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Role of Sediment Porewater in the Cycling of Arsenic in a Mine-Polluted Lake By: J. Azcue, S. Schiff, J. Nriagu

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ROLE OF SEDIMENT POREWATER IN THE CYCLING OF ARSENIC IN A MINE-POLLUTED LAKE

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Abstract

The surficial sediments of Moira Lake averaged 545 μ g.g¹ of arsenic, with maximum values close to 1 mg.g¹ at depths of 23 to 27 cm below the sediment water interface. The sediment pore water is the linking agent between the sediment solid phase and the overlying lake water. The depth distributions of total As in interstitial waters at all stations are characterized bv sub-surface maxima, with concentrations four to six times greater than in the lake waters. In all the pore water profiles examined inorganic As [As(III) + As(V)] comprised most of the As. The As(III) (arsenite) percentage ranges from 66 to 83%. Methylated-As compounds represent <2% of the total As. The strong correlation of As with Fe and Mn together suggests that both Fe and Mn are involved in the As mobility. The elevated As concentrations in bottom sediments represent a continuous "internal mining" of As towards the interface all year around. The concentration gradient of total dissolved As indicates that an upward diffusion of As towards the water column with the estimated annual fluxes being 0.8 - 3.8 μ g.cm².y¹.

INTRODUCTION

Arsenic is present in so many types of precious mineral deposits that it is used as an indicator of anomalous areas in geochemical prospecting surveys for some twenty elements of commercial importance (Boyle and Jonasson 1973). Wastes generated by gold and base metals mining thus often contain elevated concentrations of As associated with the ore or the host bedrock. Arsenic enrichments have been found in sediments near mining operations (Allan 1979; Moore 1981; Moore et al. 1991; Mudroch and Clair 1986; Mudroch et al. 1989; Wagemann et al. 1978). In general, As is not fixed permanently by the sediments, and many physico-chemical variables can alter the mobility of the deposited As. Sediment contamination of As from past mining activities has been reported in Moira Lake, Ontario, located approximately 30 km downstream of the mines (Azcue and Nriagu 1993). Gold and cobalt were actively mined on the shore of the Moira River from 1830 to 1961. Even 30 years after the mine activities ceased in the area, the concentration of As in the surficial sediments (upper 5 cm) of Moira Lake still average 545 μ g.g⁴, with maximum values being up to 1 mg.g¹ (Azcue and Nriagu 1993). By comparison the As content of uncontaminated lake sediments is about 1 to 5 μ g.g¹ (Allan and Ball 1990; Penrose 1974).

Previous investigations of the mobility of the deposited As in mine-polluted sediments have primarily focused on vertical transport of the dissolved and particulate As (Moore et al. 1991).

However, once the As is deposited in the surficial sediments it can be recycled back to the water column or buried deeper in the sediment column. Sediment porewater is the medium of As transport within the sediments, and plays a key role in the linkage between the lake water and the bottom sediments. Sediments can function as either a source of porewater As due to dissolution and desorption reactions or as a sink of porewater As due to precipitation and adsorption reactions. Arsenic concentrations have been determined in porewaters of marine sediments (Andreae 1979; Edenborn et al. 1986; Peterson and Carpenter 1986) and freshwater sediments (Aggett and O'Brien 1985; Belzile and Tessier 1990; Farmer and Lovell 1986; Oscarson et al. 1981; Peterson and Carpenter 1986). However, few studies have yet linked the concentration of the different As species in porewaters with the As levels in sediments and overlying waters.

The speciation of As in porewater remains a controversial topic. A wide spectrum of As(III):As(V) ratios has been reported in the literature, and in some areas the ratios are very divergent from what would be expected from inorganic thermodynamic calculations. Several authors (Anderson and Bruland 1991; Seyler and Martin 1989) have detected arsenite in oxic waters in greater amounts than would be predicted from inorganic thermodynamic calculations. Also, arsenate has been identified in anoxic systems (Andreae and Froelich 1984; Emerson et al. 1979; Peterson and Carpenter 1986). In this paper, we examine the vertical

distribution of total As and As species in pore water, and the internal fluxes of As in the sediments of Moira Lake. The possible interactions of As with Fe and Mn compounds are examined by studying the distribution of Fe and Mn in the same compartments.

MATERIAL AND METHODS

Moira Lake is a shallow lake, located in eastern Ontario (44°30'N, 77°27'W) (Figure 1). It is divided by a constriction into two separate zones; the west (215 ha) and the east (615 ha) basins. The physico-chemical characteristics of the lake and the sampling methods for the sediments have been described previously (Azcue and Nriagu 1993). The samples discussed in the present study were collected at four different stations of Moira Lake: two in the west basin (WA and WB) and the other two (EC and ED) in the east basin (Figure 1).

