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Impact of abandoned mine tailings on the arsenic concentrations in Moira Lake, Ontario

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Abstract

Arsenic has accumulated in the different compartments of Moira Lake for the last 160 years, since mining and mineral processing began in the area. The annual total fluvial input of arsenic (As) to the lake is approximately 3.5 tonnes. The dissolved As concentrations in the water show seasonal differences, with an average concentration of 62 μg/L during the summer, and 22 μg/L in winter. The As bound to particles represent approximately 8% of the total As burden in the water column. Arsenic bound to the organic humic, fulvic and lipid fractions represents approximately 1% of the total As in Moira Lake waters. The dissolved As profile of interstitial waters are characterized by subsurface maxima with concentrations four to six times greater than the lake waters. Inorganic As makes up the majority of the As in all the porewater profiles examined. The upward diffusion of As-enriched interstitial waters can explain the distribution of As(III) and As(V) in the overlying lake water. The diffusion upward through the hypolimnion of the arsenite originated in the interstitial water explain the thermodynamic disequilibrium in the distribution of As species in the surface waters of Moira Lake.

1. Introduction

Reported background concentrations of As in sediments range from 0.6 μg/g (Walters et al., 1974) to 50 μg/g (Farmer and Lovell, 1986), with a global average of 3 μg/g (Pershagen, 1983). The difference in the background values reflects the divergence in the As contents of rocks in different regions. Due to its peculiar, geochemistry and widespread distribution, As is used as an indicator in geochemical prospecting for gold, silver, uranium, and copper, among others (Boyle and Jonasson, 1973). Moira Lake is located in an area in Ontario known in the 1860's as the *Valley of Gold*. The lake has received elevated inputs of As, heavy metals, and other elements since the 1830's when mining and mineral processing began in the area. Hematite and magnetite ores were mined from 1837 to 1910, a

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lead mine operated from 1898 to 1906 in the Madoc township, and in 1866 gold was discovered in Eldorado and Deloro area (Mudroch and Capobianco, 1980). By 1900 gold was mined, milled and smelted at Deloro and the As wastes in the ore found a market as a pesticide component. In 1914 the first cobalt produced commercially in the world was manufactured at Deloro, and As was an important by-product. The last mine in this region closed down in 1961, due to the slumping demand for cobalt and As, and large amounts of refining slag, calcium arsenite, arsenic trioxide, ferric hydroxide tailings, and other miscellaneous tailings and chemical wastes were abandoned on the site.

In 1979 the Ontario Ministry of the Environment began treating the metal-rich leachates that were draining into the Moira River from abandoned mine wastes, removing an average of 15 tonnes of As yearly (Azcue, 1992). Groundwater, containing anywhere from 50 to 3,000 mg/L As, and surface water, is collected by a concrete dike along the Moira River and pumped to a clay-lined equalization pond for treatment with ferric chloride and lime. The sludge, ferric arsenate, is then pumped from the bottom of the clarifier to holding lagoons. The average daily As loadings have decreased from 35 kg in 1979–82 to 6.1 kg in 1989 (OME, 1990).

Arsenic is present at high concentrations in numerous lakes due to human activities (Anderson and Bruland, 1991; Faust et al., 1983; Mudroch and Clair, 1986; Nriagu, 1983; Seyler and Martin, 1989; Wagemann et al., 1978). However, there is a scarcity of data on the concentration of the different As species in natural waters. Thus, the study of As in different natural water systems, comprising local peculiarities, is needed in order to better understand the factors involved in the cycling of As. Moira Lake provides a unique environment for the study of the factors involved in the speciation and geochemical cycle of As. The high As concentration allowed the analyses of water samples without preconcentration, consequently reducing the risks of reagent and analytical contamination.

2. Materials and methods

Moira Lake, located in eastern Ontario (44°30′N, 77°27′W), is the first major enlargement in the Moira River system approximately 100 km north of Lake Ontario into which it drains (Fig. 1). The lake is situated at the contact zone between Precambrian rocks of plutonic, metasedimentary, and metavolcanic origin, exposed in the northern part of the basin, and is underlain by as much as 83 m of Paleozoic limestone in the southern part of the basin (Sibul et al., 1974).

