



Indian and Northern  
Affairs Canada

Affaires indiennes  
et du Nord Canada

#16 Yellowknife Airport,  
Yellowknife, NT X1A 3T2

Your file    Votre référence

November 3, 1995.

Our file    Notre référence

Mr. Erik Madsen  
Superintendent, Environmental Services  
Royal Oak Mines Inc.  
N.W.T. Division  
P.O. Bag 3000  
Yellowknife, NT X1A 2M2

N1L2-0040  
N1L2-0043

Dear Mr. Madsen:

Enclosed are two recently published papers on Miramar Con's Meg-Peg-Keg system that I thought might interest you.

If you have any comments or questions on the papers, you should direct them to the respective authors.

Sincerely,

David S. Jessiman

Water Resource Officer  
Yellowknife District  
N.W.T. Region

cc: Water Resources, Yk.

encls/2.

Canada



ELSEVIER

The Science of the Total Environment 155 (1994) 237–252

the Science of the  
Total Environment

An International Journal for Scientific Research  
into the Environment and its Relationship with Man

## Arsenic transport in a watershed receiving gold mine effluent near Yellowknife, Northwest Territories, Canada

D.A. Bright<sup>\*a</sup>, B. Coedy<sup>b</sup>, W.T. Dushenko<sup>a</sup>, K.J. Reimer<sup>\*a</sup>

<sup>a</sup>*Environmental Sciences Group, Royal Roads Military College, FMO Victoria, British Columbia, V0S 1B0, Canada*

<sup>b</sup>*Water Resources Laboratory, Indian and Northern Affairs, P.O. Box 1500, Yellowknife, N.W.T., K1A 2R3, Canada*

Received 18 January 1994; accepted 20 January 1994

### Abstract

The presence of abnormally high concentrations of arsenic in sediment and water samples collected from a chain of small lakes afforded a unique opportunity to investigate the environmental partitioning and speciation of inorganic arsenic in fresh water. The distribution of arsenic in water, surface sediment (0–5 cm depth) and associated pore water downstream of the discharge differed from that expected due to conservative dilution and/or sediment adsorption from a point-source. Inorganic arsenic in the water column, sediment particulates and pore water exhibited a maximum concentration ~4–6 km downstream of the gold-mine input. Arsenite (As(III)) was the predominant arsenical in the sediment pore water throughout the watershed, whereas arsenate (As(V)) comprised the vast majority of dissolved arsenic in water column samples. Arsenite was not detected in the mine effluent, but was found in increasing concentrations in the water column with increasing downstream distance from the discharge pipe. There are two possible mechanisms for the downstream redistribution of historical arsenic inputs in this system: (1) bulk movement via sediment/particulate transport; and (2) redissolution from sediments during early diagenesis, followed by upward diffusion and transport to downstream areas. Sediment distributions of other substances which are 'tracers' of the gold-mine effluent (e.g. antimony, copper, gold, nickel, zinc, sulphate and chloride ion) were examined in order to distinguish between these mechanisms. Collectively, the data indicate that the arsenic distribution in surficial sediments of the study area is controlled partially by the bulk movement of sediments, followed by burial with less contaminated sediments in the upper reaches of the watershed. Particulate concentrations of arsenic contributed significantly to the total arsenic concentrations in the water column downstream of the gold-mine discharge (up to 70% of total As concentration). The extremely high concentrations of arsenicals in sediment pore water (up to 68.9  $\mu\text{M}$ ) and the overlying water column (up to 7.3  $\mu\text{M}$  in dissolved form) in areas further removed from the input, however, are attributable to remobilization from sediments through redox-related dissolution. This release of dissolved arsenic during sediment diagenesis may be enhanced by anthropogenically-enhanced sulfate deposition, also associated with gold-mining activity.

**Keywords:** Arsenic; Porewater; Remobilization; Diagenesis; Freshwater; Contaminant

### 1. Introduction

Arsenic can be highly toxic to various plants and animals. The toxicity, however, depends on

both the chemical speciation and on the environmental compartmentalization, i.e. the distribution of arsenicals in dissolved and particulate form, either in the water column or in the sediment [1]. Arsenic occurs in solution in natural aquatic systems in one of two oxidation states, +V and +III, and primarily in the inorganic form as the

<sup>\*</sup> Corresponding authors.

appropriately protonated forms of arsenate,  $\text{H}_3\text{AsO}_4$  (As(V)) and arsenite,  $\text{H}_3\text{AsO}_3$  (As(III)). Several recent papers have focused on arsenic in freshwater systems [2–8]. Aggett and O'Brien [2] provided the first detailed model of lacustrine arsenic cycling; in seasonally stratified lakes, dissolved arsenic is removed from the water column by adsorption onto sediments during oxic conditions but undergoes release from sediments into the hypolimnion during bouts of anoxia. Many studies have emphasized the importance of iron- and, to a lesser extent, manganese-cycling in controlling the partitioning of arsenic in lacustrine systems [2,9], in coastal marine systems [10–13], in terrestrial soils [14] and at deep ocean hot vents [15]. In these models, arsenic, as arsenate, co-precipitates with particulate or colloidal iron and manganese hydroxides under oxic conditions and is removed from solution.

Although several studies have addressed the relationships between arsenic and iron in aqueous environments, there may be other important controls of arsenic solubility and bioavailability. The decomposition of organic detritus by sulfate-reducing heterotrophic bacteria in sub-oxic sediments and water produces free sulfides and secondarily causes the reductive dissolution of arsenic, principally as arsenite. Cullen and Reimer [1] reviewed the possible controls on arsenic solubility through the further complexation as relatively insoluble arsenic sulfides, e.g. orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{As}_4\text{S}_4$ ) or arsenopyrite ( $\text{FeAsS}$ ): they concluded that, given the large number of known arsenic-containing minerals, the limited data on solubility product constants and the lack of knowledge on the rates of product formation or dissolution, the present knowledge does not allow reasonable predictions of arsenic solubility in sulfide-rich, anoxic environments. Yet, microbial sulfate reduction is the dominant process in marine environments for anaerobic decomposition of detritus and significantly influences the diagenesis of many other elements — e.g. copper, zinc, lead and cadmium [16–18] — by producing free sulfides capable of reacting to form poorly soluble metal sulfides. Sulfate concentrations in the water or sediment pore water of lacustrine systems are much lower and more

highly variable than in marine systems [19] and sulfate reduction is therefore of secondary importance for the anaerobic decomposition of organic matter compared with methanogenesis. Consequently, the relative importance of sulfate reduction for the cycling of other substances in freshwater lakes is unclear. It should be noted, however, that many anthropogenic discharges contribute nutrients such as sulfates and phosphates as well as arsenic to lacustrine systems and these may influence microbially mediated sediment diagenesis. A better understanding, therefore, of all of the major factors which enhance or limit arsenic remobilization from lacustrine sediments is required.

Knowledge of arsenic cycling is important for predicting the potential for remobilization of dissolved arsenic from materials such as mine waste and to assess the potential for biological impacts. Considerably less is known about lacustrine than marine arsenic geochemistry, in part because naturally-occurring arsenic concentrations are generally much lower than in marine systems and are near typical analytical detection limits. The watershed downstream of a gold-mine discharge near Yellowknife, Northwest Territories, Canada offers a unique opportunity to investigate environmental cycling due to the anthropogenically elevated arsenic concentrations found there. The high concentrations of arsenicals and other substances (including sulfur) also afford an opportunity to discriminate between particulate-based and solubility-based mechanisms for the downstream transport of arsenic. This study examines the downstream transport of inorganic arsenicals (as arsenate or arsenite).

## 2. Materials and methods

### 2.1. The study site

The Nerco Con Mine is one of two mining and extraction operations in close proximity to Yellowknife, Northwest Territories, Canada. The Nerco Con Mine has been in operation since 1938 and initially roasted gold-bearing ores to remove arsenopyrite — a component which interferes with the cyanide extraction of gold. Hocking et al. [20] described the local contamination of

soil and vegetation associated with aerial emissions of sulfur dioxide ( $\text{SO}_2$ ) and arsenic trioxide ( $\text{As}_2\text{O}_3$ ) produced by roasting. Wet scrubbers were installed on the Nerco Con stack in 1949, which reduced aerial arsenic emissions to 7% of the previous levels: the recovered slurry was stored in two bedrock depressions on the mine site.

The mill effluent, which at times contained arsenic, cyanide and mercury, was initially discharged into a series of shallow basins. When these basins were filled in the early 1970s, the tailings were routed directly into Pud Lake (Fig. 1). Prior to 1983, treatment of the effluent in-

involved the settlement of solids and decanting of overlying water to a small flood plain below Pud Lake containing old tailings deposits. The decanted waste water ultimately drained into Meg Lake. Effluent decanted from the Pud Lake tailings pond was re-routed in 1985 to minimize remobilization of historical tailings-deposits, and is now discharged into a drainage ditch leading directly into Meg Lake. The present treatment of mine-tailings/effluent, which also commenced in 1985, involves the addition of peroxide to oxidize cyanide to cyanate, the addition of ferric sulfate and lime to precipitate arsenic as ferric arsenate