Porewater samples at each station were recovered in situ at 1 cm intervals using the membrane (0.45 μ m cellulose membrane, Gelman Scientific, Inc.) dialysis sampler (peeper) technique (Hesslein 1976). The peepers were kept in oxygen-free doubly distilled water (DDW) until divers installed them vertically in relatively flat areas of the lake bottom. Subsamples of the water used to fill and store the peepers prior to deployment were kept for further analysis to monitor any possible contamination. To prevent possible technical problems such as oxygen contamination in the cells or

movements of the peepers after installation (October 2, 1990), two peepers were installed at each station to provide replication. The peepers were left in place for 15 days, at which time new peepers were installed. Upon retrieval, the porewaters in all compartments were quickly sucked out, using disposable syringes, and the samples were then stored at 5°C in sealed, acid leached, polyethylene vials.

The pH of the porewater in each compartment was measured immediately after peeper retrieval using micro-electrodes inserted through the membrane. Aliquots for dissolved organic carbon (DOC) measurements were taken from CO_2 -free subsamples of the acidified samples used for the trace metal analysis, and were injected into a Beckmann model 915-A total carbon analyzer. For the determination of the inorganic and methylated-As species in the porewaters, the technique published by Iverson et al. (1979) was adopted. However, dissolved As was also determined in all the eluent fractions.

The vertical diffusional As flux of dissolved As from the sediments to the overlying water may be calculated from the dissolved As gradient (dC/dZ)x,y across the sediment-water interface and Fick's first law in one dimension:

F = 0 Ds $(dC/dZ)_{x,y}$

where, F is the diffusive flux of As $(\mu g.cm^2.y^1)$, \emptyset is the porosity of the sediments, and Ds is the diffusion coefficient in porewater $(cm^2.y^1)$. In order to calculate the diffusive flux the following assumptions have to be made: a) sediment water interface is known,

b) viscosity and charge coupling effects are negligible; c) arsenate and arsenite anions are the only As species present and they have identical diffusional properties; d) there is no solid phase consumption of dissolved As near the water-sediment interface; and e) As concentration gradients are linear, so that, $(dC/dZ)_{xy}$ is equivalent to $\Delta As/\Delta Z$, or the difference in the concentrations of dissolved As across the sediment-water interface (Peterson and Carpenter 1986). The average porosity is for the surficial sediments to the depth of the dissolved As maximum. The diffusion coefficient (Ds) was estimated from the empirical relationship Ds= $O^{2}D$, where n is a constant (n=2, Lerman 1978); and D (5.3x10⁻⁶ cm².s⁻¹) is the diffusion coefficient of arsenate ion at infinite dilution, corrected to the mean annual water temperature of 7°C (Li and Gregory 1974). The accumulation of As in sediments (in mg.cm².y⁻¹) was calculated with the formula:

S = R(1-0) QC

where R is the sedimentation rate $(cm.y^{1})$, \emptyset is the porosity, g is the dry density of the sediment $(g.cm^{3})$ and C is the As concentration $(\mu g.g^{1})$ (Hamilton-Taylor 1979).

Arsenic concentrations in porewater samples, acidified with nitric acid matrix, were determined at 193.7 nm by graphite furnace atomic absorption on a Varian Spectra AA-400 in background correction mode. A nickel nitrate solution (200 mg.L¹) was used as a matrix modifier because it forms nonvolatile nickel arsenides at higher charring temperatures (Ediger 1975).

To minimize contamination, all handling of the porewater samples was carried out in portable clean laboratory. All reagents were of ultra-pure grade and were used without further purification. All glassware and Teflon materials were washed through the sequence developed by Tramontano et al. (1987), with some modifications (Nriagu et al. 1993). The accuracy and precision of the analytical techniques were evaluated by analyzing certified SLRS-2 Riverine Water Reference Material for trace metals from the National Research Council with each batch of samples.

RESULTS AND DISCUSSION

Total As, Fe and Mn profiles in pore water

The pH of sediment pore water varies between 7.4 and 8.6 and the pH profiles do not show any trend with respect to depth (Azcue 1992). The average concentration of total dissolved carbon ranged from 11.3 mg.L⁴ at station ED to 16.2 mg.L⁴ at station WA, with slightly higher values in the first centimetres in all the stations. The concentration of dissolved As in the surface waters of Moira Lake averaged 47 μ g.L⁴ in summer and 22 μ g.L⁴ in winter (Azcue 1992). The As concentrations in the top of the sediment averaged 545 μ g.g⁴, with increasing concentrations with depth and maxima close to 1 mg.g⁴ located between 23 to 27 cm depth (Azcue and Nriagu 1993).

Depth distributions of total As in porewater at the four stations of Moira Lake are shown in Figure 2. The profiles in porewater reflect the physico-chemical conditions (pH, 02, temperature, etc.) at the sampling time, being very sensitive to minor chemical changes. All the profiles are characterized by maxima below the sediment-water interface, with concentrations four to six times greater than in the lake water. In the stations WA, WB and EC the As concentration maxima are located approximately within 5 to 10 cm of the water-sediment interface. Such a profile is typical of many redox species in pore water of sediments where the surface layers are aerobic (Lerman 1978). However, it is worth noting that the precise designation of the water-sediment interface and the resultant depths may not be as accurate as the data indicate, but within a margin ±2 cm of the particular interval, because of difficulty in visually verifying the interface at the site. The mobility of the peeper in the sediment and the non-linearity of the water-sediment interface are the main difficulties.

