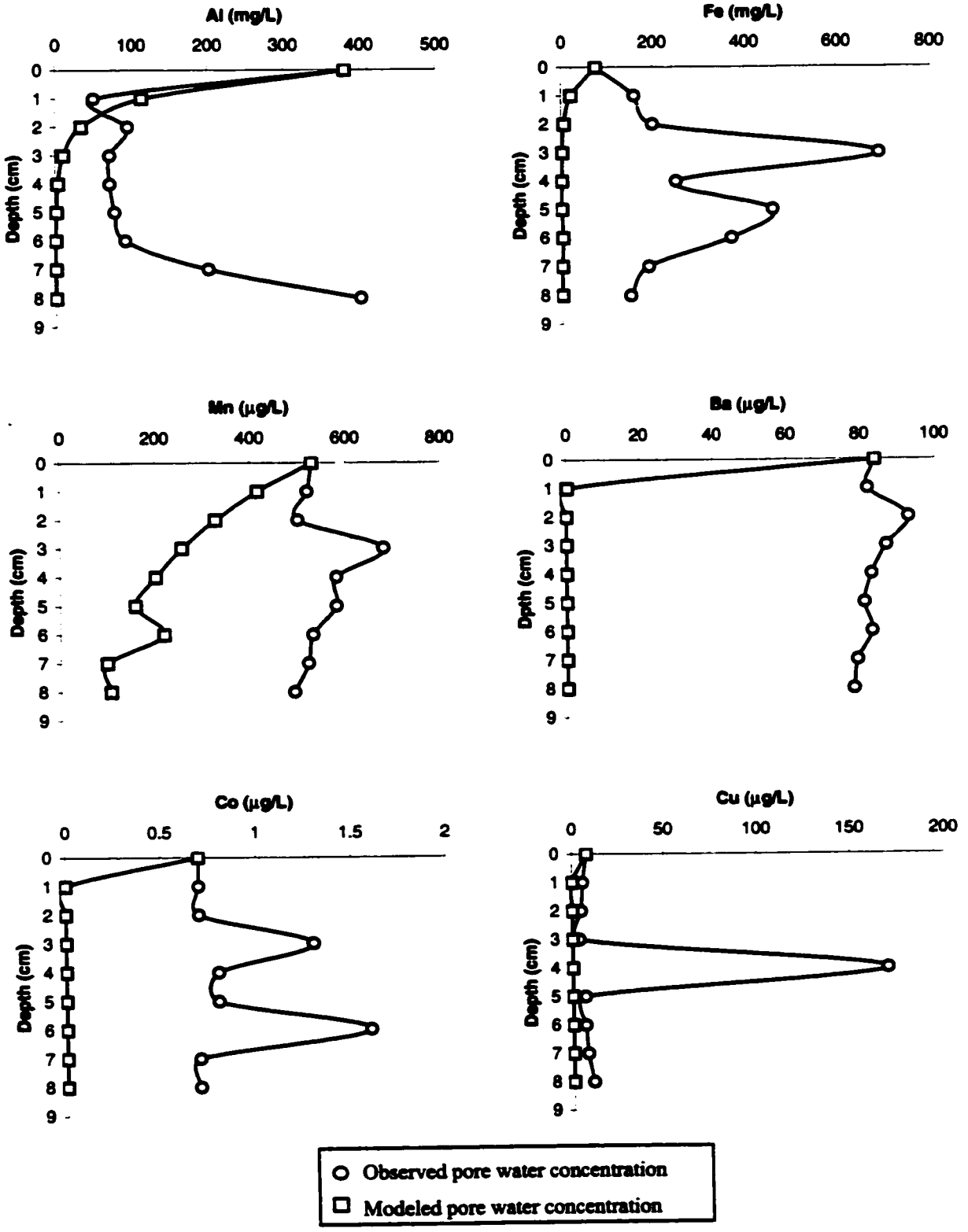

Fig. 4. a. Modeling of Al, Fe, Mn, Ba, Co, and Cu concentration profiles in the pore waters in the bioturbation zone from Lavant Long Lake.

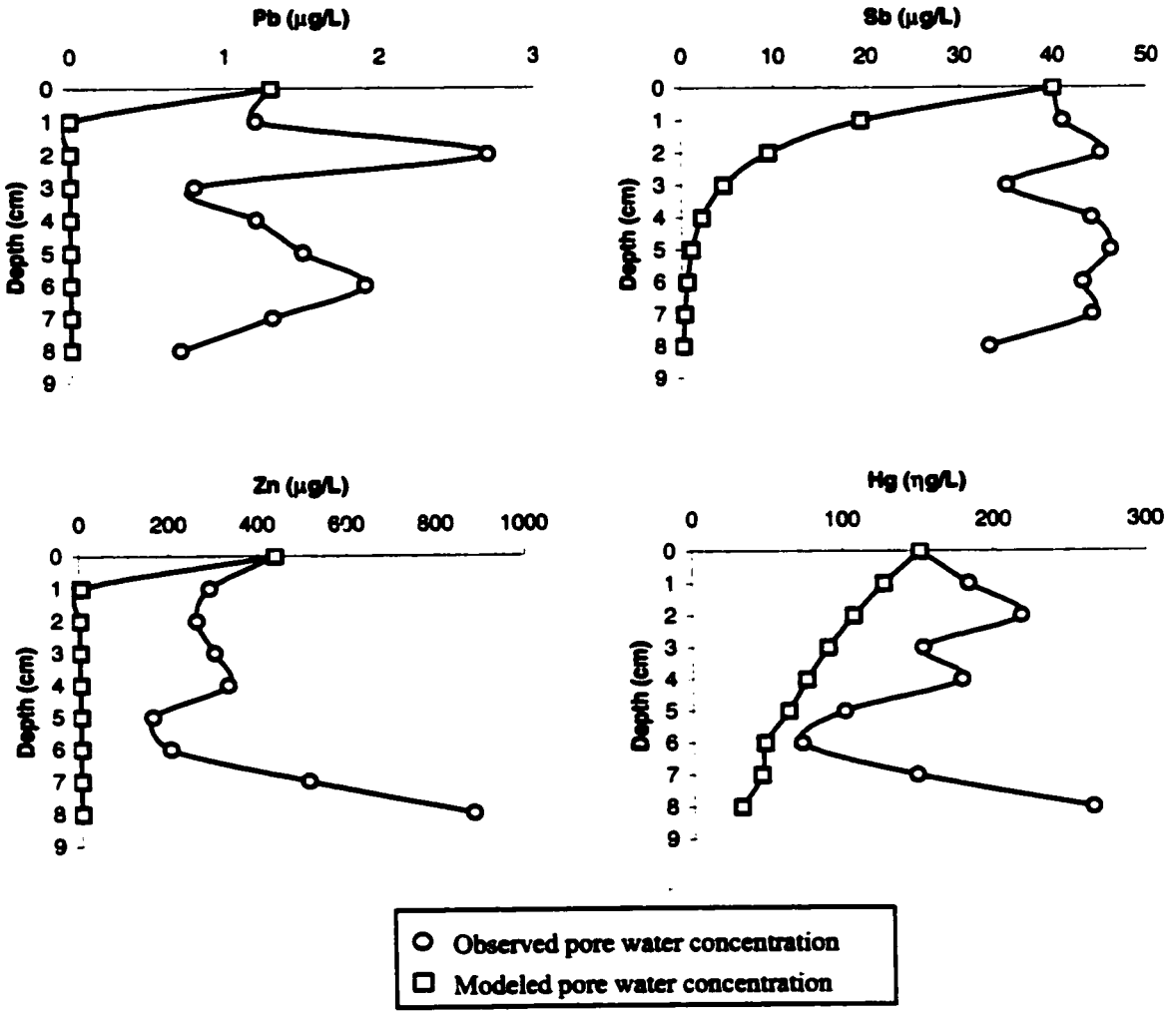

Fig. 4. b. Modeling of, Pb, Sb, Zn and Hg concentration profiles in the pore waters in the bioturbation zone from Lavant Long Lake.

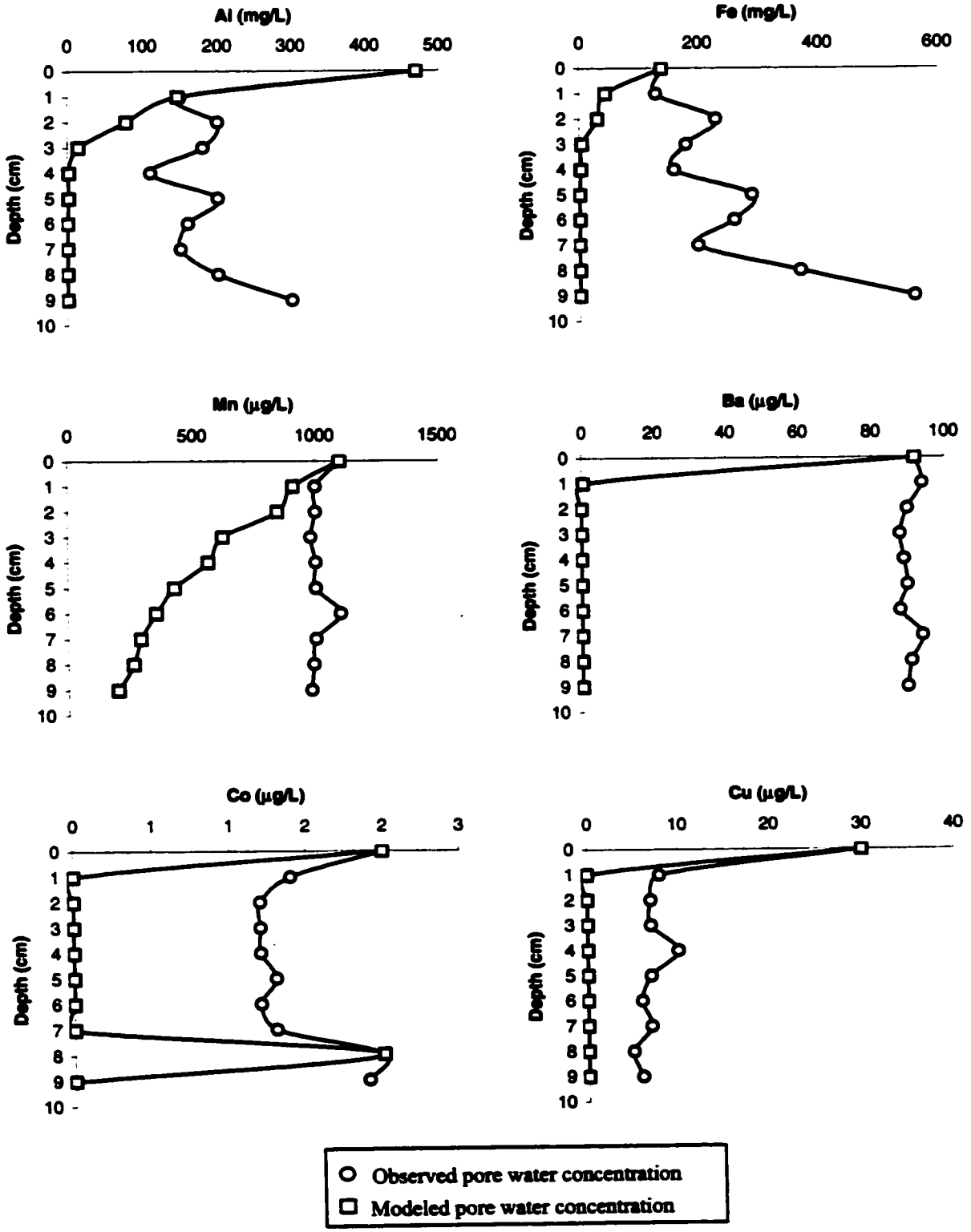

Fig. 5. a. Modeling of Al, Fe, Mn, Ba, Co, and Cu concentration profiles in the pore waters in the bioturbation zone from Perch Lake.

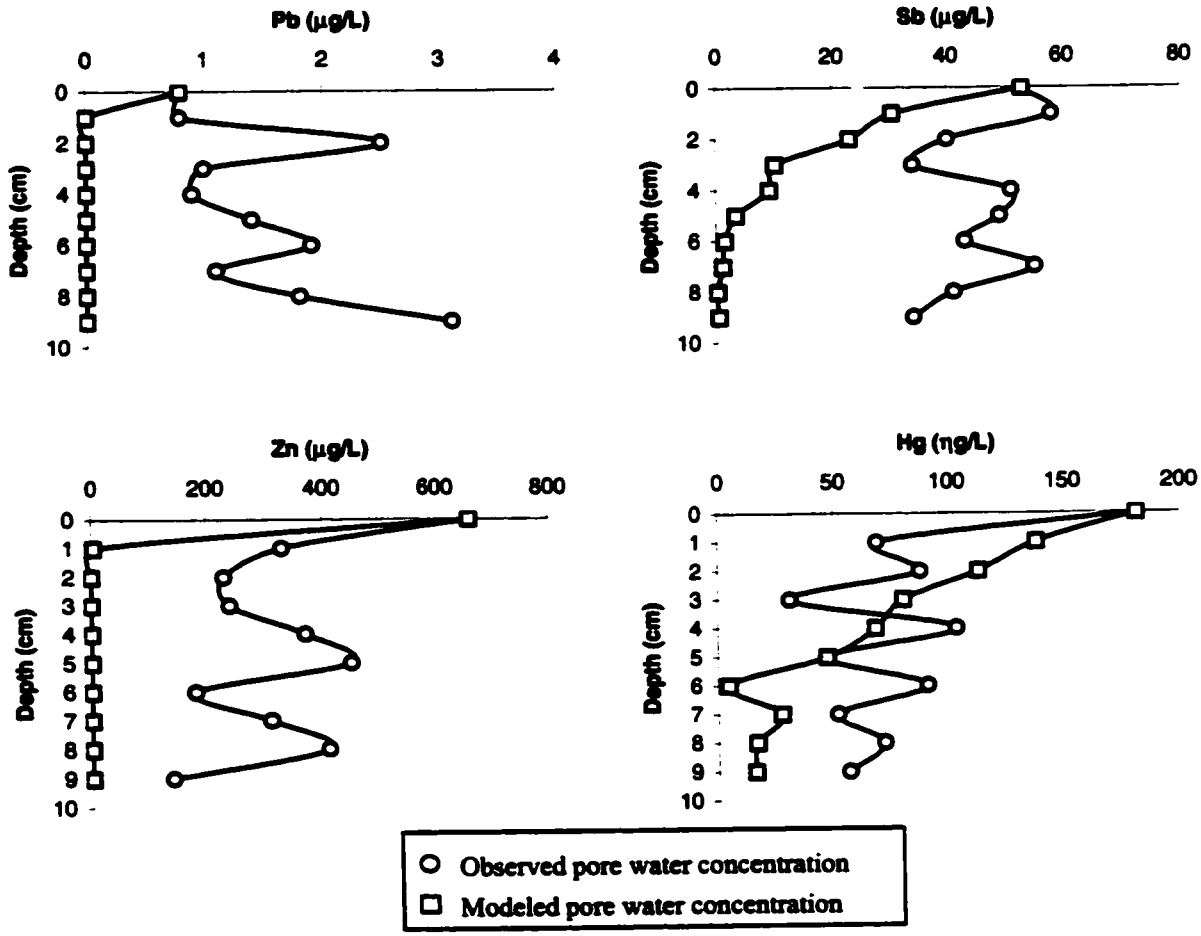

Fig. 5. b. Modeling of Pb, Sb, Zn, and Hg concentration profiles in the pore waters in the bioturbation zone from Perch Lake.

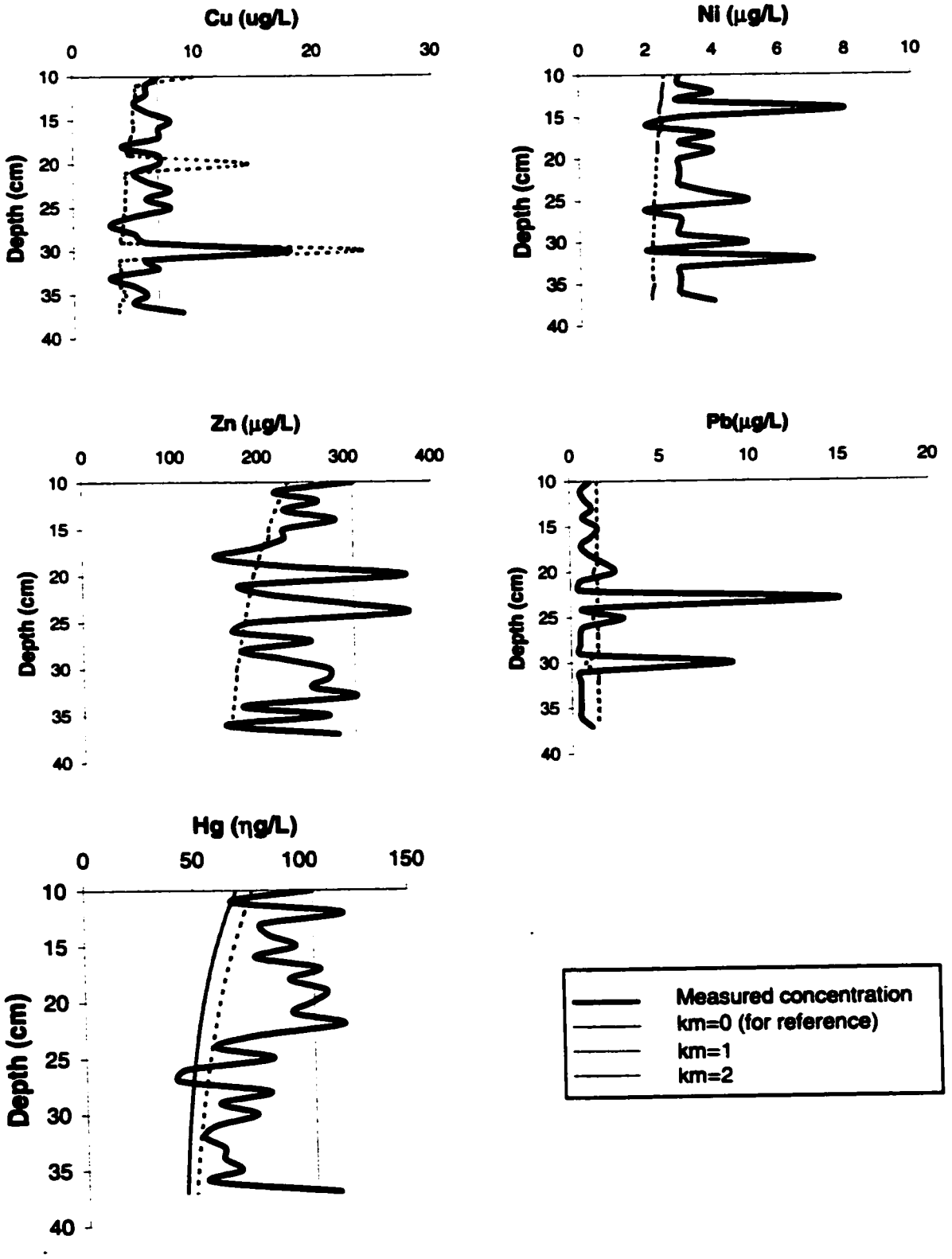

Fig. 6. Results of modeling Cu, Ni, Zn, Pb, and Hg distribution in pore waters below the zone of bioturbation in Perch Lake (K_m is the metal sulphide precipitation rate).