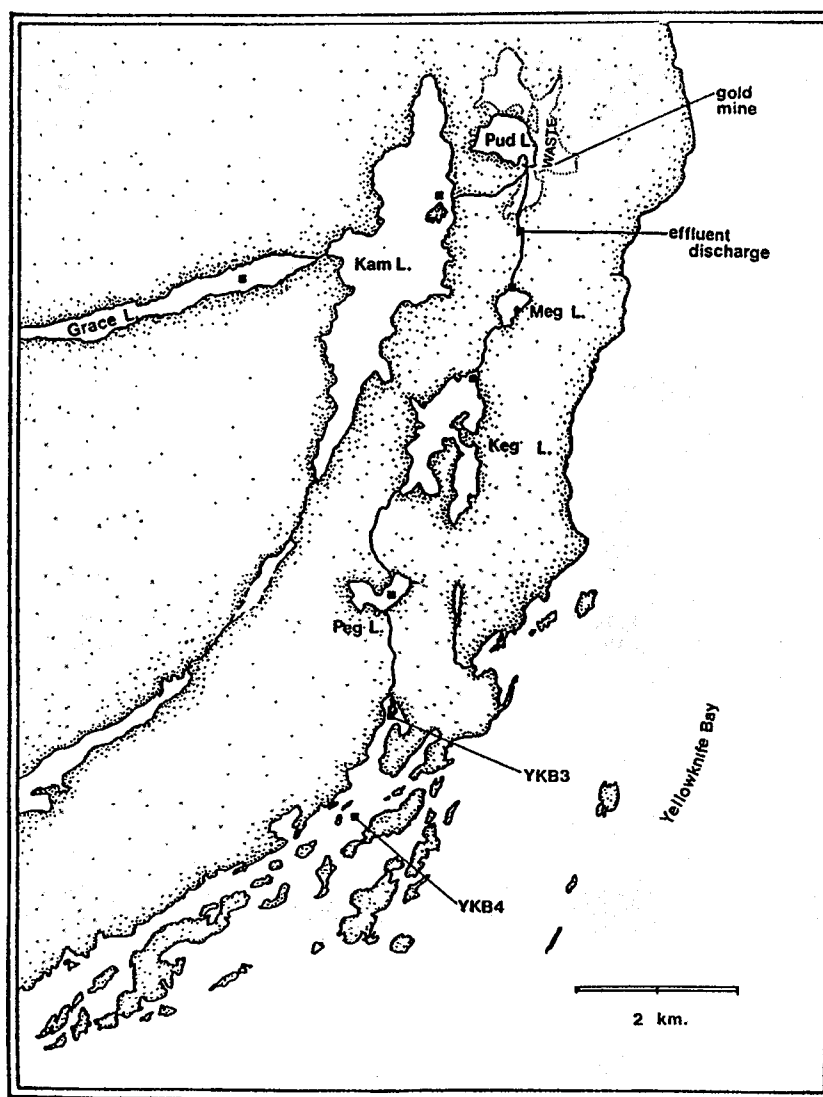


Fig. 1. Map showing the site locations for collection of sediment cores or water in the lakes near Yellowknife affected by gold mine effluent.

( $\text{FeAsO}_4$ ) and the addition of polyacrylamide flocculant to enhance sedimentation. Consequently, most of the arsenic is presently precipitated in the tailings pond and the concentration released with the effluent has declined relative to historical levels.

Meg, Keg and Peg Lakes comprise a series of shallow (< 2 m maximum depth), organic-rich lakes which eventually drain into the southwest Yellowknife Bay, Great Slave Lake. Moore et al. [21] and Wageman et al. [22] investigated the arsenic contamination in water, sediment and biota in the Meg, Keg, Peg Lake, southwest Yellowknife Bay system.

Although Kam Lake is not in the Meg, Keg, Peg Lake drainage system, it was included in this study because of its previously documented contamination by arsenic, copper and zinc [23]. Kam Lake (Fig. 1) received several accidental discharges of effluent and tailings from the Nerco Con (then Cominco Con) mine-tailings pond in the early 1970s and has also been subjected to nutrient enrichment through raw sewage discharge from Yellowknife [23]. Grace Lake, which is located farther away from the Nerco Con Mine and flows into Kam Lake via a small stream (Fig. 1), was included as a reference lake for Kam Lake and the Meg, Keg, Peg Lake system.

## 2.2. Sampling procedures

Sediment cores and surface water were obtained from one site in each of the Meg, Keg and Peg Lakes, and at three sites in southwest Yellowknife Bay near the Meg, Keg, Peg Lake discharge, during 21–29 August, 1990 (Fig. 1). Sediment cores were obtained using a 9.0-cm diameter gravity corer deployed from a small boat. The corer was constructed of either a 122-cm or 91-cm long polyacrylic tube mounted on an aluminum-alloy head with detachable lead weights and fitted with a stainless steel cutter/catcher. The ambient atmospheric temperature during the collection and transport of cores was invariably slightly lower than the actual temperature of the lake sediments; therefore, no special precautions were taken to insure that the cores remained cool. Core sediment temperatures were not observed to exceed 12°C before or during sectioning.

The cores were transported back to the laboratory within 3 h of collection and stored for a maximum of 18 h in a walk-in cooler at 4°C. The cores were then extruded from the polyacrylic core tube in a nitrogen-filled glove bag and divided into 5 cm sections with a teflon-coated knife. All core sections were squeezed through a 0.22  $\mu\text{m}$  Millipore filter under a nitrogen atmosphere using previously established techniques [24]. We have previously found that extraction of pore water from marine sediments through 0.45- $\mu\text{m}$  filters, as is often practiced, invariably resulted in lower measured concentrations of dissolved, hydride-reactive arsenicals than when extracted through 0.22- $\mu\text{m}$  filters. This paper reports only the surface sediment data, i.e. the top 5 cm of each core.

The first 5 ml of extruded pore water was discarded. The remaining pore water was split under a nitrogen atmosphere into metal-free 50 ml Evergreen<sup>TM</sup> containers. Samples to be used for the analysis of arsenic speciation, as well as phosphate, sulfate, ammonia and chloride ion were immediately frozen over dry ice.

Surface water samples at each coring location were obtained by immersing the mouth of an acid-washed 4-l polyethylene container ~30 cm below the surface. The samples were then transported to the laboratory, filtered through Whatman 934-AH filters (1.5  $\mu\text{m}$  pore size) and immediately frozen over dry ice. A parallel series of analyses was conducted on unfiltered water in order to assess potential contaminant redistribution via dissolved and suspended particulate mechanisms.

Lake water was also collected during the winter of 1991 (21 Jan. and 29 Apr., 1991), when the system was covered with a thick layer of ice or just commencing spring break-up. Water samples were obtained through a hole drilled in the ice, immediately below the lower ice surface, at stations YKB4, YKB3, the Kam Lake sediment station and ~100 m downstream of the sediment station at Keg Lake. The oxygen concentration of the water was measured using Winkler titrations in order to examine possible anoxia associated with the ice cover. Filtered and unfiltered samples were later analyzed for arsenicals as described below.

### 2.3. Analyses

**Sediment.** Elemental analyses of the solid phase of the sediment were carried out by the Analytical Services Unit at Queen's University. The following elements were measured in the sediment solid phase of cores employing neutron activation analysis (NAA): As, Al, Ca, Cl, Mn, Na, V, Br, Fe, K, Sb, Sc and Au. Concentrations of Cu, Cr, Ni, Co, Cd, Pb and Zn were determined by flame atomic absorption spectroscopy (AAS).

For AAS, previously frozen sediments were air dried and ground to a fine powder. Approximately 0.5 g dry weight of sample was digested by heating with 2 ml of nitric acid and 6 ml of hydrochloric acid in test tubes heated in an aluminum block, such that the volume was reduced to ~0.5 ml overnight. Sample volumes were then made up to 25 ml.

For NAA, previously frozen, dried and ground sediments were irradiated using the SLOWPOKE reactor facility at the Royal Military College, Kingston. The sample (0.35–1.2 g) was weighed into 1.5 ml polyethylene vials and heat sealed. A flux of  $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$  was employed and counting was accomplished using a GMC HpGe detector coupled with a Nuclear Data  $\mu$ MCA. For short-lived isotopes, including Al, Ca, Cl, Mn, Ti and V, an irradiation time of 1 min was employed, followed by a 15-min delay time and a 10-min counting time. For long-lived isotopes (As, Au, Br, Fe, K, La, Na, Sb, Sc), irradiations of 2 h followed by an 80–120-h delay time and 1.5-h counting time were used.

**Water samples.** Frozen lake water and pore water samples were transported to the Royal Roads Military College for determination of inorganic and organic arsenicals using hydride-generation/AAS methods similar to those described by Reimer [24] and modified from the methods of Andreae [25] and Braman et al. [26]. Gaseous arsines were liberated from arsenicals (arsenite, arsenate, monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsene oxide (TMAO) and others) dissolved in aliquots of pore water or water column samples by the addition of borohydride (4%  $\text{KBH}_4$ ) to a 60-ml reaction vessel, in two steps: (1) the aliquot in the reaction vessel was initially buffered with tris-HCl to pH 6 prior to the addition of borohy-

dride for the determination of As(III) species such as arsenite; and (2) following the determination of As(III) species, the sample was acidified to pH 1 by the addition of 4 M HCl to facilitate borohydride-mediated liberation of arsines from As(V) species such as arsenate, MMAA, DMAA and TMAO. As part of both steps, the arsines were purged by means of helium gas from the reaction vessel through a  $-78^\circ\text{C}$  trap employed to remove water, and then collected in a teflon U-tube immersed in liquid nitrogen. After a 5-min trapping period, the liquid nitrogen bath was replaced with a  $50^\circ\text{C}$  water bath and the trapped arsines were swept in a stream of helium through a  $50\text{--}60 \text{ cm} \times 1.2 \text{ mm i.d.}$  teflon column filled with Poropak PS 60/80 contained in a GC oven cycled from  $50$  to  $150^\circ\text{C}$ . The arsines at the distal end of the column were monitored with an Instrument Laboratories 351 Atomic Absorption Spectrophotometer in a hydrogen air flame within a quartz cuvette. The detection limits were observed to be 0.2 ng for arsenite and 0.4 ng for arsenite, MMAA, DMAA and TMAO. The arsenical concentrations were found to be within 15% R.S.D. (relative standard deviation), based on the analyses of replicates. Filtered and unfiltered water samples collected for the discrimination of dissolved versus particulate arsenic levels were acidified to dissolve arsenic in particulates prior to the analysis by hydride-generation AAS for total arsenic.

Iron and manganese concentrations in pore water were determined by flame AAS. Nutrient analyses were carried out at Queen's Analytical Services Unit, Kingston. Chloride and sulfate concentrations were determined by ion-exchange chromatography. Ammonia (as N) was determined by an ion-specific electrode and phosphate (as P) by colorimetry.

