GEOCHEMICAL ASSESSMENT OF SUBAQUEOUS TAILINGS DISPOSAL IN MANDY LAKE, FLIN FLON AREA, MANITOBA

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Geochemical Assessment of Subaqueous Tailings Disposal in Mandy Lake, Flin Flon Area, Manitoba

An Acid Drainage Task Force Project in Contribution to Mend (Mine Environment Neutral Drainage)

Rescan

EXECUTIVE SUMMARY

Available evidence suggests that the post–depositional (diagenetic) chemical reactivity of mine tailings is inhibited by storage under water, and implies that such storage may provide a preferred long–term disposal option for such wastes. To assess this, we examine in this report the chemistry of interstitial waters and the associated solid phases in tailings and natural sediments in Mandy Lake, near Flin Flon, Manitoba. Mandy Lake was used as a receiving basin for tailings in the period 1943–1944. Tailings are areally widespread in the small lake and still occur in significant concentrations in surface sediments (top 5 mm) despite 46 years having elapsed since discharged ceased.

Two cores were collected in June 1990, and processed under nitrogen to extract interstitial waters. Solid–phase chemical measurements indicate that the core raised from the central basin of the lake penetrated through the tailings–rich zone into underlying, pre–mine, organic–rich (up to 15 wt. % C) natural deposits; the other core, collected near the former discharge outfall, consisted essentially of a mixture of tailings and organic–rich natural detritus. At the central basin site, dissolved iron measurements made on the pore water samples indicate that the deposits are suboxic or anoxic at very shallow depths, probably within several millimetres of the sediment–water interface. This reflects a high benthic oxygen demand at that location. An enrichment of solid–phase Mn at the top of the nearshore core, coupled with a low Fe concentration in near–surface pore waters, indicates that the surface deposits at this location are oxic.

Relative to overlying bottom water, dissolved Zn, Cu and Pb concentrations decrease with depth in the upper decimetre at the nearshore site. These distributions are attributed to precipitation of the metals as sulphide phases at depths on the order of 7 or 8 cm. Sulphate reduction with concomitant production of HS– is expected, given the evidence for shallow anoxia in the deposits, although the rate of sulphide production may be limited by the low sulphate concentration in Mandy Lake water. At the central basin site, the pore water data indicate that Zn is diffusing into the sediments, as is the case at the other location. However, near–surface dissolved Cu and Pb concentrations, although very low, are slightly higher than in the overlying bottom water, indicating that their must be a small benthic efflux of these two metals at this location. Diffusion calculations indicate that the efflux is so small as to have no measurable impact on the dissolved metal inventory in the overlying lake water.

SOMMAIRE

Les données disponibles indiquent que la réactivité chimique après dépôt (diagénétique) des résidus miniers est inhibée lorsque les résidus sont entreposés sous l'eau et qu'un tel mode d'entreposage pourrait être une meilleure solution pour l'élimination à long terme de ces déchets. Pour vérifier cette affirmation, nous examinons dans le présent rapport la composition chimique des eaux interstitielles et les phases solides associées dans les résidus et les sédiments naturels du lac Mandy, près de Flin Flon au Manitoba. Le lac Mandy a été utilisé comme bassin de réception de résidus pendant la période de 1943–1944. Les résidus sont dispersés superficiellement dans le petit lac et leur concentration est encore élevée dans les sédiments de surface (les premiers 5 mm) même si cela fait 46 ans qu'aucun résidu n'y a été déversé.

Deux carottes ont été prélevées en juin 1990, puis traitées à l'azote pour en extraire les eaux interstitielles. Les mesures chimiques pratiquées sur la phase solide indiquent que la carotte prélevée dans le bassin central du lac traversait la zone riche en résidus pour pénétrer dans les dépôts naturels sous-jacents, riches en matière organique (jusqu'à 15 % C en poids), qui sont antérieurs aux résidus miniers; l'autre carotte, prélevée près de l'ancienne décharge, consistait essentiellement en un mélange de résidus et de détritus naturels riches en matière organique. Dans le bassin central, le dosage de fer dissous dans les échantillons d'eau interstiticielle indique que les dépôts sont suboxiques ou anoxiques aux très faibles profondeurs de l'ordre de quelques millimètres sous l'interface sédiments-eau. Cela traduit une forte demande d'oxygène benthique à cet endroit. Une teneur plus forte en Mn de la phase solide dans la partie supérieure de la carotte prélevée près du rivage, ajoutée à une faible concentration de Fe dans les eaux interstitielles près de la surface, indique que les dépôts de surface à cet endroit sont oxiques.

Les concentrations de Zn, de Cu et de Pb diminuent avec la profondeur dans le premier décimètre au point de prélèvement près du rivage contrairement à leurs concentrations dans les eaux de fond sus-jacentes. Ces distributions sont attribuables à la précipitation des métaux sous forme de sulfures à des profondeurs de 7 à 8 cm. La réduction du sulfate et la production concomittante de HS– sont à prévoir, à cause de l'anoxie dans les dépôts à faible profondeur, même si le taux de production de sulfure peut être limité par la faible concentration du sulfate dans les eaux du lac Mandy. Dans le bassin central, les données sur les eaux interstitielles indiquent que le Zn diffuse dans les sédiments, comme c'est le cas à l'autre point de prélèvement. Cependant, les concentrations de Cu et de Pb dissous près de la surface, quoique très faibles, sont légèrement plus élevées que dans l'eau du fond sus-jacente, ce qui indique qu'il doit y avoir un écoulement benthique de ces deux métaux à cet endroit. Les calculs de diffusion indiquent que l'écoulement est si faible qu'il n'a aucun effet mesurable sur le bilan des métaux dissous dans l'eau sus-jacente du lac.

ACKNOWLEDGEMENTS

1.0 INTRODUCTION

The disposal of large volumes of sulphide-rich mine tailings at depth in marine and lacustrine basins is increasingly being considered as an option for permanent storage of such deposits. Implicit in this consideration is the perception that, given certain conditions, tailings may not release metals to the overlying waters at levels which could cause environmental degradation. This perception is based both on theoretical considerations (summarized in Rescan 1989) and on a limited number of published studies of the post-depositional (i.e. diagenetic) chemical behaviour of tailings in several active or abandoned deposits located mostly in western Canada (e.g. Pedersen 1983, Pedersen 1984, Pedersen 1985, Pedersen and Losher 1988, Pedersen et al. 1990, and Drysdale 1990). These accrued results illustrate reasonably well the extent to which tailings react given specific depositional conditions; however, the important task remains of determining the degree to which the extant studies can be used to predict diagenetic responses in future disposal schemes or in deposits which have been abandoned for variable lengths of time. Thus, there is a well-defined need for quality information on the long-term diagenetic activity of mine wastes, both in marine and lacustrine waters. Toward this end, in this report we present the results of a detailed investigation of the chemical behaviour of Zn, Cu and Pb in tailings discharged more than four decades ago into Mandy Lake near Flin Flon, Manitoba. This follows preliminary work carried out earlier (Rescan 1990a). The work reported here, carried out during the period June through September, 1990 complements a similar and concurrent investigation of the diagenetic reactivity of tailings being discharged at present to Anderson Lake, near the town of Snow Lake, Manitoba (Rescan 1990b).

1.1 Background to the Study

Previous work on Mandy Lake includes a recent investigation of water quality (Rescan 1990a) and a study of the revegetation of the submerged tailings carried out by Hamilton and Fraser (1978). A brief history of mining and tailings discharge activities is presented here, summarized from Rescan (1990a).

The mine was first operated during the years 1917 to 1920, with the ore being processed off-site. The ore vein was solid chalcopyrite (>20% copper) with associated gold, silver and other lower grade sulphides. The mine was opened again during 1943 to 1944.

During this time, ore was milled on site and an estimated 73,000 metric tonnes were deposited into Mandy Lake in a fan-shaped deposit from a single launder. Some spillage occurred along the shore where it has remained. The deposited tailings gradually sloped away from the east shore to about 1 m depth, then dropped off quickly into 5 m deep water.

Little data are available regarding the original condition of the tailings, which consisted primarily of pyrite with 15 to 17% sulphur and appreciable quantities of zinc and copper. Analysis of the submerged tailings in 1975 indicated minimal oxidation had occurred. Iron was present as iron sulphide and the percentage of iron oxide and sulphate present was low, with shore samples being marginally higher. Analyses of a distilled water leach of the tailings indicated that oxidized shore samples had a lower pH, higher conductivity and a higher concentration of soluble metals than underwater samples. Both shore and underwater tailings were net acid producers with the shore samples having very low acid-consuming ability. However, the underwater tailings still had a substantial amount of acid-consuming ability indicating minimal acid generation had occurred underwater.

Petrographic analysis of sediment samples carried out by Rescan (1990a) showed that the silicate fraction of the tailings consisted of angular silt-sized quartz grains, micaceous minerals, and minor hornblende, carbonate and miscellaneous silicates. Sulphide minerals present included abundant pyrite, minor sphalerite, and rare traces of chalcopyrite and possibly arsenopyrite. Pyrrhotite could not be positively identified. All sulphide minerals appeared fresh, and showed no sign of oxidation (Rescan 1990a).

Vegetation was established on the submerged tailings nearshore in 1975 but not on the tailings exposed to the atmosphere. Species found on the submerged tailings included sedges (*Carex* spp.), riverweed (*Podostemun ceratophyllum*) and spike rush (*Eleocharis* spp.). Over 90% of the shallow sloping tailings area was covered with decaying organic material up to 2.5 cm thick.

2.0   STUDY AREA AND METHODS

2.1   Study Area

Mandy Lake is located in central Manitoba (Figure 2-1) near the Saskatchewan-Manitoba border, some five km south of Flin Flon. Originally a bay off the west side of the northwest arm of Schist Lake, the Mandy Lake was enclosed when a causeway was built across the inlet to the Mandy Mine site. The lake has now hosted an abandoned pyrite-rich tailings deposits for more than four decades. During the preliminary investigation of the lake in August 1989 (Rescan 1990a), which was carried out following several years of low precipitation in the area, there was essentially no outflow from the lake. This situation changed radically by June 1990, when the outflow was major through both culverts in the northern end of the lake and as an overflow across the road immediately north of the old open pit (Sampling Location R1, Figure 2-2).

2.2   Sampling Stations

Two cores were collected from the lake in June, 1990, at sites selected to be representative of contrasting depositional facies: MD-1 (Figure 2-2) was raised from the deepest area of the central basin of the lake, approximately 200 m west of the old open pit, and MD-2 was collected from the area near the original tailings discharge location.

Hydrographic measurements (temperature, dissolved O2, conductivity and pH) were made at the central basin site (coring site MD-1), and samples were collected for water quality measurements at three locations (Figure 2-2): a) slightly upstream of the mouth of the creek issuing from nearby Phantom Lake, which flows in to the south end of Mandy Lake (Sample I1); b) from the outflow creek washing over the road immediately north of the old open pit (Sample R1); and c) from the south culvert outflow in the northeastern corner of the lake (Sample C1).

NWT

HUDSON

BAY

Churchill

CNR

Reindeer
Lake

MANDY LAKE

PROJECT
LOCATION

Thompson

M A N I T O B A

280

Flin Flon   Snow Lake

6

39

SASK

ONT

10

Lake

Winnipeg

6

50   0   100   200   300

kilometres

1   Brandon   WINNIPEG

USA
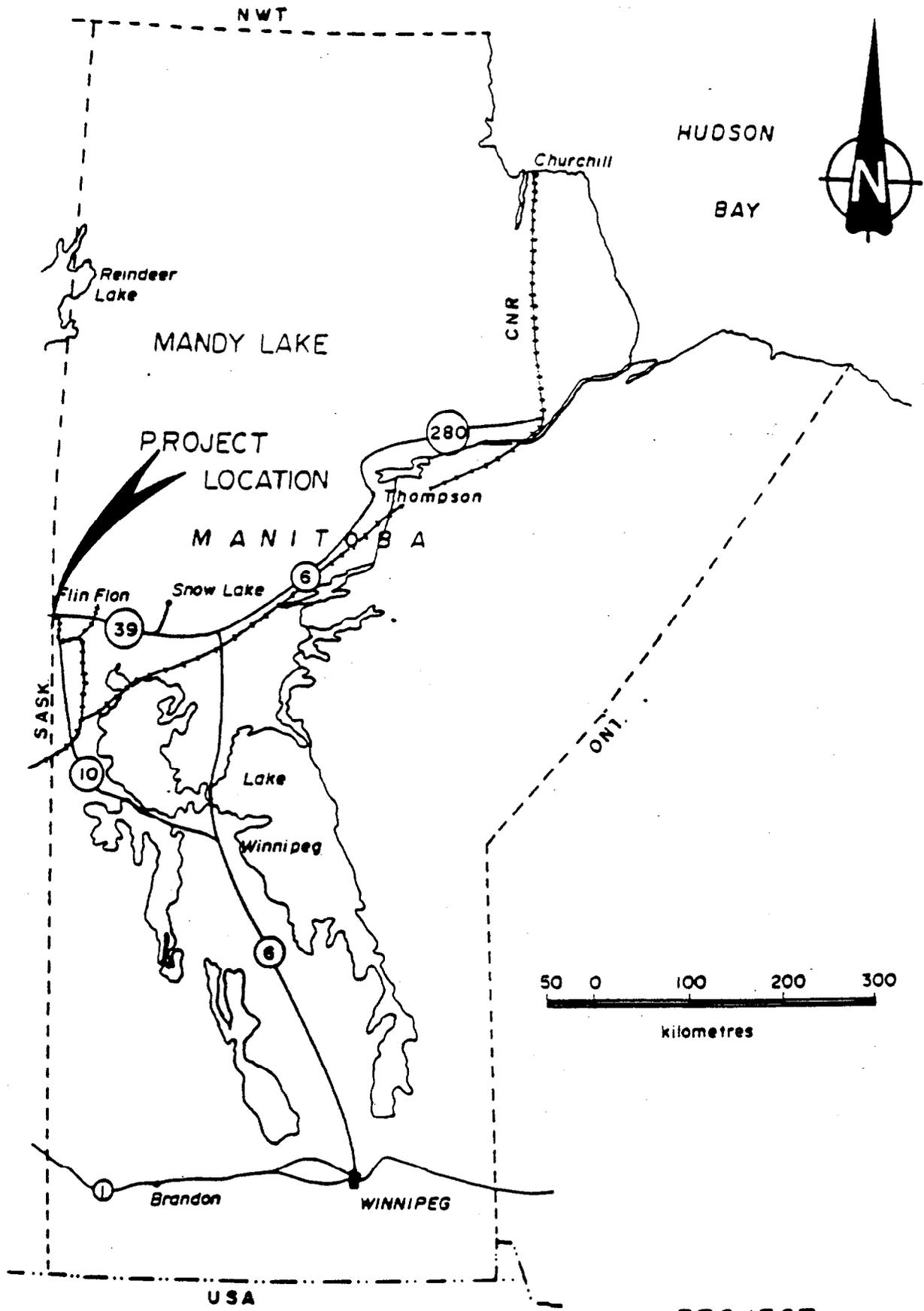
PROJECT

LOCATION MAP

Figure 2-1

Kasan

DB-R0022

ROCK OUTCROP

ROCK OUTCROP

ASPEN, SPRUCE, BIRCH

SCATTERED ROCK AND TREES

I1

CULVERT
no flow

▲⊕ MD-1

(5.5m)

⊕ MD-2

(5.4m)

BOAT LAUNCH

V1

CULVERT

C1

R1

★
V2

CULVERT

POWER LINE

PIT

●CULVERT

CULVERT
no flow

LARGE ROCK OUTCROP

SCHIST LAKE (NORTHWEST ARM)

| 0 | 50 | 100 | 150 | 200 |

METRES

LEGEND

▲ D.O./Temperature Profiles

⊕ Core Location

■ Inflow Site (water)

★ Vegetation Site

● Outflow Site (water)

BATHYMETRY DATA

Mean Breadth ($\bar{b}$)	223 m
Length (l)	1070 m
Maximum Depth (z_m)	5.5 m
Mean Depth ($\bar{z}$)	3.6 m
Area (A)	239,000 m²
Volume (V)	853,000 m³
Shoreline (L)	3,200 m
Shoreline Development (SLD)	1.8

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VANCOUVER, B.C.   CANADA

FIGURE 2-2: SAMPLING LOCATIONS

DWG: MANDY LAKE

2.3 Study Methods

2.3.1 Core Collection and Processing

Cores (8.8 cm in outside diameter) were collected using butyrate tubes and the lightweight stainless-steel catcher- and cutter-free gravity corer described by Pedersen et al. (1985). All sampling operations were carried out from an 18' fiberglass speedboat equipped with an electric winch. The winch permitted smooth deployment and recovery of the corer. As a result, cores of very good quality were recovered.

