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ARSENIC FORMS IN MINE-POLLUTED SEDIMENTS OF MOIRA LAKE, ONTARIO

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The sediments of Moira Lake, Ontario, have accumulated large quantities of arsenic and toxic metals since the 1830's when mining began in its drainage basin. Despite the fact that the mine activities ceased in 1961, leachates from the abandoned mine wastes still deliver large quantities (about 3.5 $Mg.y^{-1}$) of arsenic to the lake. The As concentrations at the top of the sediments average about 545 $\mu g.g^{-1}$, with maximal concentrations of about 1000 $\mu g.g^{-1}$ occurring at depths of 23-27 cm. Approximately 56% of the As in the sediments is bound to the iron and manganese oxides. Observed changes in the profiles of As bound to the different chemical fractions suggest that some of the oxide-bound As is being converted to the residual phases. In view of the dominant form of As in the sediments, changes in the Eh or pH may trigger the release of large quantities of As to the overlying water.

INTRODUCTION

Moira Lake has been contaminated with arsenic (As) since the 1830's when mining and mineral processing began in its drainage basin. By 1900, gold was mined, milled, and smelted at Deloro; and the As wastes in the ore found a market as pesticides. In 1914, the first cobalt produced commercially in the world was manufactured at Deloro, and As was an important byproduct (Bowles 1982). The plant at Deloro closed down in 1961, due to the slumping demand for cobalt and arsenic, but large amounts of refining slag, calcium arsenite, arsenic trioxide, ferric hydroxide tailings, and other miscellaneous tailings and chemical wastes remained on the site. The effects on the surface waters remained so severe that in 1979 the Ontario Ministry of the Environment began treating the metal-rich leachate that was draining into the river from abandoned mine wastes. The treatment removes about 15 tons (Mg) of As per year (Azcue 1992). In spite of this remedial measure, approximately 3.5 Mg of As, most probably from the waste pits and mine tailings at Deloro, are still reaching Moira Lake each year (Azcue 1992).

High concentrations of As in polluted sediments of lakes have also been reported in many places. The sediments of the Great Slave Lake in Canada, which receive wastes from gold mining, contain over 2 800 µg.g^{-1} As (Mudroch et al. 1989). Union Lake in USA, close to an As manufacturing plant, show As concentrations of up to 2 290 µg.g^{-1} (Faust et al. 1983). Lake sediments from the mining area of Sudbury (Canada) have been found to contain up to 650 µg.g^{-1} (Nriagu 1983; Palmer et al. 1989). Analysis of Lake Lansing sediments (Michigan), affected by herbicides applications, found As concentrations of 265 µg.g^{-1} (Siami et al. 1987).

Sediments used to be considered a final sink for the arsenic pollution being loaded into lakes. However, several studies (Aggett and Kriegman 1988; Belzile and Tessier 1990; Camacho-Ibar et al. 1992) suggest that the As are not necessarily fixed permanently by the sediments, and that many physicochemical reactions can alter the mobility of the deposited As. After the sediment is deposited, changes in the redox conditions can alter the mobility and bioavailability of the As reservoir. Regeneration of As from sediments is of concern in view of the well-known toxicity of As to the aquatic biota.

This report uses a five-step sequential extraction procedure to evaluate the potential retention and mobility of As pollution in Moira Lake sediments. It is possible that, even if the river loadings are stopped, enough As will be released from the large reservoir in the sediments to maintain the As in the water column at high levels for a long time.

MATERIAL AND METHODS

Moira Lake, located in eastern Ontario (44°30'N, 77°27'W), is the first major enlargement in the Moira River (approximately 100 km) which discharges into the Bay of Quinte on the northern shore of Lake Ontario (Fig. 1). Moira Lake is a shallow lake (mean depth 4.4 m) divided by a constriction into two separate basins, west (215 ha or 2.15 km^2) and east (615 ha or 6.15 km^2).

The sediment cores were collected by divers from the eastern (EC) and western (WB) basins using Plexiglas tubes of 9-cm diameter. The tubes were tightly closed with Nylon stoppers to minimize perturbation of the sediment during transport to shore. All cores were sectioned in the following sequence using a hydraulic extruder: every 1 cm from 1 to 10 cm; and every 2 cm from 10 to 30 cm. All the cores were approximately 30 to 40 cm long; with a deposition rate of 0.25 cm.y^{-1} (Cornett et al. 1992), the cores represent material deposited during the past 140 y. The sediment fractions were kept in sealed plastic bags at 4°C during transport to the laboratory where they were frozen until analysis.