The depth-distribution of total dissolved As at station WA (Figure 2), the closest station to the river input, shows that after the initial peak at approximately 5 cm depth, As remains in solution at very high concentrations, 241 μ g.L⁻¹. In contrast, the As concentrations in porewaters from stations WB and EC, drop off rapidly beneath the redox transition. At approximately 23 cm depth in station WB, the concentration of dissolved As reaches a second

peak of 42 μ g.L¹. Because pH, total dissolved carbon and concentrations of Fe and Mn do not show noticeable changes at this depth, the As release to pore water in the 20 to 30 cm interval in station WB is likely associated with peculiar features of the particular sediments.

The profile for total As at station ED has a very distinct shape: the increase starts at 10 cm depth and reaches a maximum of 225 μ g.L¹ at 35 cm depth, before dropping off to 48 μ g.L⁴ (Figure 2). The profile which could indicate the formation of a mixed sediment layer in the upper cm of the sediment of station ED can be attributed to the burrowing activity of benthic organisms (bioturbation) at the station. This high degree of mixing in the surficial sediments presumably results in the location of the As maximum at approximately 30 cm depth.

The profiles of dissolved Fe and Mn in stations WA, WB and ED of Moira Lake are shown in Figure 4. Due to analytical problems, results from station EC are not available. Iron and Mn concentrations in porewaters are higher closer to the Moira River. Under reducing conditions Mn may be mobilized before Fe and, in oxygenated conditions, will persist in water longer than Fe (Forstner and Wittmann 1981). The Fe and Mn profiles in porewaters from Moira Lake show strong similarities. Consequently any release of As to porewater due to Mn dissolution may be masked by re-adsorption onto Fe oxyhydroxide phases. Similar conditions were

observed in Lake Washington by Peterson and Carpenter (1986). The Fe and Mn distributions (Figure 3) are similar to that of the total dissolved As (Figure 2). The release of solid phase As to the porewaters may be dominated by Fe and Mn adsorption-desorption processes. The dissolved Fe and Mn concentrations are not depleted at depth in station WA. 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 As which is sorbed onto these components, should be released together with the reduced soluble Fe²⁺ and Mn²⁺. 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.

Arsenic speciation in sediment pore water

The concentrations of inorganic arsenite [As(III)], arsenate [As(V)], monomethyl-arsenate [MMAA, CH_3 -AsO₂OH), and dimethyl-arsenite [DMAA, $(CH_3)_2AsOO$] (Table 1) provide additional information on the behaviour of dissolved As in porewaters. MMAA and DMAA concentrations were determined at several depths in porewaters from station WB and ED. Due to analytical problems, results for inorganic speciation at station ED are only available to 16 cm depth. *Measured* total dissolved As is designated by As_T while Σ As represents the sum of the two inorganic As species (arsenate and arsenite), as well as the methylated species when analyzed. The agreement between As_T and Σ As, taking into

consideration that the coefficient of variation for the triplicate analyses of the porewaters ranged approximately from 2 to 18% leads to the conclusion that contributions by other As species are negligible.

Methylated As compounds at station WB represent <2% of the total As, and even a smaller percentage at station ED (Table 1). Previous studies (Diamond 1990; Wong et al. 1975) have also reported low concentrations (<10%) of methylated As-compounds in the porewaters of Moirá Lake. Since only few samples were analyzed for methylated As compounds, only general conclusions can be made from these results. The low concentrations of methylated-As compounds in porewaters can be explained by the elevated As concentrations in the sediments from Moira Lake (up to 1 mg.g⁴), that may be inhibiting the activity of microorganisms capable of As methylation. This is in agreement with the findings of several authors which have documented the inhibition of bacteria-mediated production of methyl-As (Anderson and Bruland 1991; Huysmans and Frankerberger 1991; Manning and Ash 1979; Reuther 1992).

In all the porewater profiles examined, inorganic As [As(III) + As(V)] accounts for most of the As. The percentage of As (III), the most toxic form, ranges from 66% at station ED to 83% at station WB. The slightly higher percentage of As(V), the stable form in oxic waters, in the first centimetres of station ED is consistent with the penetration in this station of oxic overlying

water into the sediments. The invariable presence of significant amounts of arsenite in the oxygenated upper centimetres of all the porewater profiles, as well as the presence of arsenate even in the reduced zones of the profiles further demonstrate a departure from equilibrium conditions in Moira Lake. This thermodynamic 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. The incomplete summer stratification and thoroughly mixing of Moira Lake waters during spring and fall explain the further presence, in surface oxygenated waters, of 20 to 30% of such sediment-derived arsenite. The arsenite profiles in water column for stations WB and EC are shown in Figure 4.

Arsenic fluxes in pore water

Arsenic porewater profiles (Figure 2) indicate an upward flux of As from deeper sediment depths towards the sediment water interface. Upward diffusion of As from the sediment porewater to the overlying water column is indicated by the higher hypolimnetic concentrations in summer time when the lake is stratified, compared with the early fall when the lake is isothermal. The As(III) concentrations, as well, were much higher in the hypolimnion (averaging 60%), compared with the epilimnion (averaging 25%) during the stratification (Figure 4).