Cores were sealed with a full column of supernatant water immediately after removal from the corer, logged, and transported hand-held to minimize disturbance back to a laboratory set up in the assay and process chemical laboratory at the HBM&S smelter in Flin Flon. Detailed core logs are listed in Appendix A.

Interstitial water samples were extracted from the cores in the temporary laboratory. Special techniques to avoid oxidation artifacts were employed during sampling (e.g. Bray et al. [1973]); each core was extruded directly into a nitrogen-filled glove bag by gradually jacking up an o-ring-sealed piston inside the barrel. The supernatant water on the top of the core was carefully removed by siphoning prior to the extrusion, with the exception of the lower 10 cm of water which were removed with a syringe once the core was secured in the nitrogen atmosphere. A sample of this core-top water was collected for each core and was subsequently analyzed as "supernatant" water. In each case, processing commenced within two hours of collection of the core. Samples were sequentially sliced from the core, placed into 250 ml N_2-filled centrifuge bottles, sealed, removed from the glove bag, and centrifuged for 20 minutes at approximately 1200 RFC (Relative Centrifugal Force). The bottles were then placed in another N_2-filled glove bag, the supernatant water in each was decanted into a polypropylene syringe barrel, and the water was expressed through Nuclepore™ 0.45 mm polycarbonate membrane filters into 30 ml sample bottles. Five to 20 ml were typically recovered, the smallest volumes corresponding to the thin sample intervals used near the top of each core. Ultrapure Seastar concentrated HNO_3 was added immediately to the samples in proportion to their volume to bring the pH to 2. All plasticware and filters were rigorously acid-washed in a Class 100 laminar flow bench as follows. Virgin plasticware (except pipette tips) was: 1) wiped outside and rinsed inside with reagent grade chloroform to remove grease and soluble organic residues; 2) soaked at least 1 day in

hot (40°C) 20% reagent-grade HNO_3; 3) rinsed twice with distilled, deionized water (DDW); 4) soaked at least 1 day in 0.1% Seastar ultrapure HNO_3; 5) rinsed once in DDW; 6) soaked at least 1 day in 0.1% Seastar ultrapure HNO_3; 7) rinsed once in DDW; and 8) dried covered in a drying oven.

In order to obtain high resolution profiles to define diagenetic reactivity in the upper few centimetres of the sediments, 5 mm sample intervals were used for the top two cm, one cm increments were used for the next several cm, and 3 cm-thick slices were selected at intervals below the upper decimetre. Approximately 16 samples were collected from each core.

All samples were returned to U.B.C. for analysis. The sediment samples were frozen and freeze-dried. An aliquot of each was ground in a tungsten carbide disc mill prior to preparation for X-ray fluorescence, CNS, and coulometric analysis. All analytical methods and quality control procedures are described in Appendix B.

2.3.2 Water, Sediment Grab and Vegetation Sampling and Analysis

Hydrographic sampling was carried out using a PVC Van Dorn bottle equipped with Neoprene o-rings, and a portable, submersible temperature and dissolved oxygen probe. Conductivity and pH were measured on the water samples immediately after recovery. The three water quality samples were collected in acid-washed 1 L Nalgene polypropylene bottles by submerging the bottle by hand into the flow in each case, rinsing several times, and then filling by submergence. The samples were immediately stored on ice and kept cool for return to Vancouver.

The samples were analyzed by Analytical Services Laboratories Ltd. (ASL) of Vancouver, B.C. Parameters determined included pH, specific conductivity, turbidity (NTU), total dissolved solids and total suspended solids, as well as anions and nutrients including alkalinity, sulphate, chloride, reactive silica, total phosphorus, nitrate/nitrite, ammonia and total organic carbon. Standard analytical methods were used (APHA 1985).

Dissolved metals were analyzed by various atomic absorption and emission spectroscopy methods as follows:

- Inductively coupled argon plasma (ICP) emission spectroscopy for higher concentration elements

- Graphite furnace atomic absorption spectroscopy for low concentration elements

- Hydride generation atomic absorption spectroscopy for arsenic

- Cold vapour atomic absorption spectroscopy for mercury

In addition to the water samples, one sediment sample was collected from under an organic mat in less than 0.5 m of water at Site V1 (Figure 2-2). Two pondweed samples (*Potamogeton* spp. leaves and stems) were collected from Sites V1 and V2 (Figure 2-2) to permit an assessment of the metal content of the local lacustrine vegetation. The sediment sample was analyzed by HCl/HNO_3 digestion and a combination of atomic absorption spectrophotometry (AAS) and ICP emission spectrometry, and metal levels in the vegetation were determined by AAS following a distilled water wash and subsequent digestion by HNO_3/H_2O_2. The analyses were carried out by ASL.

A multiple extraction leach test was performed on a sample collected from the upper several centimetres of a duplicate core raised at Site MD-1. The sample was extracted from the core in a nitrogen-filled glove bag and stored frozen and freeze-dried prior to analysis. The extraction test was performed by ASL and the method used was similar to those utilized in other aquatic studies (Forstner and Wittman 1983; Engler et al. 1974). In a multiple extraction the mildest extraction is completed first, solids are recovered by filtration and washed, and subsequent extractions, are conducted until the sample has been subjected to an entire predetermined series of extractants. The following extractants were used, and are identified in terms of their anticipated reaction with metals in the solids:

Water Soluble Phase

Distilled water extractant;

Exchangeable Cations

1 molar ammonium acetate at pH 7;

Weak Acid Soluble Phase

1 molar sodium acetate at pH 5;

Easily Reducible Phase

0.1 molar hydroxylamine hydrochloride + 0.01 molar nitric acid at pH 2;

Moderately Reducible Phase

0.2 molar ammonium oxalate + 0.2 molar oxalic acid at pH 3;

Difficultly Reducible Phase

0.5 molar sodium citrate + 0.1 molar sodium dithionite;

Oxidizable Phase

30% hydrogen peroxide + 1 molar ammonium acetate acidified to pH 2.5 with nitric acid;

Total Extractable

Nitric/perchloric/hydrofluoric acid digestion.

Note that the results of the extraction tests must be evaluated with caution, as they are subject to severe methodological artifacts as noted by Nirel and Morel (1990). The operationally-defined phases thought to be extracted by each of the sequentially-applied reagents provide only a general indication of compositional fractions potentially present.

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3.0 RESULTS

3.1 Water Quality, Sediment Grab and Vegetation Samples

Water column profiles of temperature and dissolved oxygen are presented in Figure 3-1 and the data are listed in Table 3-1. Oxygen concentrations were high in the upper 4 m of the water column at the time of sampling, but bottom waters in the lake were severely depleted. A steep oxycline occurred between about 3.75 and 5 m depth (Figure 3-1), in the lower portion of the rather diffuse thermocline. Given that the lake must turn over in the spring thaw, the oxygen depletion observed in late June reflects the high benthic oxygen demand associated with the organic-rich sediments on the bottom. A similar oxygen profile was seen in August 1989 (see Rescan 1990a); therefore, it may be that oxygen depletion is a typical condition for Mandy Lake bottom waters in the summer.

Water quality parameters measured on the inflow and outflow samples indicate that there is little difference in the dissolved salts or metals concentrations between the water entering and leaving Mandy Lake. As well, there appears to be little temporal variation in water quality. The chemistry of the inflow, which is derived from nearby Phantom Lake, was very similar in June 1990 and August 1989 (Table 3-2). The sole exception in this comparison is the Zn concentration which was lower by a factor of three (0.052 vs. 0.160) in June 1990 compared to 10 months earlier.

As noted by Rescan (1990a), Mandy Lake water is moderately hard with a hardness of approximately 87 mg L^{-1} as CaCO$_3$. The waters have a nearly neutral pH (approximately 7.5), and an alkalinity of approximately 70 mg L^{-1} as CaCO$_3$. Sulphate and chloride concentrations are low (approximately 16 mg L^{-1} and 5 mg L^{-1}, respectively). Dissolved metal concentrations in both inflow and outflow waters are generally low with only arsenic, copper and zinc being consistently above detection limits. Arsenic concentrations ranged from 0.006 to 0.008 mg L^{-1}, copper concentrations were 0.005 mg L^{-1}, and zinc concentrations in all three samples were ~0.053 mg L^{-1}. Because the metal concentration (particularly Zn) in the inflow at the south end of the lake is almost exactly the same as observed in the outflow near the north end, it appears that metal levels in the inflow may be contributing to lake water concentrations more than the release of metals from bottom sediments. This observation is justified by the

Table 3-3

Sediment Grab Sample and Vegetation Analytical Data, Mandy Lake, June 1990, and August 1989

	Sediment Site V1 June 1990	*Potamogeton* Site V1 June 1990	*Potamogeton* Site V1 August 1989	*Potamogeton* Site V2 June 1990	*Potamogeton* Site V2 Duplicate June 1990	*Potamogeton* Site V2 August 1989
Al	27300					
As	1150	4.1	80.3	1.05	1.05	8.0
Ca	5100					
Cd	13.8	2.7	3.8	1.9	1.8	0.45
Cr	47.4					
Co	86.6					
Cu	3030	35	98.8	25	25	15.3
Fe	69500					
Hg	5.56	0.06	0.3	0.05	0.05	0.075
Mg	11400					
Mn	516					
Mo	<5					
Ni	28.5	1.05	2.5	0.45	0.4	1.15
Pb	580					
V	48.1					
Zn	12400	479	1205	226	226	129

All results expressed in $\mu g\ g^{-1}$, dry wt.

3.2   Sequential Extraction Results

A single sample consisting of the upper 4 cm of sediments from Site MD-1 was subjected to a sequential, multiple extraction leach test as described in Section 2.3.2. Contact with oxygen was prevented as much as possible while the sample was in a wet state, as it was collected under nitrogen, immediately frozen in a nitrogen-flushed plastic bag, and freeze-dried under vacuum before the extractions were performed. Although we are aware of the difficulties inherent in interpreting the results of such tests (e.g. Nirel and Morel 1990), we feel that, with some qualifications, the results are useful in identifying the phases present in the sediments and the expected degree of reactivity of the submerged tailings. All data are listed in Appendix E.

Only 11-12 μg g-1 of zinc and essentially no copper were extracted by a distilled water leach. This is remarkable considering that the sediment sample contained on the order 23,000 μg g-1 Zn and 3,300 μg g-1 Cu. In contrast, high proportions of both metals were extracted by the strongly oxidizing H_2O_2/ammonium acetate/nitric acid leach. This behaviour is consistent with sulphide minerals being the primary host for zinc and copper in the deposits. The fact that essentially very little Zn and no Cu were released to distilled water reinforces the conclusion drawn from the concentrations of the metals in pore water samples (Section 3-4) that the tailings on the lake floor are essentially unreactive and unoxidized. Similar observations apply to other metals measured in the leach test. Pb, Co Hg and Cd were undetectable in the distilled water extract, despite the fact that all four of these metals occur in anomalously high concentrations (relative to expected backgrounds) in the Mandy Lake sample. A very small amount of arsenic was released to distilled water (~1% of the total; Table E-1), but a substantial proportion of the total was extracted by the strongly oxidizing leach. This implies that the dominant host for As is a sulphide phase, probably arsenopyrite, which was a minor constituent of the Mandy Mine ore.

Note that the results obtained for this study differ significantly from those reported previously (Rescan 1990a). This is because no effort was made to collect the 1989 samples under a nitrogen atmosphere or to store them frozen prior to analysis. Oxidation of the contained sulphide minerals during storage is believed to be responsible for the high concentrations of metals extracted by the distilled water leach in the previous study. This contrast between the past and the present work reinforces the

necessity to prohibit or inhibit exposure of tailings to oxygen in order to foster low diagenetic reactivity.

3.3 Solid-phase Chemistry of Cores

The concentrations of major (Fe, Ti, Ca, K, Si, Al, Mg, P and Na) and minor elements (Zn, Pb, Cu, Ni, Co, Mn, Ba, Cr, V, Sr and Rb) were determined by X-ray fluorescence spectrometry as described in Appendix B. Results are listed in Appendix C.

Core MD-1 consists of two contrasting strata: nearly three decimetres of tailings mixed with organic-rich sediments overlie about 12 cm of natural deposits; the latter contain a very high proportion of organic matter. These strata are compositionally well-defined by Zn, Cu and Pb profiles (Figure 3-2) and organic carbon, nitrogen and sulphur distributions (Figures 3-3 and 3-4). Zinc and copper levels average 5 and 0.4 wt. % respectively in the upper 20 cm of the core, and decrease to much lower values in the lower decimetre. Pb and Co are also enriched in the tailings (Figures 3-2 and 3-5) but Ni, Cr and Rb are depleted (Table C-2 in Appendix C). Organic carbon concentrations range up to nearly 15 wt. % in the lower portion of the core, indicating an organic matter content on the order of 30 wt. %. The sulphur content is very high in the pyritic-tailings-rich upper half of the core, reaching levels of nearly 9 wt. % (Figure 3-4). The iron distribution with depth tracks that of sulphur, clearly indicating that pyrite is the major host for both elements where tailings are abundant.

Zinc, copper and lead values reach exceptionally high levels in Core MD-2, which was collected near the former tailings discharge point. Zn concentrations exceed 13 wt. % at about 33 cm depth in the core; at the same horizon, Cu levels are on the order of 2 wt. % (Figure 3-2). The concentrations of both metals are variably lower throughout the remainder of the core (Table C-2). These distributions, in conjunction with the organic carbon, nitrogen and sulphur profiles (Figures 3-3 and 3-4), indicate that the lower portion of the core (below about 16 cm depth) consists of exceptionally metal-rich tailings, which are notably depleted in organic matter, while the upper section is comprised of a mixture of tailings and natural sediments. A tailings-rich band (containing up to 6 wt. % Zn and > 14 wt. % S) occurs between 3 and 7 cm depth.