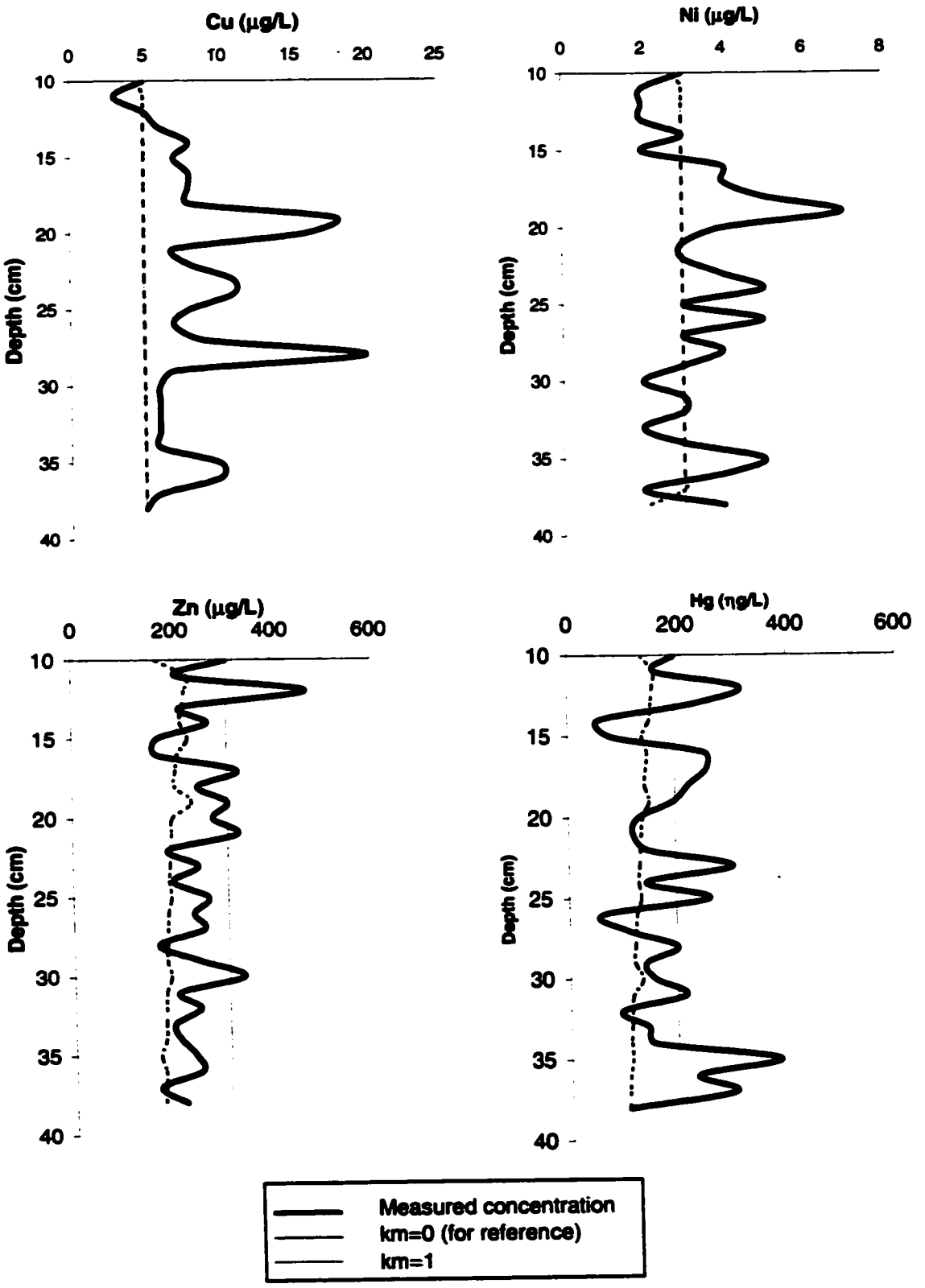

Fig. 7. Results of modeling Cu, Ni, Zn, and Hg distribution in pore waters below the zone of bioturbation in Lavant Long Lake (K_m is the metal sulphide precipitation rate).

Table 1 Sequential extraction scheme.

Fraction	Reageant	Source
F1: Humic material	0.1 M $Na_4P_2O_7$ (pH 10)	Hall and Pelchat, 1997
F2: Amorphous Fe oxides	0.25 M $NH_2OH.HCl$	Chao and Zhou, 1983
F3: Crystalline Fe oxides	1 M $NH_2OH.HCl$ in 25% CH_3COOH	Chester and Hughes, 1967
F4: Sulphide/insoluble organics	$KClO_3$-HCl-HNO_3	Chao and Sanzalone, 1977
F5: Silicates	HF-$HClO_4$-HNO_3	Tessier *et al.*, 1979

Table 2. Precision based on 33 pairs of replicates .

	Precision
Elements	%RSD (33 pairs)
Al	6%
As	6%
Ba	6%
Ca	6%
Cd	8%
Ce	12%
Co	17%
Cr	13%
Cs	10%
Cu	13%
Dy	9%
Er	8%
Eu	10%
Fe	8%
Ga	8%
Gd	9%
Hg	10%
Ho	9%
K	6%
La	11%
Lu	10%
Mg	8%
Mn	10%
Mo	13%
Na	9%
Nb	12%
Nd	11%
Ni	8%
P	10%
Pb	10%
Pr	11%
Rb	8%
Sb	9%
Sc	10%
Sm	9%
Sr	16%
Tb	8%
Ti	8%
Tl	12%
Tm	9%
U	8%
V	6%
Y	6%
Yb	9%
Zn	12%
Zr	7%

Table 3. Organic carbon and total sulfur content in the sediments from Lavant Long Lake, Perch Lake and Big Dam Lake. Note the low sulfur content in Big Dam lake.

Lavant Long	Depth (cm)	C (+/-0.2)(%)	S (+/- 0.2) (%)
	0	12.17	0.4
	2	11.89	0.5
	4	19.28	0.72
	6	14.33	0.41
	8	15.88	0.55
	15	14.41	0.85
	20	19.92	0.85
	25	14.83	0.73
	30	18.82	0.88
	35	13.35	0.71
	40	15.75	0.66
Perch	**Depth (cm)**	**C (+/-0.2)(%)**	**S (+/- 0.2) (%)**
	0	10.91	0.86
	2	7.95	0.75
	4	10.2	0.95
	6	14.06	1.2
	8	11.7	1.03
	10	11.27	0.86
	12	10.06	0.87
	14	11.81	1.12
	16	13.66	1.29
	18	11.59	0.96
	20	10.86	0.94
	25	16.26	1.35
	30	15.52	1.18
	35	14.97	1.21
	40	16.23	1.26
	45	12.57	1.02
	50	12.74	0.98
Big Dam	**Depth (cm)**	**C (+/-0.2)(%)**	**S (+/- 0.2) (%)**
	0	11.48	<0.01
	2	6.71	<0.01
	4	10.46	<0.01
	6	10.27	<0.01
	8	11.56	<0.01
	10	11.29	<0.01
	12	7.34	<0.01
	14	8.43	<0.01
	16	10.72	<0.01
	18	7.05	<0.01
	20	11.67	<0.01
	25	12.03	<0.01
	30	12.52	<0.01

Table 4. Model parameters, their values and sources.

Symbols	Definition	Value	Source
C_o	Concentration of dissolved compound insediment/water interface	Variable	Measured
C_i	Concentration of dissolved compound in lake pore water	Variable	Measured
D_B	Biodiffusion coefficient	1.3×10^{-6} cm^2 sec^{-1}	Assumed (Lerman, 1977)
D_s	Molecular diffusion coefficient	Variable	Li and Gregory, 1974; Vanysek, 1996
ϕ	Average sediment porosity	0.97 for Lavant Long Lake	Measured
		0.98 for Perch Lake	Measured
ρ_s	Average sediment density	0.14 g cm^{-3} (Lavant Long)	Measured
		0.15 g cm^{-3} (Perch)	Measured
K_{Me}	Equilibrium adsorption constant	Variable	Measured from profiles (sequential extraction results)
ω	Sedimentation rate	0.31 cm yr^{-1} (Lavan Long)	Measured
		0.33 cm yr^{-1} (Perch Lake)	Measured
K_m	Metal sulphide precipitation constant	Variable	Measured or assumed

General Conclusions

The main objectives of this study were to investigate a) the role of the organic matter, oxides (amorphous and crystalline), sulphides and silicates in trace metal distribution in lake sediments, b) the importance of trace metal atmospheric and geological fluxes in remote lakes c) the role of organic matter transformation in trace metal distribution in lake sediments and d) the role of biogeochemical processes controlling metal cycling in lakes.

The investigation of the role of sediment geochemical composition in trace metal distribution showed the important role played by organic matter and the silicate fraction in trace metal distribution. In fact, statistical tests showed a positive correlation between elements with high affinity to the mineral fraction (i.e. Cr, Mn, Fe, Co, Ni) and Al contents and a negative correlation between elements with high affinity to the organic fraction (i.e. Hg, Pb, Cd, Cu, Zn) and Al. These tests also showed a negative correlation between the group of elements with high affinity to the mineral fraction and organic C content and a positive correlation between the group with high affinity to the organic matter and the organic C contents. These correlation tests were confirmed by the sequential extraction results, which showed a strong geochemical relationship between the soluble organic and the oxide fractions and the group of elements formed by Pb, Hg, Cd, Cu, and Zn on one hand, and between the silicate fraction and the group of elements formed by Cr, Mn, Fe, Al, and Ni on the other. These findings suggested that the enrichment of the group of elements formed by Hg, Pb, Cd, Cu, and Zn in the surface sediments from the 20 lakes is related to their affinity to organic matter and to the role played by the oxide fractions in surface sediments and not to an increased loading of these metals to the lakes.

The importance of the geological contribution to trace elements to lake sediment budget as raised in the first manuscript following the observed similarity between trace metal contents and their distribution in the soil B-horizon and in lake sediments was investigated based on mass balance approach and on the use of sediment traps to measure trace metal fluxes in two remote lakes. Results from this study showed that in both lakes, the geogenic metal flux exceeded the atmospheric flux. This finding was consistent with the Hg, Pb, Cd, and Cu, occurrence at high level in the bedrock and in the postglacial deposits in the watersheds of both study lakes. Moreover, the association of high amounts of some elements such as Cu, Fe, Hg, Sb with the sulphide fraction in the sediments collected in the traps was consistent with their occurrences as sulphide minerals in the watersheds of the study lakes and support the high geogenic metal flux. Our study showed, using sediment traps, that in remote lakes trace metal flux from geological weathering sometimes exceeds atmospheric flux with a ratio higher than 9:1 (geogenic to atmospheric) and thus higher than the widely acceptable range 1/2 to 1/3 (geogenic to atmospheric ratio) from other studies.

Following the finding of a strong relationship between some trace metal enrichment in surface sediments and the organic matter content, it was important to investigate how HS content and their transformation affect their interaction with trace elements. Therefore, a study of HS from Lavant Long Lake, Perch Lake, and Big Dam Lake was carried out. This study was conducted by developing an HS extraction procedure and using HS characterization approaches including E4/E6 ratio and ^{13}C NMR. Results showed HS transformation with depth. Correlation tests between the content of trace elements

associated with the soluble organic fraction (HA and FA) and the abundance of COOH and OH functional groups in HA and FA with depth, showed positive correlation. The transformation of HS as shown by mean of increasing aromaticity, decreasing HA and FA content, increasing C/N ratio and organic carbon content and decreasing E4/E6 has direct implication on trace element cycling in lake sediments. In fact these transformation occur on the account of a decrease of COOH and OH functional groups and result in the release of important amounts of trace elements to the pore waters. It was thus the first time that an approach using a combination of sequential extraction results and HS characterization results demonstrated the effects of organic matter transformation on metal cycling.

The role of biogeochemical processes controlling metal cycling in lakes was quantitatively investigated based on both field observations and theoretical assumptions, and trace metal diagenesis was investigated using diagenetic modeling approaches. The steady state diagenetic model was an appropriate choice based on evidence from Manuscript 2, and 3, and on the fact that both Lavant Long and Perch Lakes were remote lakes and isolated from any point sources of metals, such as domestic and/or local industrial inputs. In fact Manuscript 2 showed that geogenic fluxes significantly exceeded atmospheric fluxes, suggesting no major historical changes in terms of trace metal deposition into the lakes. Moreover, Manuscript 3, showed the evidence of the diagenetic processes resulting in trace metal release to the pore waters as a result of HS transformation with depth. Results from this study showed that in the zone of bioturbation, in Perch Lake the predicted concentrations for Co, Cu, and Hg were close to

their observed concentration in the pore waters. In Lavant Long Lake and in Perch Lake (for the rest of the elements), trace metal concentrations predicted by the model were generally lower than observed. This suggested that a release of trace elements to the pore waters occurred, consistent with the findings from Manuscripts 3. Below the zone of bioturbation, comparison of the predicted and the observed trace element concentrations in the pore waters showed no significant difference for Cu, Ni and Pb (in Perch Lake). In the case of Zn and Hg, however, the difference between the predicted and the observed concentrations was significant suggesting that there were a number of processes controlling the release and the mobilization of trace element that the model did not account for. Further work is hence needed to shed the light on these processes in order to develop appropriate diagenetic models for trace element, such as Hg, in lake sediments. In Big Dam Lake, the low SRB was in favour of Hg availability for other Hg methylating bacteria. This observation helps understanding why high Hg content occur in common loons in Kejimkujik Park. However further work is needed to shed the light on the principal bacterial community (ies) responsible for Hg methylation.

This study has deep implications on the way one perceives or interprets trace metal enrichment in lake sediments. In fact, it was demonstrated that trace metal total concentrations did not necessarily reflect their sources or the importance of their fluxes but instead was a results of the geochemistry of the sediments. These conclusions raise the question regarding the use of lake sediments as tools to study the historical fluctuations of trace element input into the environment without investigating the role of the sediment geochemical composition such as, organic matter content, the role of

different phases in trace metal distribution, and/or taking into account other diagenetic processes such as the release of trace metal from sediments to pore waters as demonstrated in Manuscript 2.

Finally, this study showed that there are both methodological and conceptual problems when evaluating the importance of atmospheric and geogenic trace metal fluxes globally based on lake sediment records. First the global natural background from previous studies did not include high (natural) occurring anomalies in remote areas and second the methods used presented inherent problems mostly due to neglecting post depositional processes. The importance (as shown by the number of processes and the high trace element concentrations in the pore waters Manuscript 3 and 4) and complexity (as shown by the difficulty of predicting trace metal concentrations in the pore waters by using diagenetic models as shown in Manuscript 4) of these processes were clearly shown in this study. Although present, the post-depositional processes have never been considered when modeling long range atmospheric transport to remote areas. In the light of the results of this work, further work towards the understanding of these processes and their consideration when modeling long range atmospheric transport to remote areas seems necessary.

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Appendices

Appendix 1-1
Manuscript 1

	Accuracy				Precision			
	LKSD-1	LKSD-2	LKSD-3	LKSD-4	LKSD-1 (n=7) RSD	LKSD-2 (n1=9, n2=5) RSD	LKSD-3 (n1=6, n2=5) RSD	LKSD-4 (n=5) RSD
Mo*	25.00%	25.00%	37.50%	6.00%	9.0%	7.7%	6.1%	15.6%
Cu*	12.38%	12.38%	5.10%	0.27%	14.4%	5.7%	6.5%	11.0%
Pb*	0.06%	0.06%	7.31%	15.98%	13.6%	6.3%	4.8%	8.7%
Zn*	3.30%	3.30%	1.87%	2.99%	12.5%	5.9%	3.4%	2.2%
Ag*	15.42%	15.42%	16.32%	15.00%	1.8%	4.5%	3.7%	11.3%
Ni*	0.97%	0.97%	0.76%	5.00%	6.7%	4.9%	9.6%	4.5%
Co*	15.69%	15.69%	13.33%	25.45%	14.7%	5.7%	7.4%	4.9%
Mn*	6.76%	6.76%	1.72%	3.63%	5.6%	3.3%	8.1%	1.9%
Fe*	2.51%	2.51%	4.19%	0.74%	5.8%	3.0%	7.1%	2.8%
As*	1.36%	1.36%	0.65%	15.17%	12.1%	4.3%	24.4%	14.1%
U	12.28%	12.28%	27.54%	3.87%	24.3%	36.7%	70.7%	11.7%
Au	96.67%	96.67%	97.78%	95.00%	0.0%	0.0%	70.7%	0.0%
Th	55.22%	55.22%	44.44%	80.39%	34.6%	19.2%	7.4%	0.0%
Sr	86.31%	86.31%	87.43%	61.45%	4.5%	6.2%	6.5%	1.9%
Cd*	18.47%	18.47%	3.06%	9.47%	3.6%	5.9%	3.0%	10.9%
Sb*	37.04%	37.04%	5.95%	18.67%	19.2%	25.8%	45.9%	12.0%
Bi	n.a.	n.a.	n.a.	n.a.	11.9%	12.6%	7.7%	9.1%
V*	22.92%	22.92%	24.24%	18.13%	6.0%	3.8%	7.7%	2.9%
Ca	n.a.	n.a.	n.a.	n.a.	7.2%	3.4%	7.9%	1.9%
P	n.a.	n.a.	n.a.	n.a.	4.9%	3.2%	6.3%	2.6%
La	12.75%	12.75%	14.42%	14.62%	6.9%	3.0%	6.1%	3.4%
Cr*	6.51%	6.51%	2.29%	2.86%	7.3%	6.4%	5.1%	2.4%
Mg	n.a.	n.a.	n.a.	n.a.	8.3%	8.1%	7.7%	2.1%
Ba	72.46%	72.46%	75.49%	58.85%	5.3%	3.3%	5.1%	1.9%
Ti	n.a.	n.a.	n.a.	n.a.	8.9%	30.5%	6.3%	7.4%
B	87.52%	87.52%	78.67%	54.55%	13.1%	36.0%	28.0%	17.9%
Al	n.a.	n.a.	n.a.	n.a.	5.2%	3.5%	7.2%	4.0%
Na	n.a.	n.a.	n.a.	n.a.	13.9%	12.9%	21.5%	0.0%
K	n.a.	n.a.	n.a.	n.a.	13.1%	5.3%	7.3%	0.0%
W	n.a.	n.a.	n.a.	n.a.	n.a	n.a	n.a	n.a
Tl	n.a.	n.a.	n.a.	n.a.	31.5%	35.4%	14.1%	42.1%
Se	n.a.	n.a.	n.a.	n.a.	16.1%	18.2%	11.7%	6.9%
Te	n.a.	n.a.	n.a.	n.a.	42.0%	34.0%	63.8%	30.8%
Ga	n.a.	n.a.	n.a.	n.a.	7.9%	6.4%	3.3%	17.3%
Hg*	11.88%	11.88%	13.45%	36.84%	8.2%	14.8%	17.3%	36.4%
TOT/C	10.22%	10.22%	9.96%	6.09%	41.0%	2.6%	3.6%	1.4%
TOT/S	7.14%	7.14%	14.29%	2.83%	44.2%	4.2%	8.8%	4.3%
ORG/C	n.a.	n.a.	n.a.	n.a.	43.1%	2.5%	3.8%	4.2%
INS/S	n.a.	n.a.	n.a.	n.a.	44.1%	5.7%	24.2%	6.3%

* Elements for which accuracy was determined according to standard values from partial extraction (Lynch, 1990). Others are either compared to standard values from "Total extraction" or not available (n.a) in the provisional standard list.
RSD (%), is referred to as the average relative standard deviation within n1, n2 or n number of replicates.
n1: number of replicates used to assess data reproducibility for all element except, Hg, Tot-C, Tot-S, Org-C, and Ins-S. n2: number of replicates used to assess data reproducibility for Hg, Tot-C, Tot-S, Org-C, and Ins-S.

