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Arsenic bioaccumulation and toxicity in aquatic macrophytes exposed to gold-mine effluent: relationships with environmental partitioning, metal uptake and nutrients

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Abstract

Arsenic concentrations in freshwater macrophytes were examined in relation to arsenic loadings in sediments (solid phase and pore water) and surface waters for a group of lakes contaminated by the discharge of mine tailings near Yellowknife, N.W.T. Lakes closest to the current discharge were highly contaminated with arsenic (up to $18\,650\ \mu\text{g g}^{-1}$ in sediments) compared with other areas. Macrophytes tended to bioconcentrate arsenic relative to sediment concentrations (up to a factor of ten), with submerged species containing much higher levels of arsenic than emergents. Differences in levels between the most common submerged (*Potamogeton pectinatus* L.) and emergent species (*Typha latifolia* L.) were attributed to differences in growth form and possible differences in the ability to exclude arsenic with increasing sediment concentrations. High environmental arsenic concentrations appeared to have negative effects on *Typha latifolia*, as suggested by decreased stand height, necrosis of leaf tips and reduced micro-nutrient concentrations in root tissues of copper, manganese, and zinc. Phytotoxic symptoms in *Typha* were generally observed at sediment and water concentrations exceeding $300\ \mu\text{g g}^{-1}$ and $400\ \mu\text{g l}^{-1}$, respectively. The lack of relationships between tissue concentrations of arsenic and environmental concentrations of phosphorus (as pore water PO_4^{3-} , particulate total extractable P, or As:P ratios) did not support the hypothesis that arsenic bioavailability (as arsenate) and toxicity is related to its competition for uptake with phosphate.

1. Introduction

Arsenic occurs in solution in natural aquatic systems as either arsenite (As(III)) and arsenate (As(V)) species, or as organoarsenicals (see review by Cullen and Reimer

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(1989)). The mining and extraction of gold and other metal-bearing minerals often contributes to increased aerial and water-borne concentrations of anthropogenic arsenic (Horowitz and Elrick, 1990; Mok and Wai, 1990), as arsenopyrite is often found in association with these ores. In addition, the use of arsenical herbicides and combustion of fossil fuels has resulted in the localized arsenic contamination of soils, water, and sediment (Sanders, 1985; Cullen and Reimer, 1989). Marine and lacustrine sediments, in particular, are a major repository for anthropogenically introduced contaminants.

Dissolved inorganic arsenic is highly toxic to various plants and animals in aquatic systems (see recent experiments by Reuther (1992)); its toxicity, however, depends on its chemical species (Cullen and Reimer, 1989). Toxicity is also constrained by limits on bioavailability which, in aquatic systems, will be influenced by its redistribution between environmental compartments, including the water column, surface microlayer, sediment pore water, and sediment particulates. Much regarding the chemical 'behaviour' and toxicity of arsenic in freshwater environments, however, is still poorly understood.

Rooted aquatic macrophytes play an important role in the remobilization, cycling, and toxicity of arsenic and other metals or metalloids, as these plants are closely associated with sediments (Jackson et al., 1991) and occur at the base of the aquatic food chain. Aquatic plants have also been observed to accumulate arsenic and various metals to concentrations far in excess of environmental levels (Lee et al., 1991). Previous studies have suggested that arsenic (arsenate) bioaccumulation is intimately associated with phosphate uptake and metabolism in higher plants (Otte et al., 1990; Lee et al., 1991) and marine algae (Sanders and Windom, 1980). This has been attributed to the strong similarity of arsenate and phosphate. It has been hypothesized that the toxic effects of arsenic may arise through the competition by arsenate for phosphate uptake in plant tissues. In some cases, it has been noted that phosphate and arsenic may act synergistically in soils further to enhance arsenic mobilization and uptake (Otte et al., 1990). In others, increased phosphate in water was found to inhibit arsenic uptake (Lee et al., 1991). The apparent contrast in arsenic-phosphate interactions between studies may be related to differences in the chemical form of these substances in soil and the water column. Unfortunately, the present state of knowledge precludes any prediction of interactions between arsenic and phosphate-limited primary productivity for different macrophyte species and lacustrine systems.

This study examines the accumulation and phytotoxicity of arsenic in freshwater macrophytes in relation to arsenic levels in sediments and surface water of a system of lakes contaminated by mining effluent. The source, Nerco Con Gold Mine, located near Yellowknife, N.W.T., Canada, has been in operation since 1938. Tailings or associated effluent have caused considerable increases in the concentration of arsenic and some metals (including copper and zinc) in the water and sediments (Moore et al., 1979) and resident biota (Wagemann et al., 1978) of the Meg-Keg-Peg Lake drainage (Fig. 1). The high concentrations of arsenic encountered in this freshwater system provided a good opportunity to study the accumulation of arsenic in aquatic macrophytes and phytotoxicity using field measurements and observations. Relationships of arsenic bioaccumulation with other substances (e.g. copper, zinc, manganese and phosphorus) which serve as nutrients for aquatic macrophytes (Raven et al., 1976) were also examined to provide an indication of possible mechanisms of toxicity.