Note that in spite of the cessation of tailings discharge more than 40 years ago, metal concentrations in the near-surface sediments at both sites are much higher than would
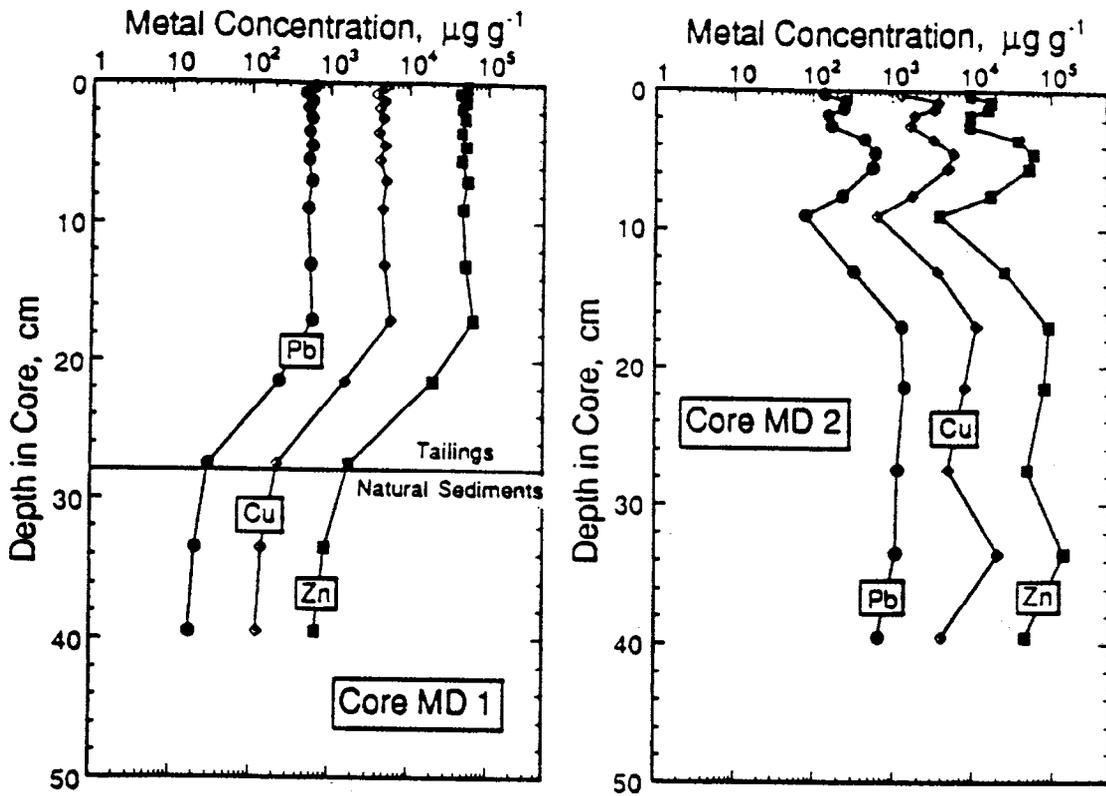
Figure 3-2 Zinc, copper and lead distributions in the sediments of two Mandy lake cores. Note the log scales on the abscissae.
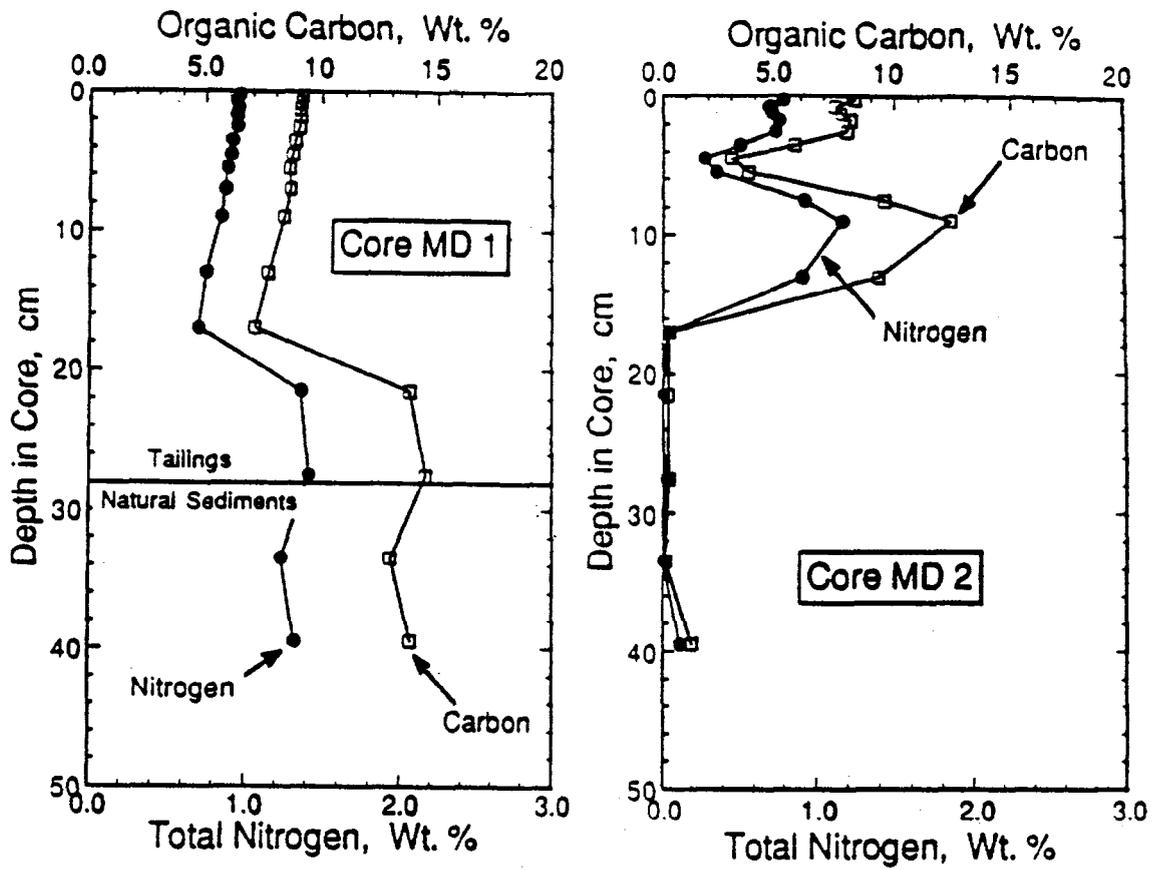
Figure 3-3 Organic carbon and nitrogen distributions in the sediments of two Mandy Lake cores.
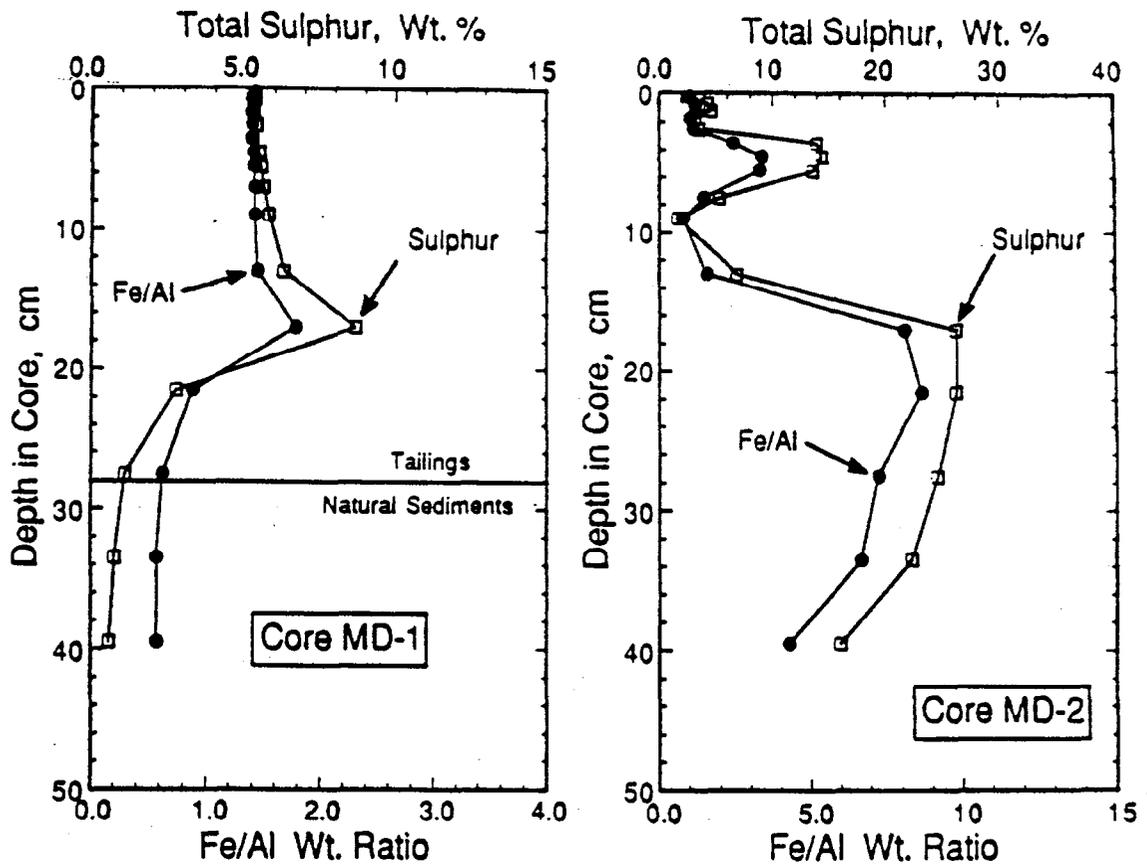
Figure 3-4 Sulphur and Fe/Al ratio distributions in the sediments of two Mandy Lake cores. Note the variable scales on the abscissae.
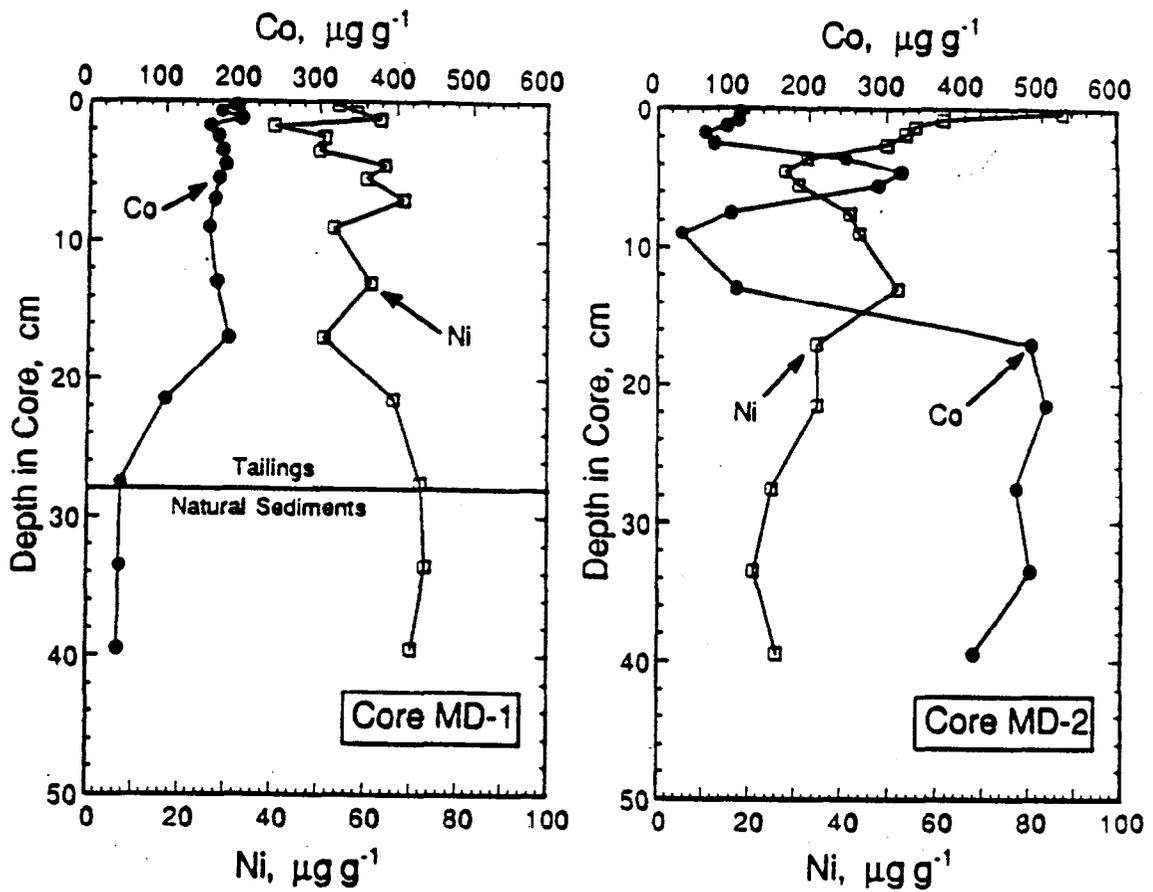
Figure 3-5   Cobalt and nickel distributions in the sediments of two Mandy Lake cores.

be expected in uncontaminated deposits. High metal concentrations were also found in recent previous work (Rescan 1990a) in surface sediments at other sites in Mandy Lake. The sulphur and Fe/Al distributions reported here indicate that these enrichments are due to the presence of pyrite-bearing tailings and not, for example, to the occurrence of alteration products or other non-tailings inputs. A relatively low rate of detrital sedimentation is to be expected in Mandy Lake, given the low fluvial input to the basin; however, the lake is meso-eutrophic (Rescan 1990a) and a significant settling flux of organic matter should be present. Thus, the tailings should have been covered by now by a veneer of natural sediments. The occurrence of tailings in the surface sediments at both sites therefore probably reflects recent slumping from the tailings fan on the lake margin near the old open pit. As noted earlier, the tailings were originally deposited in shallow water from a single launder, and formed a fan-shaped deposit which slopes away from the east shore. A map compiled by Hamilton and Fraser (unpublished manuscript, 1976) showed that in 1975 the tailings formed a shallow platform < 1.5 m deep which extended into the lake more than 50 m from the shore adjacent to the old open pit. Water depths are now on the order of a few metres where the platform previously existed, indicating that erosion by wave and ice action as well as presumed slumping have dispersed the tailings away from the original discharge site. Bioturbation by benthic infauna has almost certainly also played a role in maintaining high metal levels in surface sediments. Rescan (1990a) documented a moderately-dense profundal benthic invertebrate community in the lake characteristic of environments low in oxygen, dominated by oligochaetes (tuberficid worms) and dipteran larvae (chironomids and *Chaoborus punctipennis*). These animals will both mix and irrigate surface sediments, and serve to redistribute tailings upward.

Manganese concentrations range from a minimum of ~600 μg g^{-1} at depth in both cores, which is typical of the natural background, to about 1400 μg g^{-1} at the surface of MD-2 (Figure 3-6). The profiles in the latter core, and to a lesser extent in MD-1, suggest that there is a slight surface enrichment of Mn, which is essentially confined to the top 5 mm. As discussed in Section 4.1, this appears to be due to the presence of a manganese oxyhydroxide phase. This suggestion is consistent with the dissolved Mn profiles discussed in Section 3.4 (below).