Water content (oven dried at 40°C) and carbon content (total and organic) were determined for all the fractions of the sediment cores. The total and organic carbon were determined with a Carbon Determinator Leco, model CR-12. Density (g.cm^{-3}) of the sediment samples were determined with a Multivolume Pycnometer 1305.

Arsenic in different fractions (exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to sulfide or organic matter, and residual), was determined in the sediment cores based on the sequential extraction procedure of Tessier et al. (1979), with only slight modifications (Azcue 1992). The following extractants were employed: magnesium chloride (1M) for the exchangeable fraction; sodium acetate (1M) for the carbonate fraction; $NH_2OH.HCl$ (0.04M) for the oxide fraction; and $NHO_3+H_2O_2$ (0.02M) for the organic fraction. Wet sediments were used instead of dry samples to avoid possible chemical changes and interactions expected mainly from readily oxidizable species such as Fe(II) and Mn(II).

Extractions were performed with approximately 8 g of wet samples in centrifuge tubes. Following each extraction, the mixtures were centrifuged and the supernatants decanted. Total and residual fractions were placed in a Teflon beaker, with 6 mL of aqua regia and 1.5 mL of HF, for acid digestion in microwave oven. The samples were treated by the following microwave program: a) 3 min. at 30 psi, b) 5 min. at 50 psi, c) 5 min. at 100 psi, and d) 5 min. at 130 psi. After the microwave digestion, the samples were evaporated to dryness at about 80 to 90°C in a fumehood, and leached with HCl for atomic absorption determination. Total As, Fe, and Mn were determined in the sediment samples by atomic absorption spectrometry involving direct aspiration of the aqueous solution into an air-acetylene flame.

RESULTS AND DISCUSSION

The profiles of water and carbon contents in the sediments for both basins are presented in Fig. 2. The sediments have a high water content, with negligible intrastation variability. Although at the sediment-water interface in both stations, the carbon contents average approximately 20%, the sediment from the west basin has a higher carbon content. The difference can be explained by the higher inputs of detrital material from the Moira River in the west basin of the lake. The dry density of sediments (g.cm^{-3}) varies between 2.0 and 2.4, averaging 2.0 at station WB and 2.2 at station EC. The physico-chemical characteristics of Moira Lake are summarized in Table 1.