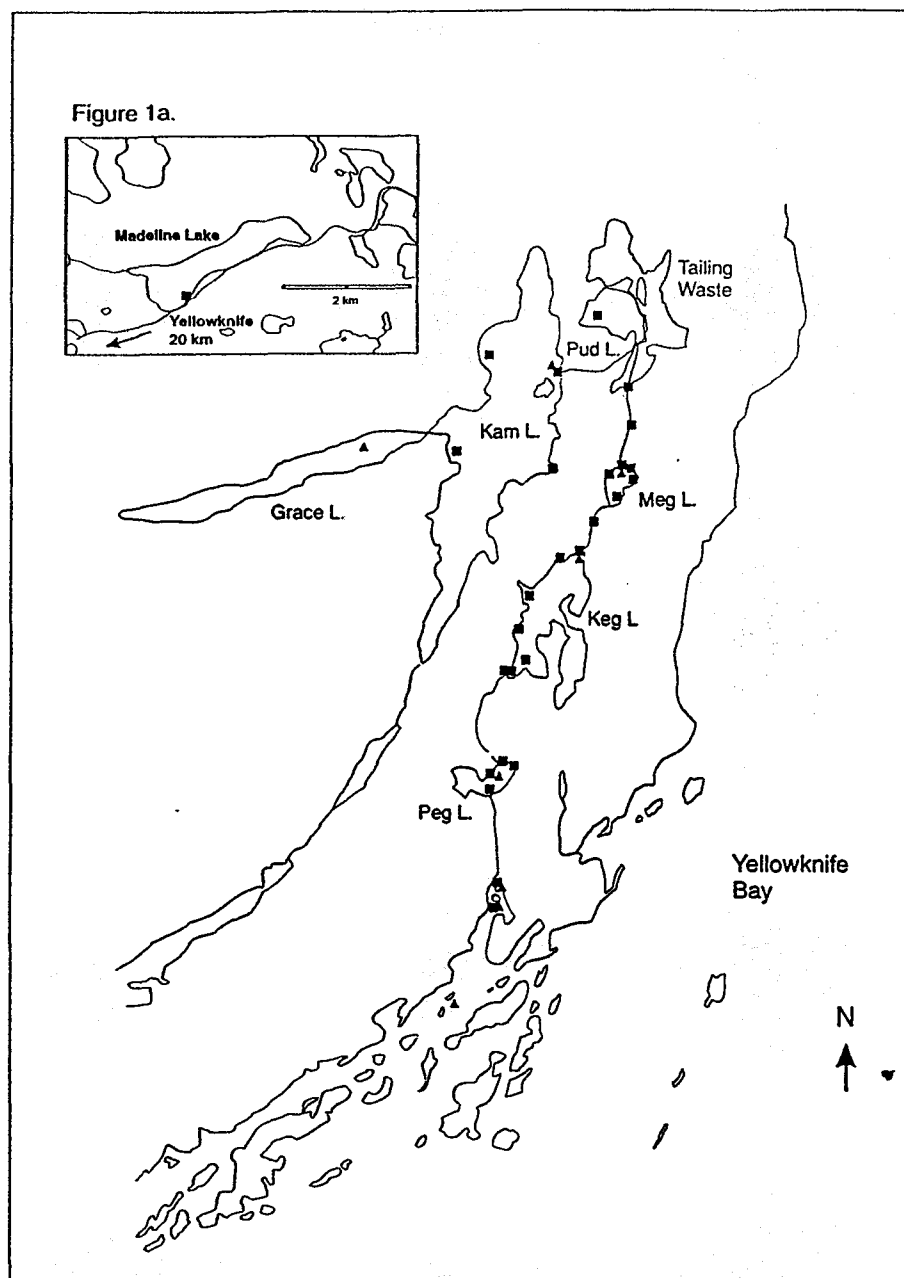


Fig. 1. Map of lake study system near Yellowknife, N.W.T., showing the 1990 deep-water (filled triangles) and 1991 shoreline (filled squares) sampling stations. A background station sampled at Madeline Lake is shown as inset (a).

2. Methods

2.1. Study sites

Tailing effluent from the Nerco Con Mine, situated south of Yellowknife, was discharged prior to 1986 into the Pud–Meg–Keg–Peg Lakes system which subsequently drains into

Yellowknife Bay (Fig. 1). At present, Pud Lake is used as a tailings pond which is periodically decanted to the other three lakes. Since 1986, decanted waste has been treated to reduce the levels of some contaminants prior to release.

Kam Lake, situated just to the northwest of the effluent system, is connected to Pud Lake by a small creek (Fig. 1). Although it is not part of the discharge system described above, the lake received several accidental discharges of effluent and tailings from the Nerco Con Mine tailings pond in the early 1970s and has also been subjected to nutrient enrichment through raw sewage discharge (Wallace and Hardin, 1975).

Grace Lake is situated further to the west and drains into Kam Lake (Fig. 1). This lake is relatively unaffected by mine waste discharge but may have received inputs through aerial deposition resulting from stack operations. This lake was used in the study as a relatively 'clean' reference site in relation to the lakes receiving mining discharge. Madeline Lake is a larger, highly productive lake located 20 km northeast of Yellowknife and is removed from the direct influences of major gold mining operations in the region (Fig. 1a inset). Its location made it suitable as a background site.

2.2. Sampling stations

A total of eight sampling stations were selected in August 1990 along the water course of the Meg–Keg–Peg–Yellowknife Bay system and in Kam and Grace Lakes (Fig. 1, triangles). Deep-water sediment cores (i.e. obtained from the open water areas of these shallow lakes), water column samples and macrophytes were collected at each of the stations, with one exception—no core sample was obtained at Station YKB2, near Yellowknife Bay (Fig. 1).

An additional 25 stations were sampled for substrate–sediments (cores) and plants in August 1991; these consisted of near-shore (shoreline) areas and connecting creeks between some of the individual lakes (Fig. 1, squares). Near-shore samples were also collected in the Pud Lake tailings and discharge (two stations), the Meg–Keg–Peg Lakes system (16 stations), Stations YKB2 and YKB3 near Yellowknife Bay (two stations), Kam Lake (four stations) and Madeline Lake (one station).

2.3. Sample collection and preparation

Deep-water sediment cores were obtained in 1990 by hand from a small boat using a gravity corer of 9.0 cm diameter with a polyacrylic barrel. These cores were transported to the laboratory, stored at 4°C for up to 16 h, and then divided into 5 cm sections in an N₂-filled glove bag.

Near-shore sediments were also collected by hand in 1991 using a polyacrylic core tube of 4.0 cm diameter. Cores were taken in sediments associated with vegetation (where present) to a maximum depth of 10 cm. These were emptied into plastic zip-lock bags and frozen for later analysis.

The sediment interstitial water was separated from the solid phase of the deep-water sediment core sections (1990) by squeezing the mud through a 0.22 μ m Millipore (Bedford, MA, USA) filter under a nitrogen atmosphere using previously established techniques (see Reimer (1989)). Pore water data from 0 to 10 cm sediment depth are reported here as this

corresponds to the zone of penetration for most rooted macrophytes. Extracted pore water was split under N_2 and decanted into 50 ml polypropylene EvergreenTM (Evergreen Scientific Inc., Los Angeles, CA, USA) containers for analysis. Samples for arsenic and phosphate analysis were immediately frozen over dry ice; the squeezed sediment was also frozen and retained for the subsequent analysis of solid-phase concentrations.

Surface water samples at each coring location in 1990 were obtained by immersing the mouth of an acid-washed 4 l polyethylene container approximately 30 cm below the surface. The samples were then transported to the laboratory, filtered using Whatman (Hillsboro, OR, USA) 934-AF filters and immediately frozen over dry ice.