The vertical diffusional As flux of dissolved As from the sediments to the overlying water (F in μ g.cm².y¹) and the accumulation of As in sediments (S in mg.cm².y¹) of Moira Lake were calculated (as shown in the material and methods) and are shown in Table 2. It is difficult to calculate the contemporary flux of As being incorporated into the sediments because of the mixing of the sediment-water interface. For this reason, present-day fluxes refer to the top 1 to 3 cm interval and excludes the surface flocculant layer. The maximum As fluxes at 22 to 26 cm depth are calculated using the maximum As concentrations. Two assumptions are also made: a) constant deposition rates during this interval, and b) the effects of the compactation of the top 20 cm of the sediments are negligible.

The data in Table 2 indicate that the As accumulation rates are similar in sediments at both basins of Moira Lake. The decrease in the As concentrations in the top sections of the sediments reflects the reduced input since the final shut-down of the mining activities in 1961. Nevertheless, the As concentrations in these surficial sediments remain quite high indicating continuing input of As from the abandoned mine site and 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. The fact that the adsorption of As by sediment fractions is reached within minutes while desorption is slow (Korte and Fernando 1991), indicates that As

will continue to accumulate in Moira Lake sediments so long as sesquioxides and other adsorbents continue to accumulate.

The calculated fluxes at all the stations in Moira Lake are shown in Table 2. Apparently, the upwardly diffusing As is inefficiently trapped near the water-sediment interface as evidenced by increased concentrations in water. Upward diffusion fluxes for Fe and Mn are observed in all the stations (Table 2). These results show that in the long term deposition of sediments, which ranges from 5.48 to 7.4 μ g.cm².y¹, is the dominant removal process for As in the lake. The total As deposition in sediments of Moira Lake is estimated to be about 190 kg.y¹, with 79% of it occurring in the larger east basin. However, the post-depositional remobilization may play an important role during the stratification period. The continuous input of dissolved As to Moira Lake and the internal input due to the high accumulation of As in the sediments are the main factors controlling the geochemical cycle of As in Moira Lake. Consequently, minimizing the fluvial input of As may not be adequate to reduce the As levels in the lake to an acceptable value. Furthermore, profiles suggest that mining of As from deeper in sediments will continue, i.e. As can not be buried because diffusional gradients are up. Arsenic will continue moving towards the sediment water interface and will enter the water column along with Fe and Mn during periods of overlying water anoxia.

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Figure Captions

Figure 1. The Moira River drainage basin of eastern Ontario and sampling stations in the study area of Moira Lake

Figure 2. Total arsenic concentrations (μ g.g⁻¹) in porewaters from Moira Lake sediments.

Figure 3. Total iron and manganese concentrations (μ g.g¹) in porewaters from Moira Lake sediments.

Figure 4. Arsenite profile (percentage of total arsenic) in water column of stations WB and EC of Moira Lake sampled on July-12, 1990. [Standard deviations expressed in %].

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Table 1-a

(Station WA)