## 3. Results and discussion

### 3.1. The spatial variation of arsenic

The input of arsenic and other contaminants into the Meg, Keg, Peg Lake discharge has undoubtedly varied during the operation of the mine, as well as seasonally. Surface sediments, nonetheless, reflect the most recent history of contaminant deposition and subsequent modifications

during early diagenesis. Likewise, although the mean residence time of water in the lakes is not known, water-borne concentrations should reflect recent inputs and geochemical processes. The downstream spatial variation in the As concentrations at the top of the water column (Table 1), in the top 5 cm of sediment, and in the corresponding interstitial water (Table 2), are displayed in Fig. 2. The vertical distributions of arsenic and other substances in the water column were not examined because the Meg, Keg and Peg Lakes do not exceed 2 m in depth and appeared to be well mixed at the time of sampling. During this investigation, organoarsenicals such as monomethylarsonic acid, dimethylarsinic acid and trimethylarsine oxide and other species not previously reported in the published literature were routinely observed in the lake water or sediment pore water at low concentrations ( $< 10\%$  of total dissolved As): these are examined in a separate paper (in prep.)

Impacts associated with gold-mine activity were clearly evident from the observed high concentrations of contaminants (Table 2). The concentrations of arsenic in the water column are amongst the highest ever documented: concentrations in the Meg, Keg, Peg Lake discharge or in Kam Lake ranged from  $\sim 0.8 \mu\text{M}$  to  $7.3 \mu\text{M}$ , compared with a range of  $0.01\text{--}0.60 \mu\text{M}$  for water from some of Europe's most polluted rivers [7] or a range of  $0.0069\text{--}230 \mu\text{M}$  in California Lakes [27]; Canadian and U.S. drinking water regulations specify an upper limit of  $0.6 \mu\text{M}$ . Given the

limited spatial extent, however, of the Meg, Keg and Peg Lakes, it is perhaps more important to examine the potential for more widespread re-distribution of arsenicals into Great Slave Lake. The water-borne concentrations of arsenic resulting from anthropogenic input in southwest Yellowknife Bay (i.e.  $0.027 \mu\text{M}$  at YKB4; Fig. 1) can be compared with levels from more remote areas. Arsenic concentrations in unfiltered samples of surface water from Kam Point, Great Slave Lake, which is  $\sim 5 \text{ km}$  away from station YKB4 in Yellowknife Bay, ranged from  $0.015$  to  $0.019 \mu\text{M}$ . The surface water arsenic concentration near Hay River, southern Great Slave Lake, was  $0.006 \mu\text{M}$  (Bright and Reimer, pers commun). The concentration of arsenic in the solid phase of surficial sediment in southwest Yellowknife Bay was  $115$  and  $174 \mu\text{g g}^{-1}$  at stations YKB3 and YKB4, respectively, compared with arsenic concentrations of  $13\text{--}14 \mu\text{g g}^{-1}$  in surficial sediments from the central basin of Great Slave Lake, as measured by x-ray fluorescence spectroscopy [32], or by standard acid-digestion, borohydride-generation, AAS techniques [33].

If the arsenic concentrations were controlled principally by a point-source input (from the effluent pipe) followed by successive dilution and adsorption to sediments, then As concentrations in the sediment and water should decrease progressively down the Meg, Keg, Peg Lake discharge. This was the case in earlier (1977/78) investigations conducted by Moore et al. [21] in the same watershed; in that instance, the highest arsenic concentrations were found in the lake nearest the effluent pipe and decreased down the watershed (Fig. 2a). Quite a different picture emerged from the more recent work presented here: the concentration of arsenic in the solid phase of surface (0–5 cm) sediments (Fig. 2a) was highest at Peg Lake ( $3090 \mu\text{g g}^{-1}$  dry wt.) and decreased both toward the effluent pipe and toward Yellowknife Bay. The arsenic concentrations measured in the study reported here were also higher than those of Moore et al. [21]; however, the data are not directly comparable because different analytical methods were employed (NAA versus AAS).

The downstream pattern of the total dissolved

Table 1  
Relative amounts of arsenic associated with particulates in the water column of the Meg, Keg, Peg Lake system

Sample	Total arsenic ( $\mu\text{M}$ )		Percent of total as particulate matter
	Unfiltered (acid-digested)	Filtered	
Effluent discharge	2.17	0.67	69.3
Meg L.	1.37	0.84	38.8
Keg L.	8.01	7.27	9.3
Peg L.	7.23	5.17	37.6
YKB2	4.09	3.03	26.1
YKB3	4.43	3.23	24.1
YKB4	0.027	0.027	0

Table 2

The spatial distribution of chemical variables in the top 5 cm of sediment and pore water along a watershed subjected to the discharge of gold mine effluent, near Yellowknife, Northwest Territories.

Variable	Station						
	Grace	Meg	Keg	Peg	YKB3	YKB4	Kam
Pore water							
(August, 1990)							
DAs-total ( $\mu\text{M}$ )	0.20	18.3	16.0	68.9	0.63	0.92	14.9
As(V) ( $\mu\text{M}$ )	0.09	8.8	3.6	28.6	0.35	0.69	3.8
As(III) ( $\mu\text{M}$ )	0.11	9.4	12.4	40.3	0.28	0.20	11.1
Fe ( $\mu\text{M}$ )	198	103	104	138	668	248	9.5
Mn ( $\mu\text{M}$ )	128	16	42	29	31	54	19
$\text{PO}_4^{3-}$ ( $\mu\text{M}$ )	7.7	17.1	11.9	21.0	7.1	< 3	27.7
$\text{SO}_4^{2-}$ (mM)	< 0.5	3.0	4.8	5.3	4.7	< 0.5	0.3
$\text{NH}_4^+$ ( $\mu\text{M}$ )	89	157	79	71	11	70	10
$\text{Cl}^-$ (mM)	1.1	120	156	153	155	18	4.8
Solid phase							
As	22.3	1160	1043	3090	115	174	2186
Sb	0.6	50.0	18.0	141	4.6	22.8	257
Fe (%)	3.34	3.35	3.94	2.65	2.93	3.66	3.90
Mn	1980	489	336	233	245	560	502
Ca (%)	1.20	3.66	1.47	2.66	11.3	1.03	1.56
Na (%)	1.10	1.16	1.41	0.98	1.01	0.75	1.27
Br	71	45	46	330	142	740	72
K (%)	1.7	1.5	2.5	0.8	1.8	2.0	2.3
Al	6.7	5.8	7.6	3.4	7.8	7.5	7.4
Au	0.04	0.79	1.58	6.75	0.13	0.37	1.49
Cu	38.9	781	151	232	38.6	147	1195
Zn	159	404	114	147	135	172	267
Pb	< 10	72	< 10	< 10	< 10	19	49
Ni	41.9	129	65.3	211	41.6	57.3	127
Co	18.4	22.2	26.8	61.3	13.7	18.0	49.7
Cr	82	74	74	40	52	40	75

Concentrations are expressed as  $\mu\text{g g}^{-1}$  unless otherwise indicated.

arsenic concentration (DAs) in surface sediment pore water closely paralleled that of the sediment solid phase (Fig. 2b). In fact, solid phase and pore water As concentrations in the top 5 cm of sediment from all sites, including Kam and Grace Lake, strongly covaried (Fig. 3; Pearson  $r = 0.88$ ,  $P = 0.009$ ,  $n = 7$ ). The near-surface As concentrations reported here did not always correspond with pore water DAs maxima in vertical core profiles; however, pore water DAs tended to correlate with solid phase As both within and between cores collected from the Meg, Keg, Peg Lake, southwest Yellowknife Bay system (Bright et al., in prep.). The Pearson correlation calculated from solid phase and pore water concentra-

tions at the depth of the pore water maxima was 0.89 ( $P = 0.008$ ,  $n = 7$ ). This contradicts the conclusion by Peterson and Carpenter [10] that pore water dissolved arsenic (DAs) is proportional to solid phase As at the depth of the pore water maximum for marine but not lacustrine sediments.

The maximum arsenic levels in the water column were also found in the Meg and Peg Lakes, ~2–6 km down the system from the discharge (Table 1, Fig. 2c).

### 3.2. Seasonal lakewater trends

Water samples were collected during the middle of winter (21 January 1991) and during the