Aquatic plants were sampled as near to the coring location as possible and included species which were common to most of the lakes. These included the emergent plant, cattail (*Typha latifolia* L.) and the submerged species, pondweed (*Potamogeton pectinatus* L.). These species could not be obtained at Grace Lake or Station YKB4 (near Yellowknife Bay), and no samples of *Potamogeton* sp. were found in Meg or Pud Lakes near the effluent point source. Additional species sampled at a few of the locations included the emergent species, water horsetail (*Equisetum fluviatile* L.); at Grace and Kam Lakes, YKB4) and arrow-grass (*Triglochin palustre* L. at Meg Lake); and the submerged species, water milfoil (*Myriophyllum exalbescens* Fern. at Grace Lake and YKB4), and bur-reed (*Sparganium* sp. also at Grace Lake). In 1991, macrophyte collection in the near-shore areas was restricted to *Typha* sp. and *Potamogeton* sp. (where available), as these species occurred most frequently.

All plant samples were picked free of debris and associated biota in the laboratory, washed thoroughly in deionized water and frozen in zip-lock bags—either whole or partitioned into roots and shoots. Analytical results represented one pooled sample from each collection site, usually comprising portions of 30 or more plants. For cattails, the root or shoot tissue from three to four plants were pooled. The average length of cattail shoots from each sampling station was recorded and served as an estimate of the cattail stand height.

2.4. Sediment analysis

Analyses of the solid phase of the sediments in 1990 and whole sediments in 1991 were carried out by the Analytical Services Unit (ASU) of Queen's University at Kingston, Ontario. Arsenic and iron were measured in the sediments using neutron activation analysis (NAA). Ground samples (0.35–1.2 g dry weight) were irradiated in heat-sealed vials using the SLOWPOKE reactor facility (neutron flux of $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$) at Royal Military College, Kingston. Counting was done using a GMC (EG&G Ortec, Oatridge, TN, USA) HpGe detector coupled to a Nuclear Data (Inc., USA) μ MCA. Long-lived isotopes (arsenic and iron) were assayed by irradiating for 2 h followed by a 80–120 h delay time and 1.5 h counting time. Flame atomic absorption spectroscopy (AAS) was used for determinations of copper, zinc and manganese following heated nitric and hydrochloric acid digestion of the sample. The exchangeable phosphorus pool in the solid phase of sediments collected in 1990 was estimated using Olsen and Dean's (1965) method for extractable phosphorus.

2.5. Water analysis

Previously frozen pore water from the 1990 cores and surface water samples were transported to Royal Roads Military College for the determination of dissolved arsenate

(As(III)) and arsenite (As(V)) using hydride-generation–AAS methods similar to those described by Reimer (1989); these were modified from the methods of Andreae (1977) and Braman et al. (1977). The detection limits were 0.2 ng for arsenate and 0.4 ng for arsenite; concentrations of arsenicals were found to be within 15% RSD (relative standard deviation) based on the analyses of replicates. Phosphate ion (PO_4^{3-}) concentrations were determined using ion-exchange chromatography by the ASU at Queen's University.

2.6. Macrophyte analysis

Plants were transported frozen to the ASU at Queen's University, dried overnight at 70°C and ground to pass through a 1 mm sieve. Determinations of arsenic and iron were obtained by NAA. Macrophyte samples were either irradiated for 1 min and counted for 10 min, following a 5 min delay, or irradiated for 1 min with a 12 min delay. Copper, manganese and zinc in plants were analysed using heated nitric and perchloric acid digestion followed by AAS.

3. Results

3.1. Inorganic element concentrations in lake sediment

Means and ranges of total arsenic and metallic element (copper, zinc, iron and manganese) concentrations in sediment samples obtained over the two study years are presented in Table 1. Sediments in lakes situated closest to the mining discharge (i.e. Meg, Keg and Peg Lakes) contained the highest total arsenic concentrations (up to 18 650 $\mu\text{g g}^{-1}$), with considerably lower concentrations towards Yellowknife Bay (Fig. 2a). Similar concentrations were also found in Kam Lake (maximum 1826 $\mu\text{g g}^{-1}$), which has received periodic mine discharges. Arsenic concentrations detected in these systems were up to two orders of magnitude greater than levels found in Grace and Madeline Lakes, which were isolated from direct mining discharge (Fig. 2a). Total arsenic concentrations tended to be greater in sediments in near-shore (shoreline) areas than in deep-water sediments in lakes where both were measured. The exceptions were Peg and Kam Lakes, where the opposite was

Table 1

Mean concentrations (standard deviations) and ranges of total arsenic and metallic elements measured in sediments from lake stations near Yellowknife in 1990 and 1991; sample size 32 stations

	Concentrations ($\mu\text{g g}^{-1}$)				
	Arsenic	Copper	Zinc	Manganese	Iron ¹
Average	1793	532	94	341	2.74
(SD)	(3304)	(627)	(49)	(399)	(1.36)
Minimum	39	19	16	23	0.53
Maximum	18 650	2217	265	2351	4.68

¹Values expressed as mg g^{-1} .