| | | * | | | | | |
|---|------------|------------|-----------------|--------|-----------|-------|---|
| | Depth | A.(III) | As(V) | (U)(V) | 8A | Total | |
| | (om) | | | | | | |
| | | | | | <u></u> | | and the second |
| | -4 | 41 | 4 | 10.3 | 45 | 47 | A CONTRACT OF A |
| | 3 | 46 | 14 | IJ | 60 | 41 | · · · · · · · · · · · · · · · · · · · |
| | -2 | 36 | 14 | 2.6 | 50 | - 44 | |
| | 4 | 28 | 1 | 28.0 | 29 | 42 | • |
| | . 0 | 40 | 4 | 10.0 | 44 | 44 | \$ |
| | L | 30 ' | 8 | 3.8 | 38 | 4 | · · · · · · · |
| • | 3 | 40 | 6 . | 67 | 46 | · 50 | · |
| | 4 | 62 | 1 | 62.0 | ů. | 82 | * |
| • | 9 S | 84 | 18 | 47 | 102 | Π | · · · |
| | 6 | 90 | 20 | 45 | 110 | 122 | |
| • | 7 | 84 | 60 | 14 | 144 | 160 | |
| | . 8 | 168 | 88 | 19 | 256 | 242 | |
| | 9 . | 112 | Q | 1.8 | 174 | .204 | |
| • | 10 | 112 | Q. | 1.8 | 174 | 224 | |
| | 11 | 114 | 44 | 2.6 | 158 | 219 | , |
| • | 12 | 180 | 110 | 1.6 | 290 | 255 | |
| | 13 | 120 | 104 | 1.2 | 224 | 235 | |
| | 14 | 176 | 60 | 2.9 | 236 | 262 | · · · · · · · · · · · · · · · · · · · |
| | 15 | 168 | 56 | 3.0 | 224 | 270 | |
| | 16 | 140 | 56 | 25 | 196 | 247 | . 1 |
| | 17 | 126 | 88 | 14 | 214 | 236 | • <u> </u> |
| | 18 | 128 | 126 | 1.0 | 254 | 223 | · · · |
| | 19 | 160 | 68 | -2.4 | 228 | 235 | •. |
| | 20 | 1,68 | 44 | 3.8 | 212 | 257 | |
| | 21 | 148 | 40 | 3.7 | 188 | 257 | |
| | 22 | 184 | 52 | 3.5 | 236 | 272 | |
| • | 23 | 168 | 44 | 3.8 | 212 | -235 | |
| | 24 | 158 | 66 | 2.4 | 224 | · 232 | |
| | 25 | 160 | 66 | 24 | 226 | 225 | |
| | 26 | 140 | 4 | 3.2 | 184. | 250 | • 、 |
| | 27 | 98 | 1 | 98.0 | 99 | 232 | |
| | -28 | 172 | 40 | 43 | 212 | 240 | |
| | 29 | 104 | 52 | 20 | 156 | 248 | • |
| | .50 | 140 | \$2 | 27 | 192 | . 205 | |
| | 31 | 72 | 60 | 12 | 132 | • 218 | • • • |
| | 32 | 196 | 44 | 45, | - 240 | 205 | |
| | 53 | 140 | 88 | 1.6 | 228 | 183 | |
| | 34 | 170 | | 3.5 | 218 | 178 | |
| | 35 | 140 | ⁷ 40 | 3.5 | 180 | 170 | |
| | 36 | 152 | 72 | 21 | 224 | 174 | |
| | 38 | 158 | Ó | 2.6 | 218 | 192 | |
| | 40 | 156 | 4 | 3.5 | 200 | 167 | · · · · · |
| | 41 | \$8 | 84 | 1.0 | 172 | 163 | . , |
| | 42 | 88 | 84 | 1.0 | 172 | 163 | · · · · · · · · · · · · · · · · · · · |
| | 44 | 112 | - 46 | 24 | 158 | 167 | × • |
| | 45 | ŚÓ | 92 | 1.0 | 182 | 1.80 | |
| | 49 | 52 | 60 | 0.9 | 112 | 152 | |

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BAs = sum of the amenio species

Total As - Total dissolved assenio

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| | | • | | Station WI | B . | • | | |
|-------|---------------|------------|------------|-------------|-------------|--------------|-------------|-------------|