At both locations, and in all samples where the nitrogen content exceeds about 0.3 wt. %, the C:N wt. ratio ranges between ~9.5 and 11 (Figure 3-7). There is little evidence of systematic variation with time at the two sites; however, the average ratio at MD-1 is
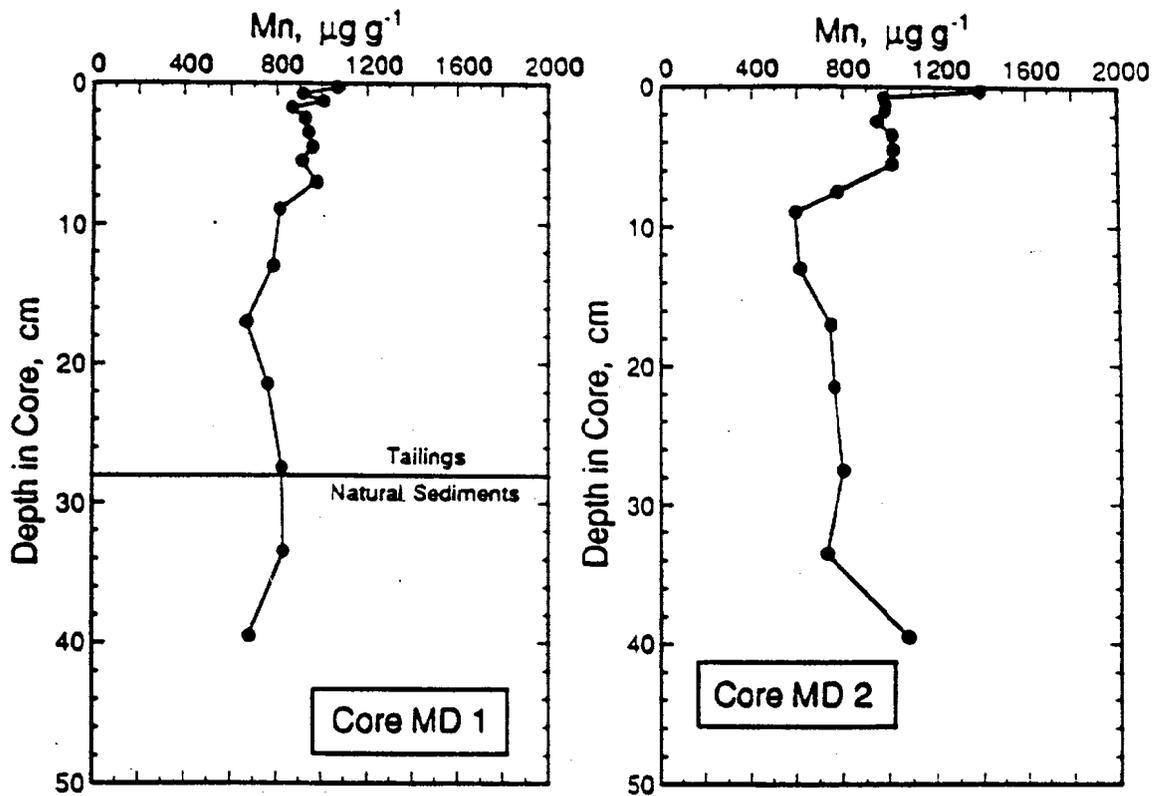
Figure 3-6 Manganese distributions in the sediments of two Mandy Lake cores.
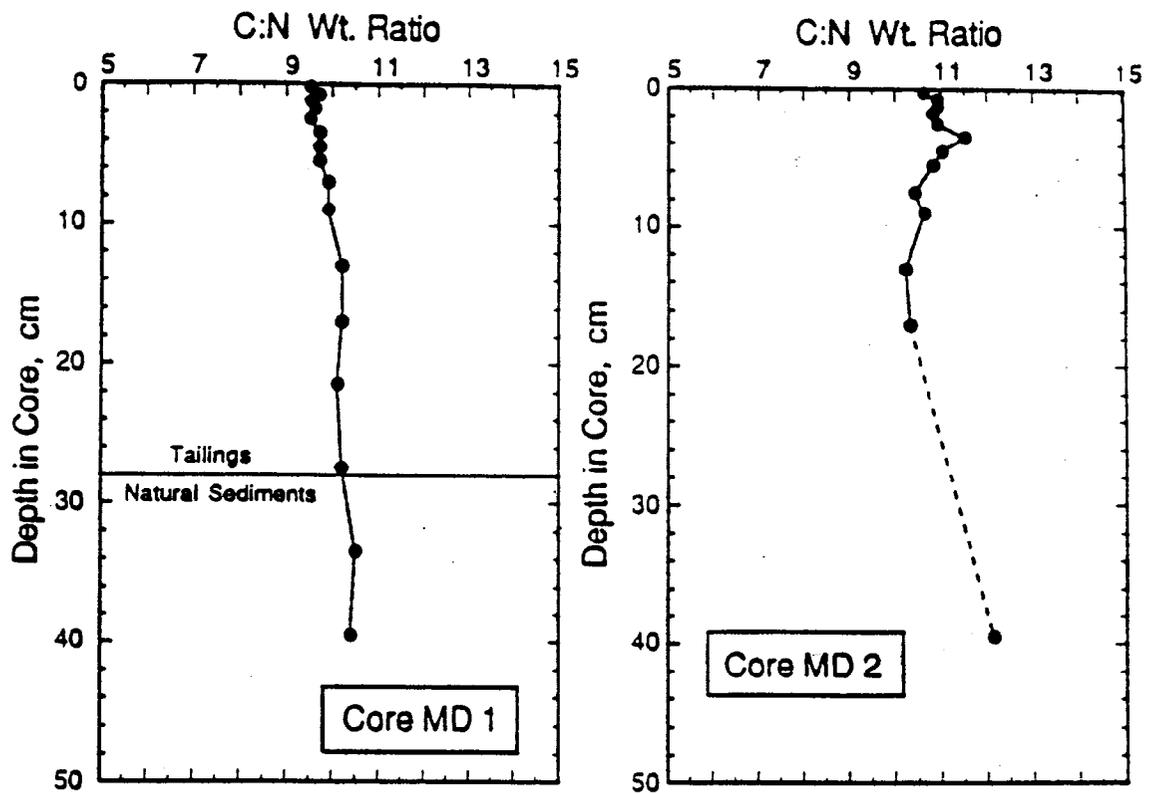
Figure 3-7   C:N ratio distributions in the sediments of two Mandy Lake cores.
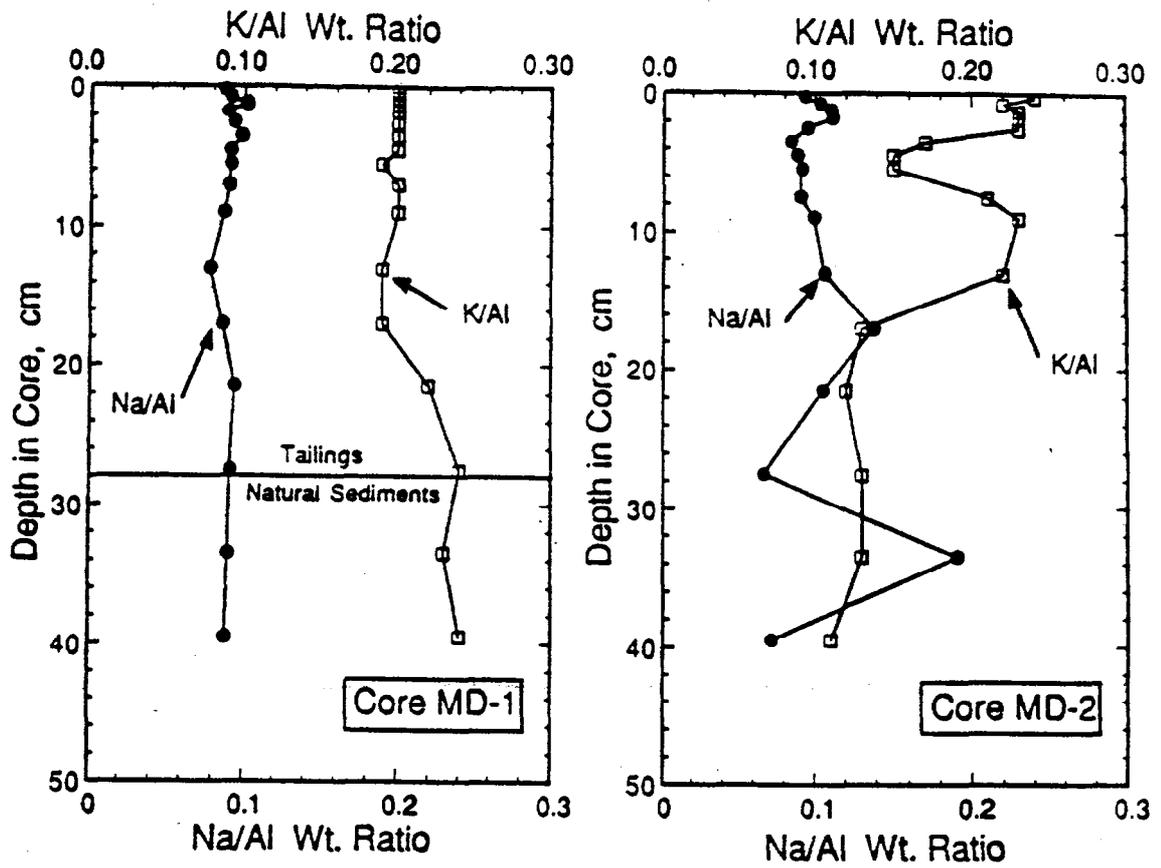
Figure 3-9 K/Al and Na/Al distributions in the sediments of two Mandy Lake cores.
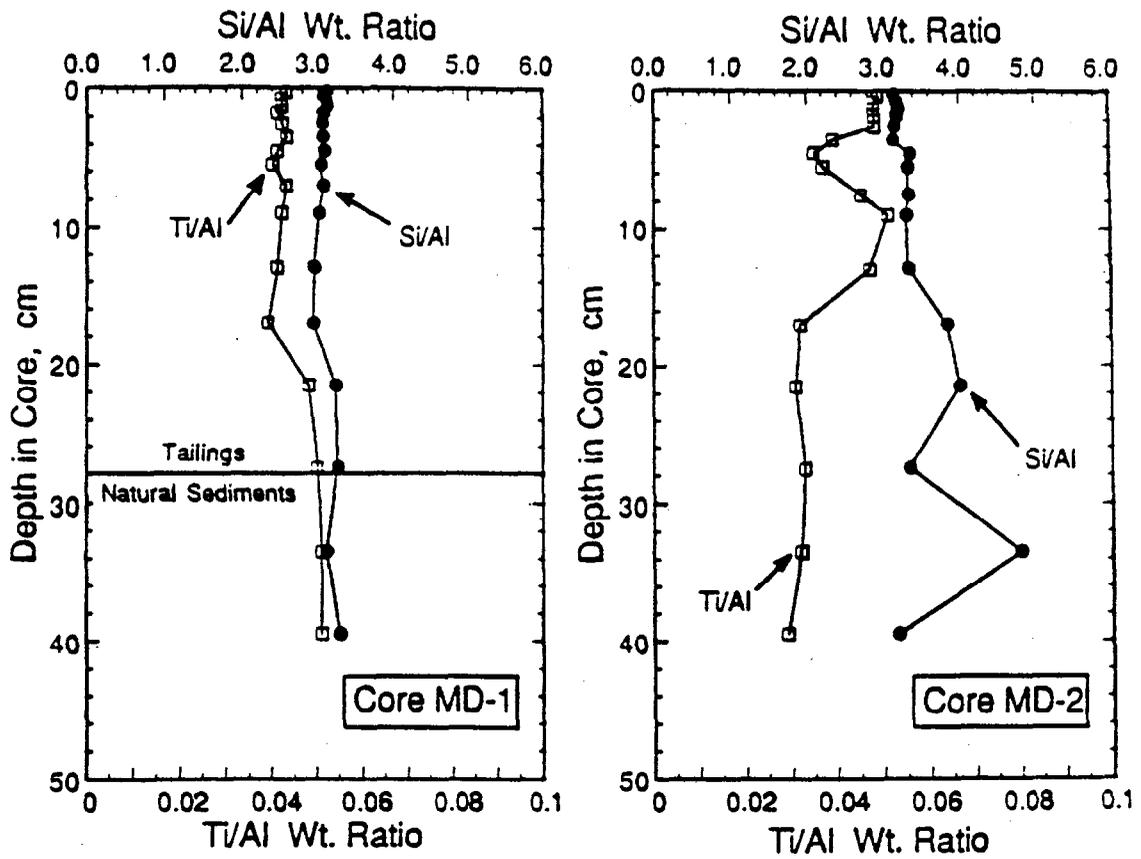
Figure 3-10 Si/Al and Ti/Al distributions in the sediments of two Mandy Lake cores.

Dissolved Fe and Mn profiles are shown in Figures 3-11 and 3-12 respectively. Concentrations of ~4 μmol L^{-1} Fe and ~6 μmol L^{-1} Mn were measured in the supernatant water at Site MD-1, and ~1 μmol L^{-1} for both metals at MD-2. These levels are considerably higher than concentrations measured in outflow and inflow waters at the time of coring, which were consistently <0.01 μmol L^{-1} for Mn and <0.5 μmol L^{-1} for Fe. In Core MD-1 dissolved iron concentrations reach levels as high as 60 μmol L^{-1} in the near-surface zone (2.5 cm depth) and are depleted at depth. An attenuated maximum is seen in Core MD-2, where values reach about 16 μmol L^{-1} between 6 and 10 cm depth (Figure 3-11). Similar subsurface distributions are observed for manganese. In MD-1 the dissolved Mn content increases reasonably steeply to a maximum of ~16 μmol L^{-1} at 4.5 cm and decreases with increasing depth to concentrations <5 μmol L^{-1} in the natural sediments near the base of the core (Figure 3-12). The maximum in MD-2 is a centimetre shallower, and is marked by concentrations of ~6 μmol L^{-1}.

Dissolved Zn contents in the supernatant waters at both sites (Appendix D) are almost identical (~1200 nmol L^{-1}). These levels are similar to the concentrations measured in both inflow and outflow water samples (~800 nmol L^{-1}) collected at the same time as the cores. At both locations, dissolved Zn concentrations measured in the top 5 mm of the sediments are sharply lower than in the supernatant samples (Figure 3-13), and in both cores minima are observed at depths of about 1 dm. Notably low concentrations (~30 nmol L^{-1}) occur in the natural sediments at the base of Core MD-1, below a sub-bottom maximum (~1000 nmol L^{-1}) centered at a depth of 22.5 cm.

Dissolved Cu concentrations in supernatant waters at both sites differ by a factor of ~2 (Appendix D); the higher value (71 nmol L^{-1}) is very similar to the level measured in both the inflow and outflow samples (~80 nmol L^{-1}, or 0.005 mg L^{-1}, Table 3-2). In the upper decimetre of Core MD-1 dissolved Cu concentrations, although quite variable, exceed the content measured in the supernatant water by a factor of roughly two. In contrast, the dissolved Cu level decreases with depth in MD-2 (Figure 3-14), reaching minimum values of <10 nmol L^{-1} between 6 and 10 cm. As for Zn, a sub-bottom dissolved-Cu maximum occurs at a depth of about 20 cm in MD-1.