Appendix 1-2
Manuscript 1

	Sediments		Soils	
	Precision RSD	Accuracy STD	Precision RSD	Accuracy STD
Mo	0.0%	0.71	10.1%	1.41
Cu	11.9%	0.71	14.1%	1.41
Pb	3.8%	1.62	1.5%	2.13
Zn	0.9%	0.71	3.1%	3.54
Ni	4.3%	1.37	4.6%	0.21
Mn	1.1%	0.00	18.2%	3.54
Fe	14.4%	0.33	5.4%	0.05
Cd	0.7%	0.07	8.6%	0.09
Cr	2.9%	15.13	2.7%	1.63
Al	1.8%	n.a	9.6%	n.a
Hg	31.7%	10.07	5.3%	16.70
Si	7.7%	n.a	7.7%	n.a

RSD refers to the average relative standard deviation baed on 2 pairs of replicates for both sediment and soil samples.

Accuracy (STD) was calculated by comparing the measured values for LKSD-4 to the provisional values from partial extraction for the same standard.

Appendix 1-3

Manuscript 1

Detail of sequential extraction procedure

Elements bound to soluble organic:

0.5 gram of sample was weighed twice into two 50 mL centrifuge tubes (Falcon tubes). 50 mL of 0.1 M $Na_4P_2O_7$ was added to each sample. In order to suspend, the sediments were vortexed and horizontally shaken for 1 hour at a rate of 160 shakes per minute. Both samples were then centrifuged for 10 minutes at 2800 rpm. The supernatants were decanted into two clean-labeled 50 mL Falcon tubes. This procedure was repeated once more on the remaining residue. Solution was then analyzed for trace elements.

Elements bound to oxides:

Elements bound to hydrous Fe and Mn Oxides:

20 mL of 0.25 M $NH_2OH.HCl$ was added to the residue from the previous extraction. Samples were vortexed to re-suspend the particles. Samples were then heated at 60°C in a water bath for 2 hours and vortexed every 30 minutes with the cap tightened, and replaced in water bath with unloosened caps after vortexing. Samples are centrifuged for 10 minutes at 2800 rpm. Supernatants were decanted into clean, labeled 50 mL Falcon tubes. The remaining residue was rinsed with 5 mL of DDI water, capped and vortexed to re-suspend the sediments and finally centrifuged for 10 minutes at 2800 rpm. Supernatants from the rinsing operation were decanted into the same Falcon tubes. The rinsing operation was repeated once more. The whole procedure was repeated but this

time by heating residues in water bath for a 30 minutes. Solutions were analyzed for trace elements.

Elements bound to crystalline Fe oxides:

30 mL of 1.0 M $NH_2OH.HCl$ and 25%HOAc mixture was added to residues from the previous extraction and capped tightly. Samples were vortexed to re-suspend the sediments and heated in a 90°C water bath for three hours with caps tightly on. During the heating stage, pressure was vented and samples were vortexed with caps on tight. Samples were then centrifuged for 10 minutes at 2800 rpm. Supernatants were decanted into cleaned labeled Falcon tubes. Residues were rinsed with 10 mL of 25% HOAc, capped, vortexed and centrifuged for 10 minutes at 2800 rpm. Supernatants from rinsing operation were added to the labelled Falcon tubes. The rinsing procedure with 25% HOAc was repeated once more. The whole procedure was repeated another time, but this time, the residues were heated in water bath for 1.5 hours. Solutions were analyzed for trace elements.

Elements bound to insoluble organic and Sulfides:

750 mg of $KClO_3$ was added to the residues, along with 10 mL of 12 M HCl. The tubes were capped tightly and the samples were vortexed one at the time. Another 5 mL of 12 M HCl was added and the samples were capped tightly and vortexed every 10 minutes for approximately 30 minutes and 10 mL of 12 M HCl are added from time to time. 15 mL of DDI water was added to each sample and the tubes were capped and vortexed to suspend and centrifuged for 10 minutes at 2800 rpm. Supernatants were decanted into clean,

labeled Falcon tubes. 10 mL of 4 M HNO_3 was added to the remaining residues, samples were then vortexed and heated in a 90°C water bath for 20 minutes with caps on with additional vortexing every 5 minutes. Samples were vortexed to resuspended and their contents were transferred into a 50-mL Teflon pressure tubes. The pressure tubes were then centrifuged for 10 minutes at 2800 rpm. Supernatants were then decanted (added) into supernatants from the previous centrifugation operation. Falcon tubes that contained the residues before their transfer to pressure tubes were rinsed with 5 mL DDI water, capped, vortexed. Sample contents were transferred to the Teflon pressure tubes, vortexed and centrifuged for 10 minutes at 2800 rpm. The supernatant was added into the Falcon tube that recovers all the supernatants. The rinsing operation was repeated once more. Supernatants were then analyzed for trace elements.

Elements associated with silicates:

2 mL of 16 M HNO_3 are added to residues which were heated uncapped on a hot plate set at 200°C. Samples were moved from the heating plate as they evaporated down to 0.5 mL. After 5 minutes of cooling time, 2 mL of 12 M HCl was added to the residues and the samples were heated uncapped in a 90°C water bath for 20 minutes. Residues were cooled down for 5 minutes before adding 10 mL of a decomposition mixture consisting of HF:$HClO_4$: HNO_3 (5:3:2 V/V). The mixture (residues and acids) was heated capped in a 90°C water bath for 1 hour. Tubes were vented whenever they appeared bloated. Contents of the Teflon tubes were transferred into Teflon beakers using DDI water to rinse the sediments from the pressure tubes. Residues were heated overnight on a hot plate set at 70°C. In the morning, the temperature was increased to 125°C and the

samples were heated to dryness. 1 mL of 12 M HCl was added to residues, and the mixture was swirled. 3 mL of 16 M HNO_3 was then added and the mixture was swirled to dissolve the particles. Beaker walls were rinsed with DDI water once. The contents were swirled and warmed for 5 minutes on a hot plate. Residues were transferred to calibrated test tubes by using DDI water to rinse beakers. The volume was increased to the 20 mL-mark. Tops were parafilmed and solutions were mixed thoroughly. Solutions were then analyzed for trace elements.

Appendix 3-1

Manuscript 3

^{13}CNMR technique theory: a literature synthesis

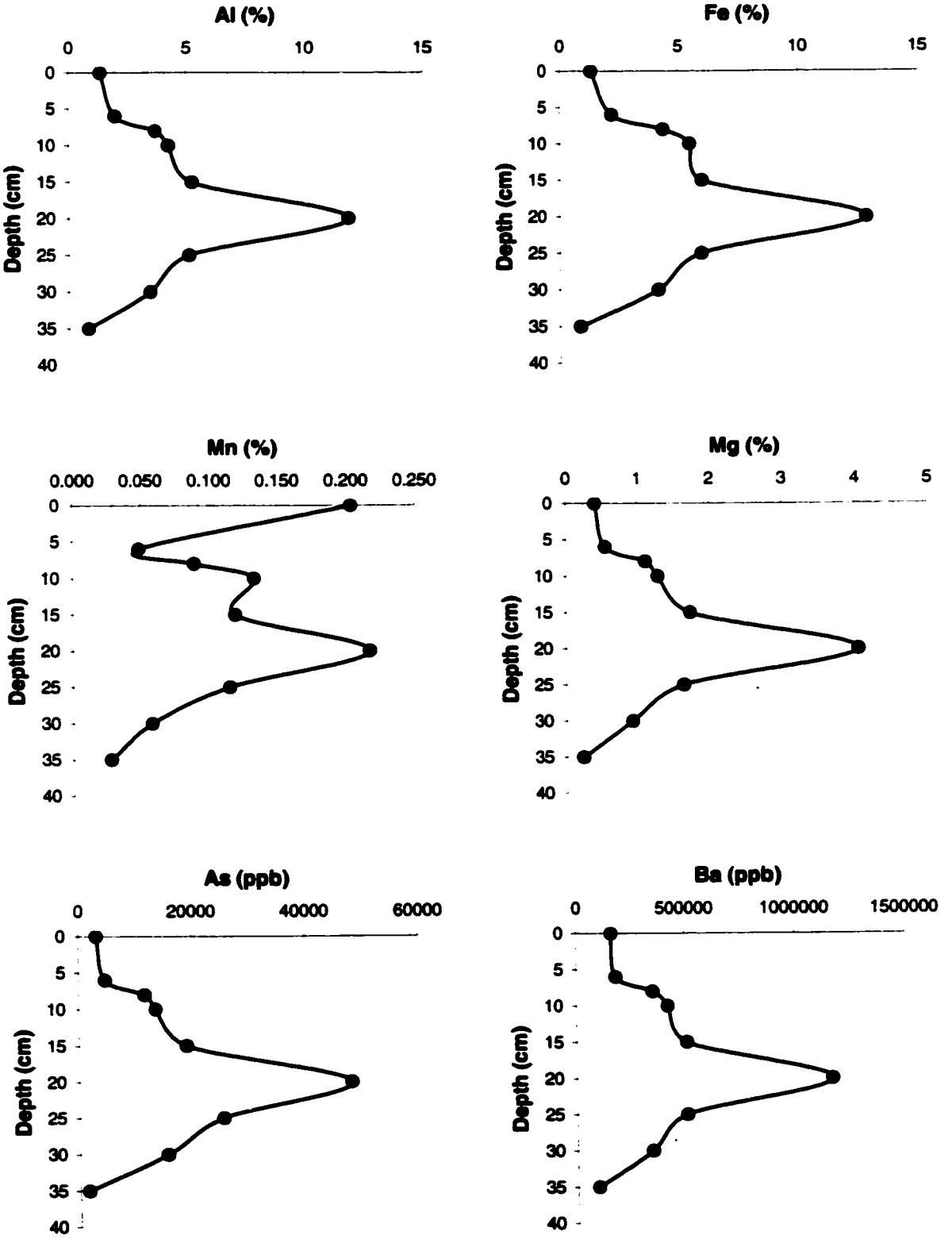
In nuclear magnetic resonance experiments, samples are placed in a uniform magnetic field and an oscillating magnetic field is applied perpendicularly. Either the steady field or the frequency of the oscillating field is varied until the resonance condition is met. At resonance, the nuclei will absorb energy from the oscillating field and undergo transition to the higher energy state. When a nucleus that possesses a spin, such as hydrogen (^{1}H) or carbon (^{13}C) atoms, exists in a chemical compound, the spinning nucleus is partially shielded by the surrounding atoms from the external magnetic field. Therefore, the effective magnetic field impinging upon the nucleus spin is altered and this in turn requires that either the stationary magnetic field or the frequency of the oscillating field be changed in order to obtain resonance. If we suppose that the stationary magnetic field is fixed as is the case for all Fourier transform spectrometers, then the frequency of the oscillating field is the parameter that will be altered in order to achieve resonance. The NMR frequency of a given nucleus is generally measured relative to a suitable standard. This type of measurement gives rise to the so-called chemical shift, ς, defined by the equation

$$\varsigma = \left(\frac{\upsilon_{sample} - \upsilon_{standard}}{\upsilon_{oscillatory}} \right) \times 10^6$$

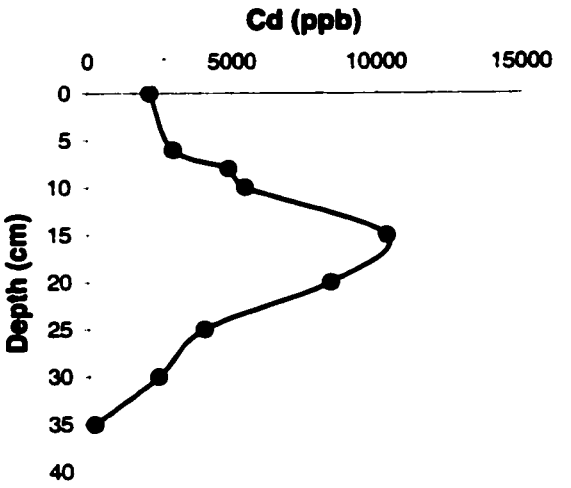
There are two types of NMR analysis, liquid NMR and solid NMR. In liquid sample NMR, the magnetic field at a nucleus consists of two components: 1- the externally applied stationary field, altered by the nuclear shielding and 2) the magnetic field induced by other spinning nuclei in the molecule (spin-spin coupling). The first gives rise to the chemical shift and the second leads to the spin-spin splitting of the chemically shifted lines. There are different spin-spin coupling mechanisms: the strongest is the dipole-dipole coupling caused by the direct interaction of the magnetic moments of spinning nuclei that are close together. This coupling can cause substantial line broadening. However, in liquids the motion of molecules averages out the dipolar effect so that the net splitting is zero. For solids, NMR spectra are much broader lines than those of liquid samples. This situation is due to anisotropic interactions in solids. The major anisotropic interaction is dipole-dipole coupling. However, the line broadening can be eliminated by high-power proton decoupling which is accomplished by irradiating the protons at their resonant frequencies so that they become activated and are no longer coupled to the ^{13}C nuclei. However, this does not eliminate broadening due to chemical shift anisotropy. The latter may be eliminated by the so-called magic-angle spinning technique. Enhanced sensitivity is also accomplished by cross polarization. By combining all the above techniques into so-called cross polarization magic-angle spinning experiments (CP/MAS), such as the one used in this study, the high-resolution solid-state NMR spectra can be obtained.

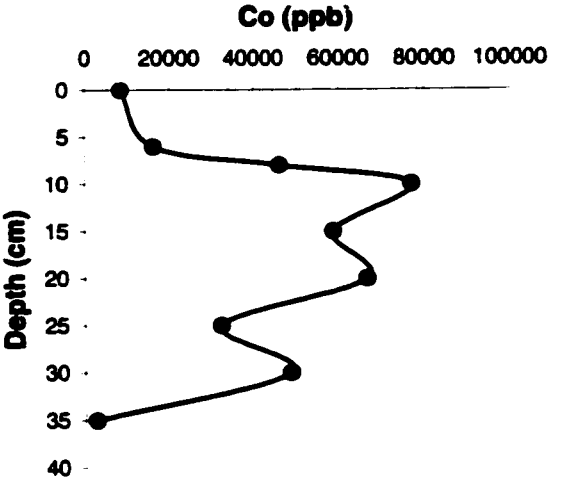
Appendix 4
Manuscript 4

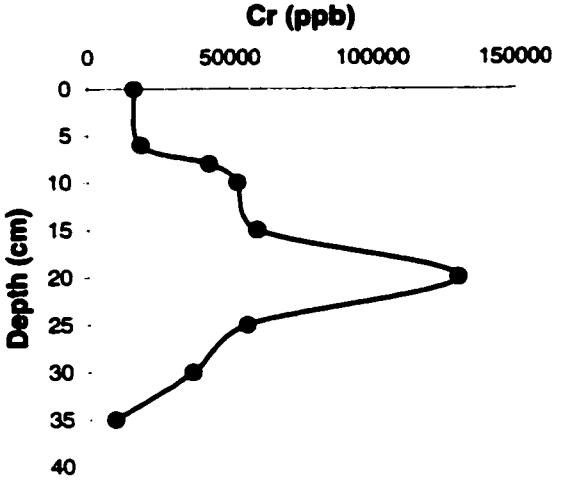
Appendix 4.1. a. Total concentrations, as a function of sediment density, of, Al, Fe, Mn, Mg, As, an in lake sediments from Lavant Long Lake.

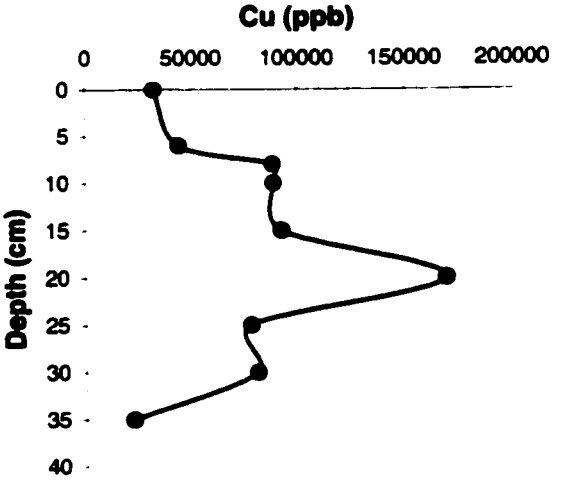


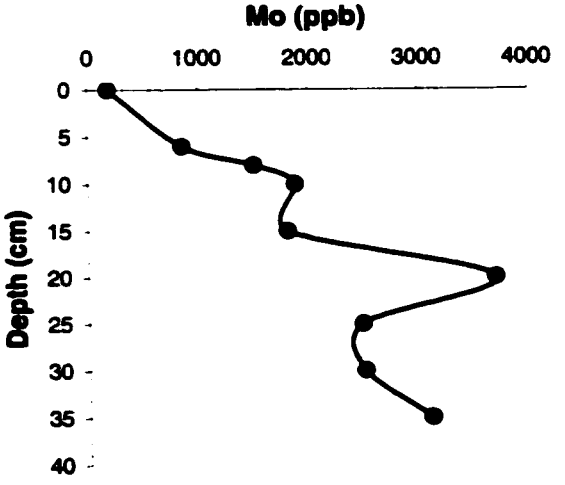
Appendix 4.1. b. Total concentrations, as a function of sediment density, of, Cd, Co, Cr, Cu, Mo, and Ni in lake sediments from Lavant Long Lake.