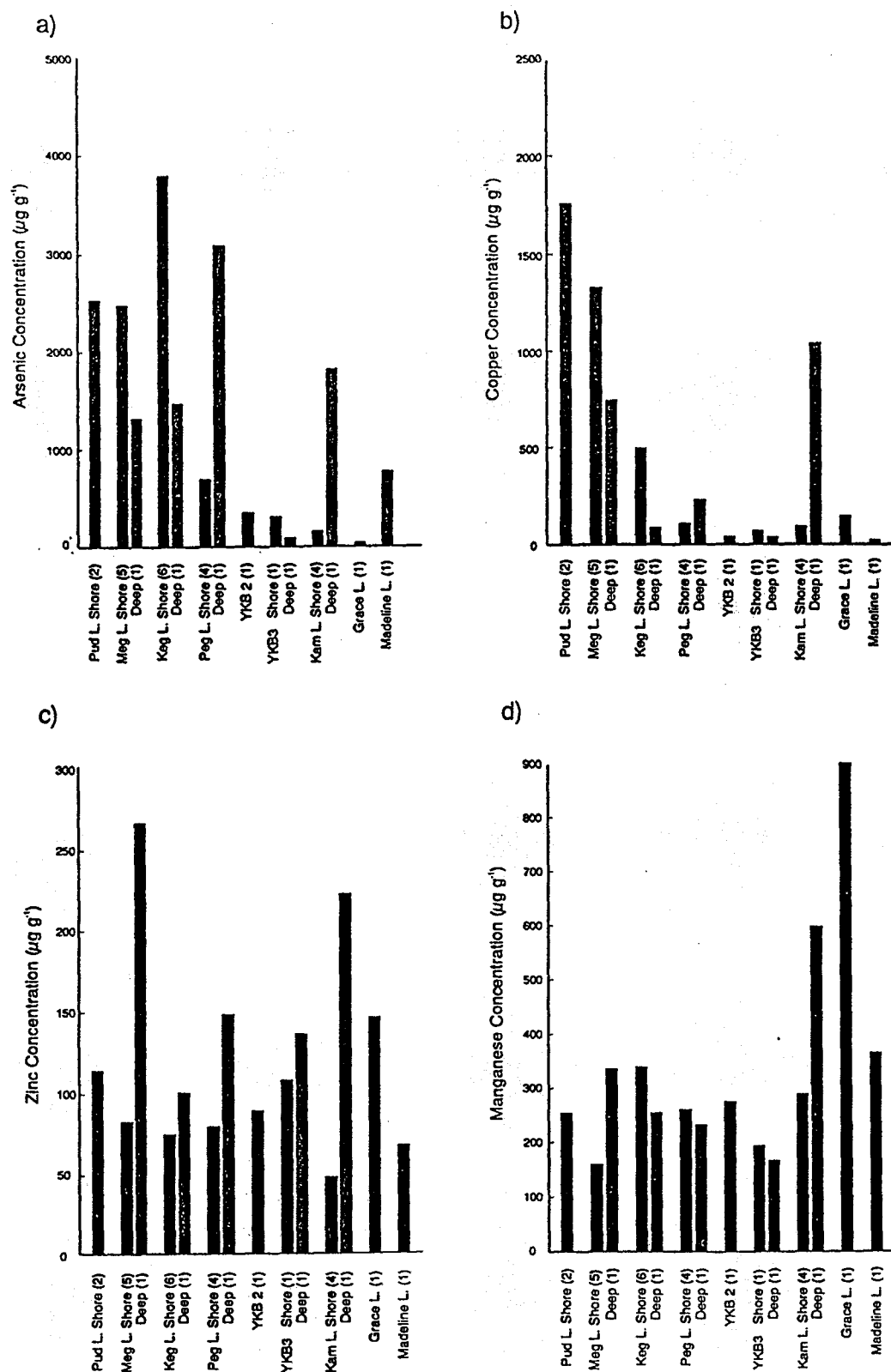


Fig. 2. Total sediment concentrations ($\mu\text{g g}^{-1}$) of (a) arsenic, (b) copper, (c) zinc and (d) manganese in deep-water and near-shore areas of lakes downstream of gold mining discharge. Grace and Madeline Lakes are provided as reference lakes.

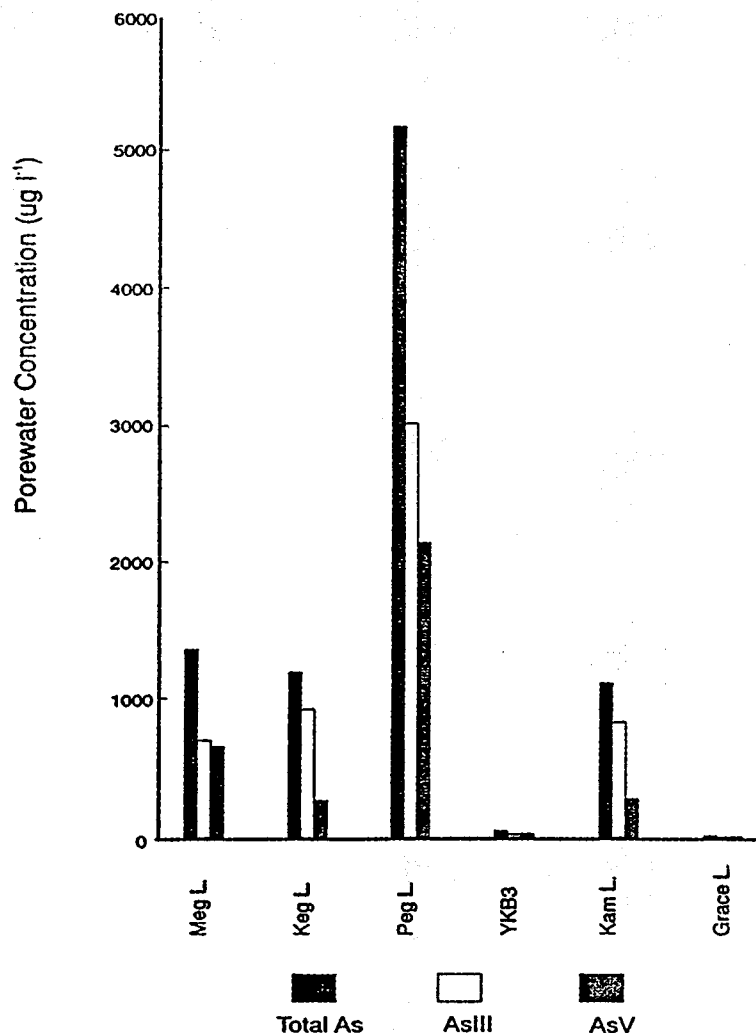


Fig. 3. Pore water concentrations ($\mu\text{g l}^{-1}$) of arsenic (total), As(III) and As(V) in deep-water sediments of lakes downstream of gold mining discharge. Grace Lake is presented as a reference.

observed (Fig. 2a). Copper in sediments (Fig. 2b) followed a similar distribution pattern to that of arsenic, whereas zinc (Fig. 2c), manganese (Fig. 2d) and iron (not shown) distributions tended to be more uniform across the study sites.

3.2. Sediment pore water and surface water arsenic

The highest sediment pore water and surface water concentrations of arsenic measured from six and seven stations (respectively) in 1990 also occurred in lakes associated with mining discharge (i.e. Meg–Keg–Peg Lakes). The highest pore water value was detected in Peg Lake (total arsenic: $4530 \mu\text{g l}^{-1}$), which was the lake farthest removed from the mine effluent discharge pipe in the Meg–Keg–Peg system (Fig. 3). Extremely high arsenic concentrations in surface water were also found in Keg as well as Peg Lakes (over $400 \mu\text{g l}^{-1}$) near the present mining discharge; a high concentration was also detected in Kam