Pb concentrations in supernatant waters (Figure 3-15) are relatively low (~2-7 nmol L^{-1}). The subsurface distributions are comparable to those for Cu; concentrations in the upper few cm of Core MD-1 are higher than the supernatant values by a factor of up
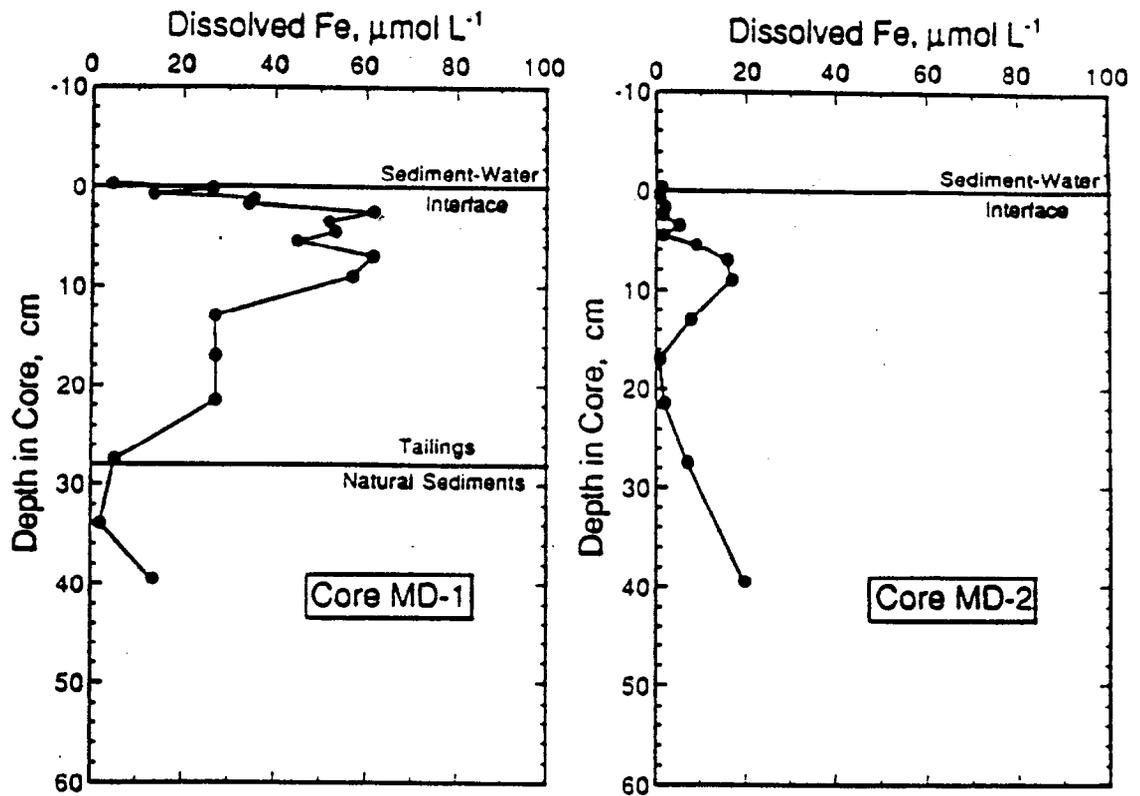
Figure 3-11 Dissolved Fe distributions in the interstitial waters of two Mandy Lake cores.
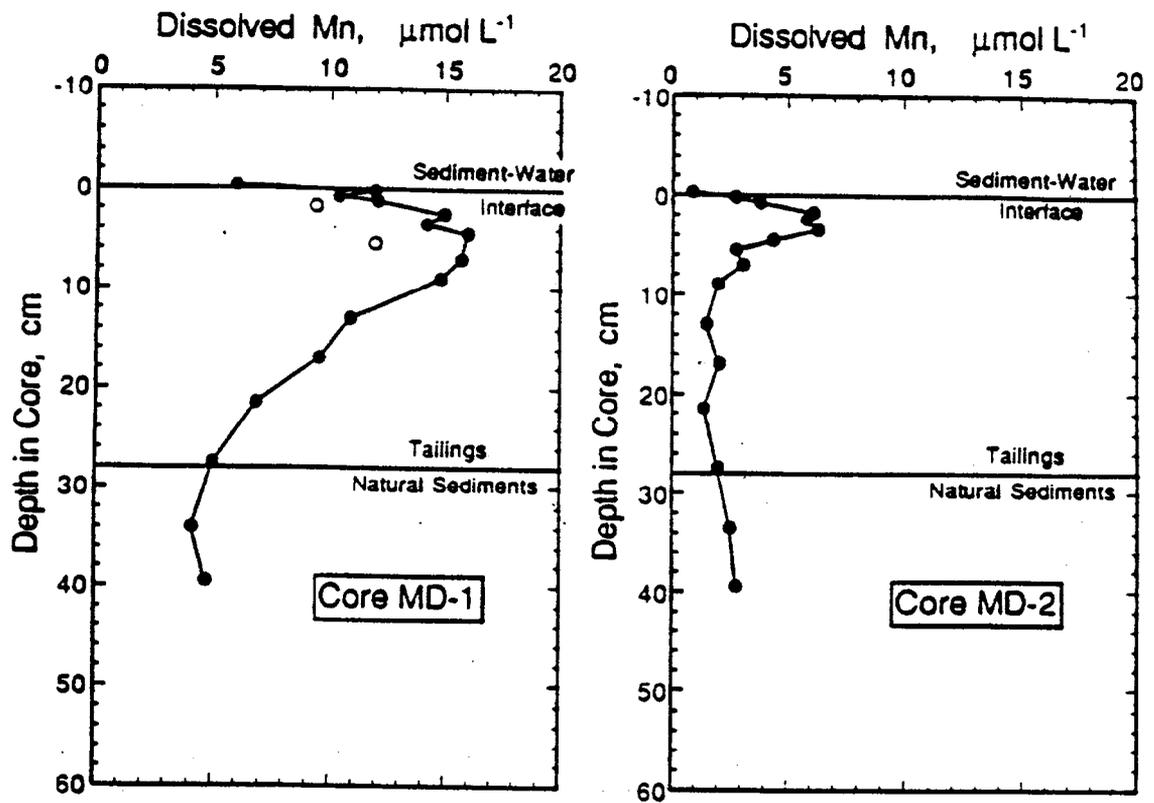
Figure 3-12 Dissolved Mn distributions in the interstitial waters of two Mandy Lake cores. The two open circles represent samples which are analytically suspect.
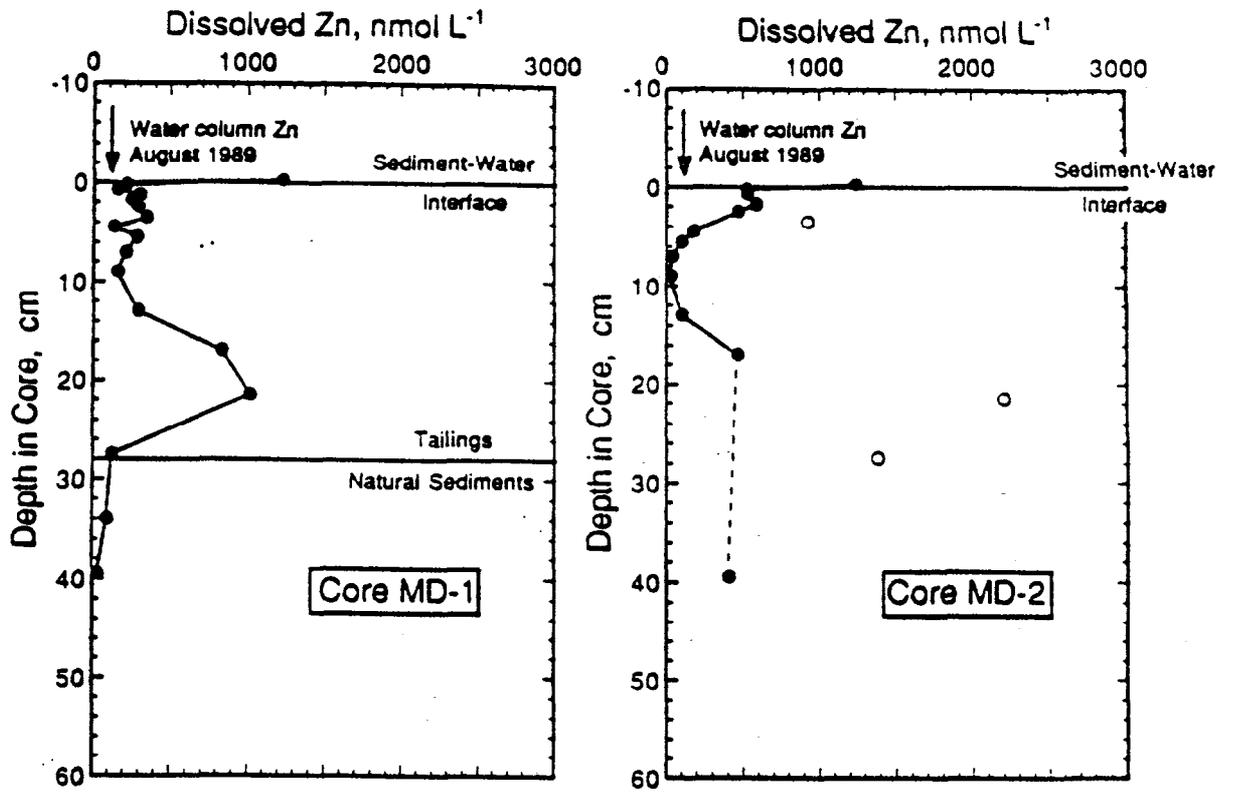
Figure 3-13 Dissolved Zn distributions in the interstitial waters of two Mandy Lake cores. The three open circles represent samples in which contamination is suspected.
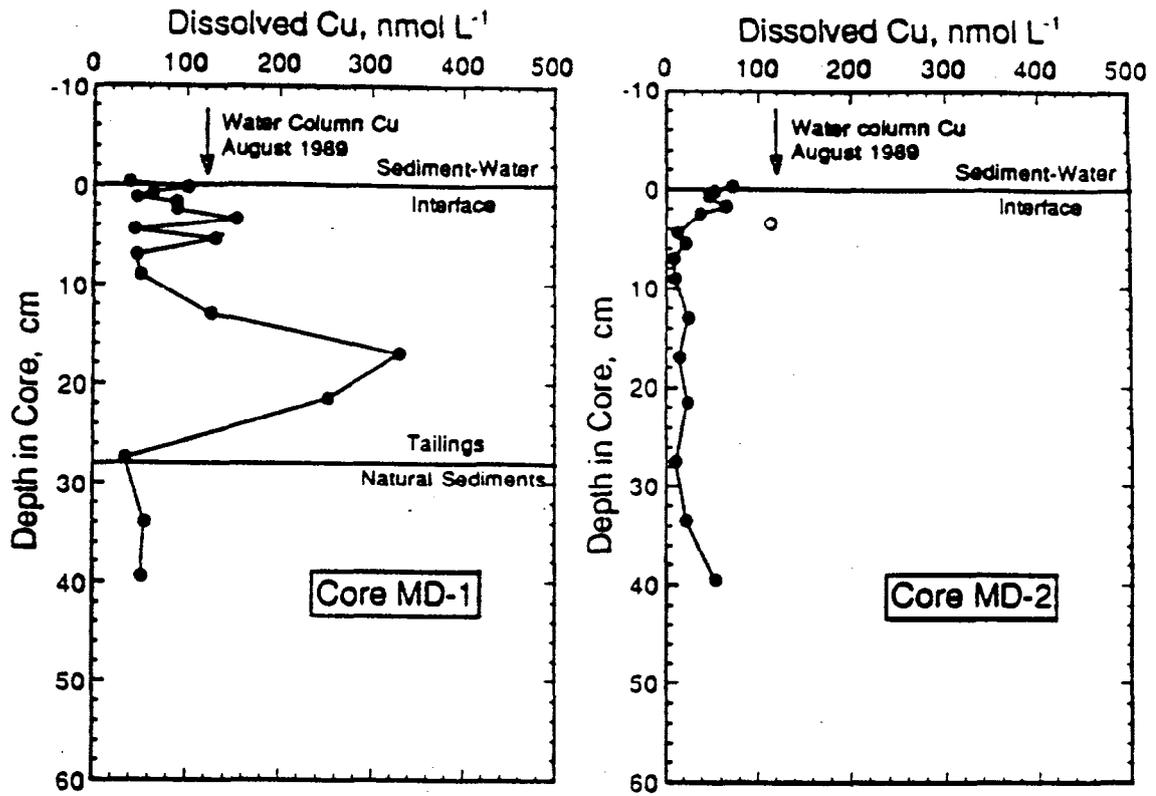
Figure 3-14 Dissolved Cu distributions in the interstitial waters of two Mandy Lake cores. The sample marked by the open circle is thought to be slightly contaminated.
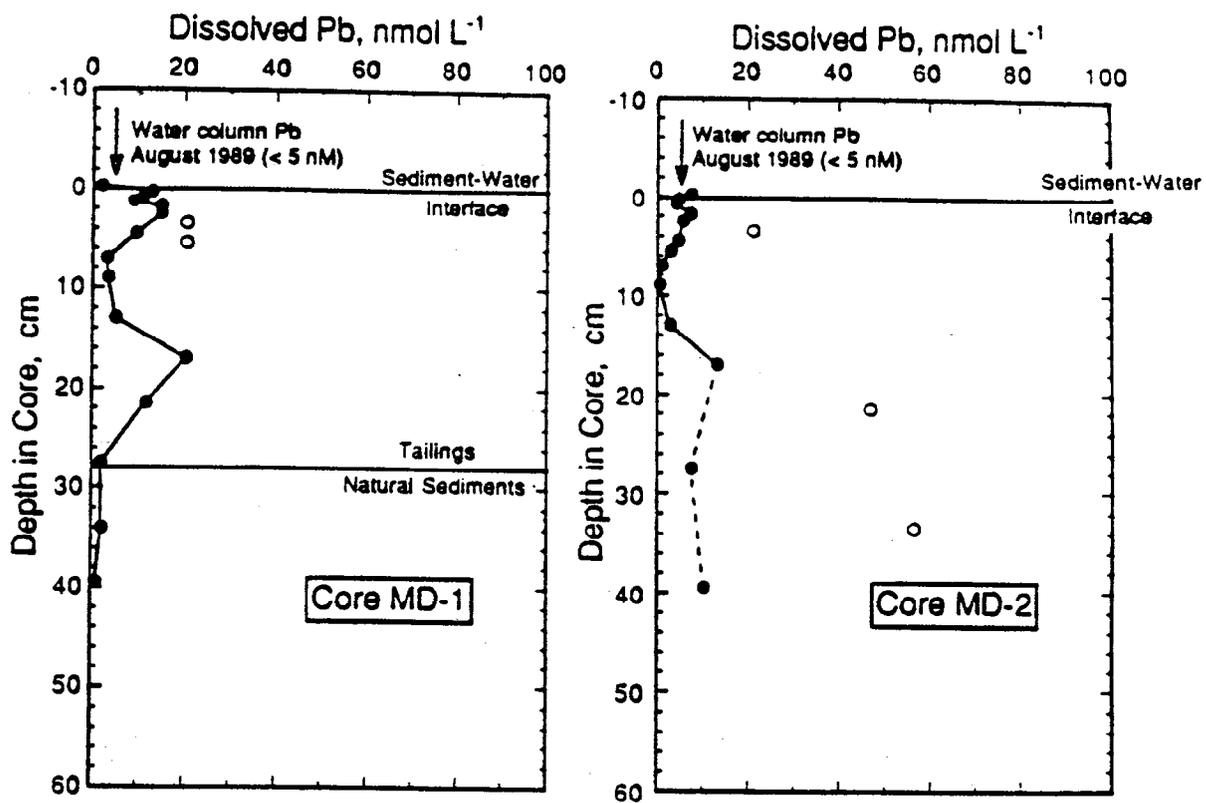
Figure 3-15 Dissolved Pb distributions in the interstitial waters of two Mandy Lake cores. Samples marked by the open circles are thought to be contaminated.

to eight, a very low level (<1 nmol L^{-1}) is observed in the natural sediments at the base of the core, and a sub-bottom maximum occurs at a depth of about two decimetres. Generally low Pb concentrations (<10 nmol L^{-1}) characterize the pore waters in Core MD-2, and as for copper a minimum is observed at about 9 cm depth. Note that three samples contained high Pb contents which are attributed to contamination (Figure 3-15).

4.0 DISCUSSION

4.1 Manganese and Iron Diagenesis

Bacterial oxidation of reactive organic matter in lacustrine sediments proceeds via a series of overlapping electron-transfer reactions in which the thermodynamically-unstable reduced carbon compounds serve as electron donors and various oxidants act as terminal electron acceptors as degradation proceeds (see review in Chapter 3 of Rescan, 1989). During oxidation, organic matter will donate electrons to orbitals of lowest available energy level as this produces the greatest free energy gain per unit of organic material oxidized. The reaction sequence proceeds in an order mandated by the net free energy yield, with aerobic oxidation (the highest-yield reaction) preceding (in thermodynamic order) denitrification, manganese and iron oxyhydroxide reduction, sulphate reduction, and methanogenesis (Froelich et al. 1979).