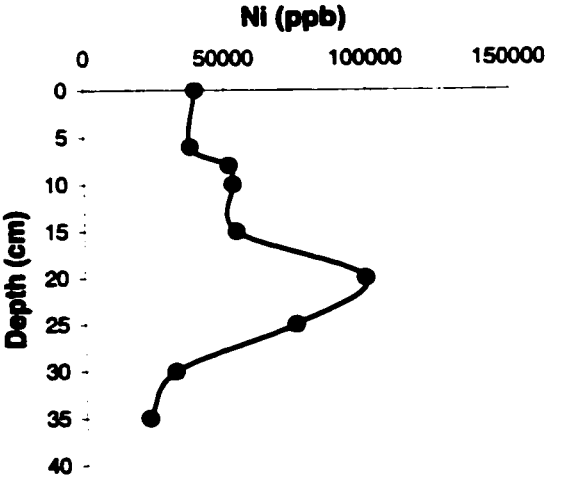




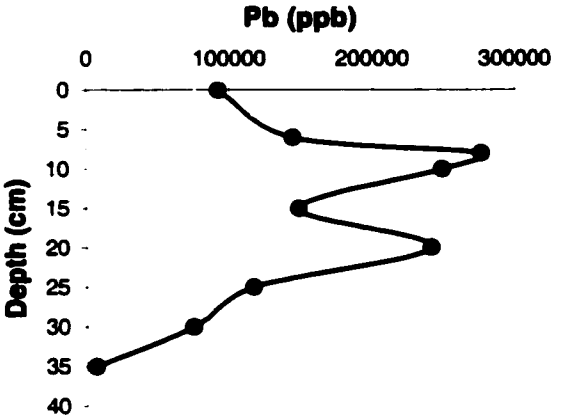


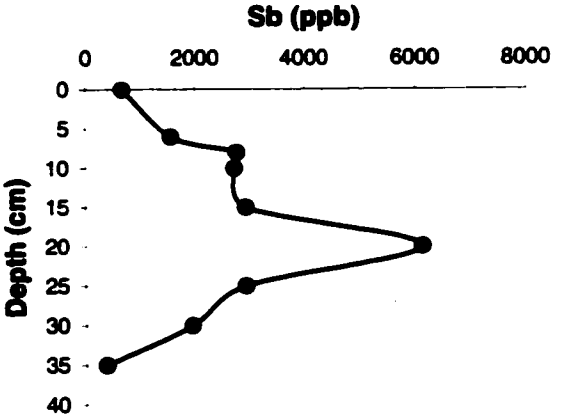


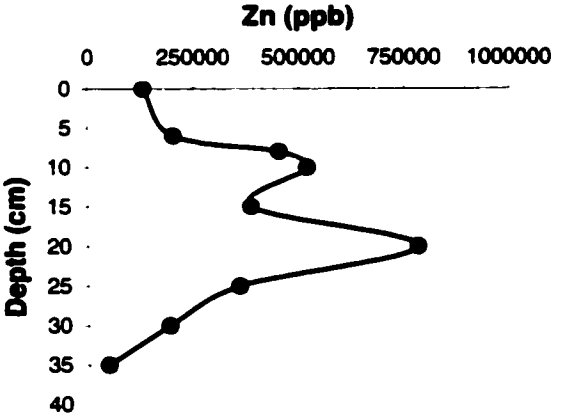


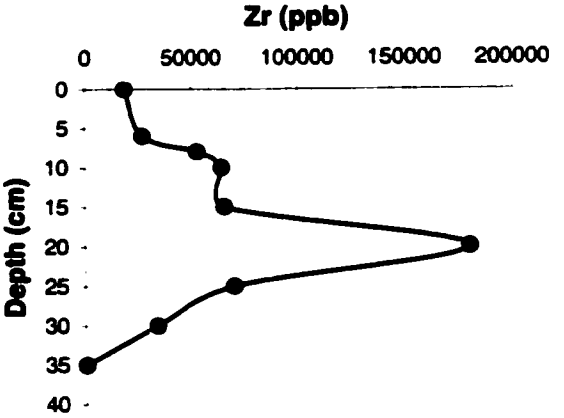


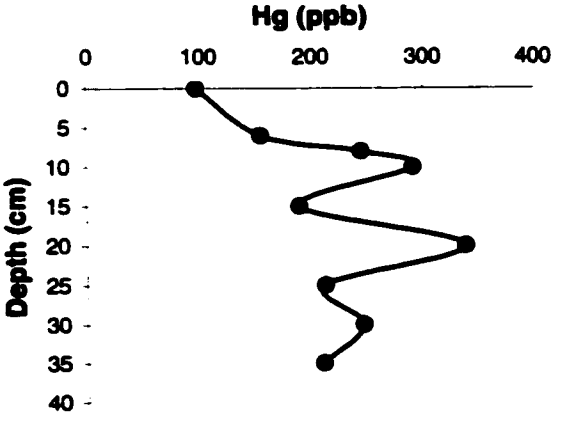
Appendix 4. 1. c. Total concentrations, as a function of sediment density, of, Pb, Sb, Zn, Zr, and Hg in lake sediments from Lavant Long Lake.



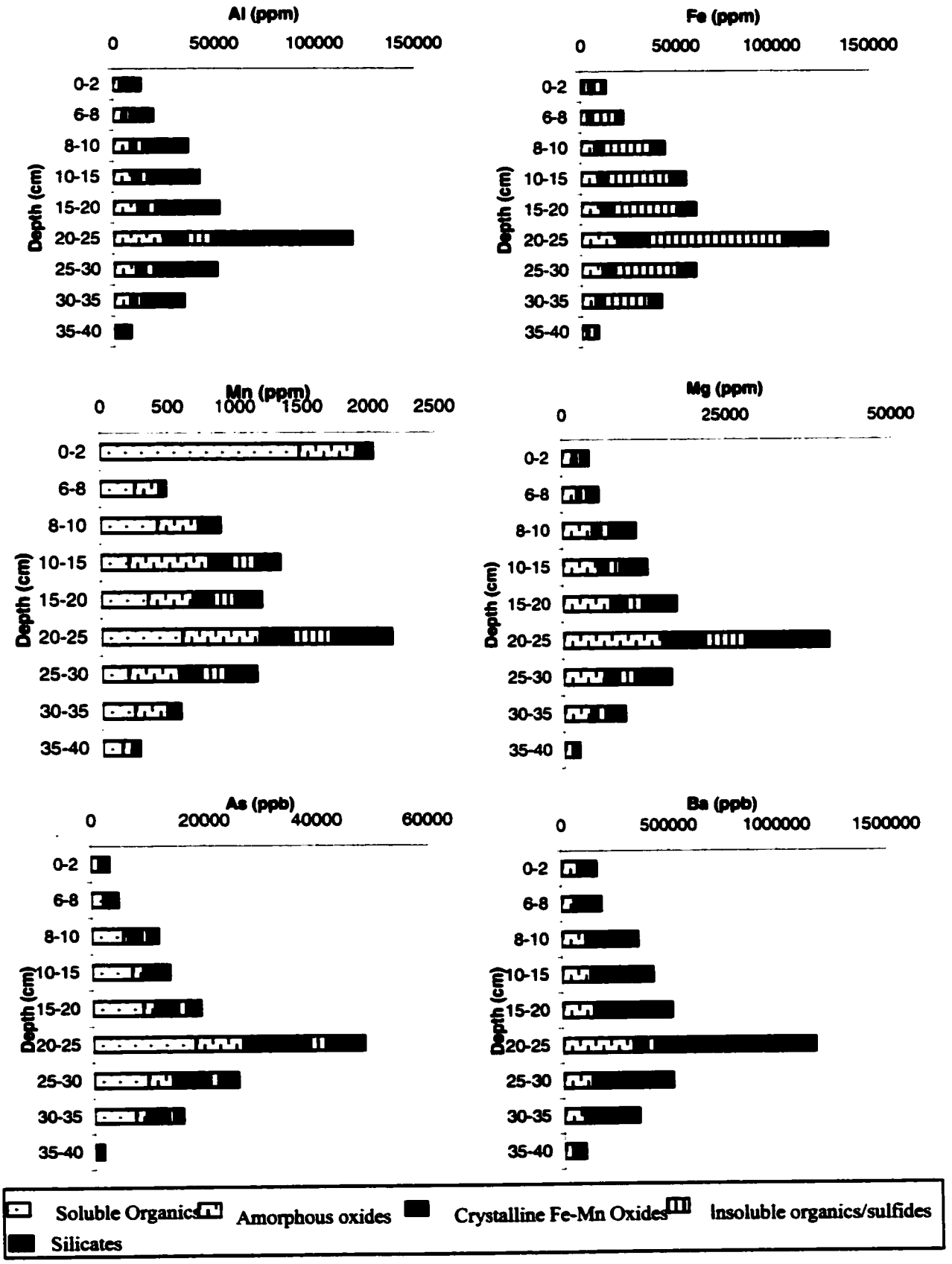




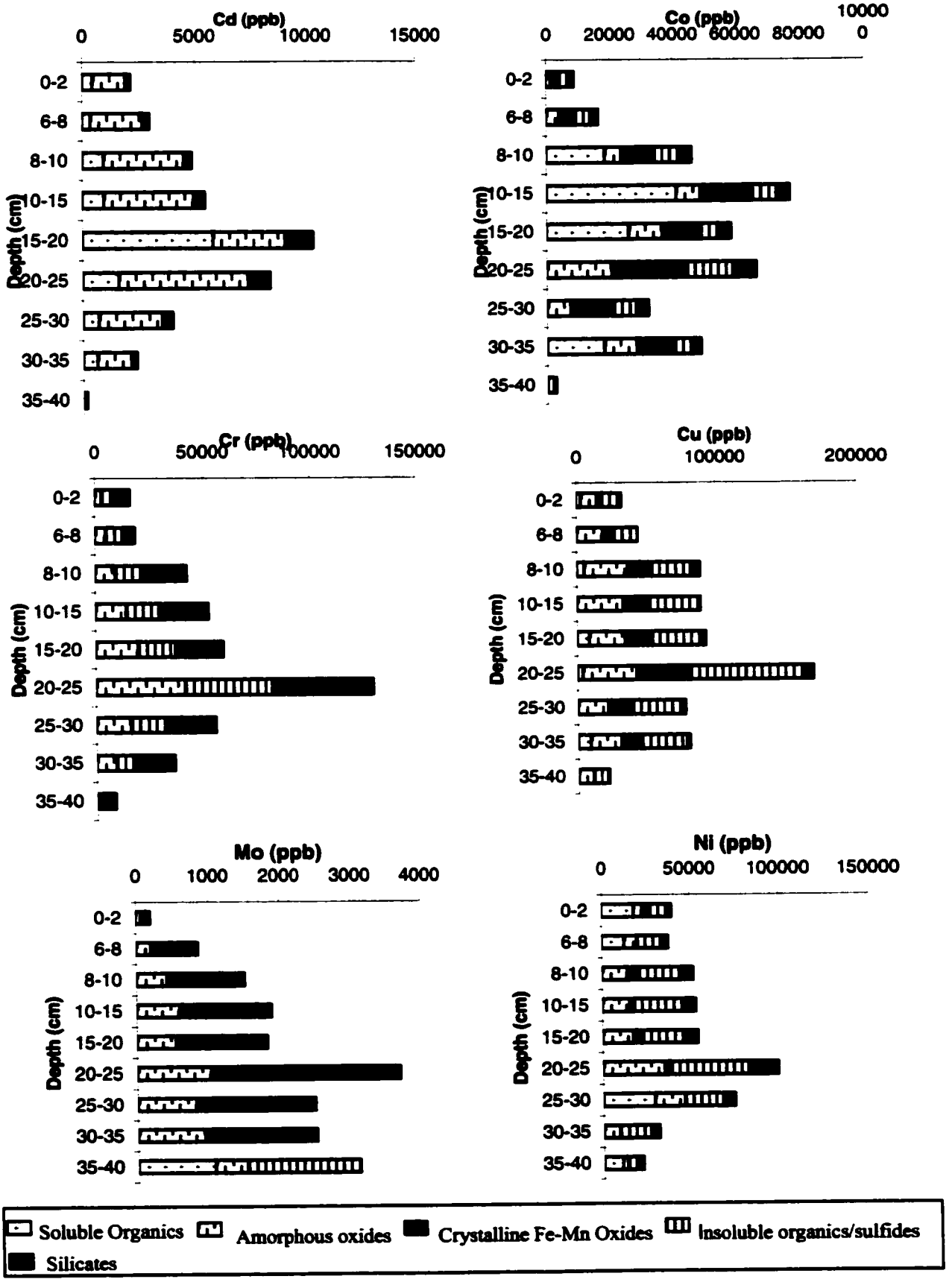




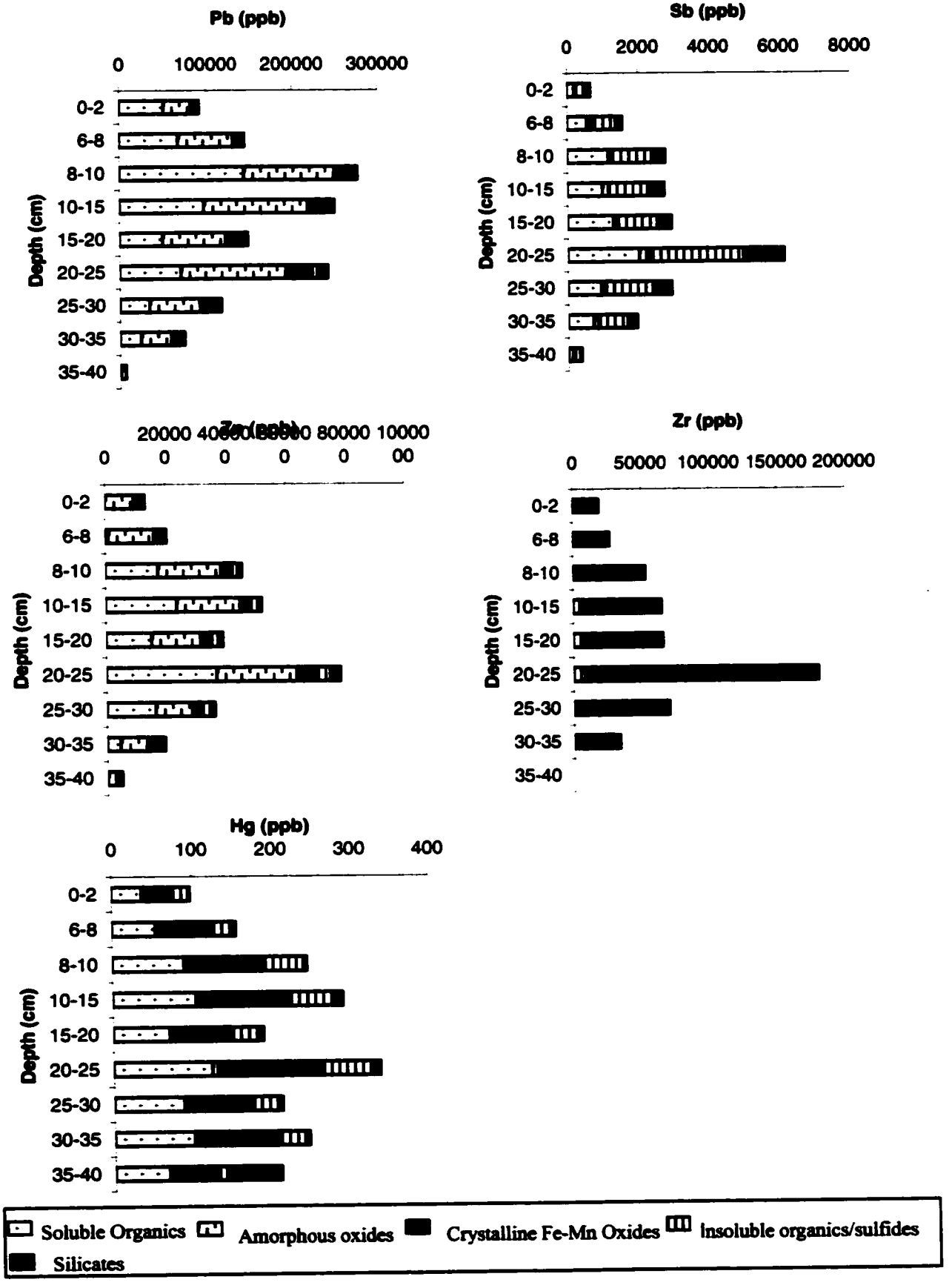
Appendix 4. 2. a. Al, Fe, Mn, Mg, As, and Ba distribution in lake sediments from Lavant Long Lak