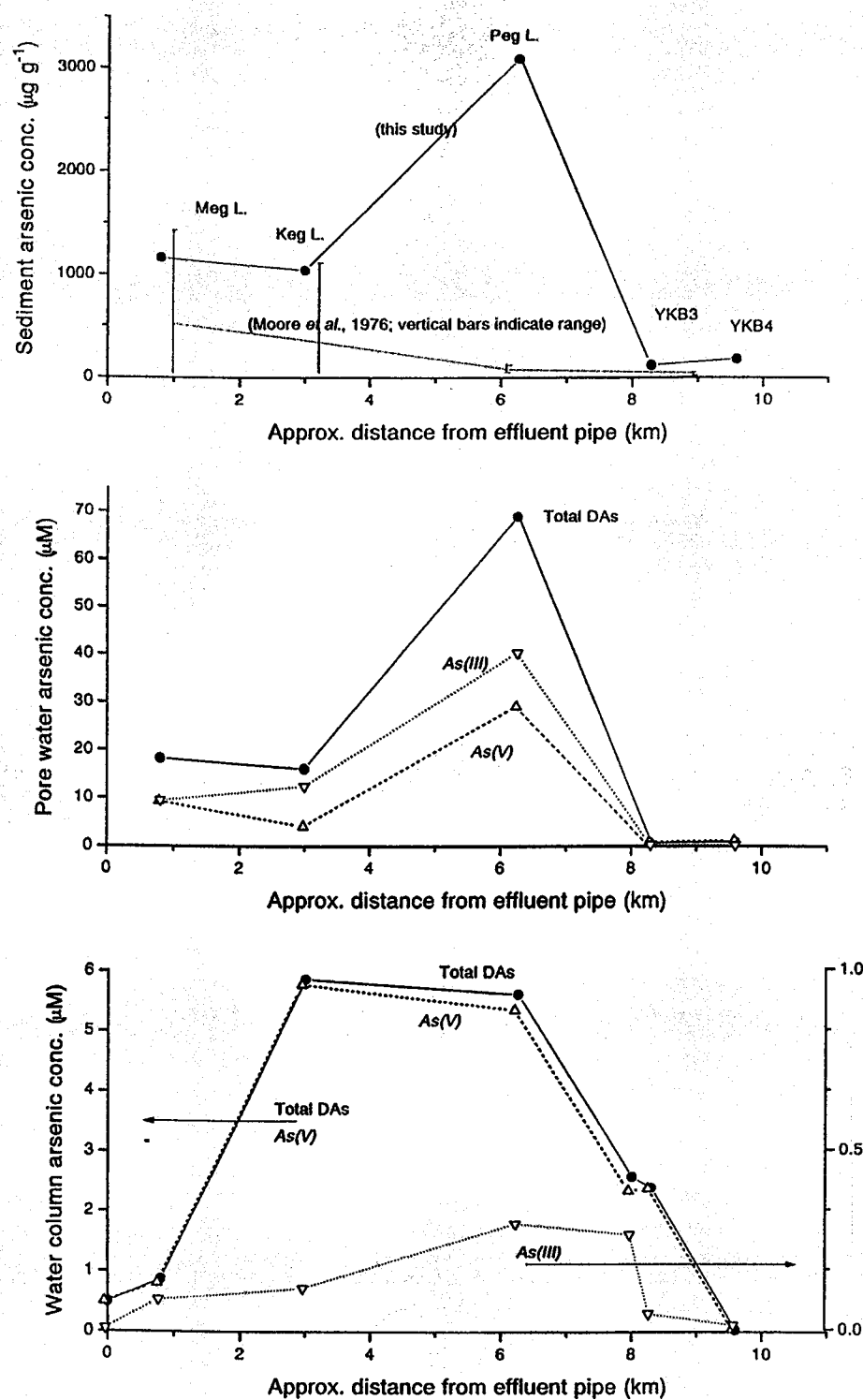


Fig. 2. The spatial distribution and chemical speciation of arsenic in the Meg, Keg, Peg Lake, southwest Yellowknife Bay discharge in (a) the solid phase of the top 5 cm of sediment, (b) the pore water of the top 5 cm of sediment, and (c) the overlying water column. The spatial patterns do not support a model of conservative dilution and/or sediment adsorption from a point-source discharge.

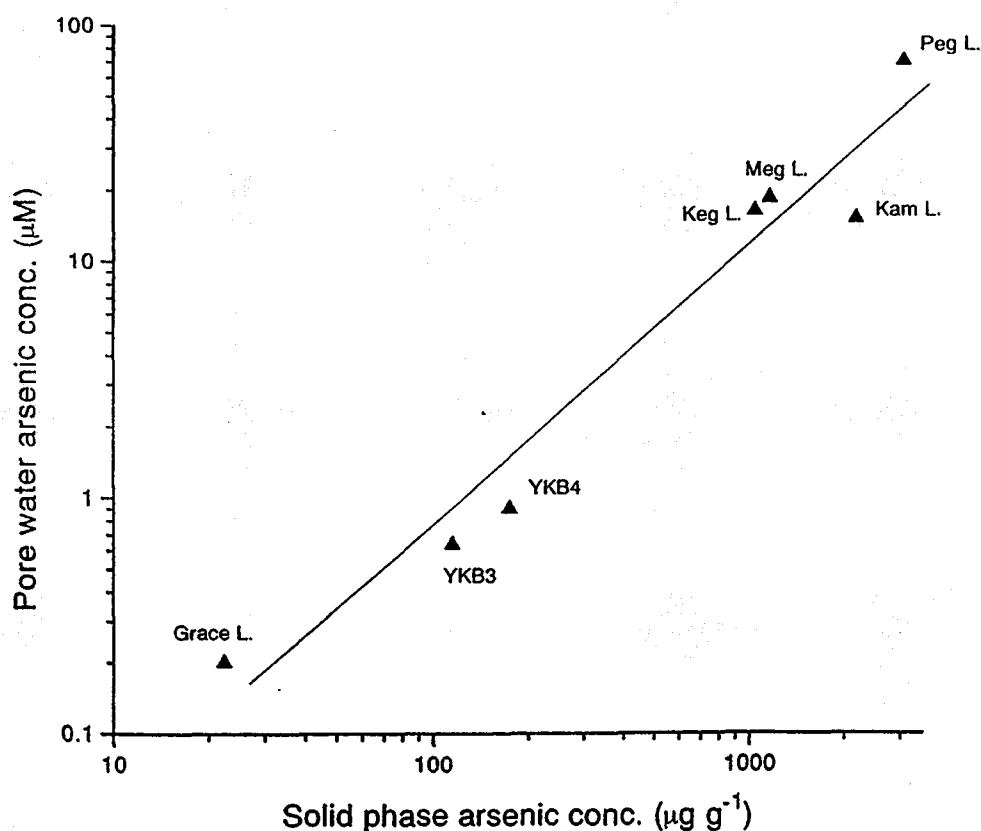


Fig. 3. Covariation of total dissolved arsenic concentration (DAs) in the pore water of the top 5 cm of sediment and the solid phase arsenic concentration. The Pearson correlation between pore water DAs and solid phase As was 0.88 ( $n = 7$ ,  $P = 0.009$ ).

early spring break-up (29 April 1992) to investigate possible seasonal trends in arsenic remobilization from sediments. The water column is sufficiently shallow in most of the Meg and Peg Lakes and in the Great Slave Lake embayment which receives the Meg, Keg, Peg Lake discharge (upstream of station YKB3), that the water froze all the way to the sediment surface during the winter. A thin ( $\sim 5$ – $10$  cm) layer of unfrozen water was found between the sediment surface and the ice at station YKB3 in January; however, the thin layer precluded drilling through the ice without disturbing the underlying sediment.

The dissolved oxygen level within the water column of Great Slave Lake at station YKB4 (Fig. 1) was  $9.7 \text{ ml l}^{-1}$  in January and  $8.1 \text{ ml l}^{-1}$  in April 1991. There was no evidence that Kam Lake was anoxic during January 1991 ( $\text{O}_2$  levels varied from  $11.2 \text{ ml l}^{-1}$  immediately under the ice to  $6.3 \text{ ml l}^{-1}$  1 m above the sediment; the depth

of the water column was 12 m). Overall, the data indicate that station YKB4 at Great Slave Lake did not experience seasonal anoxia associated with ice cover; nor was there evidence of anoxia at Kam Lake. The water column oxygen concentration at the Keg Lake site during the time of ice break-up in April was  $1.2 \text{ ml l}^{-1}$ , indicating that some under-ice  $\text{O}_2$  depletion had occurred; however, the anoxia was not severe.

The concentrations of dissolved arsenicals in lake water were as low as, or in some cases lower than those measured during the summer (i.e.  $0.027 \mu\text{M}$  TDAs at YKB4 in August 1990 compared with  $0.040 \mu\text{M}$  in January or  $0.015 \mu\text{M}$  in April;  $7.3 \mu\text{M}$  TDAs in August 1990 in Keg Lake compared with  $0.95 \mu\text{M}$  in April 1991). This would be expected, since the water column did not become severely reduced during the winter and the freeze-up of the drainage minimized the outflow of more highly-contaminated waters from

upstream. Overall, seasonal anoxia was minimal and did not contribute to the remobilization of arsenic from sediment during 1990/1991 via increased dissolution and upward diffusion.

Unfiltered lake water samples collected at station YKB4 in January or April did not contain substantially elevated levels of arsenic compared with filtered samples. The difference between unfiltered and filtered sample concentrations of total arsenic was within the analytical precision of the analysis for samples collected in January and April, suggesting that little if any was associated with particulates. In Keg Lake water collected in April, the total arsenic concentration in the unfiltered sample was  $2.9 \mu\text{M}$ , compared with  $0.95 \mu\text{M}$  for the filtered sample (i.e. the estimated percent of arsenic in the water present as particulate matter was 67%). This percentage of arsenic present as particulates was much higher than for the preceding August (Table 1), suggesting that seasonally-modified particulate transport of arsenic is important in downstream arsenic transport (see section 3.3, however).

### 3.3. Mechanisms of arsenic transport

The non-conservative downstream distributions of arsenic in the sediment, pore water and water column of the Meg, Keg, Peg Lake discharge can be partially attributed to recent declines in levels of arsenic in the mine effluent. The arsenic concentration in gold-mine effluent in August, 1990, was low in comparison with historical data, i.e.  $\sim 0.67 \mu\text{M}$  in solution (the estimated effluent discharge rate was reported by Nerco Con officials to be  $\sim 80\,000 \text{ l min}^{-1}$ ) compared with a range of  $0.53\text{--}75 \mu\text{M}$  between 1970 and 1976 [23]). This further suggests that the current spatial distribution of arsenic is primarily due to historical inputs. The downstream flux of arsenic in the Meg, Keg, Peg Lake system and remobilization of historically-deposited arsenic within the sediment might be controlled by two possible mechanisms: (1) bulk movement via sediment/particulate transport, and (2) redissolution from sediments during early diagenesis, followed by upward diffusion to the overlying water and transport to downstream areas. The distributions of arsenicals (arsenite and arsenate) as well as

other substances associated with effluent input are examined below in order to differentiate between the two possible mechanisms.

*Bulk transport of particulates.* The downstream transport of arsenic might be substantially influenced by water-borne particulates. The concentration of arsenic contained in particulates was calculated by subtracting the arsenic concentration in filtered samples from the arsenic concentration in unfiltered, acidified samples. Hence, the particulate concentrations shown in Table 1 are expressed as a percentage of the total arsenic in the water sample rather than as relative to the dry weight of filtered particulates. Particle-associated arsenic was not a significant portion of the total water column concentration at station YKB4 but accounted for  $\sim 70\%$  of the total arsenic concentration of the effluent discharge (Table 1). A general decrease in the percentage of particle-associated arsenic down the watershed suggests a net deposition of discharged particulates following effluent discharge, with very limited resuspension and entrainment beyond the Meg, Keg, Peg Lake outflow. The bulk transport of particulates, therefore, also influences the downstream arsenic flux. The rate of particulate transport of arsenic is undoubtedly related to spatial and season variations in hydrology [9] and directly influenced by effluent characteristics.