In sediments in mesotrophic or eutrophic lakes, the organic carbon content is usually sufficient to establish anoxic conditions at depths ranging from a few millimetres to one decimetre. The resulting chemical zonation is therefore characterized by a decreasing redox potential with depth and the release to interstitial solution of a number of reaction products. Two such products are dissolved manganese and iron. Because Fe oxyhydroxide reduction commences almost as soon as O_2 has been depleted, the depth at which Fe^{2+} first appears in pore water is a reasonably precise indicator of the sub-bottom oxic-anoxic boundary (Rescan 1989). MnO_2 reduction and associated addition of Mn^{2+} to pore water occurs at slightly shallower depths, thus, at a slightly higher oxidizing potential. The presence of Fe and Mn oxide phases in near-surface sediments has important implications for the diagenetic behaviour of heavy metals, given that both oxyhydroxides are effective at scavenging metals from solution (Kadko et al. 1987).

There is no indication in the present study that iron oxides are enriched in the surface sediments at either of the sites sampled. However, the background level of iron is very high due to the concentration of pyrite in the sediments, and the presence of a small proportion of oxyhydroxide would be very difficult to detect using bulk sediment analysis. In contrast, the Mn distribution does suggest that a slight manganese excess exists in the surface sediments at both locations. This is illustrated in Figure 4-1; the highest Mn/Al ratio (which is essentially insensitive to dilution by such components as
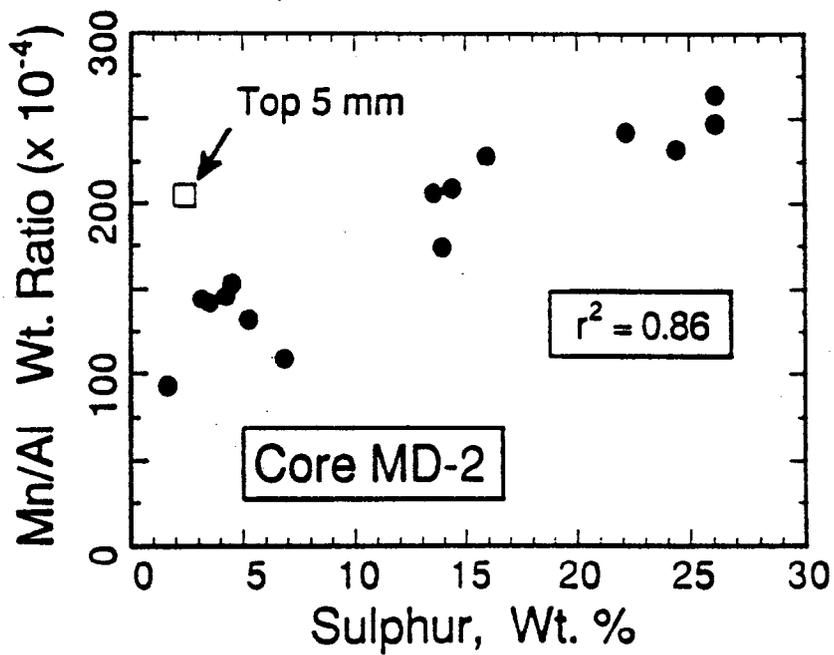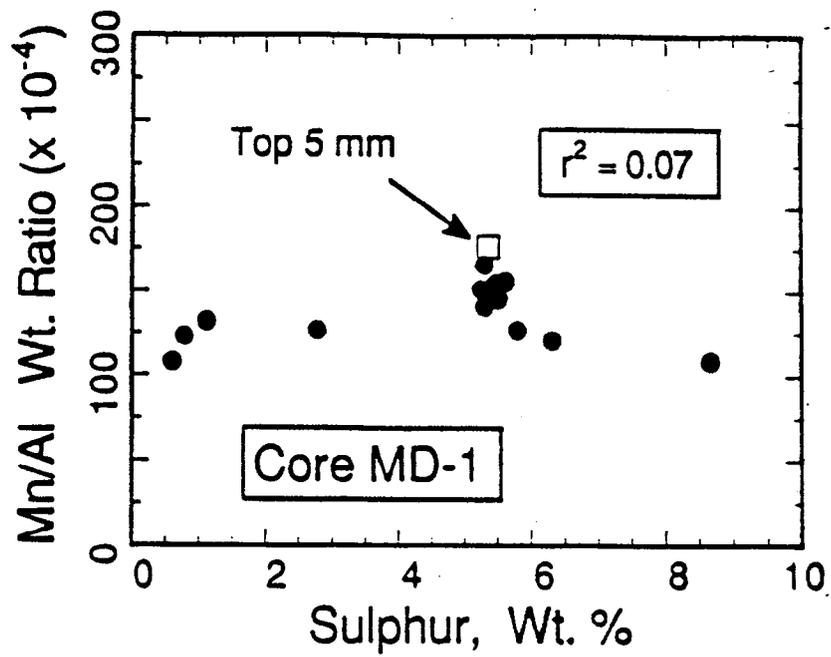
Figure 4-1 The relationship between Mn/Al and sulphur in the sediments of two Mandy Lake cores. The open square marks the topmost sample (0-5 mm depth) in each core. Note the variable scales on the abscissae.

organic matter) occurs at both sites in the topmost sample (0-5 mm). Below 5 mm depth in Core MD-2, the Mn/Al ratio correlates well with the sulphur content, indicating that the relatively coarse tailings deposited at this site are a dominant host for manganese. No such correlation is observed in the sub-surface sediments in Core MD-1, suggesting either that the fine-grained tailings accumulating at this location contain relatively less manganese, or that the aluminosilicate fraction of these sediments contains a higher proportion of Al-rich clay minerals.

The suggested presence of some manganese oxydroxides in the surface sediments and their apparent absence at depth is in general consistent with the dissolved manganese distributions in both cores, which indicate release of Mn to solution at shallow sub-bottom depths. The profiles (Figure 3-12) indicate that dissolution commences within a depth of about 2 cm in both MD-1 and MD-2. In contrast, the dissolved iron profiles show that dissolution commences at a greater depth in MD-2, where Fe levels remain low in the upper 5 cm (Figure 3-11). Given that, at neutral pH, dissolved iron is much more susceptible to oxidation in the presence of molecular O_2 than Mn, the occurrence of dissolved Mn and essential absence of iron suggest that the pore waters in the upper few centimetres at Site MD-2 are slightly oxidizing or suboxic rather than anoxic. The presence of "excess" solid-phase Mn in the upper 5 mm apparently confirms that oxic conditions prevail very close to the surface. The spatial similarity of the dissolved iron and manganese profiles in the upper decimetre at Site MD-1 indicate that the near-surface deposits at this location are less oxidizing than at Site MD-2. Indeed, unlike the case in MD-2, relatively high Fe concentrations occur in the topmost pore water sample (0-5 mm) at MD-1. Such an occurrence can only be sustained if either the sediments are sub- or anoxic, or if the oxidation rate is too slow to permit quantitative oxidation *in situ* of the iron which is diffusing upward from the concentration maximum at 4 cm depth. However, given that the data in Figure 4-1 suggest that manganese oxyhydroxides are present in the upper 5 mm at Site MD-1, albeit at a low concentration, we conclude that the surface deposits at this location are mildly oxidizing.

It is important to note that the apparent occurrence of an oxic surface layer of some 5 mm thickness in Mandy Lake sediments contrasts with the tailings and natural deposits on the floor of Anderson Lake (see Rescan [1990b]) where anoxia prevailed within millimetres of the sediment-water interface. This difference, although not profound, is thought to be reflected by the distribution of dissolved Zn, Pb and Cu in near-surface pore waters, as discussed in Section 4.2.

4.2 Zinc, Copper and Lead Diagenesis

It is clear from analysis of the water quality samples collected at the same time as the cores that Mandy Lake water is slightly contaminated with respect to zinc (Section 3.1). Zn concentrations in both inflow (from Phantom Lake) and surface outflow samples in mid-June 1990 were ~750 nmol L^{-1}. Copper levels at the same time were roughly 80 nmol L^{-1}. Concentrations of similar order were measured in the supernatant samples in both cores (~1200 nmol L^{-1} Zn in both cores and 37 and 71 nmol L^{-1} Cu in MD-1 and MD-2, respectively). Lead was not detectable (<5 nmol L^{-1}) in outflow waters in June 1990; in the supernatant water samples from MD-1 and MD-2, respective Pb concentrations of ~2 and 7 nmol L^{-1} were measured. Note that the concentrations of Zn and Cu in the water column were quite different in August 1989 when both were on the order of 110 nmol L^{-1}. Pb levels were at or near detection limit in August 1989 (Rescan 1990a) and below the limit (<5 nmol L^{-1}) in June 1990. The available data are insufficient to define the reasons for the observed year-to-year variations in metal concentrations in the lake water, but such variations are important in that they will influence the distributions of metals in near-interface pore waters, and could establish non-steady-state conditions with respect to both the overlying water and the interstitial waters and associated solid phases.

At Site MD-2, the distributions with depth of all three dissolved metals are similar; concentrations in supernatant water are relatively high, and levels decrease with depth in the deposits to a minimum near one decimetre, before increasing to varying degrees toward the base of the core. Note, however, that such distributions are contingent both on the nature and extent of diagenetic reactions at shallow depths, as well as variations in the metal concentrations in the overlying water. The ten-fold increase in the Zn concentration in near-bottom water between August 1989 and June 1990, for example, is probably responsible for the relatively high concentrations of dissolved Zn seen in the top 4 cm of the core. It is clear that when the cores were collected in June 1990, Zn was diffusing into the deposits from the overlying water and being consumed at depth. Given a bulk diffusion coefficient (corrected for porosity and tortuosity) for Zn^{2+} at 6 °C of ~4.5 x 10^{-6} cm² sec^{-1} (calculated from the data in Li and Gregory, 1974), it would take roughly seven months for Zn^{2+} to diffuse downward 9 cm (from the interface to the minimum at 9 cm depth). Thus, the decline in concentration between the interface and the concentration minimum may reflect ongoing adjustment toward the establishment of diffusive steady-state with the increased zinc concentration in the overlying bottom

water. However, if steady-state is assumed, the convex-downward form of the zinc profile in MD-2 indicates that the metal is being consumed from solution at depths on the order of 7 or 8 cm. Presumably, precipitation of authigenic ZnS or coprecipitation of Zn with FeS or FeS_2 is responsible for the depletion, given that the sediments appear to be anoxic at these depths (dissolved Fe first appears in significant concentrations in pore water at 5.5 cm depth). The assumption of steady-state is in fact reasonable given that the copper and lead profiles also show concentration minima at the same depth in the core (Figures 3-14 and 3-15), and their concentrations in the overlying water did not change as radically as that of zinc between August 1989 and June 1990; thus, the decrease with depth in the upper decimetre of dissolved Cu and Pb must also reflect consumption and not a non-steady-state artifact.

Comparison of the pore water distributions at MD-2 with solid-phase chemistry indicates that the tailings-rich band between 3 and 6 cm depth is not releasing metals to solution. In addition, the upper portion of the organic-rich stratum between 5 and 15 cm depth appears to be the locus of metal removal. This is not surprising given the high oxidant demand (thus sulphate reduction and sulphide production) expected to be fostered by the organic-rich layer.

Slightly higher dissolved metal concentrations appear to be present in the lower two decimetres of Core MD-2. The integrity of these data is somewhat questionable, given that two of the samples are thought to be contaminated for Zn and Pb (Figures 3-13 and 3-15). Nevertheless, the organic carbon concentration in the "pure tailings" in the bottom two decimetres in the core is low and if the associated rate of sulphate reduction is minor as a consequence, then the slightly enriched metal levels might reflect an equilibrium between metal release from the tailings to pore water and limited removal under sulphide-deplete conditions.

The subsurface Zn concentrations in the top decimetre in Core MD-1 are very low ($\sim$200 nmol L^{-1}), amounting to about one-fifth of the level in the overlying supernatant sample. Unlike the profile in MD-2, however, there is no gradual decline with depth; the concentration decreases abruptly between the supernatant water and the uppermost pore water sample. As at Site MD-2, this distribution indicates that at the time of sampling there was no efflux of zinc to the overlying water column, and in fact, Zn had to be diffusing into the sediments. It is not clear in this core what phase(s) are responsible for the Zn extraction from solution. It was argued earlier that there is a

slight enrichment of oxides in the upper few mm, which may be scavenging metals, but the presence of dissolved Fe and Mn enrichments in the 0-5 mm pore water sample suggests that anoxic conditions exist very near the surface at this location. The sediments at this location are certainly highly anoxic at greater depths: methane bubbles were observed throughout the core below the 12 cm level (Appendix A). It follows that dissolved sulphides could be responsible for limiting the Zn concentration in pore water in the upper horizons of the core (as well as at depth, but see below). In contrast to the Zn distribution, copper and lead concentrations are slightly enriched relative to supernatant water in the upper few centimetres of the core. The enrichments are small, but they do indicate that there is a slight efflux of both metals to the overlying water column. Dissolved copper levels are generally higher throughout the upper 30 cm of Core MD-1 than in MD-2. This observation also applies to Zn and Pb, although the contrast is less profound for these metals. All three metals are significantly enriched in a band between 15 and 25 cm depth, where the organic carbon content increases to about 15 wt. %.

The nature of the contrasts in dissolved metals distributions both within and between the cores implies that complexation of Cu, Pb and Zn with dissolved organic matter (DOM) is influencing the diagenetic behaviour of these elements. Organic matter contents are high throughout the sediment column at MD-1, and dissolved sulphate levels in the overlying lake water are low. Therefore, it is reasonable to suggest that the production rate of HS- in pore water is sulphate-limited. Under such conditions, DOM will have a proportionately greater influence on dissolved metal distributions. Thus, it follows that the Cu and Pb enrichments (relative to supernatant water) in MD-1, albeit very low in absolute terms, particularly in the upper decimetre, might reflect competition between limited precipitation of authigenic sulphide minerals and complexation by DOM in these organic-rich deposits. This supposition is supported by the behaviour of Zn, which, although having a comparatively lower affinity for organic ligands in solution (Stumm and Morgan 1981), occurs in pore water at significant levels throughout the upper 25 cm, even in the methane-bearing horizons below 12 cm. If sulphide was present even at low concentrations at depth in the deposits, the metal levels would be significantly lower, as seen, for example, in pore waters extracted from cores collected in sulphate-replete Anderson Lake (see Rescan, 1990b).

In order to estimate the potential impact on Mandy Lake water quality of the benthic effluxes of Pb and Cu from the sediments at Site MD-1, diffusive fluxes across the sediment-water interface are calculated from Fick's first law:

$$J = -\phi(K_c/F)(\,C/\,x)$$

where f is the porosity (assumed here to be 1, since the water content in the organic-rich natural sediments was very high; the flux will be only slightly overestimated by the adoption of 100% porosity). Kc is the diffusion coefficient for each metal (from Li and Gregory, 1974) corrected for estimated average *in situ* temperature (6 °C); the metals are presumed to occur largely as divalent ions - no allowance is made for complexation in the calculations. The coefficients are thus 4×10^{-6} cm^2 sec^{-1} for Cu and 5.5×10^{-6} cm^2 sec^{-1} for Pb. C/ x is the concentration gradient calculated as the concentration difference between the supernatant water (2.5 mm above the interface) and the mean dissolved metal concentration in the top 5 mm of the sediments (taken to be at a depth of 2.5 mm; thus x is 0.5 cm). F is the formation factor (Manheim, 1970) which takes into account the tortuous diffusion path of an ion in wet sediments. Given the high water content of the uppermost sediments at each core site, we estimate the formation factor to be only slighly greater than unity; thus F is taken to be 1.1. No corrections are applied here for the possible electrical coupling of the divalent metal ions to the fluxes of major ions (see Lasaga 1979), since the latter are unknown. In eastern Canadian lakes, Carignan and Tessier (1985) found that correcting for the coupling effect required a relatively small adjustment in the calculated flux for Zn^{2+} (about +10% in one lake, and -7% in another). Since we have no major ion data, we have chosen to ignore this small potential effect on our calculated fluxes. The flux calculations are listed in Table 4-1.