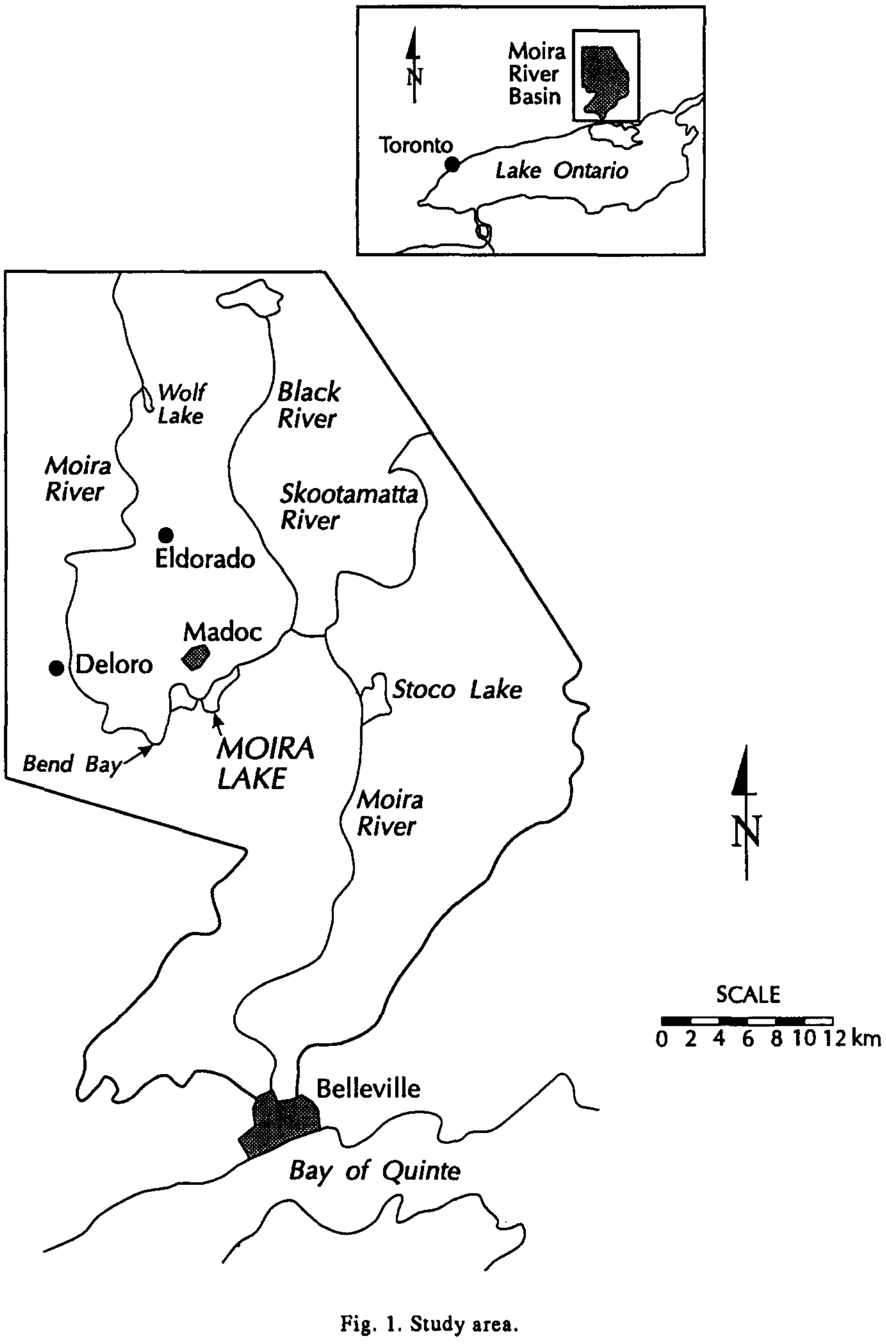


Fig. 1. Study area.

Sediments represent a significant repository of As in Moira Lake, with concentrations in solid phase being about 10^4 times higher than in overlaying waters. High total As concentrations are found in the sediment cores which show an increase with depth and maximal values of about 1000 $\mu g.g^{-1}$ at depths of 23 to 27 cm (Fig. 3). These values contrast with typical background levels of 1 to 5 $\mu g.g^{-1}$ for unpolluted lakes (Allan and Ball 1990; Pershagem 1983). The lower As concentrations in the upper sections of the sediments coincide with the decline of the mining activities and the final shut-down in 1961. However, the very high As concentrations found at the top of the sediments (450 $\mu g.g^{-1}$ in WB and 640 $\mu g.g^{-1}$ in EC) indicate continuing inputs of As pollution to the system, most probably from the abandoned mine tailings at Deloro. The average As concentration for station EC is 723 $\mu g.g^{-1}$ and is slightly higher than 623 $\mu g.g^{-1}$ found in station WB. Further transport and resuspension of the fine-