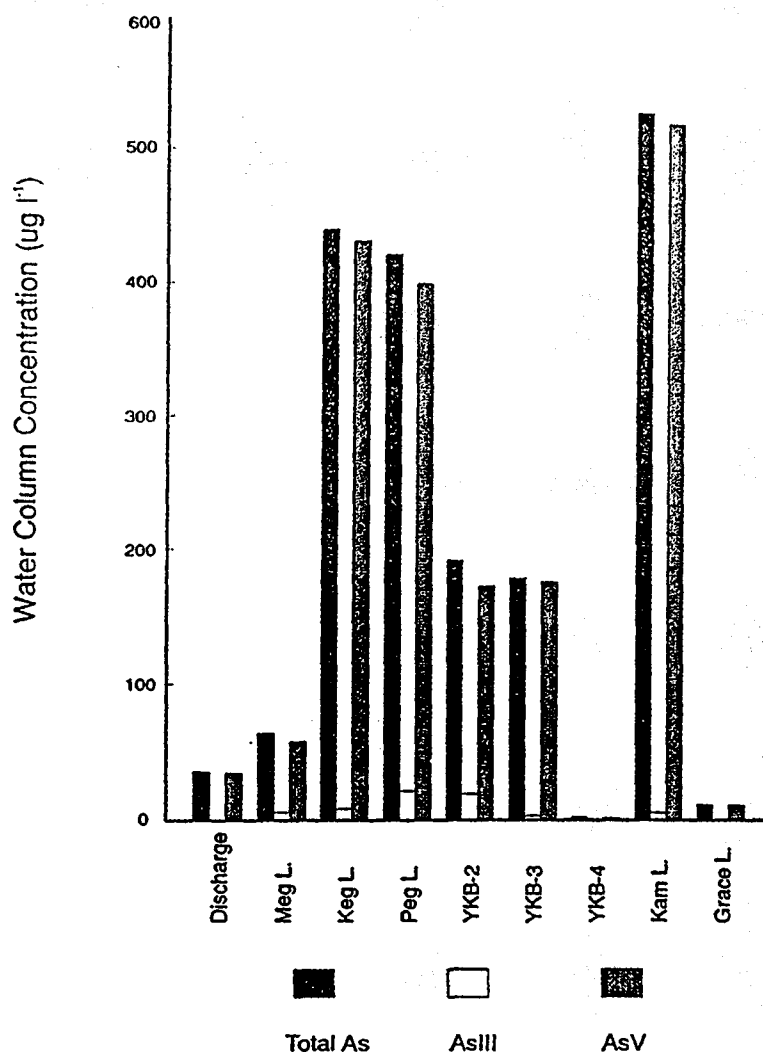


Fig. 4. Water column concentrations ($\mu\text{g l}^{-1}$) of arsenic (total), As(III) and As(V) in lakes downstream of gold mining discharge. Grace Lake is presented as a reference (see text).

Lake ($525 \mu\text{g l}^{-1}$), which has received periodic discharges in the past (Fig. 4). Sediment pore water and surface water concentrations found in the mining discharge were up to 300 times and 45 times (respectively) those detected in Grace Lake.

Distributions of arsenite (As(III)) and arsenate (As(V)) in sediment pore water were similar to total solid-phase arsenic across the systems studied, but pore water concentrations of arsenite were consistently higher than arsenate in the top 10 cm of sediment (Fig. 3). The reverse trend was found for concentrations of arsenite and arsenate in surface water (Fig. 4).

3.3. Accumulation in macrophytes

The highest concentrations of arsenic were found in the most commonly occurring submerged species, *Potamogeton pectinatus*, with levels up to $4990 \mu\text{g g}^{-1}$ (at Keg Lake

Table 2

Mean concentrations (standard deviations), ranges and concentration factors for arsenic measured in aquatic macrophyte tissues collected from various lake stations near Yellowknife in 1990 and 1991; plant concentration factor values (from sediments) exceeding one signify bioconcentration

Species and tissue	Average concentration (SD) ($\mu\text{g g}^{-1}$)	Range	Concentration factor (range)
<i>Typha latifolia</i>			
Shoots ($n=26$)	17.2 (31.9)	< 1.0–38	0.04 (0.0001–0.37)
Roots ($n=26$)	232 (206)	14–98	0.59 (0.005–2.80)
<i>Potamogeton pectinatus</i>			
Whole plants ($n=13$)	1219 (1220)	190–4990	2.93 (0.20–9.79)
Shoots ($n=2$)	751 (423)	328–1173	2.05 (0.38–3.73)
Roots ($n=2$)	592 (128)	464–719	2.75 (0.23–5.27)
<i>Equisetum fluviatile</i>			
Shoots ($n=3$)	34 (40)	5.5–91	0.10 (0.05–0.15)
Roots ($n=3$)	352 (369)	45–871	0.82 (0.48–1.15)
<i>Myriophyllum exalbescens</i>			
Whole plants ($n=3$)	143 (113)	30–255	1.27 (0.14–2.90)
<i>Triglochin palustre</i>			
Shoots ($n=1$)	40	–	0.04
Roots ($n=1$)	470	–	0.41
<i>Sparganium</i> sp.			
Shoots ($n=1$)	28	–	3.41
Roots ($n=1$)	133	–	0.72

Station 7); this far exceeded arsenic concentrations in any of the other species measured (Table 2). This submerged macrophyte contained As concentrations up to three orders of magnitude higher than roots or shoots of the most commonly occurring emergent, *Typha latifolia*, where they co-occurred (e.g. 41 and 98 $\mu\text{g g}^{-1}$ arsenic in cattail shoots and roots, respectively, from the same Keg Lake station). Other submerged species also tended to contain higher concentrations of arsenic.

Root tissues of all species analysed, except *Potamogeton* sp. (subdivided into roots and shoots at only two sites) tended to accumulate higher levels of arsenic than shoots (Table 2). This was particularly evident in *Typha* sp. (i.e. average root concentration: 232 $\mu\text{g g}^{-1}$ vs. shoots: 17.2 $\mu\text{g g}^{-1}$) for which the largest sample size was obtained ($n=29$, Table 2).

3.4. Spatial patterns of arsenic distribution in macrophytes among stations

Arsenic concentrations in root tissues of the most extensively occurring emergent species, *T. latifolia* tended to be greater in lakes closest to the present tailings discharge at Pud Lake (Fig. 5a). The highest levels were encountered in plants from Meg (maximum $790 \mu\text{g g}^{-1}$) and Keg Lakes (maximum $680 \mu\text{g g}^{-1}$), which corresponded to arsenic distribution patterns in sediments (see Fig. 2a). Concentrations in root samples from Peg Lake, Pud Lake, stations near Yellowknife Bay (YKB2 and YKB3) and Kam Lake were lower and less variable across sites, but still elevated relative to background levels at Madeline Lake (Fig. 5a). A similar distribution pattern occurred in *Typha* sp. roots (Fig. 5b).