The downstream distributions of As, Sb, Au, Ni and Co in surface sediment were all similar in that the maximum concentrations were encountered downstream in Peg Lake rather than Meg Lake, which is closest to the effluent discharge (Table 2). In addition, the concentrations in the Meg, Keg and Peg Lakes were higher than in Grace Lake or at station YKB4, an observation consistent with anthropogenic enrichment. In contrast, Cu, Zn, Pb and Cr exhibited concentration maxima in Meg Lake. Table 3 shows the significant ( $\alpha = 0.05$ ) Pearson correlations for various metals/metalloids based on solid phase concentrations in the upper 5 cm. Zinc was significantly correlated only with copper. On the other hand, As concentrations were correlated with those of Sb, Au, Ni and Co.

The difference in downstream distributions of the two groups of elements could reflect a di-

Table 3

Correlation matrix of solid phase metal levels in the top 5 cm of cores from the Meg, Keg, Peg, Kam and Grace Lakes and southwest Yellowknife Bay

	As	Sb	Al	Fe	Mn	Au	Cu	Zn	Ni	Co	Cr
As	1.00										
Sb	0.80	1.00									
Al			1.00								
Fe				1.00							
Mn					1.00						
Au	0.87		-0.85			1.00					
Cu		0.80					1.00				
Zn							0.76	1.00			
Ni	0.94		-0.86			0.87			1.00		
Co	0.97	0.83				0.86			0.88	1.00	
Cr											1.00

Only those correlations which are significantly  $> 0$  ( $\alpha = 0.05$ ) are shown. For all correlations, sample size ( $n$ ) = 7.

chotomy in their diagenetic behaviour; i.e. a greater relative affinity of Cu, Zn, Pb and Cr for adsorption onto and/or complexation with particulate organic matter and humic substances and a decreased potential for remobilization. Nissenbaum and Swain [29] concluded that  $H_2O_2$ -extractable humic substances in coastal marine sediments contained significant portions of Cu and Zn; humic substances were less important for Ni, Co or Pb complexation, and were not significantly associated with Fe or Mn.

If the sediments along the watershed were influenced primarily by chemical diagenetic processes, governed in turn by solubility controls, then the composition of any given portion of sediment would vary according to redox conditions and other local variations in the chemical milieu. Conversely, if the sediments were influenced primarily by bulk transport, then the mineralogical composition of sediments down the system should be largely conservative, varying only according to local differences in physical sorting and additional downstream inputs. The historically-deposited sediment associated with old effluent discharge and tailings washout should have a distinct 'fingerprint'. If bulk transport is the principal mechanism of the downstream arsenic flux, then the present surficial sediments in Peg Lake, which exhibit the maximum concentrations of arsenic, should more closely resemble historically-deposited sediment than do the surficial

sediments closer to the source. This can be tested directly using solid-phase sediment data.

The similarity of sediment composition based on the concentrations of the first 12 elements listed in Table 2 (As, Sb, Fe, Mn, Ca, Na, Br, K, Al, Au, Cu, Zn) was examined using a multivariate technique, principal components analysis (PCA). The actual analysis was carried out with the statistical program SYSTAT 5.0, using the data from surficial sediment samples as shown in Table 2, as well as data from subsurface samples (not shown) from cores collected at the Meg, Keg, Peg and Kam Lakes (at depths in 5 cm increments). A total of 17 sediment samples were examined. Principal components analysis is particularly useful for multivariate pattern recognition; the similarity of specific samples can be visualized directly by examining their positions on a reduced (usually two or three dimensional) plot, the axes of which are linear combinations of the original  $n$  variables.

The first four principal components of the PCA captured 84.8% of the between-sample variation in the original data set (37.4%, 26.6%, 11.7% and 10.2% for principal components 1–4, respectively). Fig. 4 shows the positions of the surface (0–5 cm) and subsurface samples ( $> 5$  cm) on the first two principal components, which account for most of the variation in the data set. The positioning of the sediment samples on the third and fourth principal component did not exhibit any additio-

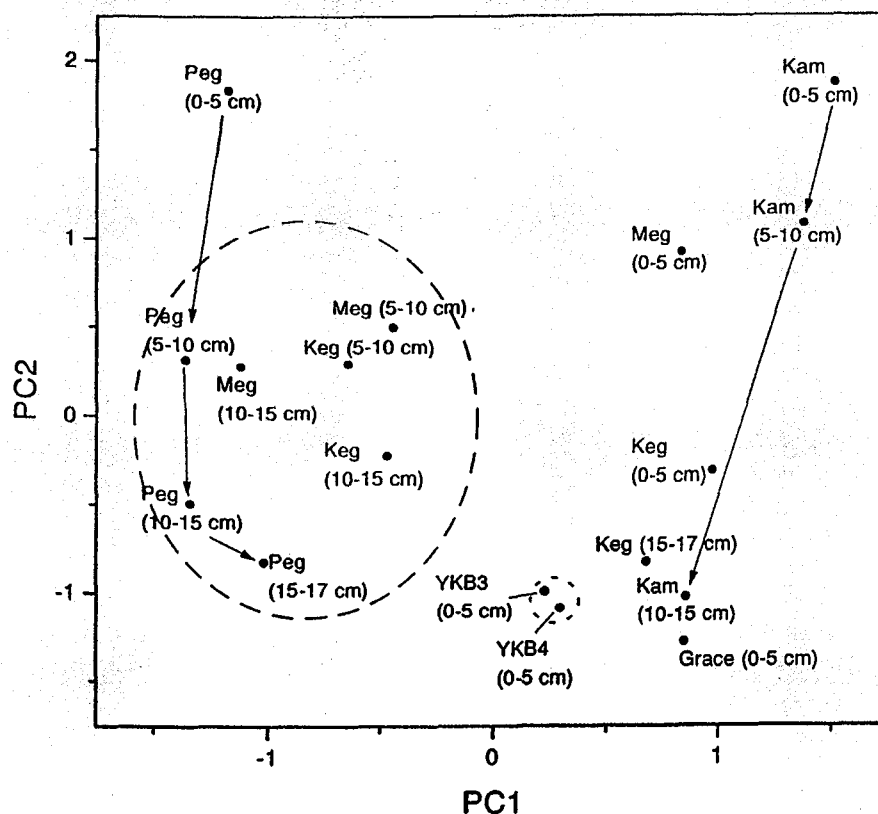


Fig. 4. Principal components analysis of the particulate sediment composition of surficial (0–5 cm) and subsurface (> 5 cm) sediments along the Meg, Keg, Peg Lake, Yellowknife Bay discharge, near Yellowknife, Northwest Territories.

nal discernible patterns. The important features of Fig. 4 are as follows: (1) the subsurface sediments from the Meg, Keg and Peg Lake cores, except for the 15–17 cm depth sample from Keg Lake, form a distinct cluster to the left of the plot; these are therefore similar in elemental composition; (2) sediment samples from Kam Lake and Grace Lake were distinct from the Meg, Peg, Keg Lake subsurface sediments based on the first principal component. The Yellowknife Bay surficial sediments were similar in composition to each other; (3) surficial sediments from the Meg and Keg Lakes are different in composition from the subsurface sediment. The Peg Lake surficial sediment is more similar to the underlying sediment; (4) there is a strong relationship between the sample scores on principal component two and depth in the sediment. This is particularly evident for the Peg Lake and Kam Lake cores.

The observation that the Meg, Keg and Peg Lake subsurface sediment samples form a group

distinct from the Kam and Grace Lake samples (based on principal component one) is not surprising, since Kam Lake and Grace Lake lie on a different geological stratum than the other lakes [22]. Collectively, the first principal component appears to show differences in geological composition. The similarity of the Meg, Keg and Peg Lake subsurface sediments are most likely due to a common historical origin/depositional regime. The less-accentuated similarity of Peg Lake surficial sediments to this group also suggests a similar origin; it is plausible that the composition of the Peg lake sediments is more reflective of earlier, bulk movement of historically-contaminated deposits farther up the system. The dissimilarity of Meg and Peg Lake surficial sediments to the deeper sediments, however, can be attributed to the capping of the old sediments in the upper reaches of the watershed by sediments deposited subsequent to the adoption by the mine of different control technologies in the mid-1980s. Indeed, the maximum concentrations of arsenic

found in the Meg and Peg Lake sediment cores occurred in the 5–10-cm increment, while downstream cores exhibited surficial arsenic maxima (Bright and Reimer, in prep.), which is also consistent with a postulated capping of historically-contaminated deposits. The composition of sediment samples along the Meg, Keg, Peg Lake, Yellowknife Bay discharge is therefore consistent with a particulate transport mechanism. The seasonal data indicate that particulate-based transport in Keg Lake was important during the spring break-up compared with the preceding August. In addition, the final sampling data in April occurred before the period of maximum stream flow, when particulate-based transport would be maximized.

The strong relationship between the second principal component and depth in the sediment deserves a critical examination. This might also be explained by progressive changes over time in the composition of particulate inputs; however, the effluent control technologies underwent punctuated rather than progressive changes (see above). The vertical sediment variations strongly suggest a secondary modification of sediment composition based on chemical diagenesis. Vertical redistributions of elements in recent sediments associated with microbial decomposition, oxidation-reduction gradients, dissolution-precipitation and vertical diffusion in sediment pore water are widely accepted in the literature. The PCA suggests that chemical diagenesis, i.e. solubility-based transport, may also be an important mechanism determining the sediment composition.

*Remobilization associated with sediment diagenesis (solubility-based controls).* Bulk transport of sediments may have contributed to the downstream flux of arsenic and other contaminants in the Meg, Keg, Peg and Great Slave Lake system; nonetheless, the high concentrations of dissolved arsenic in the water column are only indirectly related to sediment redistribution since they further involve redissolution.