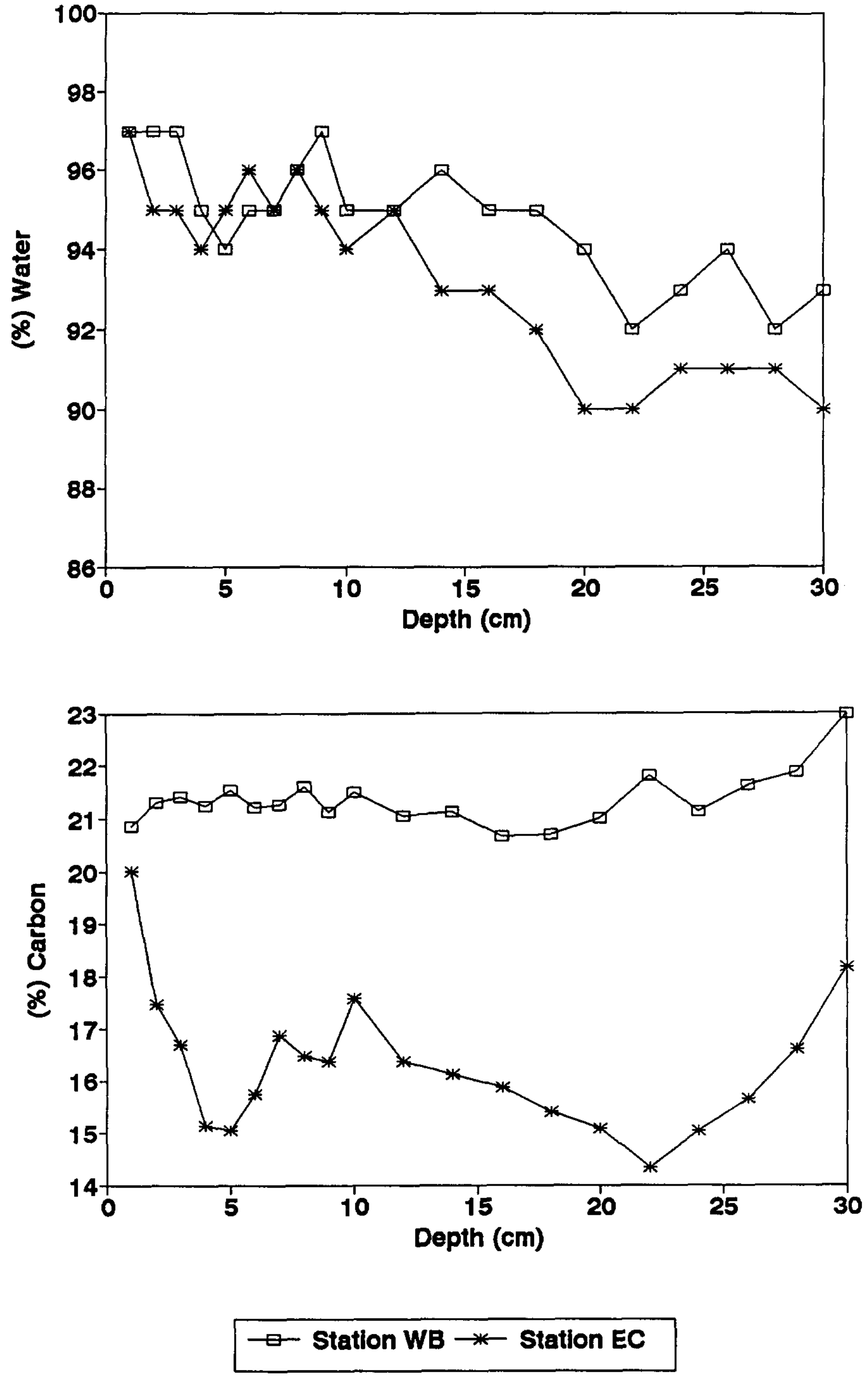


Fig. 2. Water and carbon content of the sediments from Moira Lake.

grained size particles can explain the higher As concentrations in sediments and suspended particles of the east basin.

The profiles for total Fe and Mn in the sediment cores are shown in Fig. 3. The average total Fe concentrations are 45×10^3 $\mu g.g^{-1}$and 50.5×10^3 $\mu g.g^{-1}$ for stations WB and EC, respectively. The lack of any deep peak in the Fe concentration in the sediments, in contrast to the maximum As concentrations observed at approximately 20-cm depth, probably reflect the fact that mining wastes do not control the accumulation of Fe in the sediments.

Table 1. Physico-chemical characteristics of Moira Lake.

	Lake Average	s.d.
Surface area (ha)	830	---
Water volume ($\times 10^4$ m^3)	987	---
Mean depth (m)	5	---
Water residence time (years)	0.34	---
pH	8	0.3
Summer temperature (C)	25	---
DOC ($mg.L^{-1}$)	11.8	---
Conductivity ($\mu mho.cm^{-1}$)	286	40
Total alkalinity ($mg.L^{-1}$)	133	18
Total phosphorus ($\mu g.L^{-1}$)	37	57
Nitrogen (kjedahl $\mu g.L^{-1}$)	531	126
TDS	167	84
Chlorophyll a ($\mu g.L^{-1}$)	10.3	4.7
Dissolved arsenic ($\mu g.L^{-1}$)	56	17
Particulate arsenic ($\mu g.g^{-1}$)	864	277
Bottom sediments ($\mu g.g^{-1}$)	673	71

Total Mn in sediments shows a very similar trend in both basins, with peaks at the sediment-water interface (Fig. 3). Manganese concentration in the top centimeters at station EC reaches 5 691 $\mu g.g^{-1}$. The near-surface enrichments of the Mn indicate diagenetic precipitation at the oxic interface. The fact that the vertical movement of Mn in sediments is more pronounced than that of Fe, reflects the higher sensitivity of Mn to changes in the redox conditions. The accumulation of Fe and Mn are less influenced by the mine wastes compared to As. Since the total As concentration is <3% of the (Fe+Mn) concentrations in these sediments (Fig. 3), a significant correlation should not be expected between the levels of As and (Fe+Mn).

The five geochemical fractions used in this study have widely been adopted in the investigation of the accumulation and possible mobilization of trace metals in sediments (Moore et al. 1988; Nirel and Morel 1990). The sequential extraction data for As in sediments of Moira Lake, like the results of any other sequential extraction procedure, unavoidably suffer from a certain lack of selectivity (Tessier et al. 1979). Consequently, the observed distributions should be regarded as operationally defined by the methods of extraction. However, even after considering these limitations, when compared with information obtained by the analysis of total sediments, the advantage of sequential extraction is considerable.