Moira River supplies most of the water to the lake, with a mean water residence time of approximately 0.34 years, and as low as 4.38 years in the summer (Water Survey of Canada, 1977). Moira Lake has two basins, west and east, that are 215 and 615 ha in area, respectively. Both basins mix thoroughly during spring and fall; transient thermoclines develop during the summer at deep locations in the two basins. At times of low flow in summer and winter, there is minimal circulation between the basins. Lake water pH (8.0 ± 0.3), alkalinity (133 ± 18 mg/L as $CaCO_3$) and conductivity (286 ± 40 μS/cm) were all high due to the calcareous bedrock. Thermal stratification and high productivity during summer depleted oxygen levels in the deep locations of the basins. Samples were collected at four different stations, two in the west basin and the other two in the east basin.

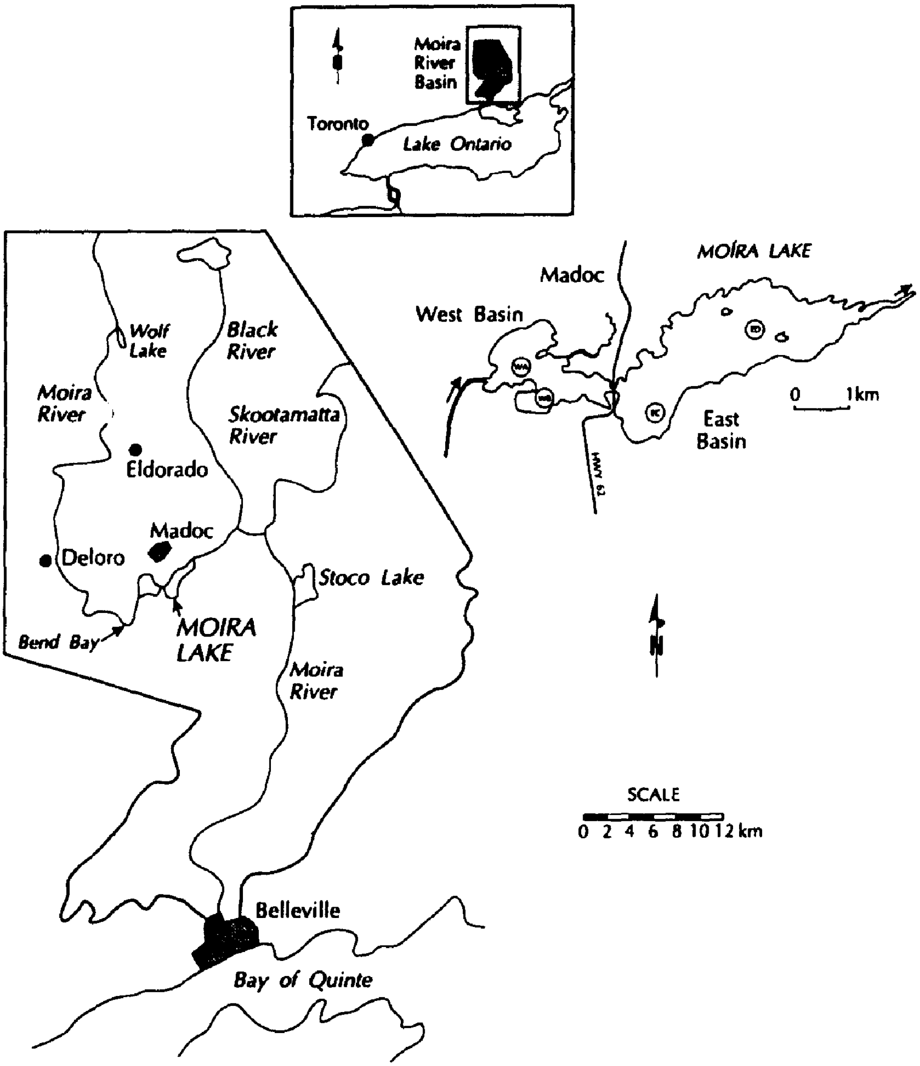

Fig. 1. Moira Lake drainage basin and study area.

Surface (20 cm depth) water samples were collected along the Moira River. Water samples were collected in Moira Lake using a battery-operated pump (Fluid Metering, Inc), at every meter of depth, and were deposited in acid-clean 1-L teflon bottles. Large volumes of water (±50 L) were pumped at two different depths and were collected in acid washed 20-L high density polyethylene containers for the isolation of the organic fractions. Immediately after collection, the water samples were filtered on shore through 0.45 μm membrane filters and were acidified to pH 2 using HCl. This was conducted in a portable clean-laboratory, equipped with a positive pressure HEPA filter, which was specifically designed for trace metal analysis (Nriagu et al., 1993). Samples for As speciation were stored in the dark at 4°C using the precautions described by Andreae (1977). Tallman and Shaikh (1980) confirmed that under these conditions samples can be retained for at least three weeks without significant interconversion of As(III) and As(V) or loss of total As. For the speciation of inorganic arsenate and arsenite the technique of Ficklin (1983) was adopted. The methods developed by Thurman and Malcolm (1981) and Kennicutt and Jeffrey (1981), with some modifications and innovations for As determination (Azcue, 1992), were adopted to study the interactions of As with humic, fulvic and lipid compounds.