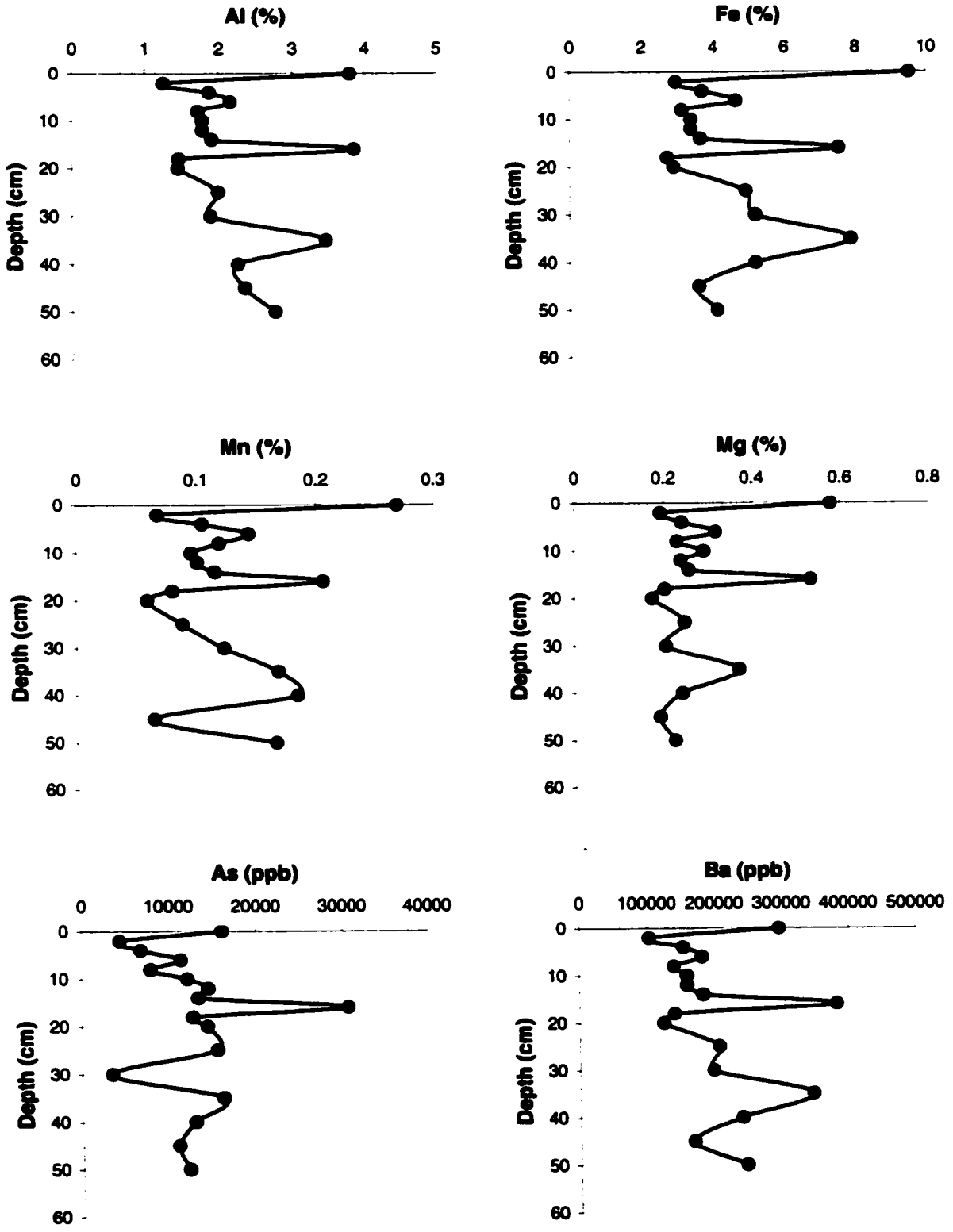
Appendix 4. 2. b.Cd, Co, Cr, Cu, Mo, and Ni distribution in lake sediments from Lavant Long Lake



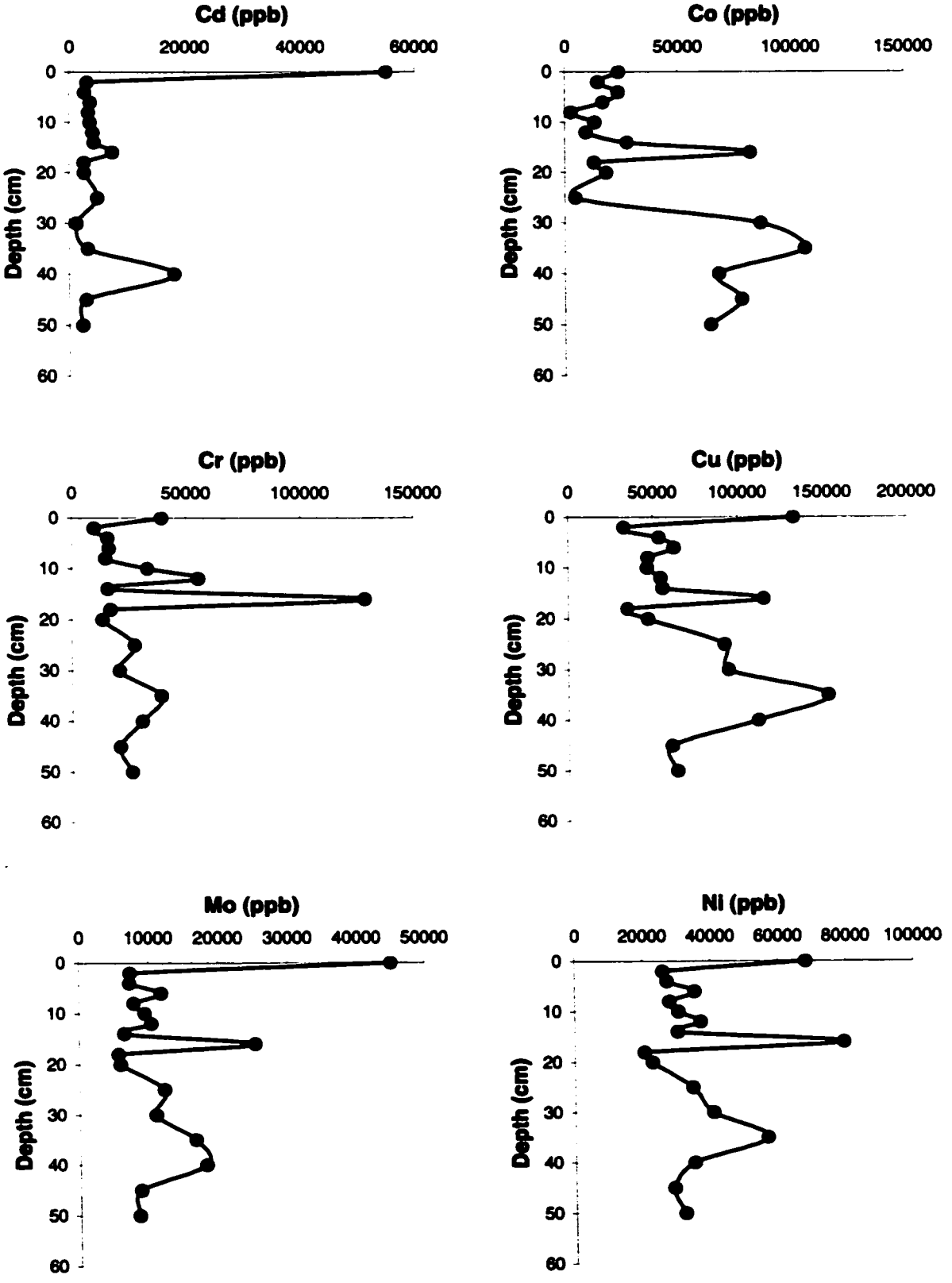
Appendix 4. 2. c. Pb, Sb, Zn, Zr, and Hg distribution in lake sediments from Lavant Long Lake.



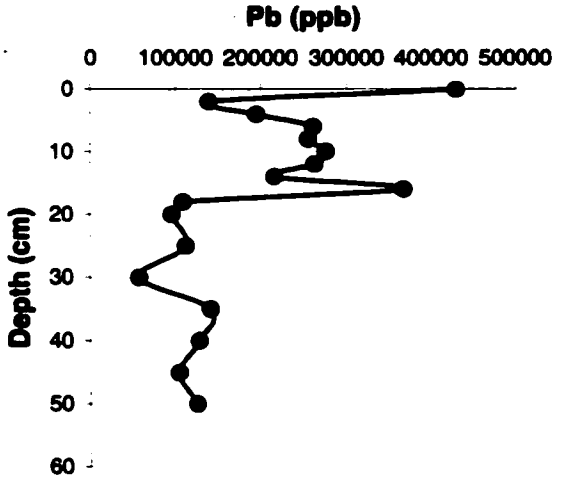
Appendix 4. 3. a. Total concentrations, as a function of sediment density, of, Al, Fe, Mn, Mg, As, and Ba in lake sediments from Perch Lake.

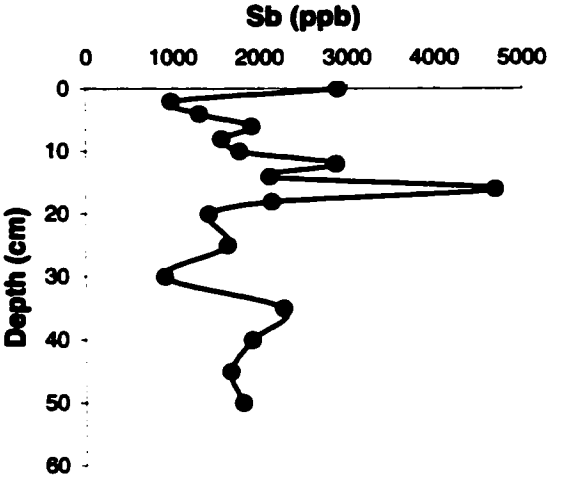


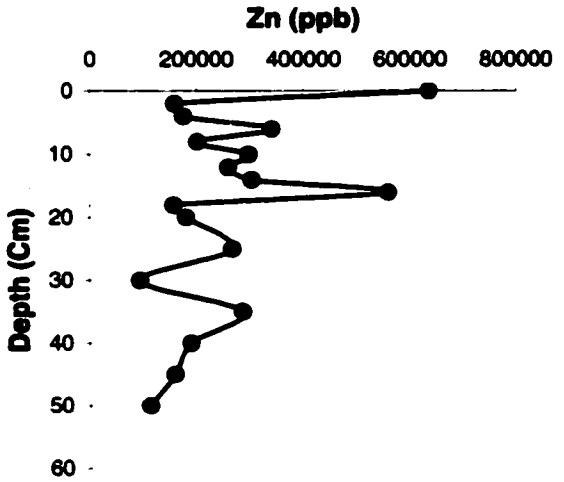
Appendix 4. 3. b. Total concentrations, as a function of sediment density, of, Cd, Co, Cr, Cu, Mo, and Ni in lake sediments from Perch Lake.

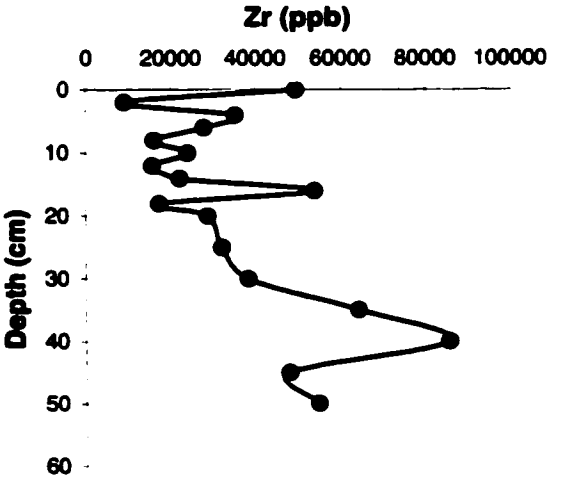


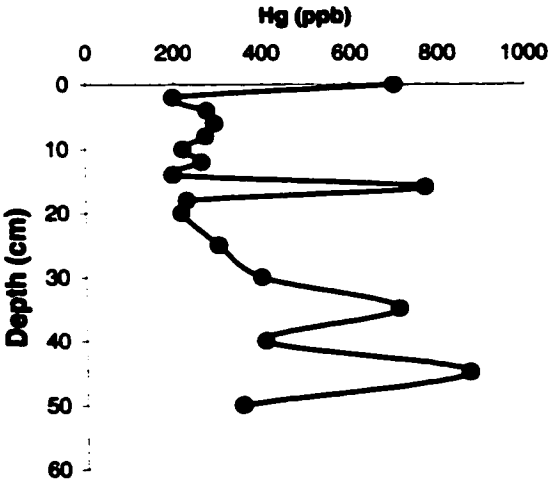
Appendix 4. 3. c. Total concentrations, as a function of sediment density, of, Pb, Sb, Zn, Zr, and Hg in lake sediments from Perch Lake.