| | Depth | A.(23) | A4(V) | MMAA | DMAA | (W)(W) | BA | Total As |
| | (000) | <u> </u> | | | · | | | · · · · · |
| | -11 | Π | 16 | 0 | • | 4.8 | 97 | 70 |
| | -10 | 66 | 34 | . 0 | 4 | 1.9 | 104 | 78 |
| | -9 | 52 | 38 | 2 | 0 | 14 | ¥2 101 | 79 |
| • . | -6 2 | л Л | - 46 16 | 2 | v, | 38 | 77 | â |
| | -1 | · 01. | 10 | | 6.6 8.6 | 33 | 60 | 70 |
| | -s | 2 | 26 | | . 3 | 20 | 84 | a |
| | 4 | 57 | - 24 | 4 | 2 | 1.5 | ଶ | . 60 |
| | 3 | , લ | 16 | . 64 | 5.8 | 3.8 | π | 90 |
| | -2 | 40 | 24 | 0 | 2 | 1.7 | 66 | 84 |
| · . · | -1 | 42 | 18 | ٥ | 2 | 23 | 62 | 62 |
| | 0 | 40 | 18 | 8 | 4 | 22 | 70 | 50 |
| ~ | 1 | 56 | 18 | 8 | 4 | 31 | 86 | 86 |
| | 2 | 92 | 18 . | 4 | 4. | , | 118 | 125 |
| | 3 | 118 | 24 | 4 | 4 | 49 | 150 | 125 |
| | 4 - | 106 | 18 | 54 , | 1 4 | 59 | 124 | 133 |
| | S | 114 | 58 | 84 | 2.4 | 3.0 2.4 | 132 | 139 |
| | | <u>~</u> | 20 | | <u></u> | - 11 | 82 | 145 |
| | | 49 | 14 14 | 0 | Ň | / 14 | | 144 |
| | | 112 | . 21 | | | 53 | 133 | 138 |
| | . 10 | 110 | | | 2.8 | 2.6 | 152 | 144 |
| - | n | 145 | 4 | | 8.8 | 363 | 149 | 135 |
| | 12 | 138 | 12 | 8.8 | 1.8 | 11.5 | 150 | 130 |
| | 13 | 112 | 10 | 8.8 | 8.4 | 11.2 | 122 | 99 |
| | 14 | 105 | 4 | 8-8 | 5.8 | 265 | 110 | 83 |
| | 15 | 136 | 1 | 10 | 0 | 136.0 | 147 | 87 |
| | 16 | 56 | 2 1 | 10 | 0 | 28.0 | 68 | 45 |
| | 17 | 92 | 1 | | 4 . | 92.0 | 93 . | . 48 |
| | 18 | 66 | 6. | PA . | 5.6 | 11.3 | 74 | - 39 |
| | 19 | 60 | • | . 5. | R.A. | 120 | 04 41 | 2/ 94 |
| • | 20 | . 64 | | | | 34.0 | * | 50 |
| | а 27 | | | | | | | 21 |
| | 23. | 48 | 4 | | | 12.0 | 52 | 19 |
| · · . | 24 | | عد | | 34 | 2.2 | 0 | 21 |
| | 25 | | | 2 | 4 | ŚS | 56 | 21 |
| | 26 | 8.6 | 3.8 | 2 | 4 | 2.6 | 6 | - 15 |
| | 27 | 15 | 6 | 84 | هم | 27 | 22 | 16 |
| | 28 | 8.8 | هغ | 2.8 | sia | 24 | 0 | 11 |
| | 29 | 12 | 1 | 3.4 | B.A | 12.0 | 13 | 14 |
| | 30 | 5.8 | <u>na</u> | 84 | 8.4 | 8.8 | 0 | 10 |
| , | 31 · . | 11 | 2 | 2 | 2 | 55 | 17 | 10 |
| • | 32 | 2.8 | | | 8.8 | 54 | 0 | • |
| · · | 33 , | 12 | . 4 | 8.8 | 2.5 | . 10 | 16 . | 12 |
| | 34 | 8.4 | 11.8 | 5.4 | | | U A | |
| | 30 86 | | | | 54 | | 0 | |
| • | 257 | 10 | 2 | 0 | 0 | 5.0 | 12 | 6 |
| | . 38 | 2.0 | - | . 0 | 0 | R.A. | 0 | 5 |
| | 39 | -28 | 1 | 2.4 | 8.8 | 28.0 | 29 | 6 |
| | 40 | 5.8 | . 54 | 84 | 2.8 | . | 0 | 6 |
| | 41 | 21 | . 2 | ' nà | 3.8 | 10.5 | 23 | 9 |
| | 42 | n.a | 2.8 | 0 | 2 | 5.6 | . 21. | 9 |
| | 43 | 16 | 1 | 0 | 2 | 160 | 19 | 9 |
| | 4 | <u>nia</u> | sia . | 24 | 3.8 | 0.a | 0 | 8 |
| • | 45 | 1 | 2 | 5.0 | 5 .8 | 0.5 | 3 | 9 |