Variations of the concentrations of the different fractions of As with depth are shown in Figs. 4 and 5. The first extraction, the exchangeable fraction, should remove the weakly bound As by anion-desorption and dissolution of oxidic coatings. Despite the fact

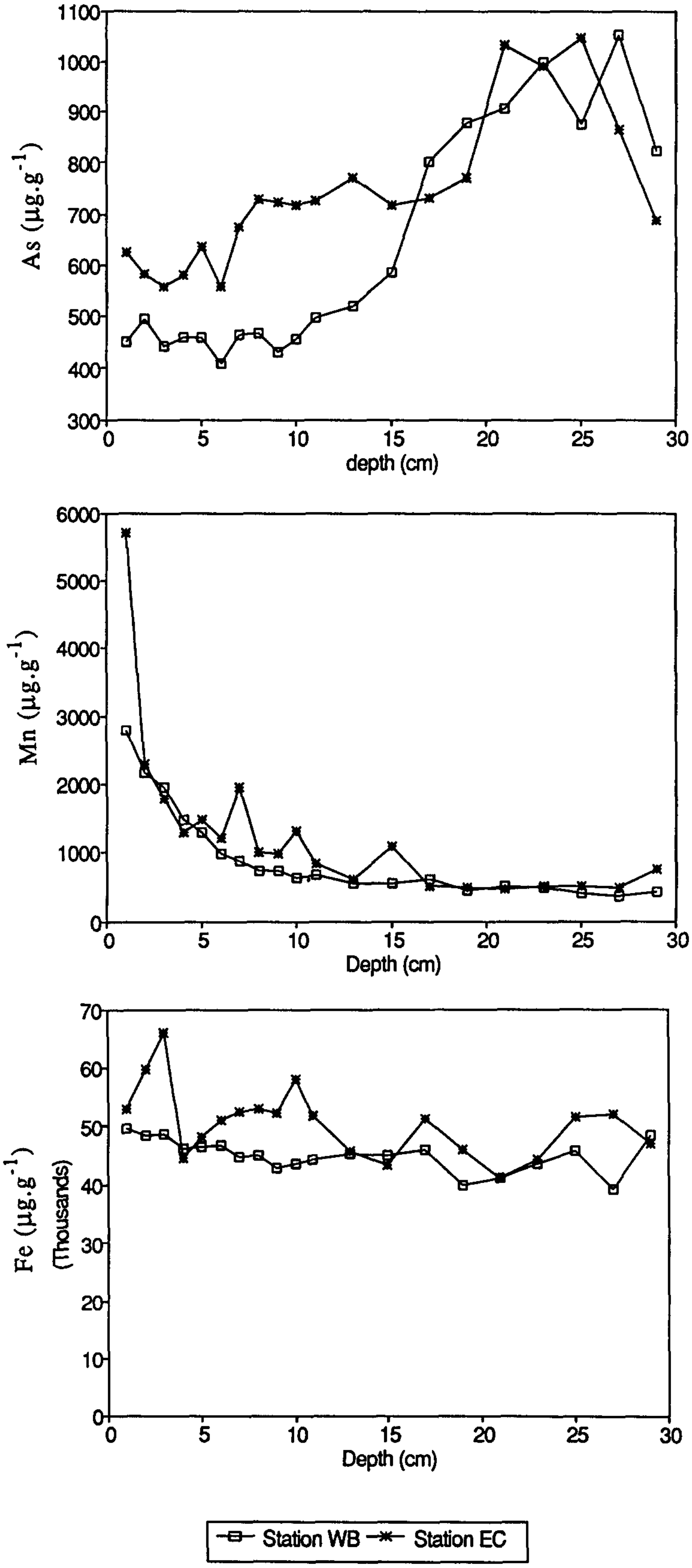


Fig. 3. Profiles of total arsenic, iron, and manganese in Moira Lake sediments.