The highest concentrations of arsenic in whole plants of *P. pectinatus*, the most extensively occurring submergent, were found in Keg Lake (maximum of $4990 \mu\text{g g}^{-1}$), which was closest to the discharge (Fig. 5c). Levels at this lake were up to 26 times the background concentration found in Madeline Lake ($190 \mu\text{g g}^{-1}$). Average arsenic levels in *Potamogeton* sp. from other lake stations were also elevated relative to the background (Fig. 5c).

3.5. Sediment–tissue relationships

Only copper in cattail (*Typha* sp.) roots and near-shore sediments (solid phase) measured in 1991 were found to share a significant positive relationship ($r=0.79$, $P<0.001$, $n=20$) across the different lake stations. No other significant correlations between tissues and sediment were found for the other elements (including arsenic) in *Typha* sp. roots or shoots ($r\leq 0.38$, $P\geq 0.09$, $n=20$).

Significant positive correlations between inorganic element concentrations in sediment and plant tissue were found for arsenic ($r=0.83$, $P=0.006$) as well as copper ($r=0.90$, $P<0.001$) for *Potamogeton* sp. tissue collected in 1991. No other statistically significant correlations were detected.

Root concentrations of arsenic in cattails appeared to decrease with increased pore water arsenic concentration based on measurements at five deep-water sediment stations in 1990, although the correlation was not statistically significant ($r=-0.77$, $P=0.22$). No such relationship was found for shoots. The correlations between arsenic in cattail roots and pore water arsenate and arsenite ($r=-0.59$ and $r=-0.51$, respectively) yielded similar results to total arsenic, but were also not significant. Concentrations of arsenic in *Potamogeton* sp. were not correlated to arsenic concentrations in the water column or sediment pore water; r values ranged from -0.02 to 0.34 ($P\geq 0.65$).

Although the correlations between concentrations of micronutrients (copper, zinc and manganese) in *Typha* sp. roots, and environmental arsenic concentrations (i.e. pore water, sediment and water column) were not all statistically significant and the sample size ($n=5$) was very small, the correlations were consistently negative (Table 3). Zinc and manganese had the highest coefficient (r) values. Correlation coefficients of shoot metal concentration and environmental arsenic concentrations were all considerably less than for root tissue ($P>0.13$). The only exception was the zinc level in *Typha* sp. shoots, which was significantly negatively correlated both with pore water arsenic concentrations (total arsenic: $r=-0.89$, $P<0.05$; arsenite: $r=-0.87$, $P=0.05$; arsenate: $r=-0.90$, $P<0.05$) and solid-phase As concentrations ($r=-0.92$; $P<0.05$). For *P. pectinatus*, only the manganese

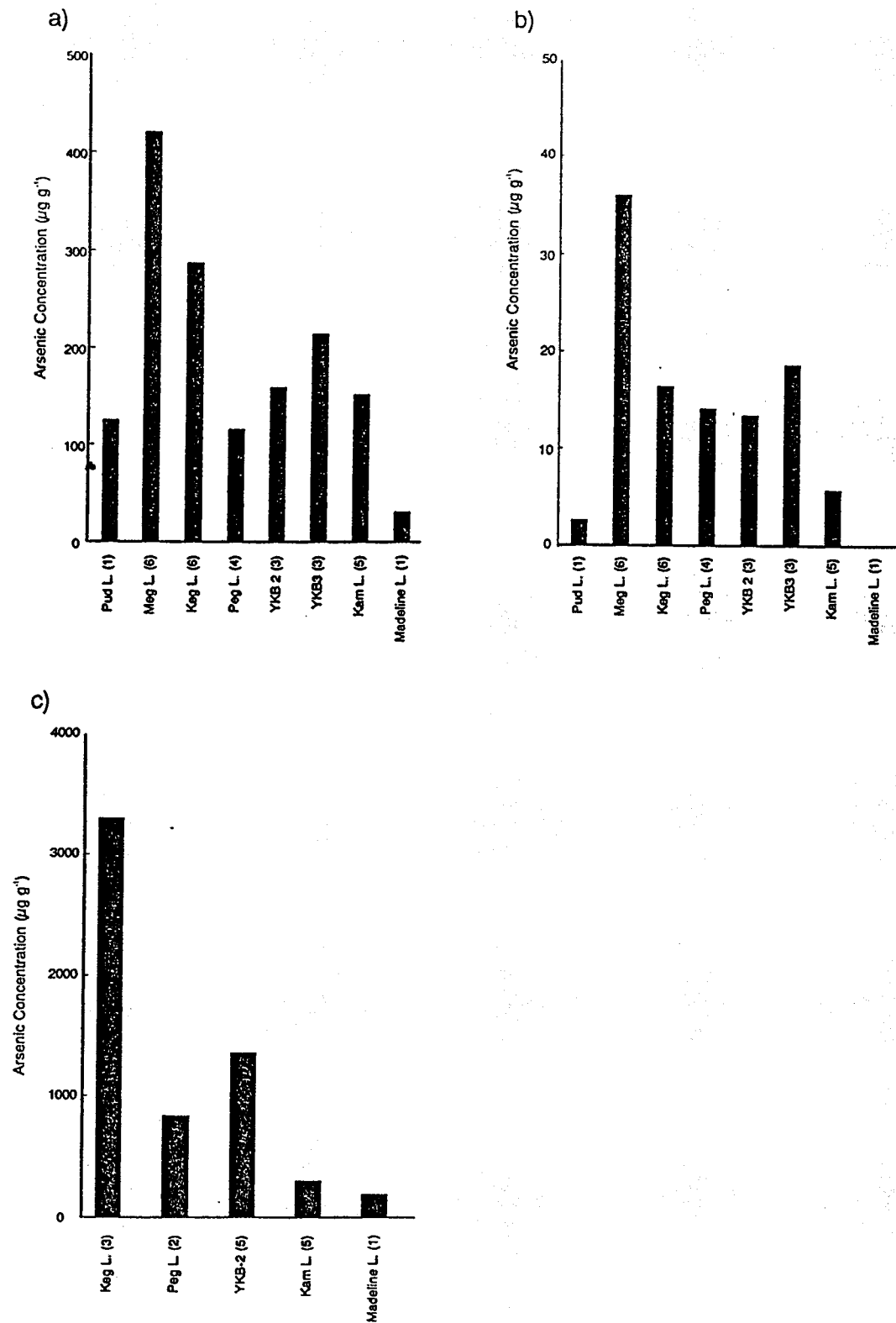


Fig. 5. Concentrations of arsenic ($\mu\text{g g}^{-1}$) in (a) root tissue and (b) shoot tissue of *Typha latifolia*, and (c) whole tissue of *Potamogeton pectinatus* (where sampled) in lakes downstream of gold mining discharge. Madeline Lake is presented as a reference (see text).