In 1990, total dissolved arsenic concentrations of 7.3 and 5.2  $\mu\text{M}$  were found in the surface water of Keg and Peg Lake, respectively (Fig. 2c). All dissolved inorganic arsenic in the effluent was

released as arsenate; no arsenite was detected ( $< 0.0005 \mu\text{M}$ ). The water column of lakes downstream of the effluent pipe also contained arsenate as the dominant dissolved arsenical, but, as shown in Fig. 2c, the water column concentration of arsenite increased with increasing distance from the discharge.

Arsenite was the dominant dissolved arsenical in the upper 5 cm of sediment in the Meg, Keg and Peg Lakes, indicating that these sediments were reduced close to the sediment-water interface. With the exception of Meg Lake, the ratio of arsenite to arsenate in the upper 5 cm decreased away from the discharge pipe (Fig. 5). This indicates that the oxidation-reduction potential of near-surface sediments was lower in the upper reaches of the system and is possibly modified by the anthropogenic input of other substances (e.g. sulfates, see below) that influence microbial decomposition during early diagenesis.

Reduction of sediments at or near the sediment-water interface enhances dissolution of arsenic from particulates and upward diffusion, principally as arsenite ( $\text{As(III)}$ ) [2]. The downstream increase in concentration of arsenite in the water of the Meg, Keg and Peg Lakes probably results from diffusion across the sediment-water interface; alternate explanations that the water column inorganic arsenate-arsenite conversions were carried out by bacteria or phytoplankton [1,28] are less likely. The water column concentration of DAs at station YKB3 was actually higher than that of the underlying sediment pore water, i.e. 2.4  $\mu\text{M}$  compared with 0.60  $\mu\text{M}$  (Fig. 2) and probably originated from sediment pore water DAs in upstream sediments.

Based on thermodynamic considerations, the tendency would be for the chemical conversion of arsenite to arsenate in the well-oxidized water column and adsorption onto particulate iron and/or manganese hydroxides, followed by sedimentation. The process of arsenic migration during summertime oxygenated conditions may, therefore, consist of the reductive dissolution of arsenic from sediments, upward diffusion, downstream transport, re-oxidation and removal from solution. Indeed, this is consistent with the model of arsenic cycling developed by Aggett and

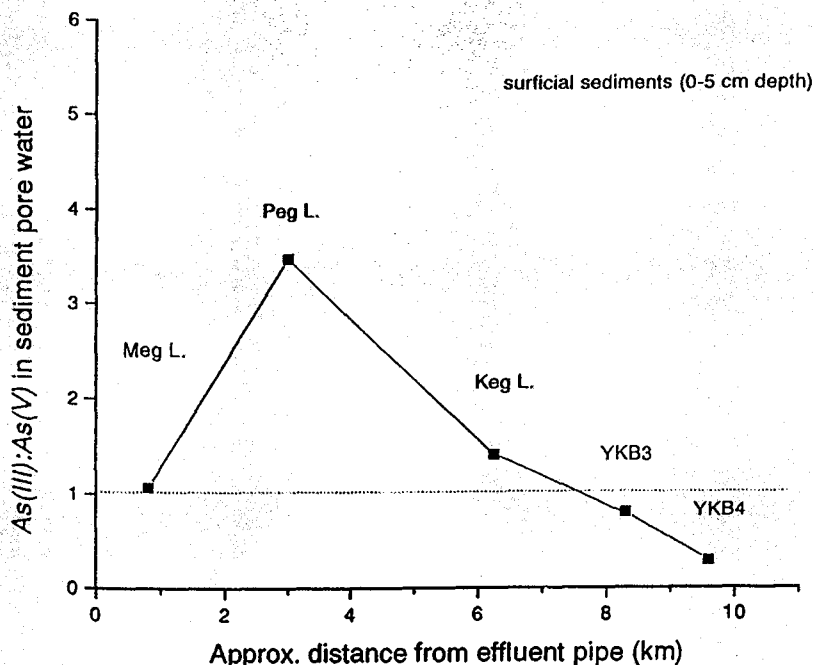


Fig. 5. Spatial trend in the arsenite:arsenate ratio (As(III):As(V)) in surface sediments (0–5 cm) of the Meg, Keg, Peg Lake system.

O'Brien [2]. The rate of downstream flux would, therefore, depend on the magnitude of upward diffusion in sediments based on reductive dissolution and the rate of oxidation and association with iron and manganese hydroxides. The persistence of arsenite in the oxic water column at non-equilibrium concentrations [1,31] probably influences the rate of downstream migration of historically deposited arsenic loads by delaying re-adsorption and removal to sediments. Based on the lack of any seasonal anoxia in 1991 in the Meg, Keg, Peg Lake, Yellowknife Bay system, it is suspected that remobilization via dissolution from sediments primarily occurs chronically throughout the months of active flow, rather than as punctuated events.

Table 2 shows the spatial distribution of some of the other substances associated with the Nerco Con discharge. The main geochemical source of chloride ion,  $\text{Cl}^-$ , in terrestrial aquatic systems is subterranean [30] and mining often results in the release of  $\text{Cl}^-$  from the lithosphere to the hydrosphere. The elevation of  $\text{Cl}^-$  concentration in the

surficial sediment pore water of the Meg, Keg and Peg Lakes relative to the Great Slave Lake or Grace Lake, therefore, reflects the input of mine waste into the Meg, Keg and Peg Lakes (Table 2).

Sulfate and phosphate concentrations in pore water also tended to be higher directly downstream of the effluent discharge than in Grace Lake or farther out in Yellowknife Bay (YKB4: Table 2). Enhanced sulfate concentrations of 3000–5000  $\mu\text{M}$  were probably attributable to the addition of ferric sulfate to mine tailings (see section 2.1.). Fresh water lakes typically exhibit sulphate concentrations of 10–300  $\mu\text{M}$  compared with 3000–30 000  $\mu\text{M}$  for brackish and saline systems [30]. The sulfate input from the Nerco Con effluent pipe, or aerial deposition, could potentially enhance microbial sulfate reduction and associated processes; for example, enhanced sulfate reduction could decrease the depth at which sediments become reduced and increase the upward mobility of arsenic, as As(III) and/or soluble thioarsenite species similar to that

observed in marine studies [1]. This might be particularly important in lakes which are organic-rich, such as the Meg, Keg and Peg Lakes.

#### 4. Conclusions

The concentration of dissolved arsenic in the water of the Meg, Keg, Peg Lake, southwest Yellowknife Bay system appears to be controlled by the remobilization of arsenic from historically-contaminated sediments rather than through present day mining inputs. The downstream flux of arsenic-contaminated sediments may be at least partially controlled by the bulk movement of particulates. The sediment-water column flux of arsenic, as well as water-borne input into Great Slave Lake, however, probably varies as a function of the reductive dissolution of arsenic in near-surface sediments, the rate of upward diffusion and the rate of re-oxidation and association with sediments or suspended particulates in the water column. Arsenic input into Great Slave Lake, however, has not contributed to extreme elevations of sediment or water column arsenic concentrations at distances > 1 km from the source of input (ie. > 0.027  $\mu\text{M}$  in the water column or 170  $\mu\text{g g}^{-1}$  dry wt. in the sediment). It is possible that the introduction of other substances to the gold-mine waste such as ferric sulfate could alter the diagenetic changes occurring in upstream surface sediments and indirectly enhance remobilization of historical deposits. Seasonal variation could also influence downstream arsenic flux, based on possible under-ice oxygen depletion, changes in hydrology, etc.; this requires further investigation.

#### Acknowledgements

This study was supported by a Department of National Defence Academic Research Program Grant (3705-624 FUHHG) to K.J. Reimer and an NSERC-administered Visiting Fellowship in Government Labs to D.A. Bright. We also thank the staff of the Water Resources Laboratory and the Department of Indian and Northern Affairs for their financial and field support.

#### References

- 1 W.R. Cullen and K.J. Reimer, Arsenic speciation in the environment, *Chem. Rev.*, 89 (1989) 713–764.
- 2 J. Aggett and G.A. O'Brien, Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri, *Environ. Sci. Technol.*, 19 (1985) 231–238.
- 3 I.S. Seydel, Distribution and circulation of arsenic through water, organisms and sediment of Lake Michigan, *Arch. Hydrobiol.*, 71 (1972) 17–30.
- 4 W.-M. Mok and C.M. Wai, Distribution and mobilization of arsenic and antimony species in the Coeur D'Alene River, Idaho, *Environ. Sci. Technol.*, 24 (1990) 102–108.
- 5 P. Seyler, and J.M. Martin, Arsenic and selenium in a pristine river-estuarine system: the Krka (Yugoslavia), *Mar. Chem.*, 34 (1991) 137–151.
- 6 P. Seyler and J.M. Martin, Distribution of arsenite and total dissolved arsenic in major French estuaries: dependence on biogeochemical processes and anthropogenic inputs, *Mar. Chem.*, 29 (1990) 277–294.
- 7 P. Seyler and J.M. Martin, Biogeochemical processes affecting arsenic species distribution in a permanently stratified lake, *Environ. Sci. Technol.*, 23 (1989) 1258–1263.
- 8 W.W. Huang, J.M. Martin, P. Seyler, J. Zhang and X.M. Zhong, Distribution and behaviour of arsenic in the Huang He (Yellow River) estuary and Bohai Sea, *Mar. Chem.*, 25 (1988) 75–91.
- 9 C.A. Johnson and I. Thornton, Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage, *Water Res.*, 21 (1987) 359–365.
- 10 M.L. Peterson and R. Carpenter, Arsenic distribution in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, British Columbia, *Geochim. Cosmochim. Acta*, 50 (1986) 353–369.
- 11 M.L. Peterson and R. Carpenter, Biogeochemical processes affecting total arsenic and arsenic species distributions in an intermittently anoxic fjord, *Mar. Chem.*, 12 (1983) 295–391.
- 12 N. Belzile, The fate of arsenic in sediments of the Laurentian Trough, *Geochim. Cosmochim. Acta*, 52 (1988) 2293–2302.
- 13 H.M. Edenborn, N. Belzile, A. Mucci, J. Lebel and N. Silverberg, Observations on the diagenetic behaviour of arsenic in a deep coastal sediment, *Biogeochemistry*, 2 (1986) 359–376.
- 14 P.H. Masscheleyn, R.D. Delaune and W.H. Patrick, Effect of redox potential and pH on arsenic speciation and solubility in contaminated soil, *Environ. Sci. Technol.*, 25 (1991) 1414–1419.
- 15 R.A. Feely, J.H. Trefry, G.J. Massoth and S. Metz, A comparison of the scavenging of phosphorus and arsenic