Sediment porewater was recovered in situ at 1 cm intervals using the membrane dialysis sampler technique (Hesslein, 1976). The technique published by Iverson et al. (1979) was adopted for the determination of the methylated species in the interstitial water samples. The sediment cores discussed in this study were collected by divers using Plexiglass tubes of 9 cm inner diameter. 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. Arsenic in different fractions (exchangeable, carbonate, organic, oxide and residual), was determined in one core from each basin of the lake. The scheme of the sequential extraction for sediment fractionation was based on the technique of Tessier et al. (1979), with few modifications (Azcue and Nriagu, 1993).

The concentration of As in all the samples was determined at 193.7 nm by graphite furnace atomic absorption spectrophotometry on a Varian Spectra AA-400 equipped with a Zeeman GFA-96 graphite furnace and autosampler. A nickel nitrate solution (200 mg/L), used as a matrix modifier, was added in 20 μL aliquots to the standards, blanks, and samples in the graphite tube. To minimize contamination, all water and porewater sample handling was carried out in a Class-100 positive-pressure clean laboratory at the National Water Research Institute (Burlington) as described in Nriagu et al. (1993).

3. Results and discussion

The average pH is 8.0, with very little intrabasin variation, indicating extensive mixing of Moira Lake waters. The As concentration in the Moira River sampled in winter upstream of the mining area is 0.67 μg/L and the highest As concentration, 23.3 μg/L, is found just past the Deloro mining area. The As concentration remains high further downstream until the river reaches Stoco Lake (23 km downstream of Moira Lake) and the concentration drops to 3.03 μg/L. The discharge of the Black River and Skootamatta River into Moira River before Stoco Lake leads to a considerable dilution in the As levels in Moira River (Fig. 1). At 200 m offshore in the discharge area of Lake Ontario the concentration is 0.42 μg/L. The evidence is clear that even after 31 years since the shutdown of the mining activities, physico-chemical interactions of the water with the mine tailings are still transferring high concentrations of As into solution.

Moira River plays an important role in the transport and distribution of As. The still elevated As concentrations (20.4 μg/L) in the output of Moira Lake refutes the notion of Moira Lake acting as a final sink of As. Thus, the persistent input of soluble As into Moira Lake indicates the existence of a continuous source of As to the lake. The dissolved As concentrations in the lake are highest during summer, with an average surface concentration of 47 μg/L, compared with 22 μg/L in winter. The seasonal differences are produced by the changes in water flow and have been described by Diamond (1990). The dissolved As concentrations in the water samples in the two deepest stations are 38% higher closer to the

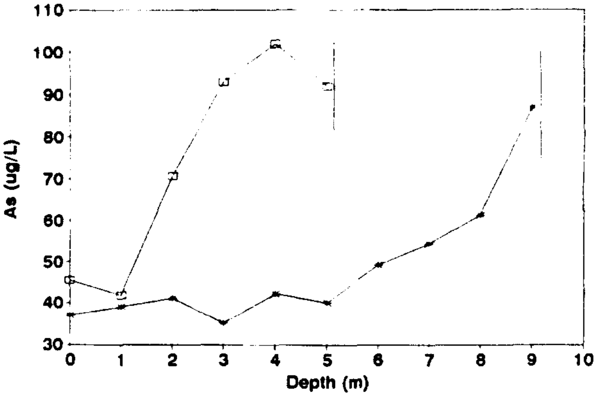

Fig. 2. Total dissolved arsenic profile in water column of Moira Lake at stations WB and EC.

bottom of the lake (Fig. 2). In the summer, the As in the hypolimnion is largely present as arsenite (60%). Even in surface waters, some arsenite (25%) can be detected. Upward diffusion through the hypolimnion of As(III) originated in the interstitial water and the incomplete stratification of Moira Lake waters explain the changes in the ratios of As(V):As(III) in the water column. The As bound to the organic fractions of the water column represents approximately 0.93 ± 0.7% of the total As in Moira Lake water. The average concentrations in bottom samples of both basins are approximately 75% higher than in surface samples.