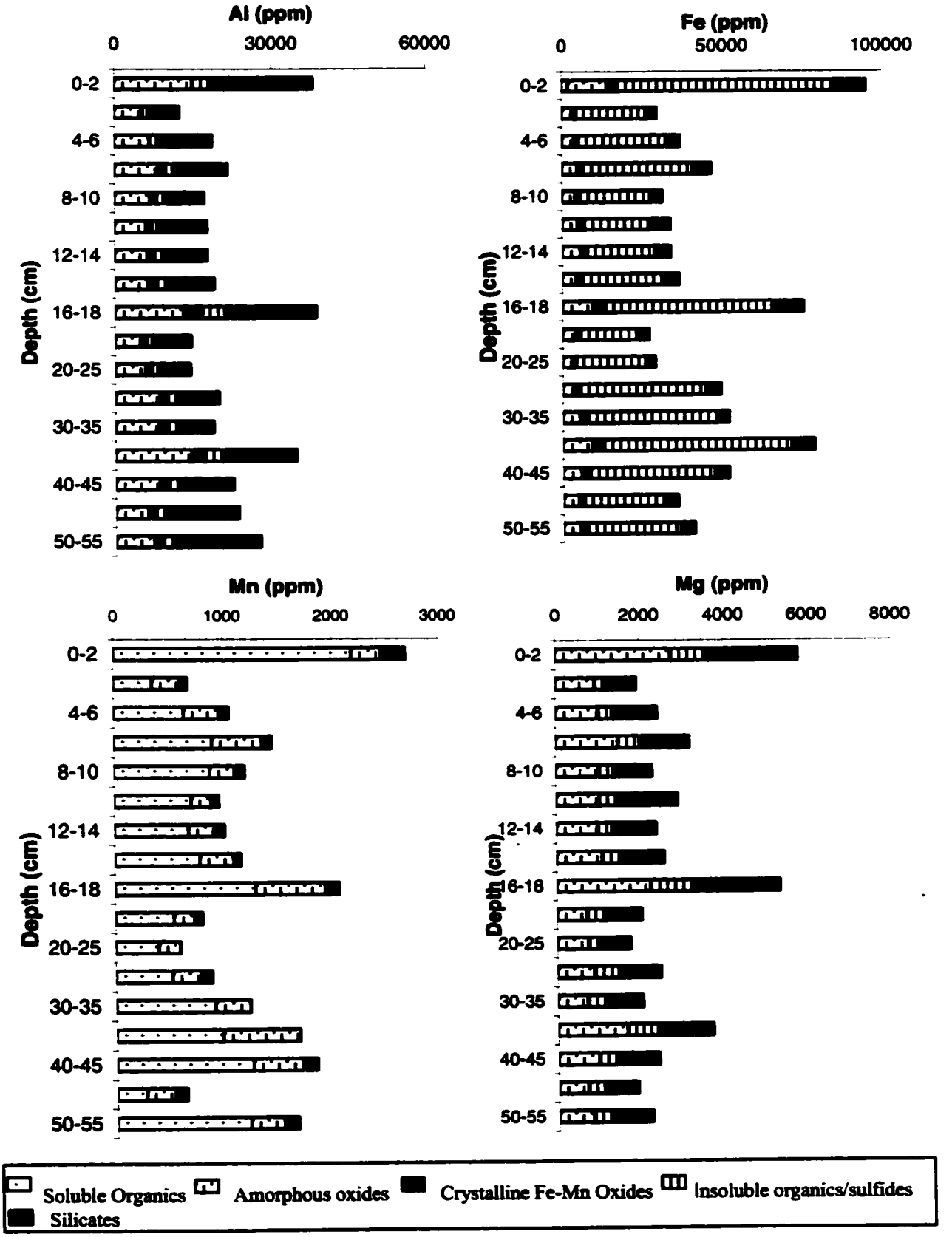




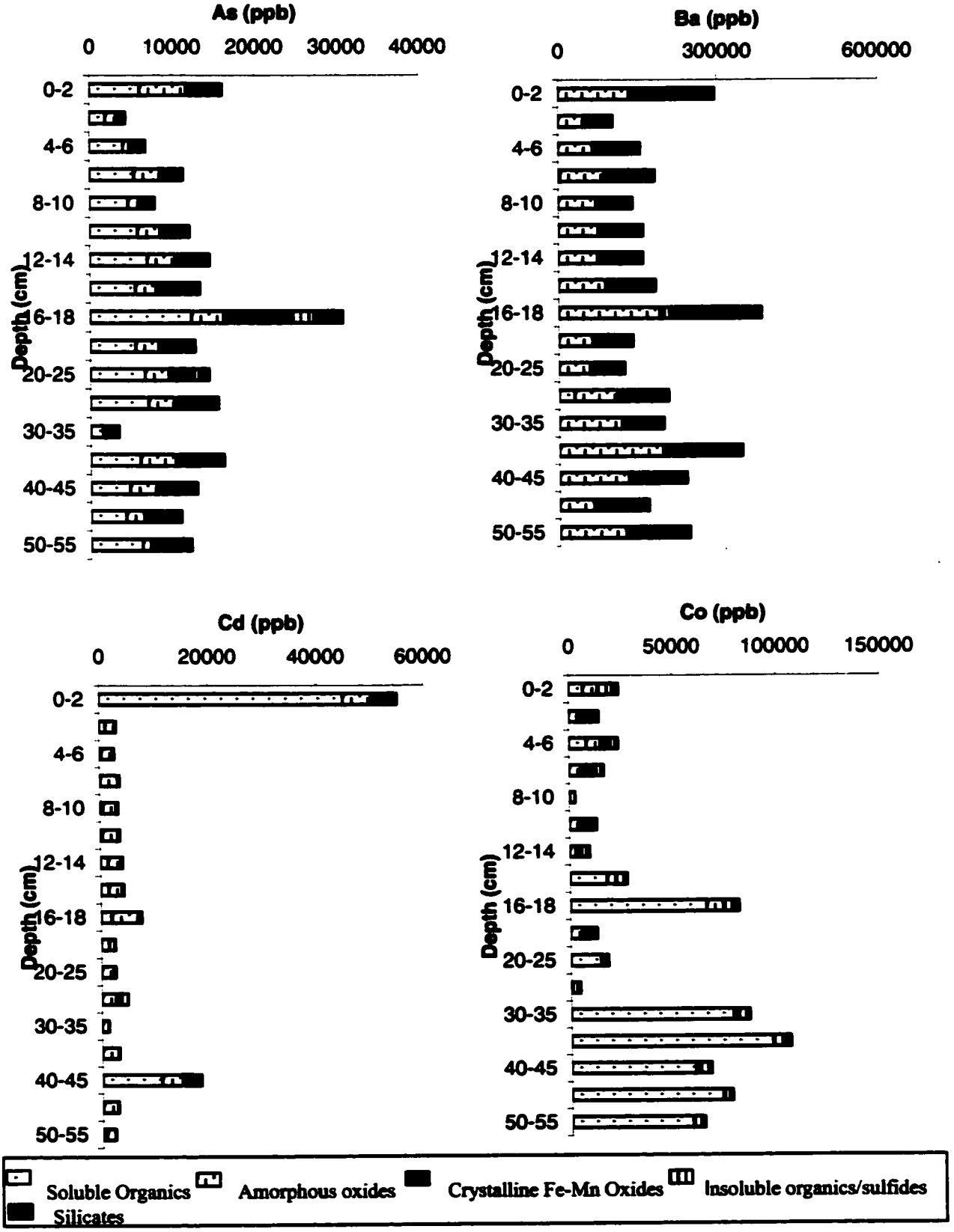




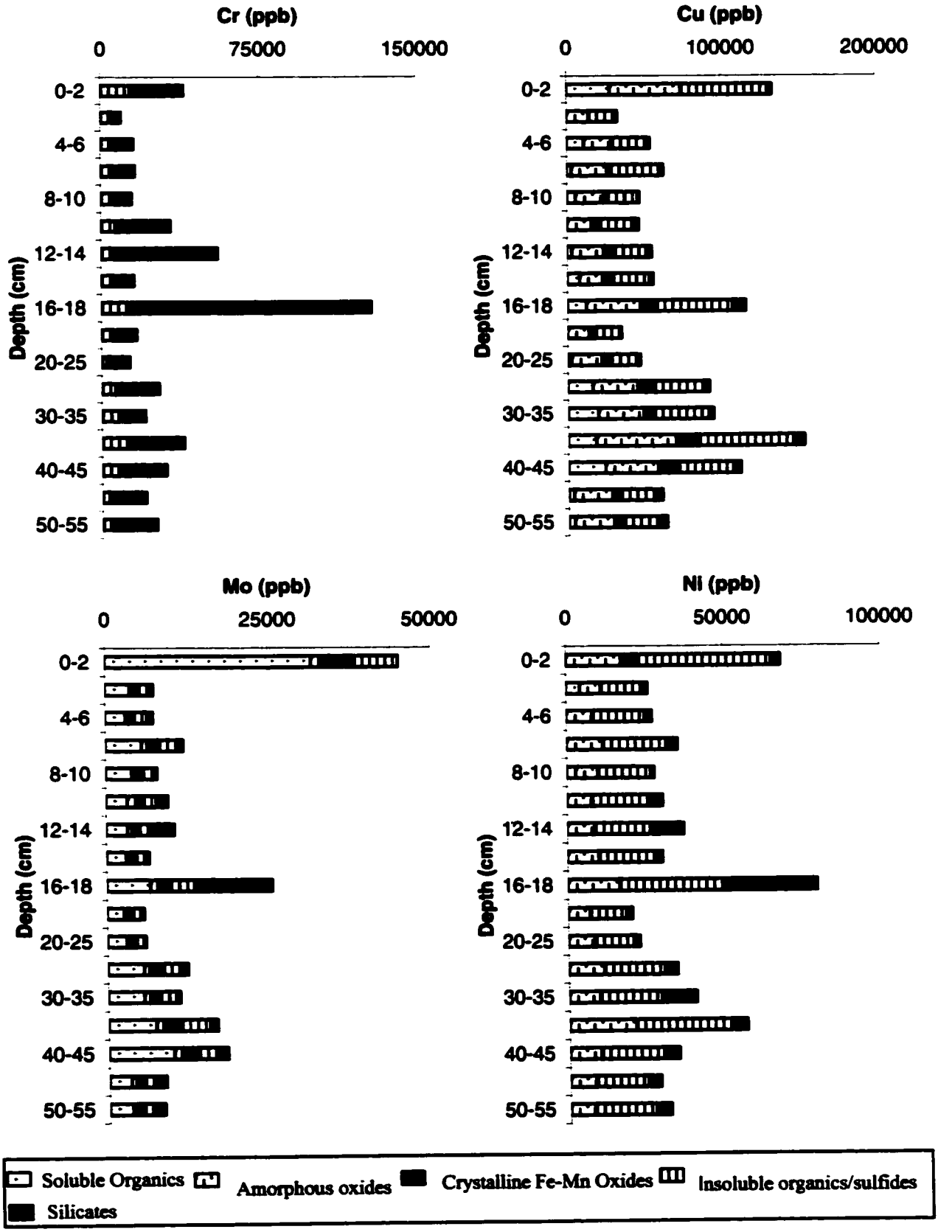
Appendix 4. 4. a. Al, Fe, Mn, and Mg, distribution in lake sediments from Perch Lake.



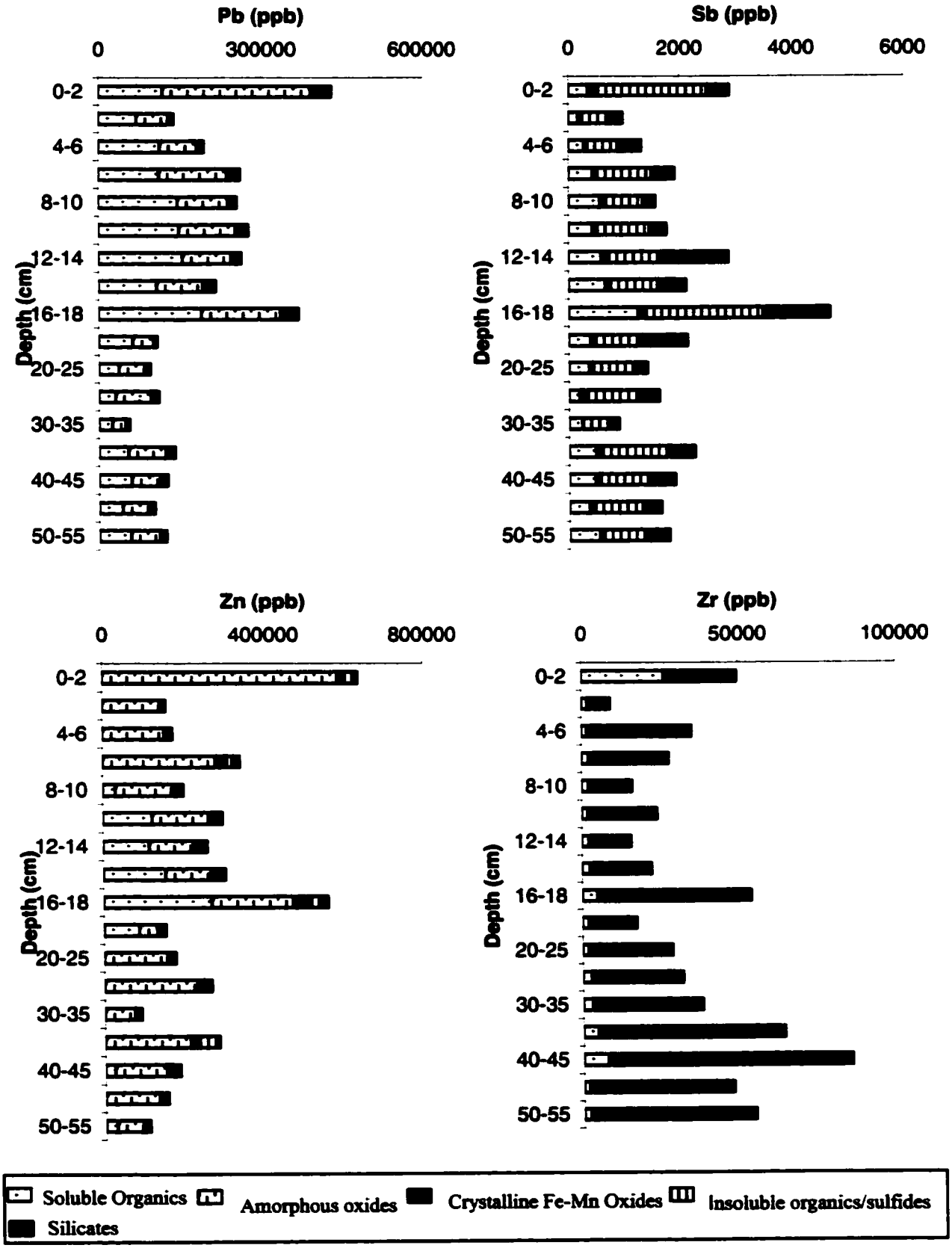
Appendix 4. 4. b. As, Ba, Cd, and Co distribution in lake sediments from Perch Lake.



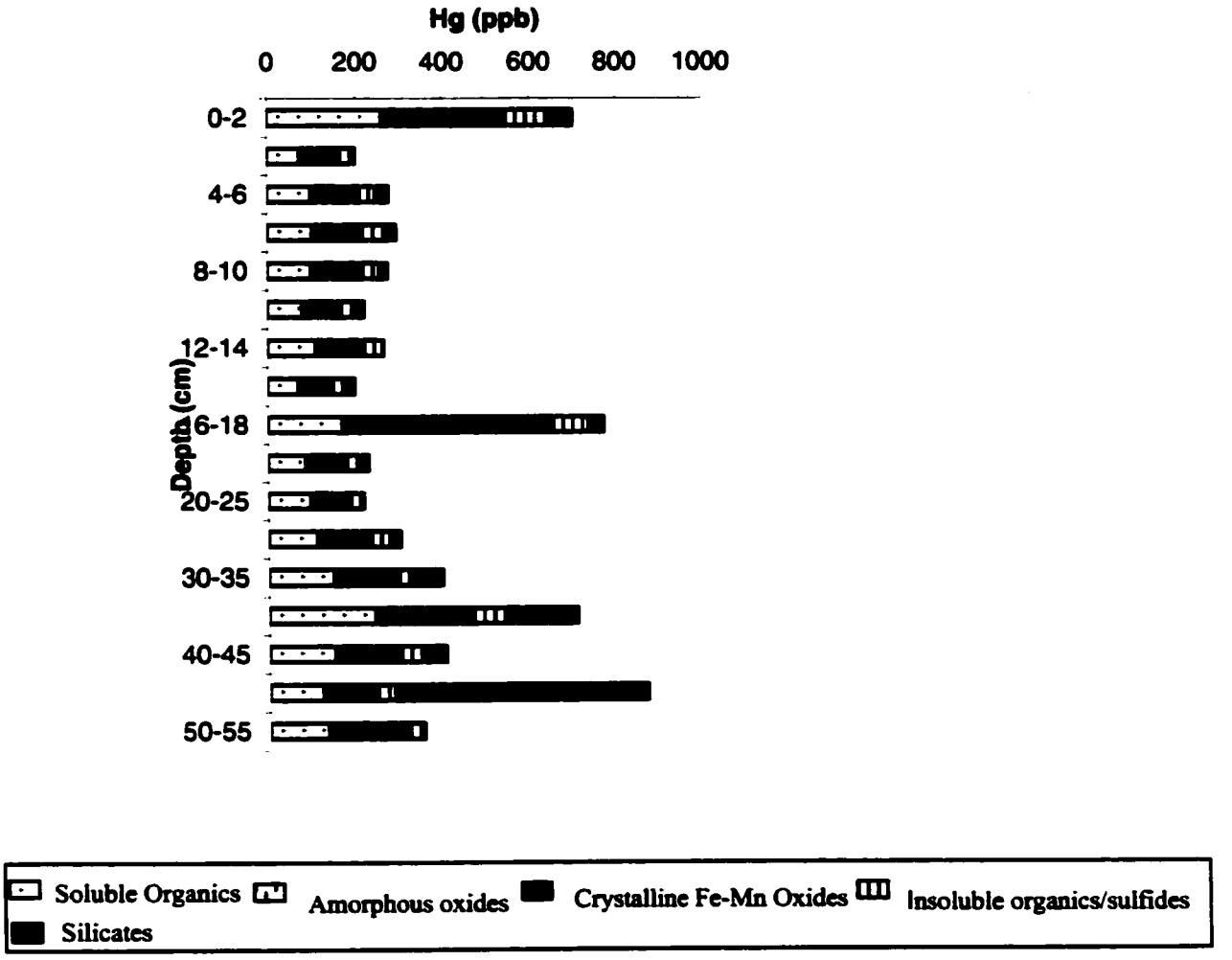
Appendix 4. 4. c. Cr, Cu, Mo, and Ni distribution in lake sediments from Perch Lake.



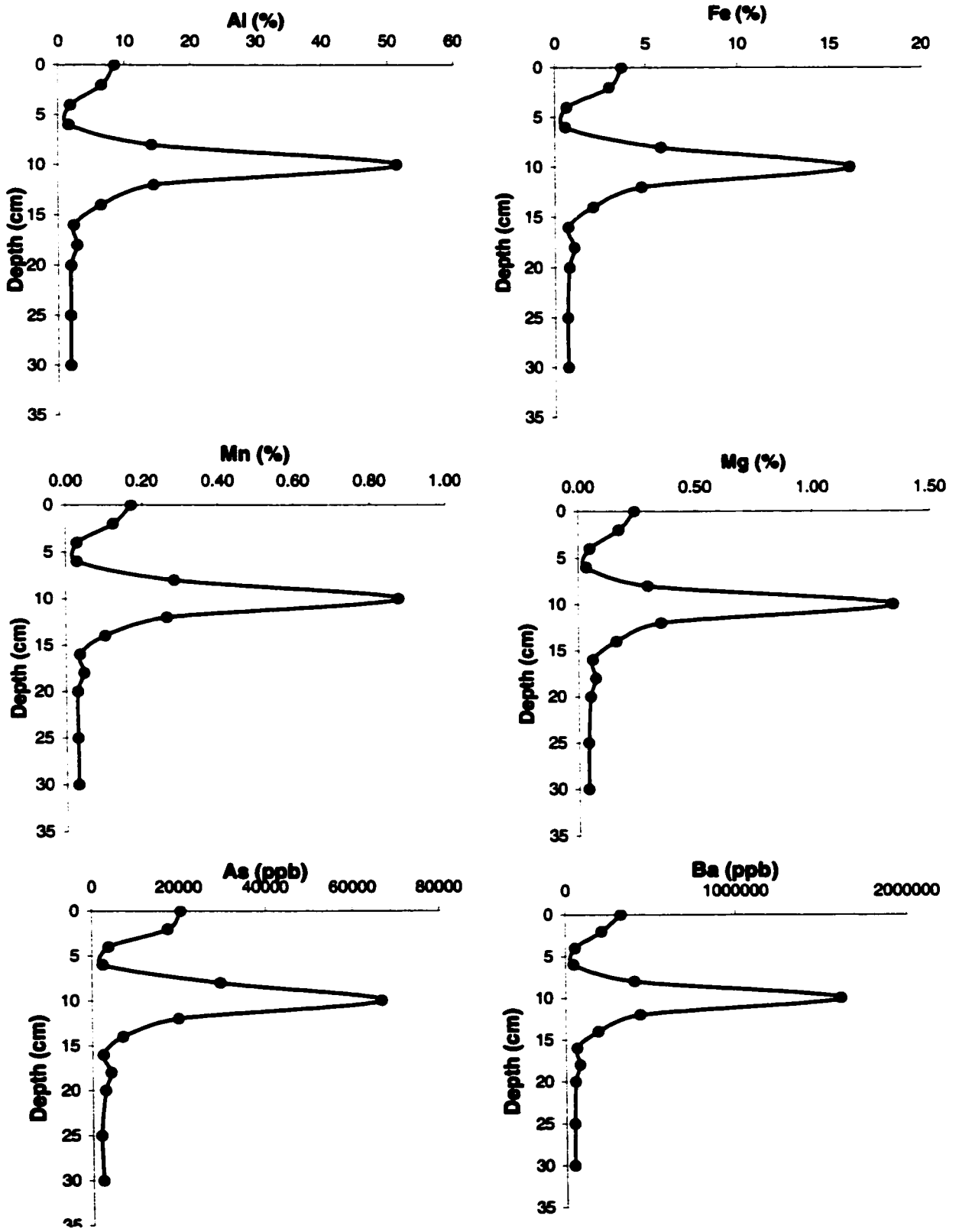
Appendix 4. 4. d. Pb, Sb, Zn, and Zr distribution in lake sediments from Perch Lake.



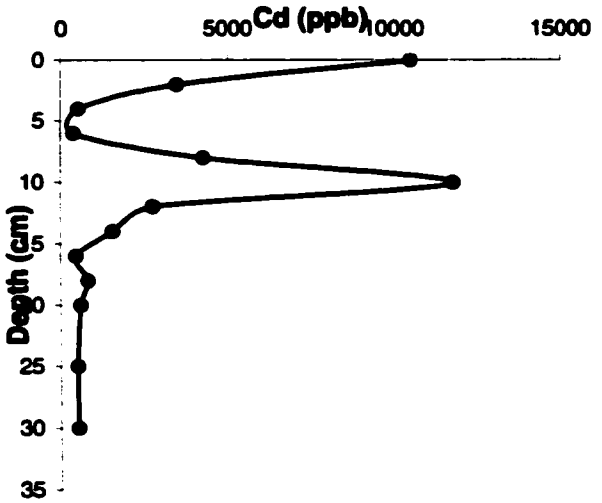
Appendix 4. e. Hg distribution in lake sediments from Perch Lake.

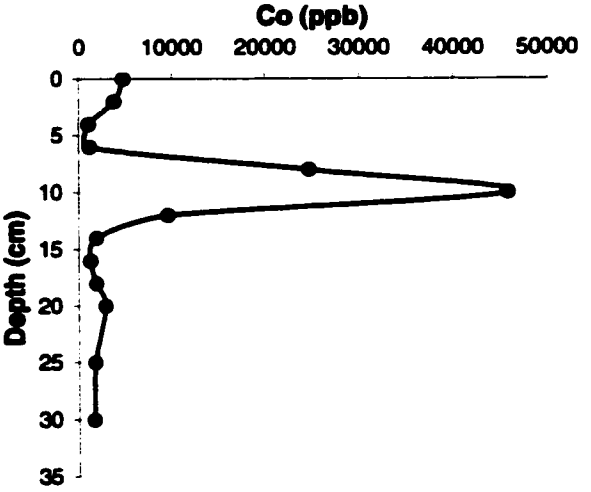


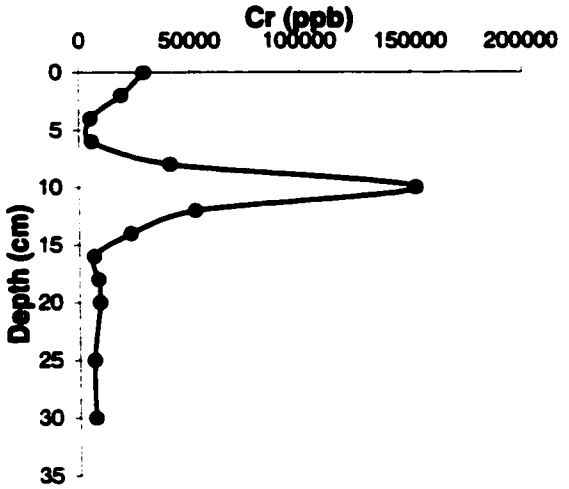
Appendix 4. 5. a. Total concentrations, as a function of sediment density, of, Al, Fe, Mn, Mg, As, and Ba in lake sediments from Big Dam Lake.