Table 3

Pearson correlations (and *P* values) between element concentrations in cattail (*Typha*, *n* = 5) roots from several lakes near Yellowknife and environmental concentrations of arsenic in 1990

Element	Sediment levels (average over 0–10 cm depth interval)				Water D As
	PW As	As (III)	As (V)	SP As	
Cu	–0.48 (0.83)	–0.55 (0.34)	–0.39 (0.52)	–0.49 (0.40)	–0.79 (0.12)
Zn	–0.76 (0.14)	–0.81 (0.10)	–0.66 (0.22)	–0.86 (0.06)	–0.66 (0.22)
Mn	–0.68 (0.24)	–0.69 (0.11)	–0.66 (0.13)	–0.56 (0.24)	–0.11 (0.80)

PW As, total dissolved pore water arsenic; As (III), pore water arsenite concentration; As (V), pore water arsenate concentration; SP As, total solid-phase arsenic concentration; D As, total dissolved arsenic in water. Probability values are indicated below by parentheses; *P* values ≤ 0.05 are statistically significant.

concentration in whole tissues of this species exhibited negative relationships with environmental arsenic (Pearson *r* value range: –0.64 to –0.95, *P* = 0.29–0.05).

The average height of *T. latifolia* stands (from the sediment–water interface to the tip of the inflorescence) tended to exhibit a negative relationship with increased sediment pore water concentrations of arsenic ($r = -0.89$, $P = 0.11$). At the same time, the estimated local height of *Typha* sp. stands was correlated with root concentrations of iron, zinc, and manganese concentrations ($r = 0.74$, 0.86 , and 0.97 , respectively; $P = 0.15$, 0.06 , and 0.007 , respectively).

Phosphate concentrations in the pore water of near-surface sediments were somewhat related to the extractable phosphorus content of dried sediments ($r = 0.79$, $P = 0.11$; $n = 5$). Arsenic uptake by neither *Typha* sp. roots nor whole *Potamogeton* sp., however, was significantly related to environmental phosphorus concentrations as measured by pore water or water column phosphate concentration, by readily extractable phosphorus in sediments, or ratios of environmental arsenic to phosphorus ($P \geq 0.25$). Correlations were indicated between *Typha* sp. shoot concentrations of arsenic and ratios of pore water total dissolved As:phosphate ($r = 0.82$, $P = 0.09$), arsenite (As(III)):phosphate ($r = 0.83$, $P = 0.08$), and total dissolved As:sediment extractable phosphorus concentrations ($r = 0.76$, $P = 0.14$); $n = 5$ for all correlations.

4. Discussion

4.1. Environmental distribution and bioavailability of arsenic

Lakes near Yellowknife, N.W.T., which receive gold mining discharge were highly contaminated with arsenic, as well as several other elements, compared with background systems in the region (i.e. Grace and Madeline Lakes). In fact, environmental arsenic concentrations in the sediment and water of Meg, Keg and Peg (and Kam) Lakes were

among the highest published values for lacustrine systems; for example, an observed maximum water column concentration of $525 \mu\text{g l}^{-1}$ compared with $251 \mu\text{g l}^{-1}$ reported by Lee et al. (1991) in Malaysia, or $250 \mu\text{g l}^{-1}$ found by Mudroch and Capobianco (1979) in Canada.

Elevated levels of dissolved arsenic in the water column as well as the sediments (i.e. pore water and solid phase) suggested that remobilization from historically contaminated sediments via dissolution associated with sediment diagenesis has occurred (see Bright et al. (1994)). Surface sediments (0–10 cm depth) in the lakes tended to be reducing, as suggested by the high ratio of arsenic III:V in pore water; arsenate predominates in the overlying water column. Such conditions tend to increase the solubility and mobility of arsenic and other contaminants from the sediments (Campbell et al., 1988) and, therefore, increase the potential for arsenic to enter the aquatic food chain. Arsenite (As(III)) is also reported to be more toxic than arsenate (As(V)) to aquatic organisms (Cullen and Reimer, 1989).

Higher concentrations of arsenic encountered in near-shore sediments relative to deep sediments at Meg and Keg Lakes and YKB3 were probably due to differences in sediment–substrate composition. The organic matter content of near-shore areas in these shallow lakes is considerably higher than in sediments removed from the shore, owing to the presence of large *Typha* sp. mats resulting from the dense proliferation of roots, rhizomes and detritus. The large number of potential binding sites for arsenic and other elements afforded by organic matter complexes in such substrate (Campbell et al., 1988) might explain the higher concentrations detected in the near-shore areas of these lakes.

The tendency for macrophytes to accumulate and, in many cases, bioconcentrate arsenic from the sediments in these lake systems confirmed that much of the environmental arsenic occurred in a highly available form. Concentration factor values (i.e. the ratio of the concentration in plant tissue to the concentration in sediments; Table 2) provide a means for assessing the relative bioaccumulation of arsenic by individual macrophyte species in a given locale. Submerged macrophyte species (particularly *P. pectinatus*) in this system showed a much greater potential to accumulate arsenic than emergents (e.g. cattail, *Typha* sp.). Similar results have also been found for submerged and emergent plants studied by Reay (1972) in naturally enriched waters, although no explanation is offered. Differences in arsenic accumulation observed here were probably related to the different growth forms and associated uptake physiology exhibited by emergent and submergent species in this system. *Potamogeton* sp. differed markedly from *Typha* sp. and other emergent species in that its foliage is entirely exposed to the surrounding water. Although root tissue is generally acknowledged to be the main route for metal or metalloid uptake in submerged macrophytes (see Jackson and Kalff (1993), Barko et al. (1991)), leaf uptake may also be significant in systems where the concentration in the surrounding water column is high (Guilizzoni, 1991); such was the case in some of the lakes studied here. Thus, foliar uptake may account for the higher arsenic levels detected in submerged species.

The availability of contaminants to resident biota is influenced by their environmental partitioning between various compartments, e.g. sediment particulates, pore water, and the water column. The ability to assess the relative influence of different compartments on the uptake of arsenic by different aquatic plants, however, was limited by a strong intercorre-

lation between arsenic concentrations in sediment (solid phase), pore water, and the water column ($r \geq 0.88$, $P \leq 0.009$, $n = 5$).