Average concentrations of As bound to suspended particles in the west basin are 7.4 ± 1.4 μg/L at the surface and 10.7 ± 1.5 μg/L at the bottom. In the east basin it is much lower and uniform, being 3.7 ± 0.7 μg/L at both surface and bottom. The amount of suspended material in the west basin (9.1 mg/L) is much higher than in the east basin (3.7 mg/L). The much higher load of suspended particles in the west basin is directly related to the proximity to the mouth of Moira River. The higher particulate load (approx. 30%) in the deepest samples can be related to the resuspension of smaller particles and to the decomposition of material present in the bottom. The As bound to particles represents approximately 8% of the total As in Moira Lake waters. The higher As concentration in suspended particles from the east basin, 1,067 μg/g compared with 675 μg/g in the west basin (Table 1), has been explained by recycling of As from deeper in sediments to surficial sediments, both by diffusional gradients and by release to overlying water column, and subsequent incorporation into sediment particles (Azcue et al, 1994).

Porewater is a medium of As transport, and plays a key role in the linkage between the lake water and the bottom sediments. The dissolved As profile in sediment porewater at all the stations is characterized by sub-surface maxima with concentrations four to six times greater than the lake waters (Table 1). The concentrations obtained for the porewater reflect the physico-chemical conditions (pH, O_2, temperature, etc.) at the sampling time, being very sensitive to minor chemical changes. The strong linear correlation of dissolved As with dissolved Fe and Mn in the porewaters of Moira Lake, suggests that adsorption–desorption of As onto Fe and Mn oxides exerts some control on the mobility of As (Fig. 3). With continued sedimentation the surface oxides are buried and subjected to a reducing environment where they become unstable. When the hydrous Fe and Mn-oxides are reduced

Table 1

Concentration of arsenic species in dissolved fraction (μg/L) of lake water and porewater, and bound to particles (μg/g) in Moira Lake sampled on summer 1990. Data presented as arithmetic mean with standard deviation and range

	West basin	East basin
Dissolved		
As(III) (range)	36.5 ± 24 (10.9–74.7)	21.6 ± 15.1 (7.4–54.1)
As(V) (range)	37.3 ± 10.7 (26.3–58)	26.4 ± 5.2 (18.8–32)
Organic-As (range)	0.84 ± 0.57 (0.01–1.52)	0.56 ± 0.33 (0.01–1.08)
Suspended particles		
average (range)	675 ± 148 (495–921)	1067 ± 270 (768–1565)
Porewater		
As(III) (range)	79.2 ± 73 (0–196)	30.4 ± 19.8 (0–98)
As(V) (range)	29.729 (0–110)	12.4 ± 13 (0–52)
Methylated As (range)	1.85 ± 2.4 (0–10)	1.6 ± 2.0 (0–8)

As which is sorbed onto these components, should be released together with the reduced soluble Fe^{2+} and Mn^{2+}. Consequently, the concentrations of As, Fe, and Mn increase together in the porewaters. The dissolved species then migrate upwards and downwards depending upon the gradient that develops. In all the porewater profiles examined, inorganic As made up the majority of the As, with arsenite percentage ranging from 66 at the east basin to 83% at the west basin. The As(III):As(V) ratios in Moira Lake waters can be explained by the introduction of large quantities of As(III)-charged porewaters into the overlying water. More information regarding the role of sediment porewater in the cycling of As in Moira Lake can be found in Azcue et al. (1994).

High total As concentrations are found in the sediment cores, with concentrations in solid phase being 10^4 times higher than in overlying waters. The average As concentrations for

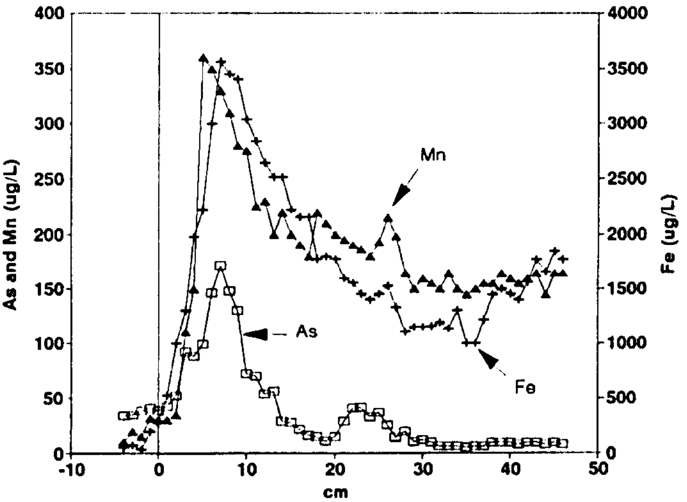

Fig. 3. Total As, Fe, and Mn concentrations in porewater from Moira Lake sediments at station WB.