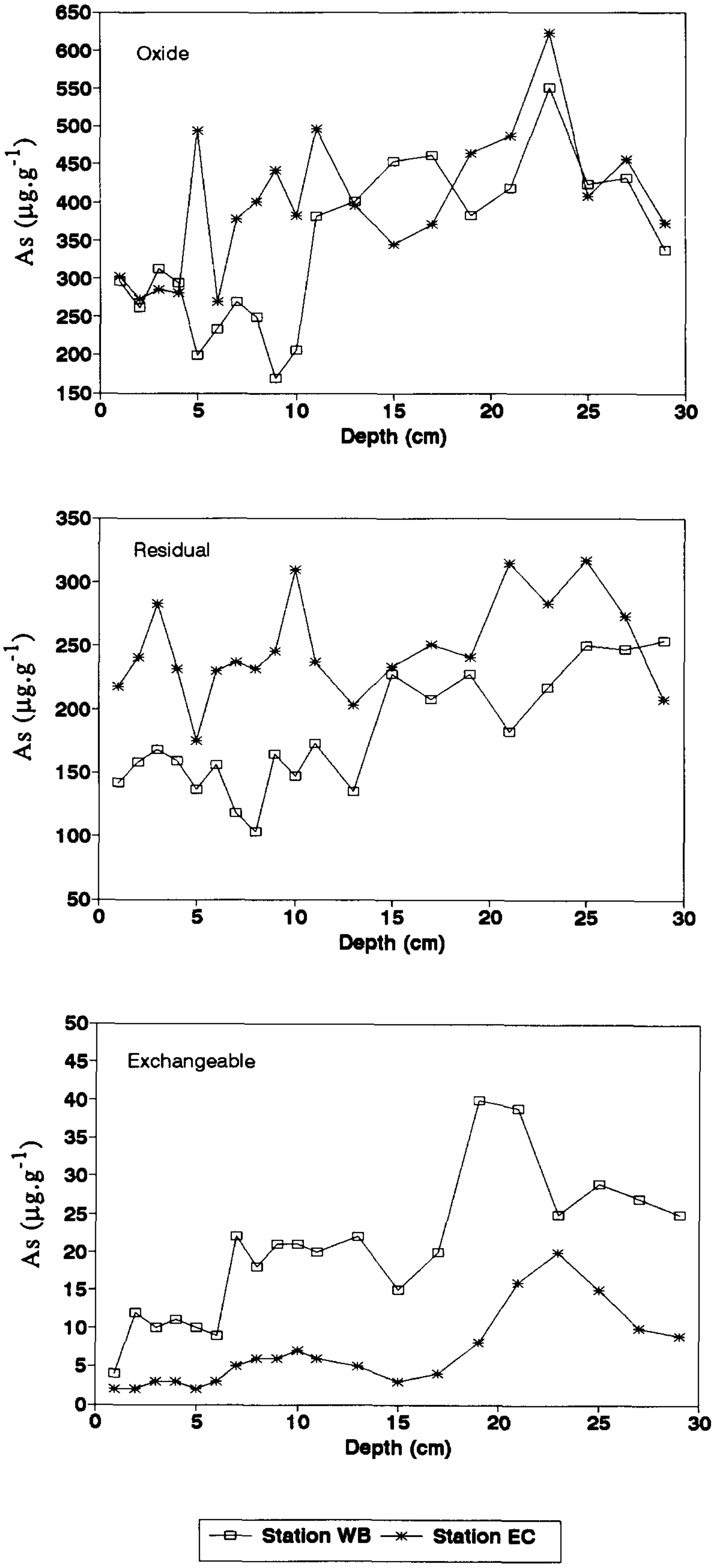
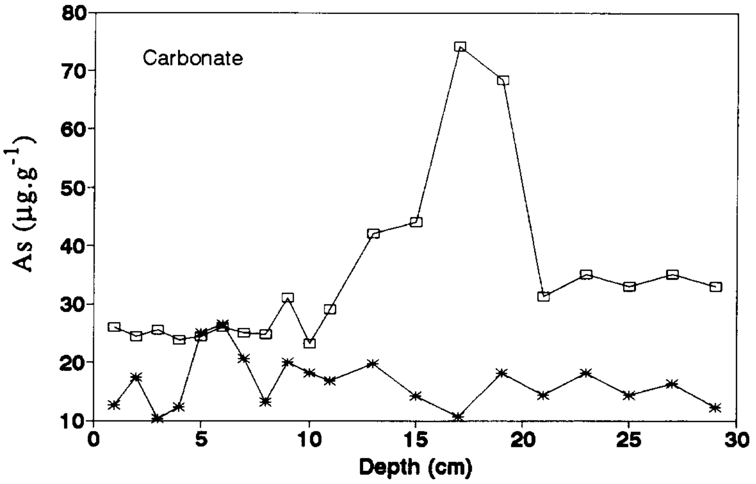


Fig. 4. Concentration of arsenic in the different chemical fractions of the sediment of Moira Lake.