MMAA = Menomethylamonie acid

DMAA - Dimethylamenis acid

Tille Le

| | | | | 00000000000 | • | | | • |
|-----------|---------------|------------|-------------|-------------|------|------------|------|----|
| | Durch | 447D) | Action | HIV | BA | Total As | | • |
| | (cm) | | | | | | / | |
| | | | | | | | | |
| | | | , , | | | | | |
| | -5 | 28 | • • | 7.0 | 32 | 44 😳 | • | |
| • | · 👍 | 26 | 18 | 14 | 44 | 48 | • * | |
| , | · | 32 | 16 | 2.0 | ~48 | 50 | | |
| | -2 | 32 | 16 | 2.0 | 48 | 56 | | |
| , | . -1 . | 42 | 16 | 2,6 | .58 | <u>\$2</u> | | 1 |
| | ί Ö | Ø | 16 | 2.5 | - 36 | 46 | | |
| | 1 | 48 | 14 | 3.4 | 62 . | 88 | | |
| | 2 | 46 | 10 | 46 | - 96 | 88 | · , | |
| | - 3 | 48 | · 12 | 2.2 | 70 | 82. | . `` | |
| | 4 | 45 | 12 | 1 3.8 | \$7 | 88 | 1 | |
| | 5 | 66 | 14 | 47 | 80 | 92 | | |
| | 6 | 98 | 2 | 45 | 120 | 160 | · · | |
| | 7 | 122 | 20 | 61 | 142 | 166 | | • |
| | , 8 | 66 | 12 | S.5 ' | 78 | 75 | • | |
| | 9 | 48 | 6. | 8.0 | 54 | 48 | • | |
| | 10 | 36 | 10 | 3.6 | 46 | 30 | | |
| | 11 | 30 | 14 | 21 | 44 | 39 | | |
| • | 12 | 34 | 16 | 21 | 50 | 36 | . , | |
| | 13 | 34 | 14 | 24 | 48 | 35 | | |
| | 24 | 30 | 12 | 25 | . 42 | 53 | | |
| | 15 | 20 | 16 | 13 | 36 | 20 | | |
| × × | 15 | 22 | 12 | · 1.8 | 34 | 30 | • | |
| | 17 | . 20 | 26 | 0.8 | 46 | 31 | | |
| | 18 | 32 | 8 | 4.0 | 40 | 40 | • | • |
| • | 19 | 12 | 10 | 1.2 | 22 | 31 | • | |
| | 20 | 18 | 16 | น | -34 | 44 | *A. | |
| | 21 | 28 | 12 | 2.5 | . 40 | 45 | | |
| | 22 | 14 | 12 | 1.2 | 26 | 31 | | |
| • , | . 23 | 24 | 1 | 24.0 | 25 | 49 | , | |
| | 24 | 36 | 1 | 36.0 | 37 | 48 | | |
| | 25 | , 38 | 1 | 38.0 | 39 | 47 | | |
| * | 25 | 32 | 8 ` | 4.0 | 40 | 53 | | |
| • | 27 | 30' | 10 | 3.0 | ¢0 | 42 | • | |
| | 28 | 30 | 1 | 30.0 | 31 | 48 | • | |
| | - 29 | 38 | 1 | 38.0 | 59 | -41 | • | |
| • • | . 30 | . 6.4 | 88 | 8.8 | 8.6 | . 31 | • | |
| | 51 | 48 | 1 | 48.0 | 49 | 47 | | |
| • | | 44 | 10 | 4 | 54 | 36 | | |
| | 33 | 3.4 | 6.4 | na. | 8.A. | 27 | (| |
| | 34 | 8.8 | 22 | | 5.A | . 12 | | ·, |
| | 35 | - 48 | . 6 | .80 | 54 | 20 | , | • |
| | . 36 | , DA | <u>1.</u> | 2.6 | 2.2 | 72 | | |
| • | 57 | 20 | 8 | 25 | 28 | 12 | ~ | |
| | 58 | 8.8 | 8.0 | 8.8 | | 72 | | |
| | 39 | 12 | 6 | 2.0 | 18 | . 16 | | |
| | 40 | 2.6 | 0.0 | - 54 | 8.8 | 7 | | |
| • | 41 | 22 | 1 | 22.0 | 23 | 15 | •• | • |
| | 42 | | (14 | 5.4 | 24 | n | | |
| | 43 | 28 | 1 | 28.0 | 29 | 7 | | |
| | 44 | 1.2 | 64 | 14 | 5.6 | • 9 | | |
| | 45 | 25 | 6 | 4 | 32 | 14 | • | |
| | 46 | 0.8 | 84 | 8.4 | 0.8 | 14 | • | |
| · · · · · | 47 | 16 | 8 | 2.0 | 24 | . 23 | | |
| N | - 48 | 8.8 | 5.6 | 8.5 | 5.6 | 14 | | |
| | 49 | 16 | 4 | 4.0 | 20 | 16 | | |
| | . 50 | 5.8 | 5 . | 5.0 | 2.2 | 14 | | ς |
| | R C | 14 | 12 | 12 | 25 | 19 | | |
| | | • | | | | | • | |
| | | | | | | | | • |