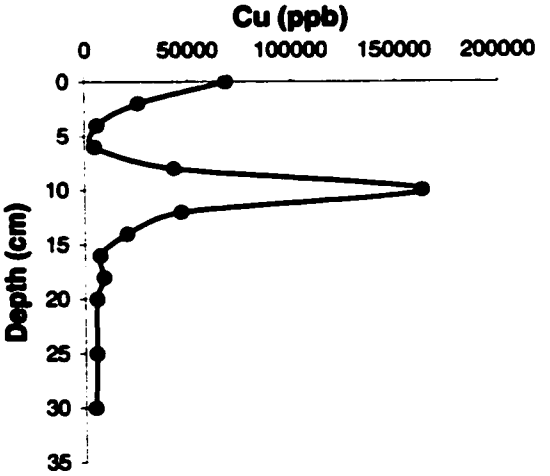


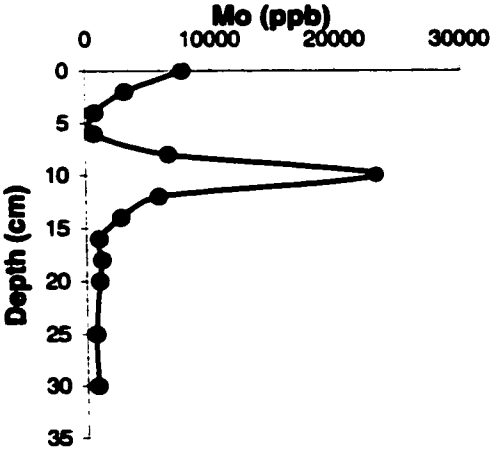
Appendix 4. 5. b. Total concentrations, as a function of sediment density, of Cd, Co, Cr, Cu, Mo, and Ni in lake sediments from Big Dam Lake.

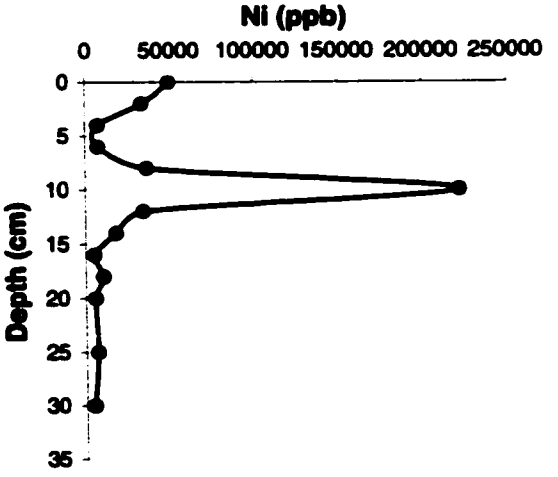




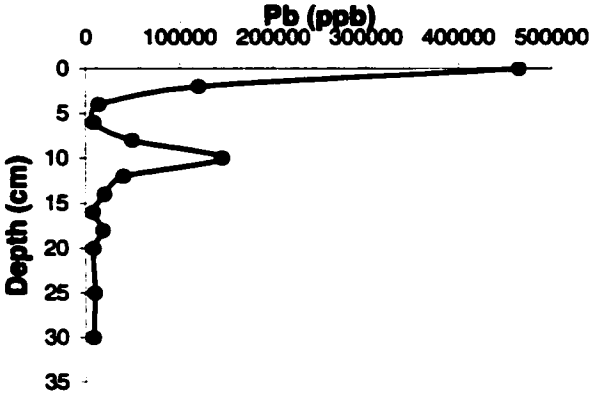


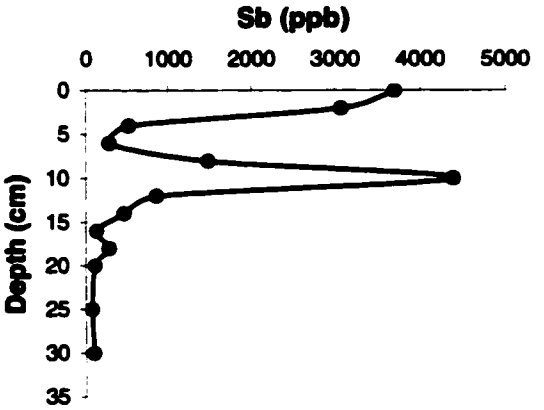


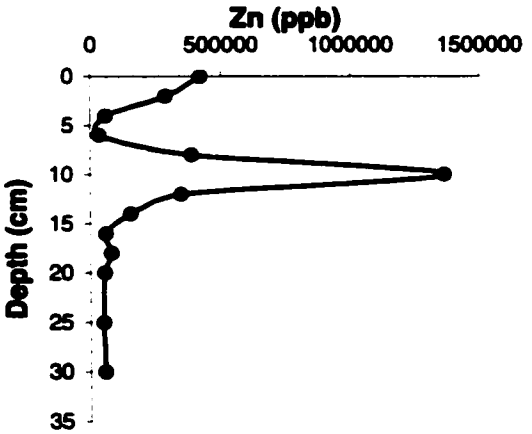


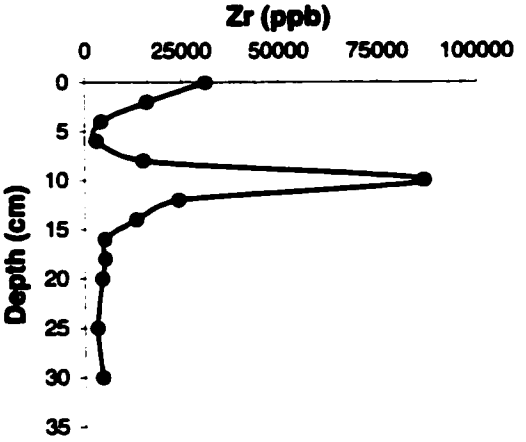


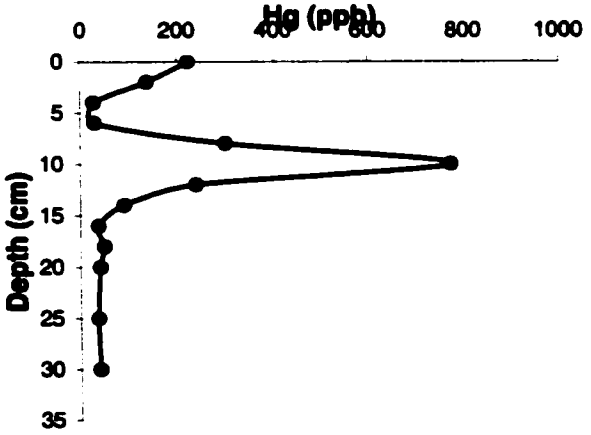
Appendix 4. 5. c. Total concentrations, as a function of sediment density, of Pb, Sb, Zn, Zr, and Hg in lake sediments from Big Dam Lake.



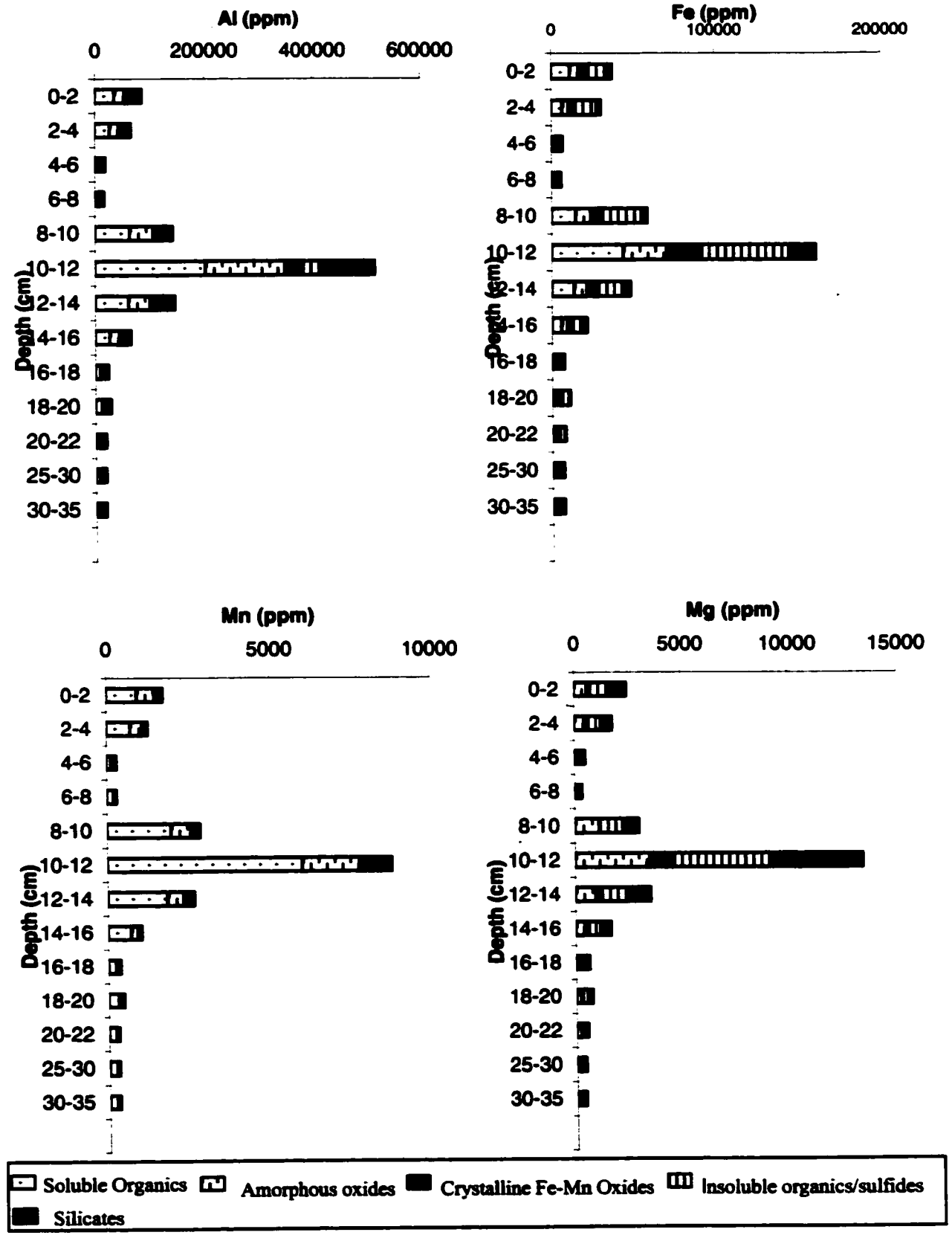




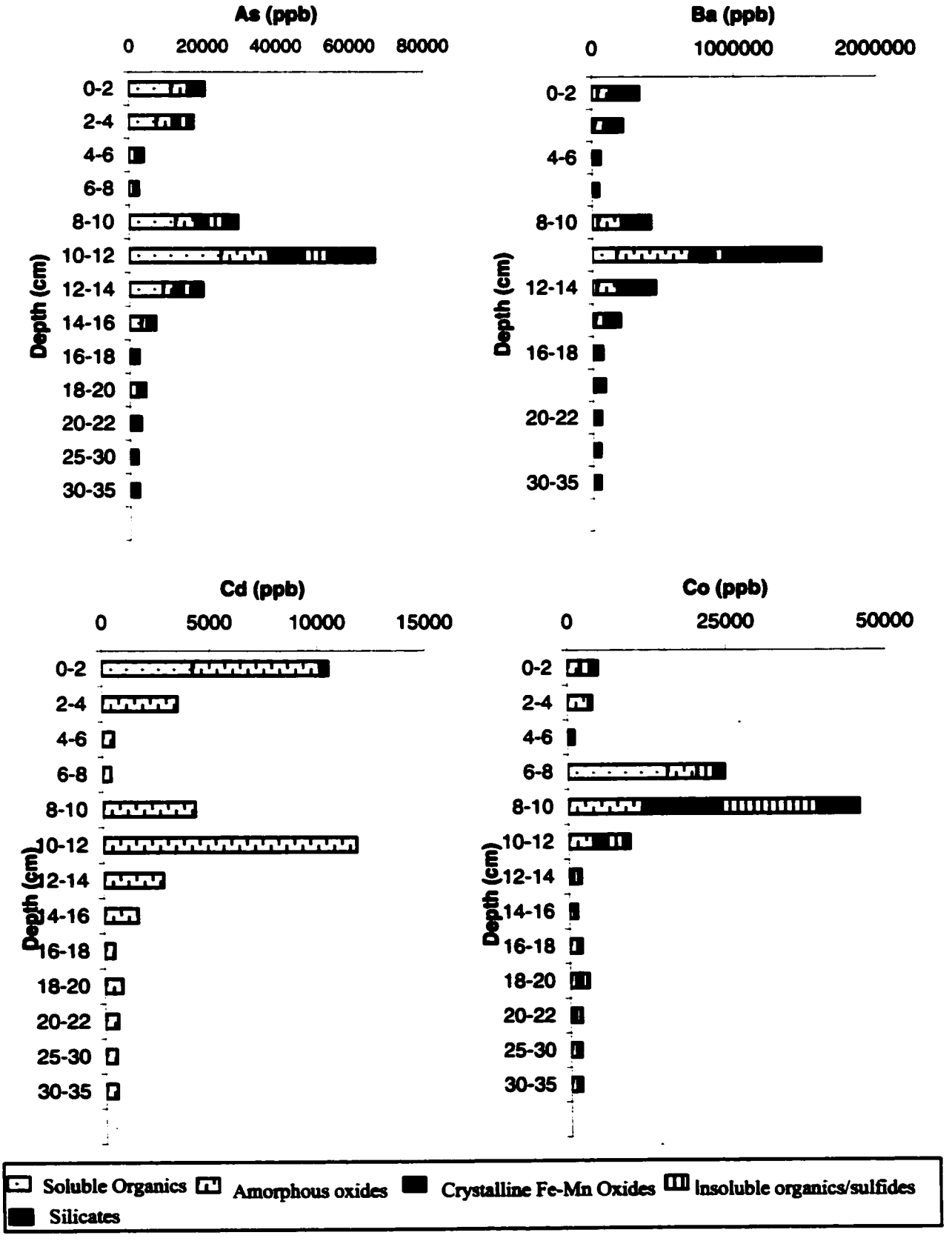




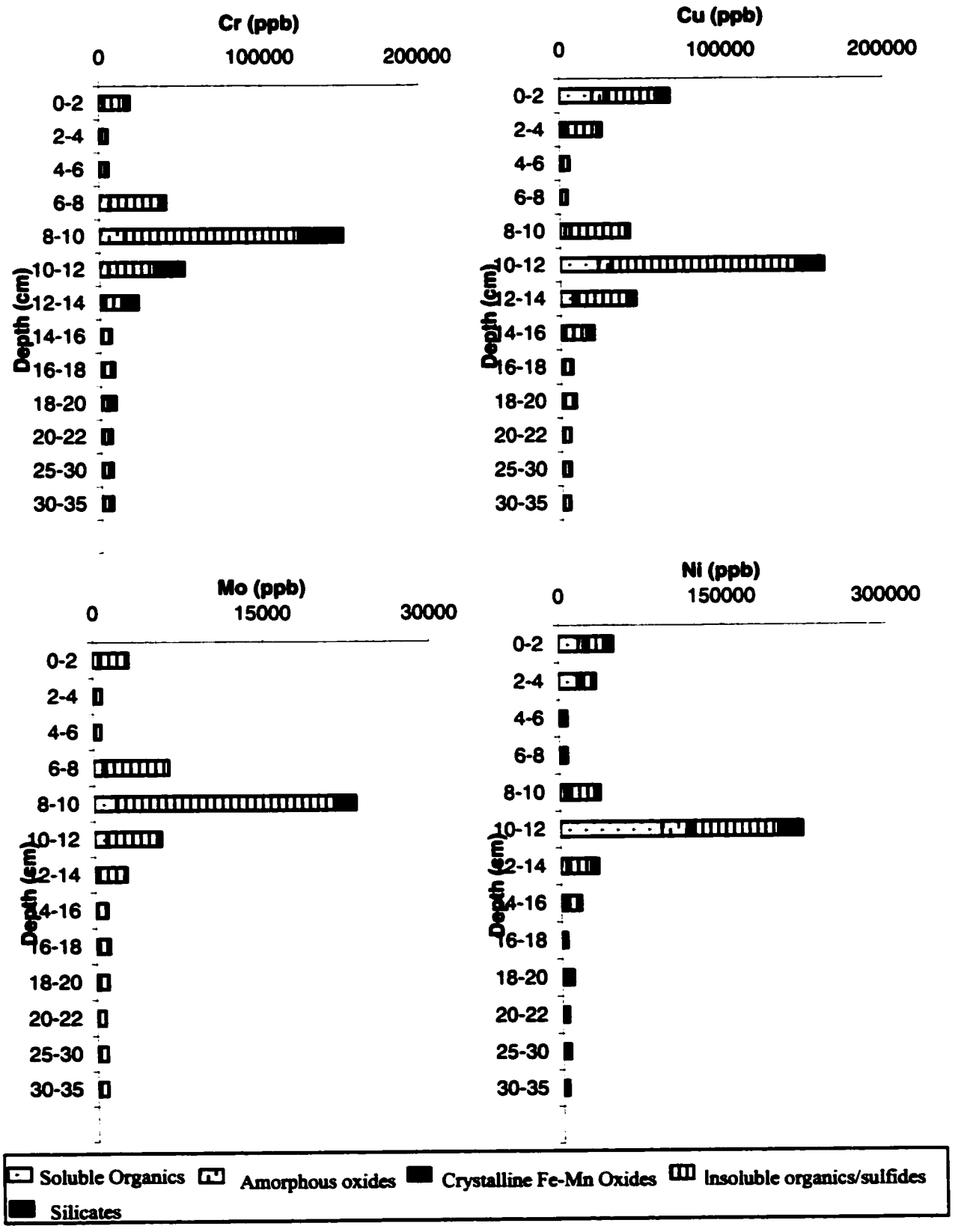
Appendix 4. 6. a. Al, Fe, Mn, and Mg distribution in lake sediments from Big Dam Lake.