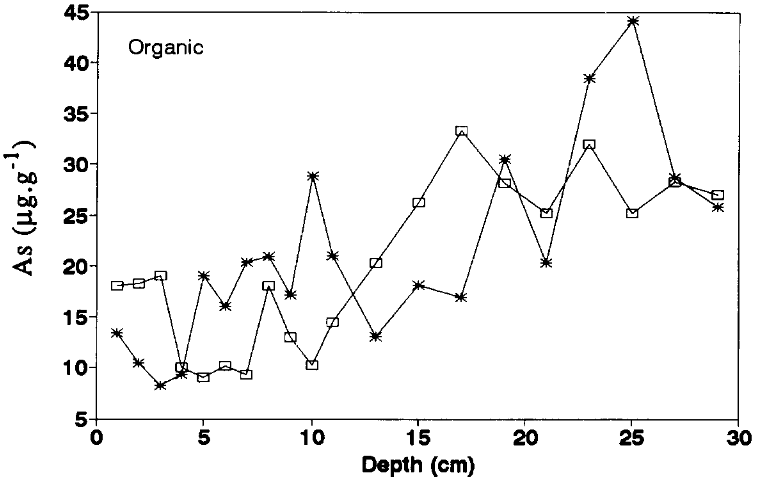


Fig. 4. Continued.

that this fraction represents less than 4% of the total As in the sediments from both stations (Table 2), it can not be ignored because it still averages 5 µg.g^{-1} in the top centimeters of the sediments and it is believed to be the most available form biologically. The essentially anionic chemistry of As, and the cationic specificity of the magnesium chloride extraction, support the low values obtained for this fraction (Fig. 4).

The second extraction should remove As bound to carbonates (Fig. 4). This fraction comprises 5.8% of the total As in station WB and 2.4% in station EC, equivalent to weight concentrations of 34 µg.g^{-1} and 16.5 µg.g^{-1} at station WB and EC, respectively. These results are in agreement with the suggestions of previous studies that the carbonate in the sediment is relatively irrelevant in the chemistry of As (Kersten 1988; Moore et al. 1988; Oscarson et al. 1981). However, it should be noted that the carbonate fraction as defined by the extraction method used is very susceptible of phase changes and matrix effects (Nirel and Morel 1990).

The amounts of As associated with the Fe and Mn oxide fraction at both stations are shown in Fig. 4 and represent approximately 56% of the total As in both stations (Table 2). This fraction clearly is the dominant form of As in the sediments. In station EC, the amount of As extracted in this fraction changed very little from the water-sediment interface to the bottom of the core, with an average concentration of 396 µg.g^{-1}. At station WB, the As concentration in the top 10 cm was 249 µg.g^{-1}, compared with 424 µg.g^{-1} in the deeper sections of the core. The station WB, where the Moira River enters the lake,

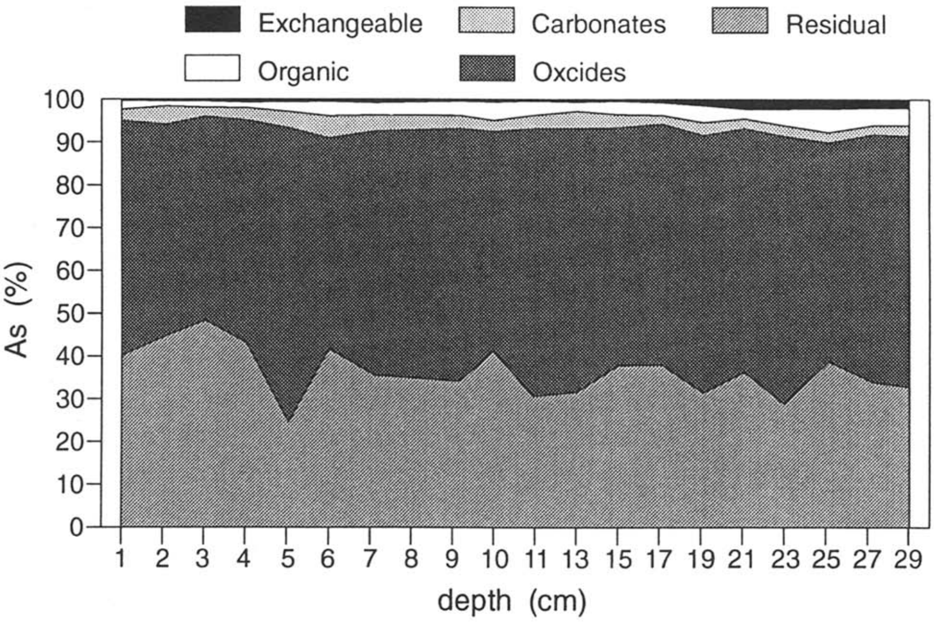


Fig. 5. Profile of arsenic percentages in sediment fractions of Moira Lake.

presumably reflects the As input source functions more closely than the station EC. In fact, the difference in the profiles in the two basins suggest extensive mobility and redistribution of As in sediments at station EC.