The potential impact of these calculated effluxes can be very roughly estimated if we assume that they are representative of the entire lake floor (obviously this is not a tenable assumption, but it does illustrate the most extreme case), the area of which is about 240×10^3 m^2 (Rescan 1990a). Integrating the flux over one year yields an addition of roughly 2.3 kg of Cu and 2 kg of Pb. Given a volume of the lake of 853,000 m^3 (Rescan 1990a), this translates into an increase of the dissolved metal content of 4 nmol L^{-1} yr^{-1} (0.25 ppb yr^{-1}) for Cu and 1 nmol L^{-1} yr^{-1} (0.2 ppb yr^{-1}) for Pb, assuming that the added metal is evenly distributed throughout the whole water column (which does turn over twice a year). Clearly, these are extremely crude estimates, particularly considering

Table 4-1

**Calculated Benthic Fluxes of Dissolved
Cu and Pb in the Central Basin of Mandy Lake
(Based on Core MD-1)**

Metal	C/2x	J
Cu	0.13	-15
Pb	0.2	-4

- = indicates a flux out of the sediment
Concentration gradient are in units of nmol
cm^{-4} and fluxes are units of $nmol/cm^{-2} yr^{-1}$

that they are extrapolated from one core, but they do serve to indicate that the impact of the effluxes on the quality of the overlying water must be negligible.

In summary, dissolved Zn, Pb and Cu concentrations in the pore waters of both Mandy Lake cores are low in absolute terms. There is clearly no efflux of the three metals from the sediments collected near the former discharge point, despite the presence of high concentrations in the solid phase, and indications that the deposits at this site are oxic in the top five millimetres. At the more distal site (MD-1) in the central basin, surface sediments are oxic to suboxic, and anoxic conditions prevail below very shallow depths. There appears to be a very slight efflux of Cu and Pb to the overlying water column, but an influx of Zn to the deposits at this site.

5.0   CONCLUSIONS

1. Despite the cessation of mining at Mandy Lake more than 40 years ago, mine tailings are widely distributed (likely due to continued slumping of tailings fan) in modern sediments on the lake floor, occurring not only near the former shallow discharge outfall, but also in the central basin 200 m to the west, as demonstrated by the measurement of high Zn, Cu, Pb, Co and sulphur concentrations in two cores.

2. Natural sediments underlying the tailings are organic-rich, with organic carbon concentrations commonly reaching nearly 15 wt. %.

3. Relatively high dissolved iron concentrations (relative to bottom water) within five millimetres of the interface in the central basin indicates that the tailings-bearing deposits at that site are suboxic or anoxic at very shallow sub-bottom depths. Nearer the shore, an enrichment of manganese in surface sediments and low dissolved Fe concentrations in near-surface pore waters reflect the presence of oxic conditions in at least the upper five mm.

4. The concentrations of Zn, Cu and Pb in pore waters at both locations are in general very low. There is clearly no efflux of the three metals from the mixed tailings and natural organic-rich sediments collected near the former discharge point, despite the presence of high concentrations in the solid phase and indications that the deposits at this site are oxic in the top five millimetres. Indeed, pore water profiles at this location indicate that dissolved metals are diffusing into the deposits from the overlying lake water. At the more distal site (MD-1) in the central basin, there must be a very slight efflux of Cu and Pb to the overlying water column, but an influx of Zn to the deposits.

5. Rough estimates of the maximum impact of the benthic effusion at Site MD-1, assuming it is representative of the lake floor as a whole, indicate that the release of Cu and Pb to the overlying water column would respectively contribute on the order of 4 nmol L^{-1} and 1 nmol L^{-1} annually. This contribution is negligible. It can be concluded that the tailings on the floor of Mandy Lake show very little or no evidence of chemical reaction 46 years after discharge.

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Appendix A: Detailed Core Descriptions

Rescan

APPENDIX A: DETAILED CORE DESCRIPTIONS

CORE MD-1

General: 44.5 cm total length, 5.5 m water depth. Good interface: slightly domed, with about 1 cm relief. Abundant zooplankton (Daphnia) in supernatant (core-top) water; no worms observed.

Detailed Description:

- 0-12 cm: olive-black silty clay, homogeneous (5Y2/1)

- 12-20 cm: grades at 12 cm to slightly lighter colour; same texture, constant to 20 cm. Methane bubbles encountered at 12 cm; persistent to bottom of core

- 20-44.5 cm (end): gelatinous, organic-rich silty clay, dark yellowish brown (10YR4/2), homogeneous to end of core

CORE MD-2

General: 47 cm total length, 5.4 m water depth. Good interface (may have been slightly disturbed?), slightly domed, with about 7 mm relief. Abundant zooplankton (Daphnia) in supernatant water. Worms present at shallow depths.

2.5 cm of grayish brown silty clay, overlying lustrous grey fine-to-medium-silt-sized tailings. Tailings show no sign of oxidation.

Detailed Description:

- 0-2.5 cm: slightly sandy to silty grayish brown clay, lumpy texture

- 2.5-16 cm: tailings present, about 50:50 with natural sediments. Tailings occasionally have lobate appearance in this interval, are obviously lustrous (presumably pyrite), and appear to be very fresh. Chironomid worm (15 mm long) observed at about 5.5 cm

- 16-44.5 (end): Homogeneous, compact, lustrous, silt-sized tailings throughout interval

Appendix B: Analytical Methods & Quality Control Data

APPENDIX B: ANALYTICAL METHODS AND QUALITY CONTROL DATA

Graphite Furnace Atomic Absorption Analysis

Dissolved metal concentrations in pore waters were determined by direct-injection graphite-furnace atomic absorption spectrophotometry using a Varian SpectrAA 300 spectrophotometer with Zeeman background correction and a PSD 96 autosampler. All determinations were conducted using pyrolitic L'Vov platforms using peak area measurements and operating conditions adapted from those recommended by the manufacturer. The autosampler was controlled by a Varian Quality Control program which ensured reproducibility. Standards were prepared by diluting 1000 ppm standard solutions with 1% twice-quartz-distilled HNO_3 in distilled deionized water. Where pore water metal concentrations were outside the linear calibration range, samples were diluted automatically by the autosampler with the same 1% HNO_3 and rerun.

Analytical precision estimates and the detection limit for each metal, defined in this study as three times the standard deviation of the mean of several blank determinations, are listed in Table B-1.

X-Ray Fluorescence Analysis

Following freeze-drying and grinding of the sediment samples to fine powders in a tungsten carbide disc mill, major and minor element concentrations were respectively measured on cast glass and pressed powder discs, using an automated Philips PW 1400 X-ray fluorescence spectrometer equipped with a Rh target anode. Glass discs were prepared using a slight modification of the method of Norrish and Hutton (1969), which eliminates the need to apply specific corrections for matrix absorption effects.

For minor elements, a method similar to that described by Harvey and Atkin (1982) was used. The samples were prepared by forming a mixture of 4 g sample and 0.5 g finely-divided wax (Hoechst Wax C) into 32-mm diameter discs in a hydraulic press. Calibration for both sets of measurements was provided by a wide range of international geochemical reference standards, with discs prepared in the appropriate way, and using the element concentrations recommended by Abbey (1980). Additional metal-rich standards were prepared for the minor element measurements on the tailings-bearing

Table B-1

Quality Control Data for GFAAS Measurement of Dissolved Metal Concentrations in Mandy Lake Pore Waters

Sample (Method)	Mn	Fe	Cu	Zn	Pb
M-07 (Normal)	14.1		158	344	20.4
M-07 (Normal)	13.3		164	310	21.4
M-07 (Std. Addition)				375	
M-27 (Normal)		15.7	7.9	39.0	0.9
M-27 (Normal)		15.9	13	36.4	0.9
M-27 (Std. Addition)			11	41.1	
Detection limit	4.5	48	8.3	1.2	1.4

Cu, Zn and Pb measurements are reported in nmol L^{-1} , and Mn and Fe in μmol L^{-1}. Normal = measurement by comparison to the linear calibration curve. Accuracy can be assessed by comparing the results determined by normal calibration and by standard additions (where sample size permitted). Detection limit is defined as three times the standard deviation of a suite of deionized-water blanks run randomly with the analyses. All detection limits are given in nmol L^{-1}.

samples, to ensure that a calibration curve could be used which was linear up to and beyond the maximum Zn, Cu or Pb concentration encountered. The highest concentrations in the synthetic standards were 96000 μg g^{-1} Zn, 19000 μg g^{-1} Cu and 4300 μg g^{-1} Pb.

Analytical precision was estimated for major elements by comparing duplicate discs made for reference sample G2 (Table B-2). Accuracy was assessed by randomly including several geochemical reference samples as unknowns in the analytical run. The results of these measurements are listed in Table B-3. As can be seen the accuracy of the major element measurements is excellent.

CNS and CaCO$_3$ Analysis

Total carbon, nitrogen and sulphur were determined using elemental analysis. Total C and N were measured using a Carlo-Erba 1106 Elemental Analyzer which combusts the sample in a stream of O$_2$, separates the combustion gases (CO$_2$ and N$_2$ reduced from NOx) chromatographically, and measures the gas concentrations (thus C and N contents) by thermal conductivity. Sulphur was determined using a Carlo-Erba NA-1500 CNS Analyzer, which employs the same methodology. The use of the two different instruments was required because the high sulphur content of the tailings swamped the C and N channels on the CNS Analyzer with SO$_2$. The analyzers are calibrated using acetanilide and the NRC marine sediment standards MESS-1 and BCSS-1. Accuracy is excellent; agreement with the recommended values for total C and N is always within analytical precision. The precision of the measurements (1σ, R.S.D.) was about 1.5%, 3% and 3% for C,N and S respectively.

Carbonate carbon was determined on all samples by coulometry using a Coulometrics Analyzer, which electrochemically measures the CO$_2$ evolved following addition of HCl to a sample. Concentrations were very low in the natural sediments (typically <0.1 wt. %), but ranged up to 0.8 wt. % in the tailings. Precision of the measurements (1σ, R.S.D.) was better than 3% for the higher carbonate carbon concentrations.

Organic carbon was determined by subtracting carbonate carbon from the total C measurements. Precision of the resulting organic C value was about ±5 % (1σ, R.S.D.).

Table B-2

XRF Major Element Quality Control Data

Standard		Fe	Ti	Ca	K	Si	Al	Mg	P	Na
NIMS	(m)*	0.95	0.00	0.46	9.39	30.03	9.37	0.28	0.052	0.20
	(r)	0.98	0.02	0.49	9.81	29.71	9.17	0.28	0.05	0.16
JR1	(m)	0.58	0.042	0.48	2.72	35.43	6.92	0.08	0.009	1.67
	(r)	0.67	0.06	0.45	2.82	35.22	6.82	0.05	0.01	1.48
JF2	(m)	0.0	0.0	0.07	8.01	30.42	10.04	0.00	0.000	1.05
	(r)	0.04	<0.01	0.06	8.37	30.44	9.75	0.003	<0.01	0.91
JG1A	(m)	1.38	0.132	1.51	2.47	34.25	7.71	0.45	0.035	1.46
	(r)	1.44	0.15	1.52	2.56	33.71	7.52	0.41	0.3	1.26
W2	(m)	7.52	0.618	7.66	0.41	23.87	7.97	3.91	0.057	0.93
	(r)	7.60	0.64	7.79	0.40	24.66	8.19	3.85	0.06	0.82
G2	(m)	1.83	0.31	1.37	2.77	32.16	8.22	0.55	0.06	1.65
G2 (Repeat)		1.83	0.30	1.37	2.79	32.32	8.09	0.49	0.06	1.51
	(r)	1.88	0.29	1.40	2.85	32.32	8.15	0.45	0.06	1.51

*Concentrations determined for geochemical reference standards in this study (m), are compared with concentrations recommended (r) by Abbey (1980).

Table B-3

XRF Minor Element Quality Control Data

Standard		Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Co ppm	Mn ppm	V ppm	Cr ppm	Ba ppm
SY2	(m)	269	236	166	87	250	7	41	12	2468	43	1	n.a.
	(r)	280	275	220	80	250	5	10	11	2480	52	12	460
BHVO	(m)	182	392	12	10	111	153	129	46	1307	354	311	n.a.
	(r)	180	420	10	n.a.	105	140	120	45	1316	300	320	135
W2	(m)	99	195	23	10	85	121	76	42	1225	279	95	n.a.
	(r)	100	190	21	n.a.	80	105	70	43	1300	260	92	175
NIMD	(m)	9	7	1	1	89	5	2031	245	1669	27	2483	n.a.
	(r)	20	3?	?	7?	90	10	2050	210	1690	40	2900	10?
MRG1	(m)	109	270	12	9	204	148	154	94	1168	360	465	n.a.
	(r)	92	178	17	n.a.	139	140	120	69	1031	326	408	10
NIMG	(m)	281	15	315	40	52	8	40	5	181	0	8	169
	(r)	300	10	320	40	50	12	8?	4?	162	2?	12	120?
NIMS	(m)	29	67	520	2	16	18	0	4	134	30	7	2501
	(r)	33	62	530	5	10	19	7	4	80	10	12	2400

*Concentrations determined for geochemical reference standards in this study (m), are compared with concentrations recommended (r) by Abbey (1980). Question marks indicate possibly unreliable values; n.a. = not available.