surface sediments are approximately 550 μg/g. The depth profiles of As in the sediments reflect the variation in As input into the lake, with maxima close to 1,000 μg/g between 23 to 27 cm depth (Fig. 4). These values contrast with typical background levels of 1 to 5 μg/g for unpolluted lakes (Allan and Ball, 1990). The very high As concentrations found at the top of the sediments indicate continuous adding of As pollution to the lake, from the abandoned tailings at Deloro and from internal source due to the high accumulation of As deeper in the sediments. The long term deposition of sediments ranged from 5.48 to 7.4 μg cm^{-2} y^{-1}. The total As deposition in sediments of Moira Lake is estimated to be about 190 kg y^{-1}, 79% of it occurring in the larger east basin. The As profiles in interstitial water indicates an intense mobilization–desorption below the interface and As will enter water column along with Fe and Mn during periods of overlying water column anoxia. Total Mn in sediments shows a very similar trend in both basins, with peaks at the sediment water interface (Fig. 4). The near surface enhancements of the Mn indicate diagenetic precipitation at the oxic interface. Upward diffusion of As from the sediments has been found during the stratification period, with the diffusive flux estimated to be 0.81 to 7.09 μg cm^{-2} y^{-1} (Azcue, 1992). Consequently, the elevated As concentrations in bottom sediments represents a continuous internal "mining" of As in the overlying water.

The sequential extraction data for As in the 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). Arsenic removed in the first extraction, the exchangeable fraction, represents 3% of the total As in the sediments (Table 2). However, this fraction can not be ignored because it still average about 5 μg/g in the top cms of the sediments and it is believed to be the most available form biologically. The Fe and Mn oxide fraction contains the highest concentrations of As, representing approximately 56% of the total As at both stations. Despite slight variations, the role of the different fractions throughout the sediment cores has not been affected by the considerable changes in the input of total As into the lake (Azcue and Nriagu, 1993).

Table 3 shows the calculated As budget for Moira Lake. Most of the As enters the Moira Lake as part of the dissolved and particulate load of the Moira River. Considering the number of assumptions made and that annual averages have been used, the small imbalance is very satisfactory. The continuous fluvial input of As (approximately 3.5 tonnes per year)

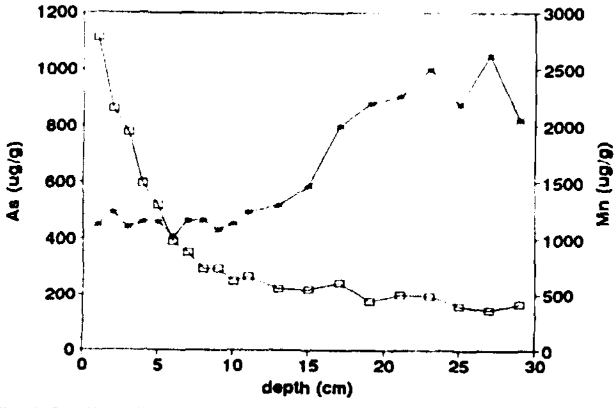

Fig. 4. Profiles of total As and Mn in Moira Lake sediments at station WB.

Table 2
Arsenic concentrations in different chemical fractions of sediments from Moira Lake

Fraction	Percentage of total arsenic	Average (μg/g) ± s.d.	Concentration range (μg/g)
Exchangeable	2.6	13.4 ± 6	(2–40)
Carbonate	4.1	25.3 ± 14	(10–74)
Organic	3.3	20.3 ± 9.4	(8–44)
Oxide	57	366 ± 103	(169–623)
Residual	33	213 ± 46	(103–317)
Total		680 ± 220	(408–1,051)

Table 3
Arsenic budget for Moira Lake

	kg As/y
Input	
Moira River (dissolved)	3,147
Moira River (particulate)	346
Domestic waste	0.5
Atmospheric	0.26
Output	
Moira River (total)	2,900
Net flux to sediment	90

to Moira Lake and the internal input due to the high accumulation of As in the lake sediments are the main factors in the geochemical cycle of As in this lake. Consequently, one can predict that the As concentrations in the lake water will likely remain high for many years to come.

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