- from seawater by hydrothermal iron oxyhydroxides in the Atlantic and Pacific Oceans, *Deep Sea Res.*, 38 (1991) 617–623.
- 16 W. Salomons, Contaminants in sediments: out of sight out of mind?, in *Environmental Contamination: International Conference-London*, July 1984, 1985, pp. 766–774.
- 17 L. Jacobs and S. Emerson, Trace metal solubility in an anoxic fjord, *Earth Planet. Sci. Lett.*, 60 (1982) 237–252.
- 18 T.F. Pedersen, Early diagenesis of copper and molybdenum in mine tailings and natural sediments in Rupert and Holberg inlets, British Columbia, *Can. J. Earth Sci.*, 22 (1985) 1474–1484.
- 19 B.B. Jorgensen, The microbial sulphur cycle, in W.E. Krumbein (Ed.), *Microbial Geochemistry*, Blackwell Scientific Publ., London, 1983, pp. 91–124.
- 20 D. Hocking, P. Kuchar, J.A. Plambeck and R.A. Smith, The impact of gold smelter emissions on vegetation and soils of a sub-arctic forest-tundra transition ecosystem, *J. Air Pollut. Control Assoc.*, 28 (1978) 133–137.
- 21 J.W. Moore, D. Sutherland, V.A. Beaubien and S.J. Wheeler, The effects of metal mines on aquatic systems in the Northwest Territories, III Cominco Ltd., Con Mine, Yellowknife, Report EPS-5-NW-79-5, 1979.
- 22 R. Wageman, N.B. Snow, D.M. Rosenberg and A. Lutz, Arsenic in sediments, water and aquatic biota from lakes in the vicinity of Yellowknife, Northwest Territories, Canada, *Arch. Environ. Contam. Toxicol.*, 7 (1978) 169–191.
- 23 R.R. Wallace, and M.J. Hardin, Chemical and biological characteristics of seepages from tailings areas at Cominco Con Mine into Kam Lake, Northwest Territories, in 1974, Report EPS 5-NW-75-3.
- 24 K.J. Reimer, The methylation of arsenic in marine sediments, *Appl. Organomet. Chem.*, 3 (1989) 475–490.
- 25 M.O. Andreae, Determination of arsenic species in natural waters, *Anal. Chem.*, 49 (1977) 820–823.
- 26 R.S. Braman, D.L. Johnson, C.C. Forback, J.M. Ammons and J.L. Bricker, Separation and determination of nanogram amounts of inorganic arsenic and methylarsenic compounds, *Anal. Chem.*, 49 (1977) 621–625.
- 27 L.C.D. Anderson and K.W. Bruland, Biogeochemistry of arsenic in natural waters: the importance of methylated species, *Environ. Sci. Technol.* 25 (1991) 420–427.
- 28 J.G. Sanders, Arsenic cycling in marine systems, *Mar. Environ. Res.* 3 (1980) 257–266.
- 29 A. Nissenbaum and D.J. Swaine, Organic matter-metal interactions in recent sediments: the role of humic substances, *Geochim. Cosmochim. Acta*, 40 (1976) 809–816.
- 30 P. Santschi, P. Hohener, G. Benoit, and M. Buchholtzen Brink, Chemical processes at the sediment-water interface, *Mar. Chem.*, 30 (1990) 269–315.
- 31 M.O. Andreae, Distribution and speciation of arsenic in natural waters and some marine algae, *Deep Sea Res.*, 24 (1978) 391–402.
- 32 A. Mudroch, R.J. Allan and S.R. Joshi, Geochemistry and organic contaminants in the sediments of Great Slave Lake, Northwest Territories, Canada, *Arctic*, 45 (1992) 10–19.
- 33 R.J. Allan, Heavy metals in bottom sediments of Great Slave lake (Canada): a reconnaissance, *Environ. Geol.*, 3 (1979) 49–58.

Reprinted from

# Aquatic botany

---

Aquatic Botany 50 (1995) 141-158

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

W.T. Dushenko\*, D.A. Bright, K.J. Reimer\*

*Environmental Sciences Group, Royal Roads Military College, FMO Victoria, B.C. V0S 1B0, Canada*

Accepted 22 December 1994



# Aquatic botany

An International  
Scientific Journal  
dealing with  
Applied and  
Fundamental  
Research on  
Submerged,  
Floating and  
Emergent Plants  
in Marine  
and Freshwater  
Ecosystems

**Aims and scope.** The journal is concerned with fundamental studies on structure, function, dynamics and classification of plant-dominated aquatic ecosystems. It is also intended as an outlet for papers dealing with applied research on aquatic plants, including reports on the consequences of disturbance of aquatic ecosystems (e.g. transplantations, influence of herbicides and other chemicals, thermal pollution, biological control, grazing and disease), the use of aquatic plants, conservation of resources and all aspects of plant production and decomposition.

## EDITORS-IN-CHIEF

C. den Hartog  
Catholic University of Nijmegen  
Laboratory for Aquatic Ecology  
NIJMEGEN  
The Netherlands

J.M.A. Brown  
35 Laurie Avenue  
Parnell  
AUCKLAND 1  
New Zealand

## EDITORIAL ADVISORY BOARD

A.D. Barnabas (Durban, South Africa)  
G. Bowes (Gainesville, FL, USA)  
J.S. Bunt (Sydney, N.S.W., Australia)  
A. Cheshire (Adelaide, S.A., Australia)  
J.S. Clayton (Hamilton, New Zealand)  
C.D.K. Cook (Zürich, Switzerland)  
S.J. de Groot (IJmuiden, The Netherlands)  
P. Denny (Delft, The Netherlands)  
F.I. Dromgoole (Auckland, New Zealand)  
J.W. Eaton (Liverpool, UK)  
J. Květ (Třeboň, Czech Republic)  
A.W.D. Larkum (Sydney, N.S.W., Australia)

Y. Lipkin (Tel Aviv, Israel)  
S.C. Maberly (Ambleside, UK)  
C.T. Philbrick (Danbury, CT, USA)  
W. Pietsch (Dresden, Germany)  
F.J. Ryan (Davis, CA, USA)  
M. Søndergaard (Hillerød, Denmark)  
D.L. Sutton (Fort Lauderdale, FL, USA)  
J.E. Titus (Binghamton, NY, USA)  
J.C.J. van Zon (Arnhem, The Netherlands)  
D.F. Westlake (Wareham, UK)  
R.G. Wetzel (Tuscaloosa, AL, USA)

## Book Review Editor

J.S. Bunt, 212 Lower Plateau Road, Bilgola, N.S.W. 2107, Australia

**Publication information:** *Aquatic Botany* (ISSN 0304-3770). For 1994 volumes 48–50 are scheduled for publication. Subscription prices are available upon request from the Publisher. Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by surface mail except to the following countries where air delivery via SAL mail is ensured: Argentina, Australia, Brazil, Canada, Hong Kong, India, Israel, Japan, Malaysia, Mexico, New Zealand, Pakistan, PR China, Singapore, South Africa, South Korea, Taiwan, Thailand, USA. For all other countries air-mail rates are available upon request. Claims for missing issues should be made within six months of our publication (mailing) date. Please address all your requests regarding orders and subscription queries to: Elsevier Science B.V. Journal Department, P.O. Box 211, 1000 AE Amsterdam, The Netherlands, Tel. (+31-20)4853642, Fax (+31-20)4853598.

US mailing notice, *Aquatic Botany* (ISSN 0304-3770) is published monthly by Elsevier Science B.V. (Molenwerf 1, Postbus 211, 1000 AE, Amsterdam). Annual subscription price in the USA is US\$ 610 (valid in North, Central and South America only), including air speed delivery. Application to mail at second class postage rate is pending at Jamaica, NY 11431.

USA POSTMASTERS: Send address changes to, *Aquatic Botany* Publications Expediting Inc., 200 Meacham Avenue, Elmont, NY 11003. Airfreight and mailing in the USA by Publication Expediting.

**In the USA and Canada:** For further information on this and other Elsevier journals please contact: Elsevier Science Publishing Inc., Journal Information Center, 655 Avenue of the Americas, New York, NY 10010, USA. Tel. (212)6333750; fax (212)6333764; telex 420-643 AEP UI.

**Back volumes:** Please contact the Publisher.

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

W.T. Dushenko\*, D.A. Bright, K.J. Reimer\*

*Environmental Sciences Group, Royal Roads Military College, FMO Victoria, B.C. V0S 1B0, Canada*

Accepted 22 December 1994

---

## 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  $\text{PO}_4^{3-}$ , 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

---

\* Corresponding authors. Telephone: (604) 363-4620/4600. Fax: (604) 363-4651. E-mail: bdushenk@post.royalroads.ca./kreimer@post.royalroads.ca.

(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.