The organic/sulfide fraction, shown in Fig. 4, constitutes about 3% of the total As in the sediments of both stations. In the top 3 cm, the As concentration is higher in the core from station WB (18.6 $\mu g.g^{-1}$), decreases to an average of 10 $\mu g.g^{-1}$ at a depth of 10 cm, then increases significantly in deeper sections. The same trend of increasing As concentrations with depth can also be observed from the sediment cores of station EC. The observed profiles for this fraction can be explained in terms of high inputs of detrital sulfidic phases by the river (surface enrichment) and progressive diagenetic formation of arsenic sulfides in older sediments (Manning and Ash 1979).

Table 2. Percentages of total arsenic in the different chemical fractions of the sediment cores at stations WB and EC.

	Station WB		Station EC	
Fraction	Avg.	(Range)	Avg.	(Range)
Exchangeable	3.4	(0.8-5.6)	0.9	(0.3-2.0)
Carbonate	5.8	(4.1-9.3)	2.4	(1.6-4.8)
Organic	3.3	(2.0-4.4)	3.0	(1.4-5.5)
Oxide	56.7	(42.5-64.6)	57.1	(48.4-69.1)
Residual	30.8	(21.8-41.2)	36.6	(24.5-48.0)

No correlation can be observed between the organically associated As fraction and the carbon content of the sediments in Moira Lake (compare Figs. 2 and 4). This is not surprising since As does not bind strongly to organic ligands in sediments and soils (Kersten 1988). The distribution of As, thus, differs from the partitioning of other elements in sediments with high organic carbon concentrations. For instance, Cornett et al. (1989) showed that the highest concentration of Ni in Moira Lake sediments was contained in the organic fraction. It should also be noted that the interpretation of the organic fraction in sequential chemical extraction experiments is very difficult because pyrite is not easily oxidizable, but rather extractable by strong acid digestion in the last residual step (Horowitz et al. 1990; Kersten 1988).

The As contained in the residual fraction of the sediments is shown in Fig. 4. The average As concentration in this fraction at station EC is 248 $\mu g.g^{-1}$, with little variation with depth. In the top 10 cm of station WB, the average As concentration is 145 $\mu g.g^{-1}$, while the deepest fractions of the core average 230 $\mu g.g^{-1}$. This fraction constitutes 31% (WB) and 37% (EC) of the total As on the average (Table 2). This fraction is generally believed to reflect the lithogenous As in sediments (Sager et al. 1990). If so, the river must be loading large quantities of arsenic-rich detrital material into the lake. The higher concentration of the residual fraction in the station EC also suggest that some of the pollutant As is being converted to the residual phases, for example, by the replacement of silica by As in the clay minerals.

The data clearly suggest that the inputs from the mines have changed the forms of As in the sediments. In premining times, one would expect the As to occur primarily in the residual and sulfide fractions. The fractional distribution of As in such sediments would be in the order residual ≥ sulfide > oxide > exchangeable > carbonate. With increased flux of dissolved As pollution into the lake, scavenging by seston becomes a major route for the delivery of As to the sediments. This is reflected in the observed predominance of the oxide fraction in the polluted sediments. The fractional distribution sequence is then changed to oxide > residual > sulfide > exchangeable > carbonate. The fact that this sequence is being maintained in Moira Lake sediments indicates that the abandoned mines still control the As cycle in the lake. The forms of As and their distribution sequence in Moira Lake are generally consistent with observations in other polluted sediments. For example, Moore et al. (1988) found that As is largely present in the organic fraction in the deeper sediments of Clark River, Western Montana, but occurs mostly in the oxide phase in the overlying contaminated sediments.

Figure 5 shows the historical changes in the combined (EC+WB) percentages of As bound to different chemical fractions in Moira Lake sediments. Two features are particularly noteworthy: a) the concentration of residual As in the polluted sediments is high, and b) there are significant incursions of the oxide fraction into the field for residual fraction. The two features suggest that some of the oxide-bound As is being converted to the residual phases. The oxide and residual fractions make up over 90% of the As in the sediments and changes in the relative proportions of the exchangeable, carbonate, or organic fractions to the two dominant fractions have been small.

Since the pollutant As is dominantly associated with the oxide fraction, changes in the Eh or pH of the sediments can trigger a regeneration of the As reservoir in the sediments. Elimination of As loadings to the lake, thus, may not guarantee a drastic reduction in the As levels in the water column. It is, however, encouraging that lake processes do result in the conversion of the oxide-bound As to the less mobile residual forms. An understanding of the conversion processes should be useful in developing proper remediation measures for Moira Lake and other As-contaminated bodies of water.

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