Table 1d

Station ED

| | | | | | | | • |
|-----|---|--|---|---|--|---|---|
| -13 | 28 | 8 | 8 | 0 | 3.5 | 44 | 42 |
| -12 | 27 | · 7 | n.a | n.a | 3.9 | 34 | 41 |
| -11 | 38 | 4 | · 2 | 2 | 9.5 | 46 | 40 |
| -10 | 27 | 4 | n.a | n.a | 6.8 | 31 | 42 |
| -9 | 28 | 6 | 0 | 0 | 4.7 | 34 | 41 |
| -8 | 26 | 12 | n.a | n.a | 2.1 | 38 | 40 |
| -7 | 21 | . 8 | · • 0 | 0 | .2.6 | 29 | 41 |
| -6 | 20 | 8 | n.a | n.a | 2,5 | 28 | 42 |
| -5 | 21 | 18 | 0 | . 8 | 1.2 | 47 | 42 |
| -4 | 21 | 8 | n.a | n.a | 2.6 | 29 | 41 |
| -3 | 16 | 24 | 2 | 0 | 0.7 | 42 | 40 |
| -2 | 16 | 8 | n.a | n.a | 2.0 | 24 | 40 |
| -1 | 17 | 12 | . 0 | 0 | 1.5 | 29 | 42 |
| 0 | 18 | 20 | n.a | n.a | 0.9 | 38 | 40 |
| 1 | 33 | 14 | 2 | 4 | 2.4 | 53 | 45 |
| 2 | 31 | 10 | n.a | n.a | 3.1 | 41 | 43 |
| 3 | 33 | 14 | 0 | 4 | 2.4 | 51 | 46 |
| 4 | 37 | 6 | n.a | n.a | 6.2 | 43 | 45 |
| 5 | 35 | 20 | · 8 | Q | 1.8 | 63 | 44 |
| 6 | 36 | 20 | n.a | n.a | · 1.8 | 56 | 47 |
| 7 | 30 | 52 | 0 | 0 | 0.6 | 82 | 51 |
| 8 ` | 35. | 52 | n.a | n.a | 0.7 | 87 | 58 |
| 9 | 30 | 30 | 2 | 0 | 1.0 | 62 | 56 |
| 10 | 30 | 44 | n.a | n.a | 0.7 | 74 | 53 |
| 11 | . 35 | 12 | 0 | · 0 | 2.9 | 47 | 64 |
| 1Ž | 48 | 8 | n.a | n.a | 6.0 | 56 | 75 |
| 13 | 60 | 12 | 0 | 6 | 5.0 | 78 | 90 |
| 14 | 73 | 20 | <u>n.a</u> | n.a | 3.7 | 93 | 102 |
| 15 | - 78 | 14 | n.a | n.a | 5.6 | 92 | 95 |
| 16 | 77 | 32 | D.8 | n.a _ | 2.4 | 109 | 106 |
| | -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 | -12 27 -11 38 -10 27 -9 28 -8 26 -7 21 -6 20 -5 21 -4 21 -3 16 -2 16 -1 17 0 18 1 33 2 31 3 33 4 37 5 35 6 36 7 30 8 35 9 30 10 30 11 35 12 48 13 60 14 73 15 78 16 77 | -12 27 7 -11 38 4 -10 27 4 -9 28 6 -8 26 12 -7 21 8 -6 20 8 -5 21 18 -4 21 8 -3 16 24 -2 16 8 -1 17 12 0 18 20 1 33 14 2 31 10 3 33 14 4 37 6 5 35 20 6 36 20 7 30 52 8 35 52 9 30 30 10 30 44 11 35 12 12 48 8 13 60 12 14 73 20 15 78 14 16 77 32 | -12 27 7 $n.a$ -11 38 4 2 -10 27 4 $n.a$ -9 28 6 0 -8 26 12 $n.a$ -7 21 8 0 -6 20 8 $n.a$ -5 21 18 0 -4 21 8 $n.a$ -3 16 24 2 -2 16 8 $n.a$ -1 17 12 0 0 18 20 $n.a$ 1 33 14 2 2 31 10 $n.a$ 3 33 14 0 4 37 6 $n.a$ 5 35 20 8 6 36 20 $n.a$ 7 30 52 0 8 35 52 $n.a$ 9 30 30 2 10 30 44 $n.a$ 11 35 12 0 12 48 8 $n.a$ 13 60 12 0 14 73 20 $n.a$ 15 78 14 $n.a$ 16 77 32 $n.a$ | 12277n.an.a-12277n.an.a-1138422-10274n.an.a-928600-82612n.an.a-721800-6208n.an.a-5211808-4218n.an.a-3162420-2168n.an.a-117120001820n.an.a133142423110n.an.a33314044376n.an.a535208063620n.an.a730520083552n.an.a9303020103044n.an.a1135120012488n.an.a13601206147320n.an.a157814n.an.a167732n.an.a | -12277nana3.9-11384229.5-10274nana6.8-9286004.7-82612nana2.1-7218002.6-6208nana2.5-52118081.2-4218nana2.6-31624200.7-2168nana2.0-11712001.501820nana0.913314242.423110nana6.253520801.863620nana6.253552nana0.793030201.0103044nana0.793030201.0103044nana0.7113512002.912488nana6.0136012065.0147320nana3.7157814nana5.61677 </td <td>121717181412229.546-10274n.an.an.a6.831-9286004.734-82612n.an.an.a2.6-6208n.an.a2.528-52118081.247-4218n.an.a2.629-6208n.an.a2.629-6208n.an.a2.629-31624200.742-2168n.an.a2.024-11712001.52901820n.an.a0.93813314242.45323110n.an.a3.14133314042.4514376n.an.a6.24353520801.86363620n.an.a0.68283552n.an.a0.774113512002.94712488n.an.a6.056136012065.078</td> | 121717181412229.546-10274n.an.an.a6.831-9286004.734-82612n.an.an.a2.6-6208n.an.a2.528-52118081.247-4218n.an.a2.629-6208n.an.a2.629-6208n.an.a2.629-31624200.742-2168n.an.a2.024-11712001.52901820n.an.a0.93813314242.45323110n.an.a3.14133314042.4514376n.an.a6.24353520801.86363620n.an.a0.68283552n.an.a0.774113512002.94712488n.an.a6.056136012065.078 |

Table 2. Mean solid phase arsenio deposition rates (S) and discolved arsenio diffusive flux (F) in ug.cm-2.y-1.

| Location | • <i>:</i> | Deposition present day (0-1 cm) | meximum (22-26 cm) | Difffuelve flux (F) | (F/S) | · |
|------------------------------------|---|---------------------------------------|-----------------------|------------------------|----------------|-----|
| Arsenio | | | | | | |
| : | WA | n.a. | D.8. | 3.85 | L.a. | |
| West.basin | MB. | 7.43 | 38.7 | 3.04 | 0.41 | • |
| · : | Ö Ü | 16.8 | 46.8 | 2.64 | 0.16 | • ′ |
| East basin | B | n.a. | | 0.77 | | • |
| lon | | | | | | |
| West basin | 8M , | 788 | ца. С | 63.6 | 0,08 | |
| East basin | E | 1,646 | n.a. | 11 | 0.007 | |
| Manganese | | | X | - | | • |
| West basin | WB | 36.8 | n.a. | 8.2 | 0.23 | |
| East basin | ß | 110 | ла. Д | 9.4 1 | 0.03 | |
| Diffusion coeffic D-As= 5.3x10E | clents (on 6 | n2/s): | | (From LI and G | iregory, 1974) | |
| D-Fe= 4.38x10 | е Ш | | ų | | | • |
| D-Mn= 4.1X10 | i i i i i i i i i i i i i i i i i i i | ·. | | | | |





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