Physiological differences in arsenic uptake between the two species were also indicated based on relationships with sediment concentrations. Only *Potamogeton* sp. exhibited a significant positive relationship with sediment arsenic. Levels of arsenic within root tissue or shoot tissue of *Typha* sp. were not positively correlated with solid-phase sediment levels of arsenic. If anything, arsenic uptake into cattail (*Typha* sp.) tissues tended to be negatively related to sediment pore water concentrations. Otte et al. (1990) has also observed a negative relationship between arsenic concentrations in marshland soils and arsenic concentrations in roots of the emergent *Phragmites australis* (Cav.) Trin. ex Stead. (common reed). The most likely explanations for this trend may be either the concentration-dependent active exclusion of arsenic (negative feedback) or a toxic inactivation of uptake sites. Necrosis of root tissue surfaces associated with arsenic toxicity could conceivably limit the uptake of arsenic and other substances from the surrounding substrate. No evidence of a similar physiological response was indicated for *Potamogeton pectinatus*, owing to the small sample size available; this may also explain why much higher arsenic concentrations were accumulated by this species. Plaque formation on root surfaces may also play a limiting role by binding inorganic elements such as arsenic (Crowder and Macfie, 1986).

4.2. Phytotoxic effects of environmental arsenic

High environmental arsenic concentrations tended to be negatively related to *Typha* sp. stand height, which suggested the possible inhibition of growth in this species by arsenic contamination. Growth reduction is the most common symptom of arsenic phytotoxicity (Kabata-Pendias and Pendias, 1992) and can be accompanied by reduced nutrient concentrations in crops (Wallace et al., 1980). The positive relationship of *Typha* sp. stand height to root tissue concentrations of nutrients (zinc, manganese and iron), as well as the consistent negative correlations between micronutrient concentrations in *Typha* sp. roots and arsenic in sediments, also suggested that nutrient uptake inhibition by environmental arsenic may have been the underlying cause of growth inhibition. Cattails collected from high arsenic sites (Keg, Peg and Kam Lakes) showed considerable die-back of leaf blades, characterized by yellowing or browning and necrosis of the tips; these symptoms might be indicative of nutrient deficiency. Such symptoms (stunted shoot growth and necrosis) along with reduced species richness were generally observed to occur where sediment and water column arsenic concentrations exceeded $300 \mu\text{g g}^{-1}$ and $400 \mu\text{g l}^{-1}$, respectively; above these concentrations, *Typha* sp. stand height decreased from 2 m to 0.5 m where the highest arsenic levels were measured (Peg Lake). Water column concentrations here far exceeded levels reported to reduce macrophyte biomass ($50 \mu\text{g l}^{-1}$) in experiments using a freshwater model ecosystem by Reuther (1992). *Typha* sp. stands occurring at locations where water column concentrations were below $200 \mu\text{g l}^{-1}$ appeared to be relatively healthy.

Inhibited uptake of arsenic by *Typha* sp. (roots) tended to be accompanied by the inhibited uptake of essential trace metals and suggested a possible mechanism of arsenic toxicity associated with reduced growth. Although the relationships were not statistically significant, owing to the small sample size, the consistent negative correlation between environmental arsenic concentration (particularly sediment pore water) and the concentration of Cu, Zn,

Mn, and Fe in *Typha* sp. roots suggest that sites of uptake of arsenic and the essential metals examined are related; it would appear that arsenic inputs were the overriding factor controlling the uptake of other metals in this study area.

The potential for sediment copper effects on the uptake of manganese in *Typha* sp. tissues was also suggested by negative relationships between (total) copper in sediments and root and shoot concentrations of manganese ($r = -0.60$, $P = 0.005$; and $r = -0.44$, $P = 0.05$; respectively; $n = 20$) (Dushenko et al., 1991, unpublished data). Copper, therefore, could also serve to compound the effects of arsenic toxicity.

It is interesting to note that the distribution of *Potamogeton* sp. was not as extensive as for *Typha* sp. In fact, *Potamogeton* sp. was not found in the mine tailings pond at Pud Lake and was nearly absent in the adjacent Meg–Keg–Peg Lakes system, where environmental arsenic was the highest. Cattails, in contrast, were found in all of these areas, which suggests a greater tolerance in this emergent species to arsenic contamination and that the exclusion of arsenic by *Typha* sp. (roots) enables it to persist at higher environmental concentrations. In *Potamogeton* sp., no such mechanism appears to exist (i.e. arsenic is taken up in proportion to the sediment levels encountered), which would limit its distribution to areas of lower arsenic concentrations further away from the discharge. The high levels of detritus and organic silt, and anthropogenic sulphate enrichment (Bright et al., 1995) observed in this system, which would result in more suboxic conditions in sediments, may also contribute to the limited growth and distribution of this particular submerged species (see Van Wijck et al. (1992)).

Several laboratory and field plot manipulation studies have focused on the competition between arsenic and phosphate for soil or root adsorption sites (Otte et al., 1990; Lee et al., 1991). It has been proposed that the ratio of arsenic to phosphate could be a major determinant of biological uptake and toxicity in plants. Direct measurements of extractable phosphorus in sediments, or of phosphate in sediment pore water in this field study provided little insight into the relationship between arsenic concentrations in macrophytes (*Potamogeton* sp. or *Typha* sp.) and those in the various environmental compartments. Although the sample size analysed was small, few trends were evident to suggest that such relationships might exist, even with a larger sample size. Positive, significant relationships were indicated between arsenic in *Typha* sp. shoots and ratios of arsenate/phosphate in the pore water or solid-phase sediment. The interaction of arsenic and phosphorus in sediments may have some indirect effect on the accumulation of arsenic in shoot tissues.

The absence of any other relationships between arsenic and phosphorus in arsenic accumulation in macrophytes of this system may be due to any number of reasons. Arsenic levels in water and sediments in these systems were considerably higher than reported in experimental arsenate–phosphate studies (Otte et al., 1990; Lee et al., 1991) and this may have obscured any relationships with phosphate. The interaction between arsenic and phosphate under natural field conditions may also be more subtle than observed in manipulated experiments. In soils and sediments, arsenic–phosphate plant relationships could be modified by effects on mycorrhizal symbionts or other microorganisms within the rhizosphere, by chemical exchanges between the sediment, roots and specialized compartments such as root iron plaques (Crowder and Macfie, 1986; St. Cyr, 1989), or by some other physical–chemical modification resulting in subsequent secondary or tertiary responses by assimilative structures of the plant (e.g. pH, Jackson et al., 1991). Consequently, field studies are

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often difficult to interpret, but are further needed to resolve the extent to which arsenate and phosphate affect each other in terms of uptake and toxicity in aquatic plants.

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