Appendix C: Sediment Chemistry Data

APPENDIX C: SEDIMENT CHEMISTRY DATA

Table C-1

Major Element Composition in Sediments From Two Mandy Lake Cores

Interval cm	Depth cm	Fe Wt. %	Ti Wt. %	Ca Wt. %	K Wt. %	Si Wt. %	Al Wt. %	Mg Wt. %	P Wt. %	Na Wt. %
CORE MD-1										
0-0.5	0.25	8.51	0.26	1.11	1.19	18.75	6.03	1.68	0.12	0.53
0.5-1	0.75	8.48	0.26	1.08	1.20	18.89	6.10	1.72	0.11	0.55
1-1.5	1.25	8.48	0.25	1.09	1.21	18.84	6.05	1.69	0.12	0.61
1.5-2	1.75	8.47	0.25	1.09	1.21	18.89	6.15	1.68	0.11	0.55
2-3	2.5	8.54	0.26	1.09	1.23	18.81	6.16	1.74	0.11	0.57
3-4	3.5	8.52	0.26	1.07	1.23	18.97	6.19	1.74	0.11	0.60
4-5	4.5	8.63	0.25	1.08	1.21	18.94	6.15	1.77	0.10	0.56
5-6	5.5	8.70	0.25	1.09	1.21	18.92	6.23	1.72	0.10	0.57
6-8	7	8.83	0.27	1.09	1.25	19.21	6.25	1.77	0.10	0.56
8-10	9	8.94	0.26	1.09	1.26	19.13	6.35	1.83	0.10	0.55
12-14	13	9.28	0.26	1.11	1.23	18.93	6.43	1.78	0.08	0.50
16-18	17	10.86	0.24	1.01	1.13	17.93	6.10	1.67	0.07	0.53
20-23	21.5	5.26	0.29	1.27	1.34	19.30	5.98	1.39	0.11	0.56
26-29	27.5	3.85	0.31	1.44	1.48	20.29	6.23	1.39	0.11	0.57
32-35	33.5	3.86	0.34	1.44	1.57	21.01	6.72	1.52	0.10	0.60
38-41	39.5	3.58	0.32	1.41	1.51	20.70	6.30	1.40	0.10	0.56
CORE MD-2										
0-0.5	0.25	6.60	0.33	1.41	1.60	21.25	6.78	1.71	0.09	0.63
0.5-1	0.75	7.55	0.32	1.44	1.50	21.20	6.69	1.73	0.09	0.69
1-1.5	1.25	7.64	0.31	1.42	1.51	20.59	6.43	1.65	0.08	0.70
1.5-2	1.75	6.75	0.32	1.42	1.59	21.52	6.79	1.69	0.08	0.76
2-3	2.5	7.31	0.32	1.44	1.50	20.88	6.64	1.70	0.09	0.63
3-4	3.5	14.00	0.23	1.67	0.98	18.11	5.81	2.13	0.06	0.49
4-5	4.5	16.30	0.17	1.79	0.72	16.18	4.85	2.01	0.05	0.43
5-6	5.5	15.97	0.18	1.80	0.73	16.25	4.89	2.04	0.04	0.45
6-8	7.5	8.39	0.26	1.54	1.24	19.37	5.83	1.68	0.08	0.53
8-10	9	4.80	0.32	1.37	1.45	20.99	6.38	1.50	0.09	0.63
12-14	13	8.75	0.26	1.52	1.23	18.63	5.62	1.53	0.07	0.59
16-18	17	24.27	0.10	2.15	0.40	11.47	3.00	1.71	0.02	0.41
20-23	21.5	24.71	0.09	2.15	0.33	11.39	2.86	1.75	0.02	0.30
26-29	27.5	24.75	0.11	2.37	0.46	11.40	3.44	2.04	0.02	0.23
32-35	33.5	19.91	0.10	1.92	0.38	14.36	3.00	1.56	0.03	0.57
38-41	39.5	19.98	0.14	2.07	0.52	14.88	4.70	2.29	0.03	0.33

Table C-2

Major Element Weight Ratios In Sediments From Two Mandy Lake Cores

Interval cm	Depth cm	Fe/Al	Ti/Al	Ca/Al	K/Al	Si/Al	Mg/Al	Na/Al	Mn/Al x10⁻⁴
CORE MD-1									
0-0.5	0.25	1.41	0.043	0.18	0.20	3.11	0.28	0.087	177
0.5-1	0.75	1.39	0.042	0.18	0.20	3.10	0.28	0.091	149
1-1.5	1.25	1.40	0.042	0.18	0.20	3.12	0.28	0.101	166
1.5-2	1.75	1.38	0.041	0.18	0.20	3.07	0.27	0.089	141
2-3	2.5	1.39	0.042	0.18	0.20	3.05	0.28	0.093	150
3-4	3.5	1.38	0.043	0.17	0.20	3.06	0.28	0.098	151
4-5	4.5	1.40	0.041	0.18	0.20	3.08	0.29	0.091	155
5-6	5.5	1.40	0.040	0.17	0.19	3.04	0.28	0.091	146
6-8	7	1.41	0.043	0.17	0.20	3.07	0.28	0.090	156
8-10	9	1.41	0.042	0.17	0.20	3.01	0.29	0.087	127
12-14	13	1.44	0.041	0.17	0.19	2.95	0.28	0.078	121
16-18	17	1.78	0.039	0.17	0.19	2.94	0.27	0.086	109
20-23	21.5	0.88	0.048	0.21	0.22	3.23	0.23	0.094	127
26-29	27.5	0.62	0.050	0.23	0.24	3.26	0.22	0.091	132
32-35	33.5	0.57	0.051	0.21	0.23	3.12	0.23	0.090	123
38-41	39.5	0.57	0.051	0.22	0.24	3.29	0.22	0.088	108
CORE MD-2									
0-0.5	0.25	0.97	0.049	0.21	0.24	3.14	0.25	0.093	205
0.5-1	0.75	1.13	0.048	0.21	0.22	3.17	0.26	0.103	146
1-1.5	1.25	1.19	0.048	0.22	0.23	3.20	0.26	0.110	153
1.5-2	1.75	0.99	0.048	0.21	0.23	3.17	0.25	0.111	144
2-3	2.5	1.10	0.048	0.22	0.23	3.14	0.26	0.095	142
3-4	3.5	2.41	0.039	0.29	0.17	3.12	0.37	0.084	174
4-5	4.5	3.36	0.035	0.37	0.15	3.34	0.42	0.088	209
5-6	5.5	3.27	0.037	0.37	0.15	3.32	0.42	0.091	206
6-8	7.5	1.44	0.045	0.26	0.21	3.32	0.29	0.090	132
8-10	9	0.75	0.051	0.22	0.23	3.29	0.24	0.099	93
12-14	13	1.56	0.047	0.27	0.22	3.32	0.27	0.106	109
16-18	17	8.08	0.032	0.71	0.13	3.82	0.57	0.137	247
20-23	21.5	8.63	0.031	0.75	0.12	3.98	0.61	0.105	264
26-29	27.5	7.20	0.033	0.69	0.13	3.32	0.59	0.066	232
32-35	33.5	6.64	0.032	0.64	0.13	4.79	0.52	0.190	242
38-41	39.5	4.25	0.029	0.44	0.11	3.16	0.49	0.071	228

Table C-3

Organic Carbon, Nitrogen, Sulphur and Calcium Carbonate Concentrations in Sediments From Two Mandy Lake Cores

Interval cm	Depth cm	CaCO$_3$ %	N %	S %	C$_{org}$ %	C/N Wt. Ratio
CORE MD-1						
0-0.5	0.25	1.76	0.96	5.35	9.14	9.5
0.5-1	0.75	1.76	0.94	5.35	9.09	9.7
1-1.5	1.25	1.56	0.95	5.29	9.03	9.5
1.5-2	1.75	1.52	0.94	5.29	9.05	9.6
2-3	2.5	1.51	0.94	5.38	8.97	9.5
3-4	3.5	1.47	0.91	5.24	8.80	9.7
4-5	4.5	1.48	0.90	5.46	8.69	9.7
5-6	5.5	1.46	0.88	5.50	8.58	9.7
6-8	7	1.43	0.87	5.60	8.62	9.9
8-10	9	1.37	0.84	5.78	8.32	9.9
12-14	13	1.53	0.75	6.30	7.67	10.2
16-18	17	1.78	0.70	8.66	7.08	10.2
20-23	21.5	0.15	1.36	2.76	13.75	10.1
26-29	27.5	0.06	1.41	1.10	14.44	10.2
32-35	33.5	0.07	1.23	0.78	12.90	10.5
38-41	39.5	0.03	1.32	0.60	13.76	10.4
CORE MD-2						
0-0.5	0.25	1.03	0.78	2.39	8.31	10.6
0.5-1	0.75	1.75	0.69	4.21	7.48	10.9
1-1.5	1.25	1.70	0.71	4.48	7.74	10.9
1.5-2	1.75	1.32	0.75	3.14	8.09	10.8
2-3	2.5	1.63	0.73	3.49	7.96	10.9
3-4	3.5	5.98	0.50	13.92	5.72	11.5
4-5	4.5	7.62	0.27	14.35	2.97	11.0
5-6	5.5	7.31	0.35	13.52	3.73	10.8
6-8	7.5	2.84	0.92	5.24	9.54	10.4
8-10	9	0.38	1.16	1.61	12.33	10.6
12-14	13	2.69	0.91	6.81	9.29	10.2
16-18	17	10.98	0.03	26.10	0.31	10.3
20-23	21.5	11.58	n.d.	26.10	0.24	-
26-29	27.5	12.82	n.d.	24.39	0.27	-
32-35	33.5	10.28	n.d.	22.15	0.10	-
38-41	39.5	11.07	0.11	15.91	1.28	12.1

Appendix D: Interstitial Water Chemistry

APPENDIX D: INTERSTITIAL WATER CHEMISTRY

Table D-1

Interstitial Water Chemistry of Two Mandy Lake Cores

Depth cm	Mn μmol L⁻¹	Fe μmol L⁻¹	Cu nmol L⁻¹	Pb nmol L⁻¹	Zn nmol L⁻¹
CORE MD-1					
-0.25	5.88	4.23	37.2	1.9	1220
0.25	11.88	26.28	100.8	12.9	208
0.75	10.30	13.39	62.6	10.9	154
1.25	11.99	35.01	45.3	8.8	298
1.75	9.32	34.06	88.1	14.9	243
2.5	14.89	61.43	88.5	15.0	291
3.5	14.12	51.62	152.0	20.5	345
4.5	15.93	52.95	42.9	9.5	133
5.5	11.90	44.68	129.8*	20.5*	281*
7	15.65	61.22	45.9	3.1	210
9	14.76	56.85	50.2	3.2	156
13	10.83	26.81	125.6	5.1	290
17	9.50	27.03	328.8*	20.3*	830*
21.5	6.79	27.03	252.1*	11.8*	1015*
27.5	4.97	5.02	33.9	2.0	121
34	4.10	1.89	55.2	2.2	91
39.5	4.70	13.46	52.0	0.9	32
CORE MD-2					
-0.25	0.84	1.17	71.0	7.3	1235
0.25	2.69	0.65	51.9	4.6	516
0.75	3.73	0.71	45.0	4.0	525
1.75	6.04	1.89	63.6	7.1	580
2.5	5.75	1.40	36.0	5.5	461
3.5	6.24*	5.05*	112.4*	20.9*	926*
4.5	4.31	1.49	11.5	4.5	176
5.5	2.73	8.81	20.1	2.8	100
7	3.02	15.64	7.9	0.9	39
9	1.95	16.63	9.4	0.4	30
13	1.46	7.71	23.3	2.7	97
17	2.00	0.82	13.6	13.0	456
21.5	1.35	1.76	22.8	46.8	2198*
27.5	1.95	6.98	9.4	7.4	1373*
33.5	2.49		21.1	56.3*	
39.5	2.73	19.40	52.5	10.1	400

*Measurements marked with an asterisk are thought to reflect contamination, based on criteria defined in the text.

Appendix E: Sequential Multiple Extraction Data

Rescan

Table E-1

Sequential Multiple Extraction of Surface Sediments (top 4cm) from Mandy Lake (Station MD-1) Duplicate A

Parameter	Detection Limit (µg/g)	Water Soluble Phase	Exchange Cations	Weak Acid Soluble Phase	Easily Reducible	Moderate Reducible	Difficultly Reducible	Oxidizable Phase	Residual Phase	Mass Balance	Total Digestion
Aluminum	4.00	<	<	17	<	1455	335	295	34255	36357	37926
%		0.0	0.0	0.0	0.0	3.8	0.9	0.8	90.3	95.8	
Arsenic	0.020	20.4	5.80	85.8	56.9	49.8	7.88	1444	602	2283	1901
%		1.1	0.3	4.5	3.0	2.6	0.4	76.0	31.7	119.6	
Cadmium	0.20	<	<	<	<	<	<	54.4	19.0	73.4	76.2
%		0.0	0.0	0.0	0.0	0.0	0.0	71.4	24.9	96.3	
Cobalt	0.30	<	1.43	3.26	0.82	5.15	1.98	49.4	63.3	125	130
%		0.0	1.1	2.5	0.6	4.0	1.5	38.0	48.7	96.4	
Copper	0.20	0.52	<	<	<	<	0.71	2622	722	3345	3225
%		0.0	0.0	0.0	0.0	0.0	0.0	81.3	22.4	103.7	
Iron	0.50	42.1	9.66	806	1123	9691	2053	13566	56173	83465	85365
%		0.0	0.0	0.9	1.3	11.2	2.4	15.9	65.8	97.5	
Lead	0.20	<	4.83	43.9	3.26	2.55	3.18	380	200	638	740
%		0.0	0.6	5.9	0.4	0.3	0.4	51.4	27.0	86.0	
Manganese	0.10	27.5	99.6	51.1	15.6	57.9	24.9	25.6	366	668	697
%		3.9	14.3	7.3	2.2	8.3	3.6	3.7	52.5	95.8	
Mercury	0.010	<	<	<	<	<	<	<	5.81	5.81	6.13
%		0.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8	
Nickel	0.40	<	<	<	<	1.69	<	3.63	27.7	33.0	33.5
%		0.0	0.0	0.0	0.0	5.0	0.0	10.8	82.7	98.5	
Selenium	0.100	0.240	0.156	0.600	0.030	<	62.6	31.0	15.0	110	87.0
%		0.3	0.2	0.7	0.0	0.0	72.0	35.6	17.2	136.8	
Zinc	0.10	11.1	140	578	355	3445	499	9184	7035	21248	22391
%		0.0	0.6	2.6	1.6	15.4	2.2	41.0	31.4	94.8	

Results are expressed as micrograms per dry gram of sediment followed by % of total. Duplicates A and B are splits of the same bulk sample. Neither molybdenum nor silver were detectable in any fraction. The "<" sign indicates that the measured value was below the detection limit.

Table E-1 (continued...)

Sequential Multiple Extraction of Surface Sediments (top 4cm) from Mandy Lake (Station MD-1) Duplicate B

Parameter	Detection Limit (µg/g)	Water Soluble Phase	Exchange Cations	Weak Acid Soluble Phase	Easily Reducible	Moderate Reducible	Difficultly Reducible	Oxidizable Phase	Residual Phase	Mass Balance	Total Digestion
Aluminum	4.00	<	<	15.7	<	1427	335	324	29362	31462	37926
%		0.0	0.0	0.0	0.0	3.8	0.9	0.9	77.4	83.0	
Arsenic	0.020	20.2	4.20	67.2	54.7	47.7	9.00	1943	388	2534	1950
%		1.0	0.2	3.4	2.8	2.4	0.5	99.6	2.6	109.9	
Cadmium	0.20	<	<	<	<	<	<	53.8	17.8	71.6	73.5
%		0.0	0.0	0.0	0.0	0.0	0.0	73.2	24.2	97.4	
Cobalt	0.30	<	1.41	2.85	0.73	5.75	2.70	54.1	52.4	120	126
%		0.0	1.1	2.3	0.6	4.6	2.1	42.9	41.6	98.6	
Copper	0.20	<	<	<	<	<	1.00	2905	614	3520	3320
%		0.0	0.0	0.0	0.0	0.0	0.0	87.5	18.5	106.0	
Iron	0.50	46.4	18.0	821	883	9853	2091	15937	48654	78302	82100
%		0.0	0.0	1.0	1.1	12.0	2.5	19.4	59.3	95.3	
Lead	0.20	<	6.27	41.8	2.69	2.90	1.36	373	217	645	725
%		0.0	0.9	5.8	0.4	0.4	0.2	51.4	29.9	89.0	
Manganese	0.10	29.1	96.9	54	13.2	58.6	25.9	34.6	326	638	656
%		4.4	14.8	8.2	2.0	8.9	3.9	5.3	49.7	97.2	
Mercury	0.010	<	<	<	<	<	<	<	6.13	6.13	6.13
%		0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	100.0	
Nickel	0.40	<	<	<	<	2.26	<	3.53	22.4	28.2	33.5
%		0.0	0.0	0.0	0.0	6.7	0.0	10.5	66.9	84.1	
Selenium	0.100	0.280	0.260	0.440	0.080	<	64.6	33.3	15.0	114	110
%		0.3	0.3	0.4	0.0	0.0	58.7	30.3	13.6	103.3	
Zinc	0.10	11.9	133	484	281	3485	570	10482	5434	20879	23988
%		0.0	0.6	2.0	1.2	14.5	2.4	43.7	22.7	87.1	

Results are expressed as micrograms per dry gram of sediment followed by % of total. Duplicates A and B are splits of the same bulk sample. Neither molybdenum nor silver were detectable in any fraction. The "<" sign indicates that the measured value was below the detection limit.