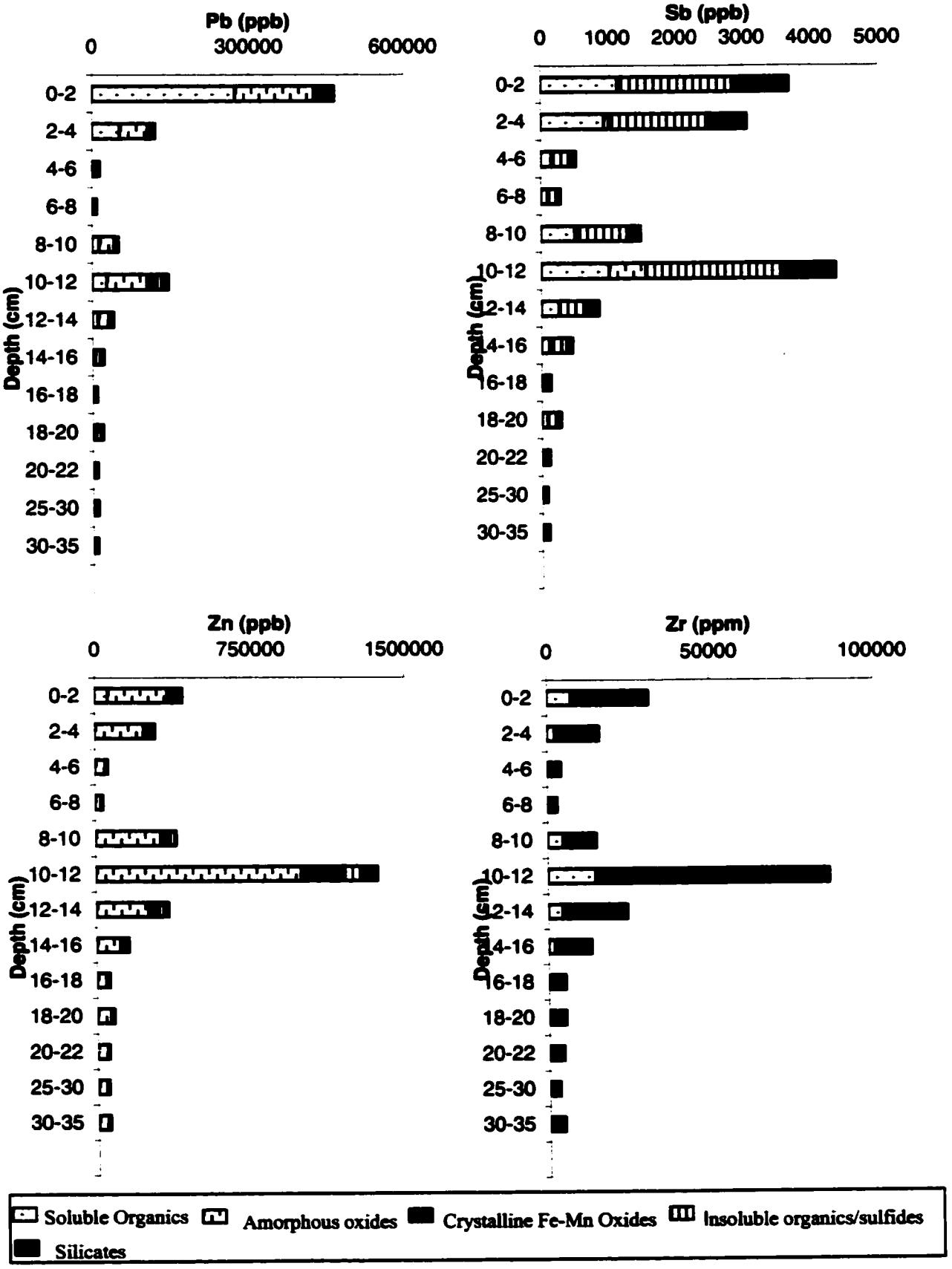
Appendix 4. 6. b.As, Ba, Cd, and Co distribution in lake sediments from Big Dam Lake.



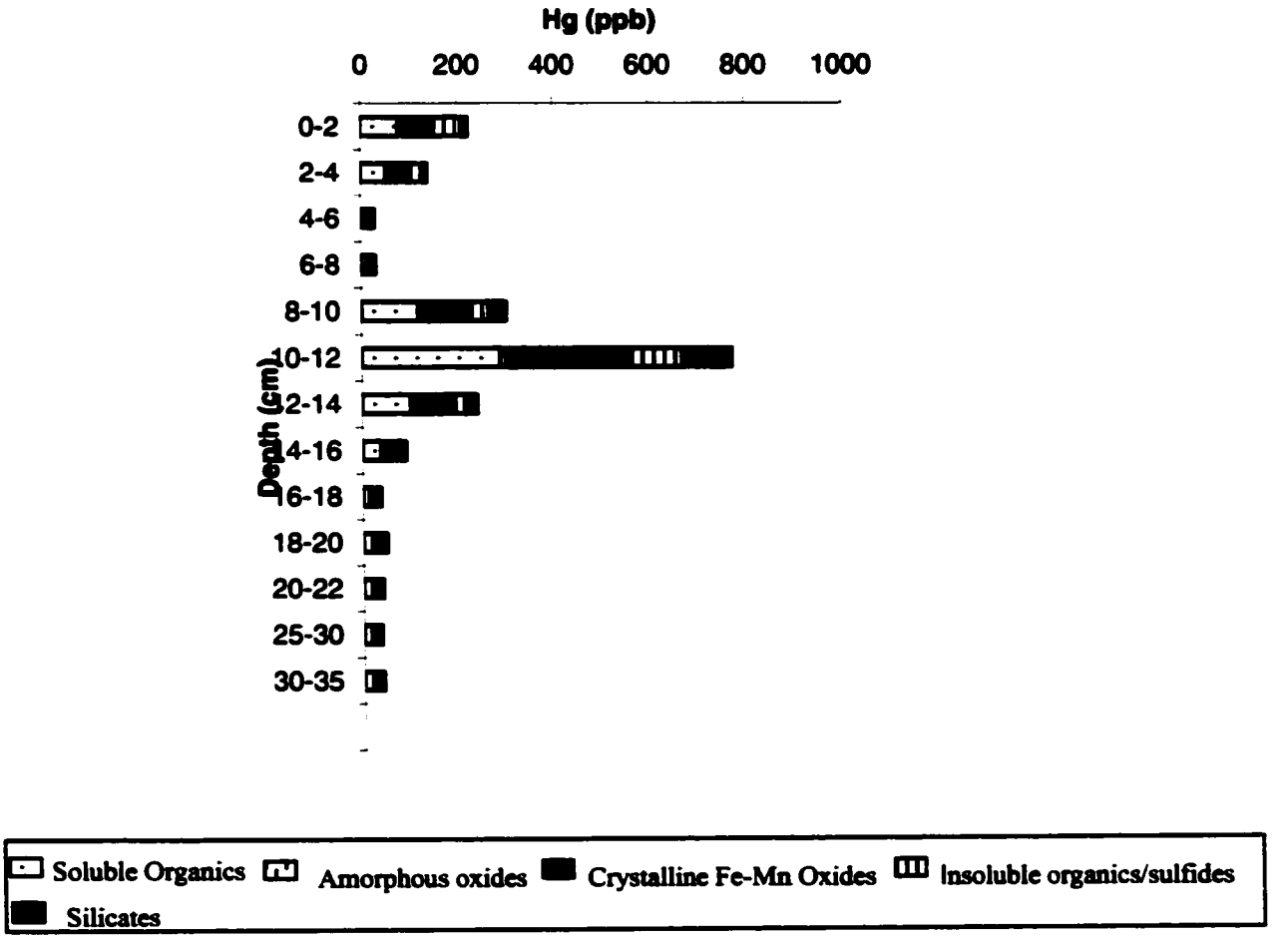
Appendix 4. 6. c. Cr, Cu, Mo, and Ni distribution in lake sediments from Big Dam Lake.



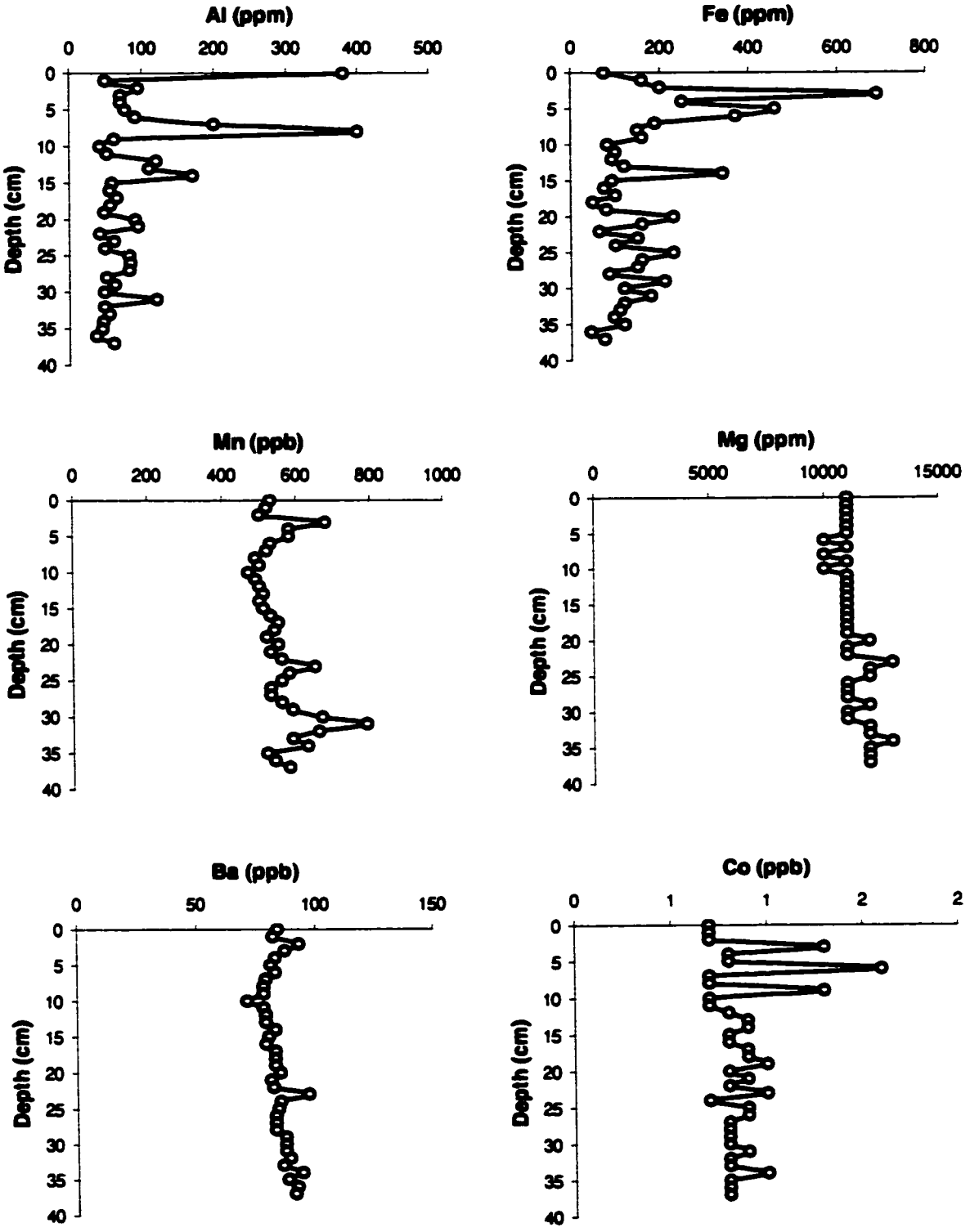
Appendix 4. 6. d. Pb, Sb, Zn, and Zr distribution in lake sediments from Big Dam Lake.



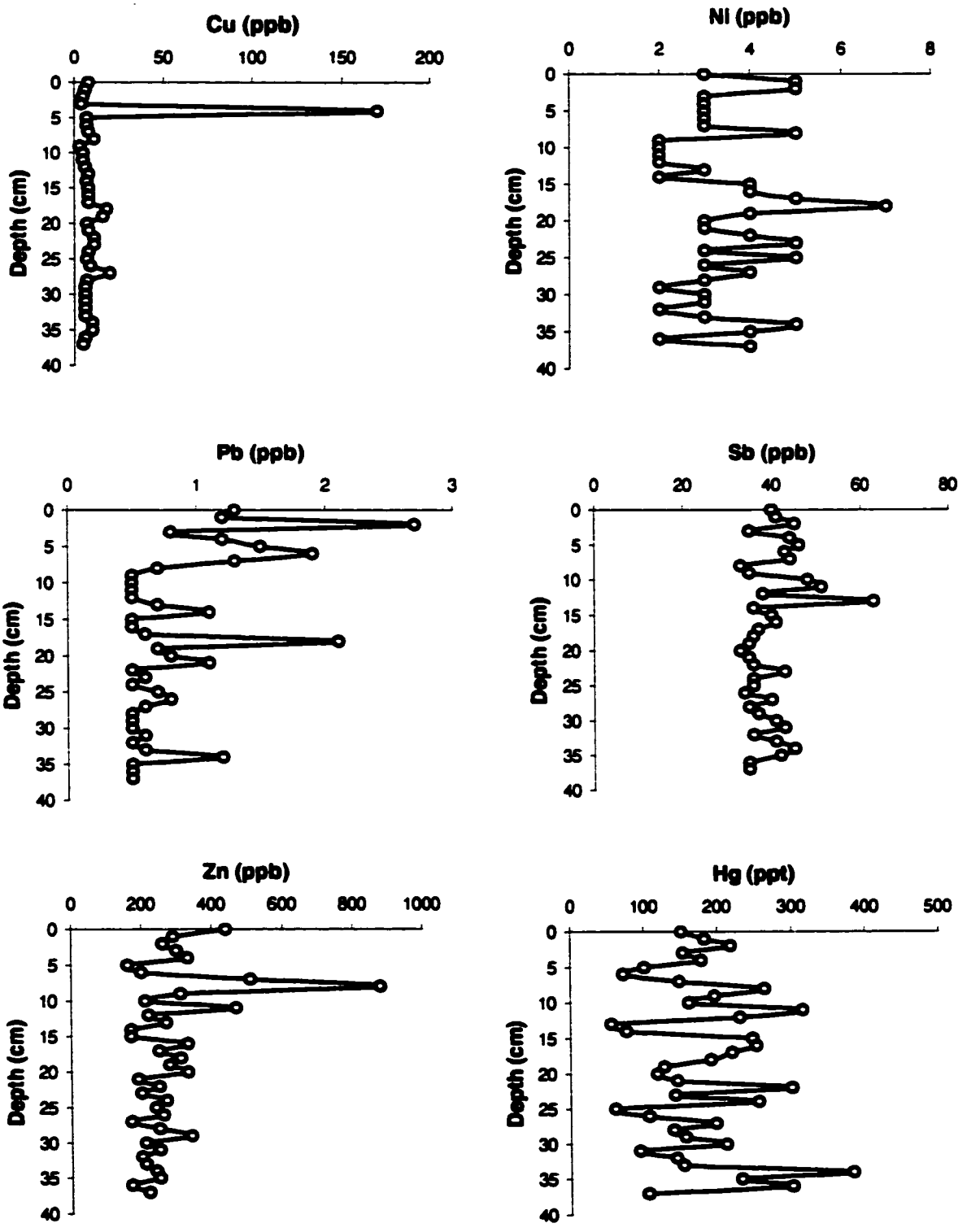
Appendix 4. 6. e. Hg distribution in lake sediments from Big Dam Lake.



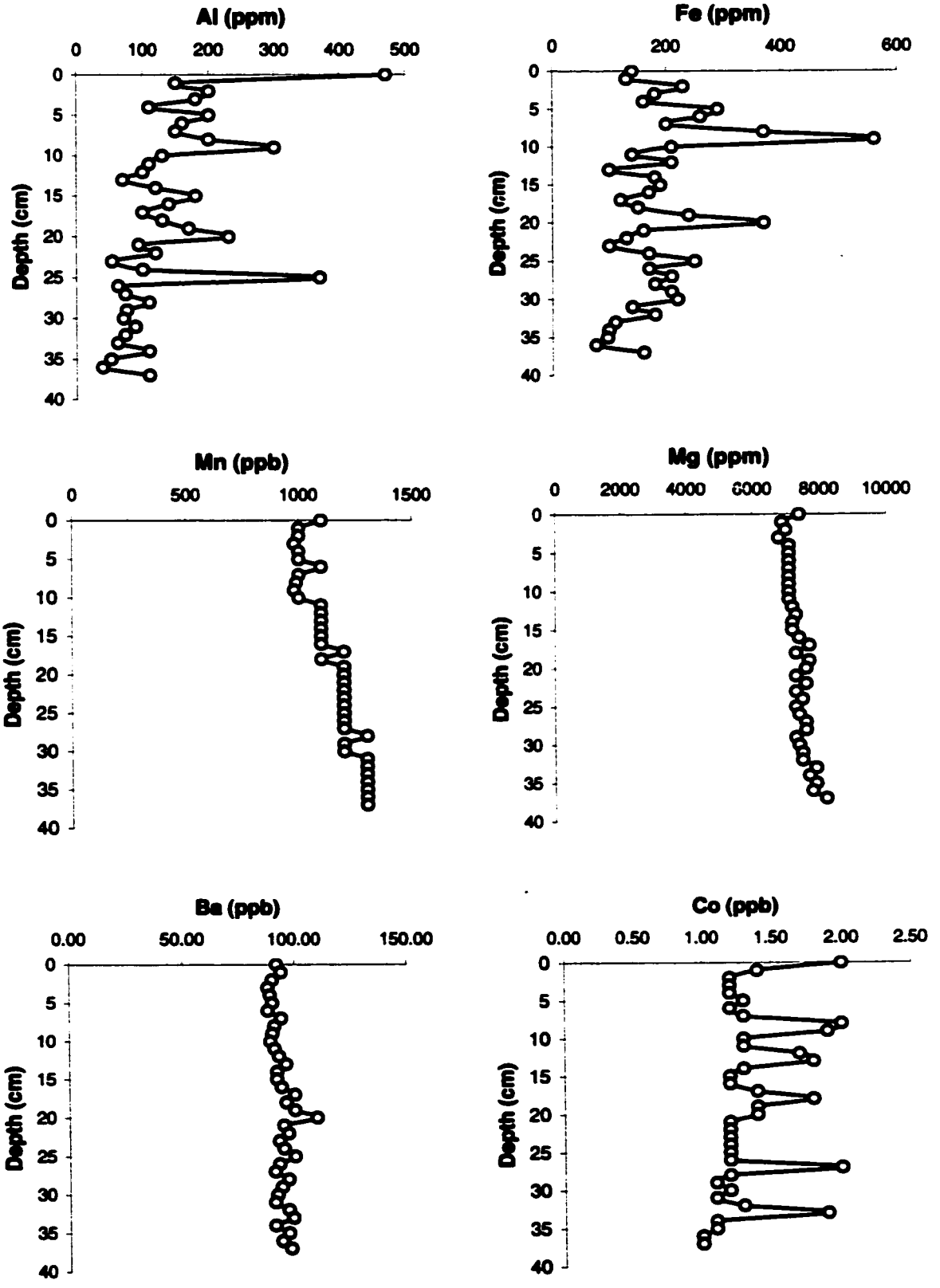
Appendix 4. 7. a. Al, Fe, Mn, Mg, Ba, and Co concentration profiles in pore waters from Lavant Long Lake.



Appendix 4. 7. b. Cu,Ni, Pb, Sb, Zn, and Hg concentration profiles in pore waters from Lavant Long Lake.



Appendix 4. 8. a. Al, Fe, Mn, Mg, Ba, and Co concentration profiles in pore waters from Perch Lake.



Appendix 4. 8. b. Cu,Ni, Pb, Sb, Zn, and Hg concentration profiles in pore waters from Perch Lake.