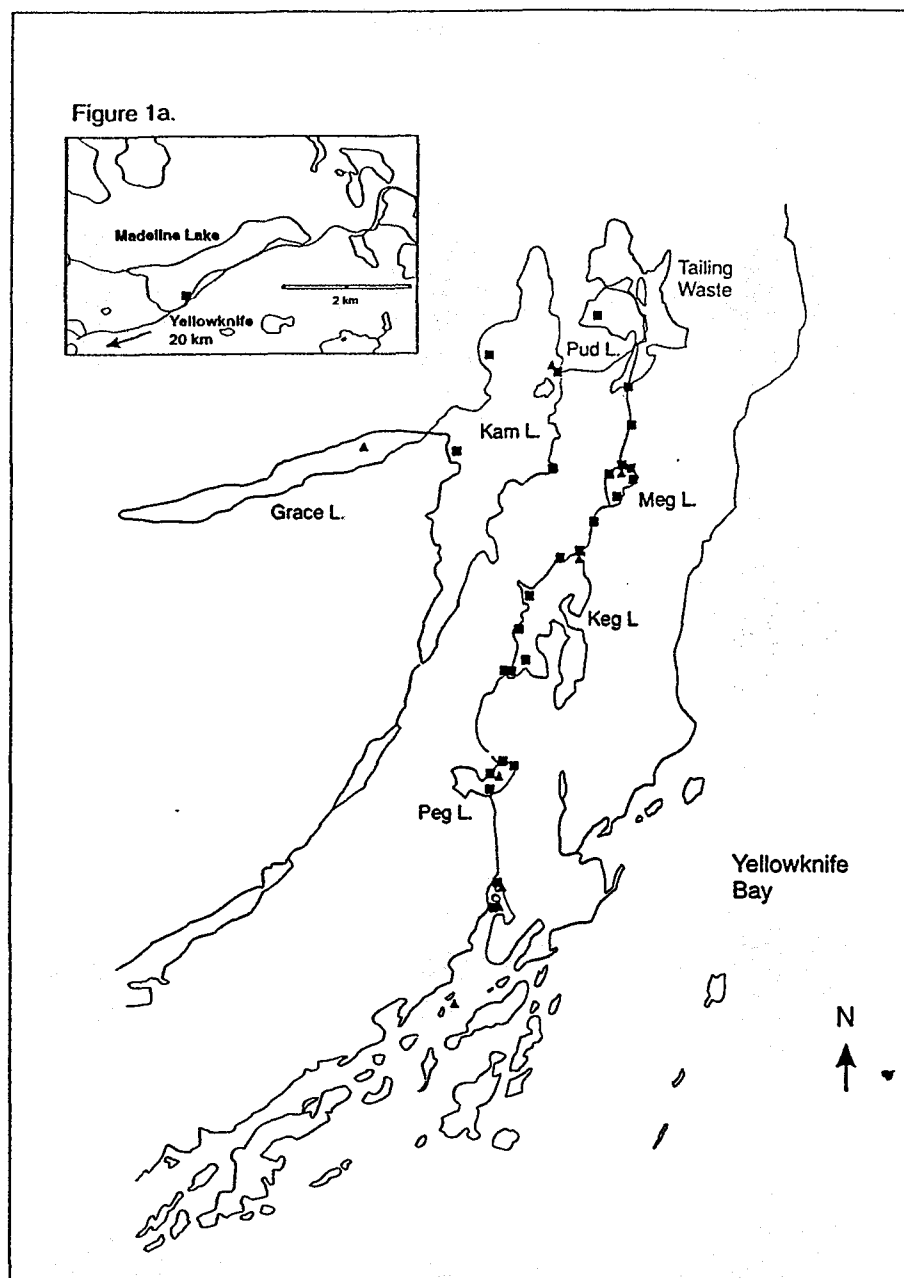


Fig. 1. Map of lake study system near Yellowknife, N.W.T., showing the 1990 deep-water (filled triangles) and 1991 shoreline (filled squares) sampling stations. A background station sampled at Madeline Lake is shown as inset (a).

## 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 N<sub>2</sub>-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  $\mu$ 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 Evergreen<sup>TM</sup> (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)  $\mu$ 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 ( $\text{PO}_4^{3-}$ ) 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 <sup>1</sup>
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

<sup>1</sup>Values expressed as  $\text{mg g}^{-1}$ .

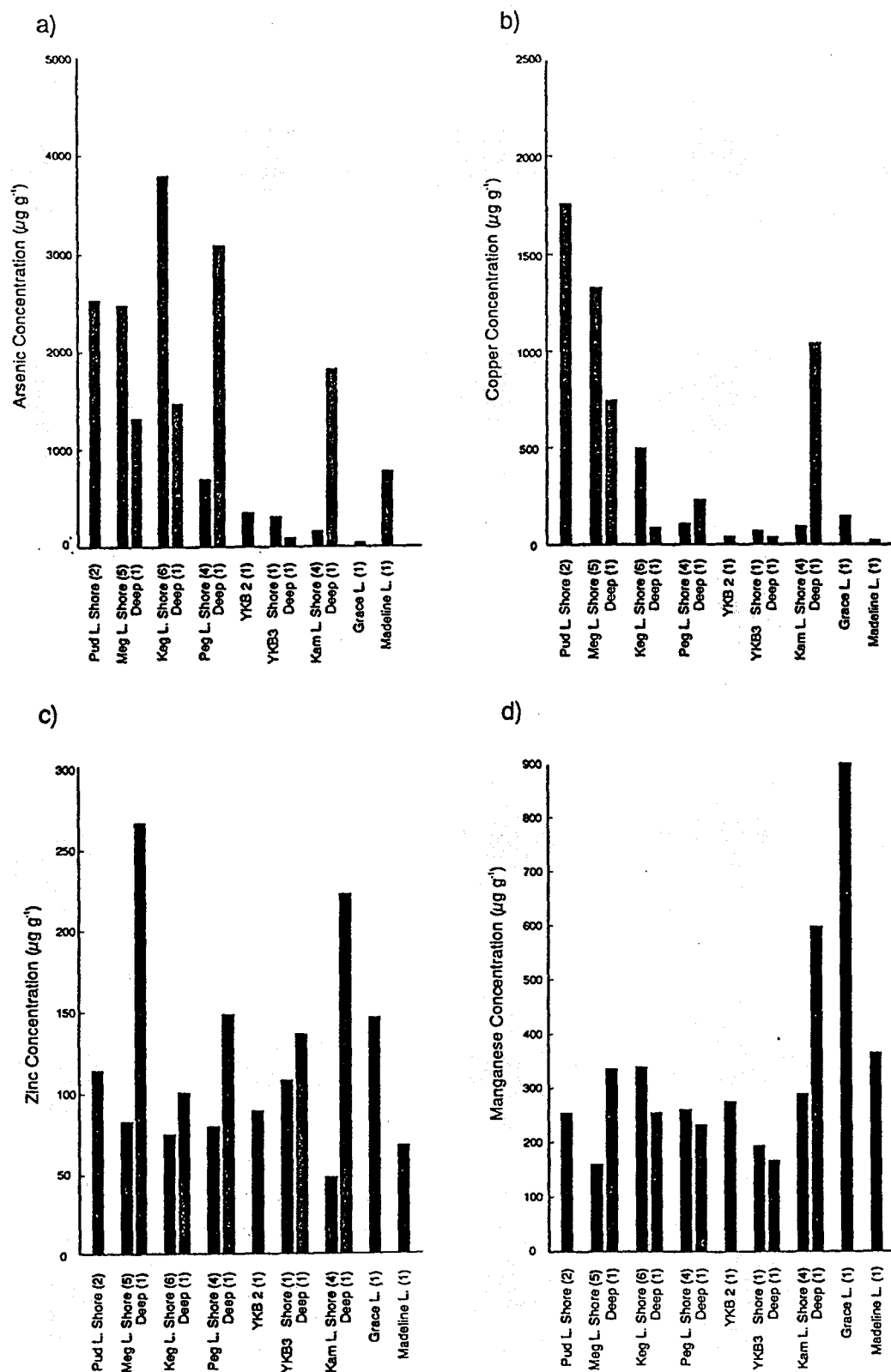


Fig. 2. Total sediment concentrations ( $\mu\text{g g}^{-1}$ ) of (a) arsenic, (b) copper, (c) zinc and (d) manganese in deep-water and near-shore areas of lakes downstream of gold mining discharge. Grace and Madeline Lakes are provided as reference lakes.

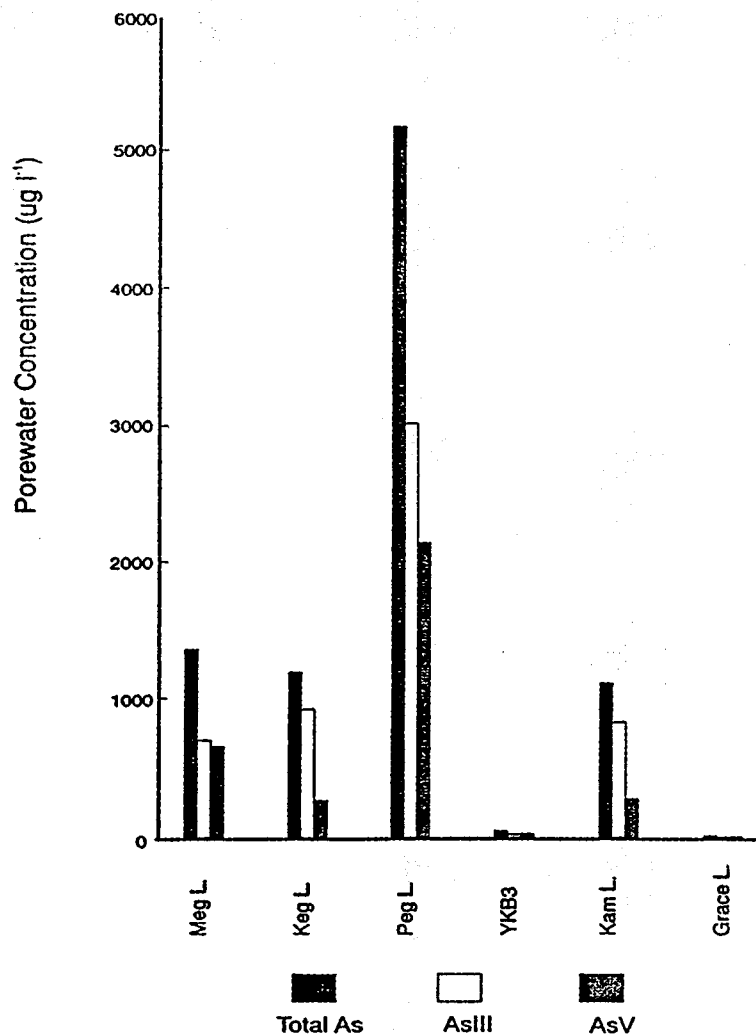


Fig. 3. Pore water concentrations ( $\mu\text{g l}^{-1}$ ) of arsenic (total), As(III) and As(V) in deep-water sediments of lakes downstream of gold mining discharge. Grace Lake is presented as a reference.

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

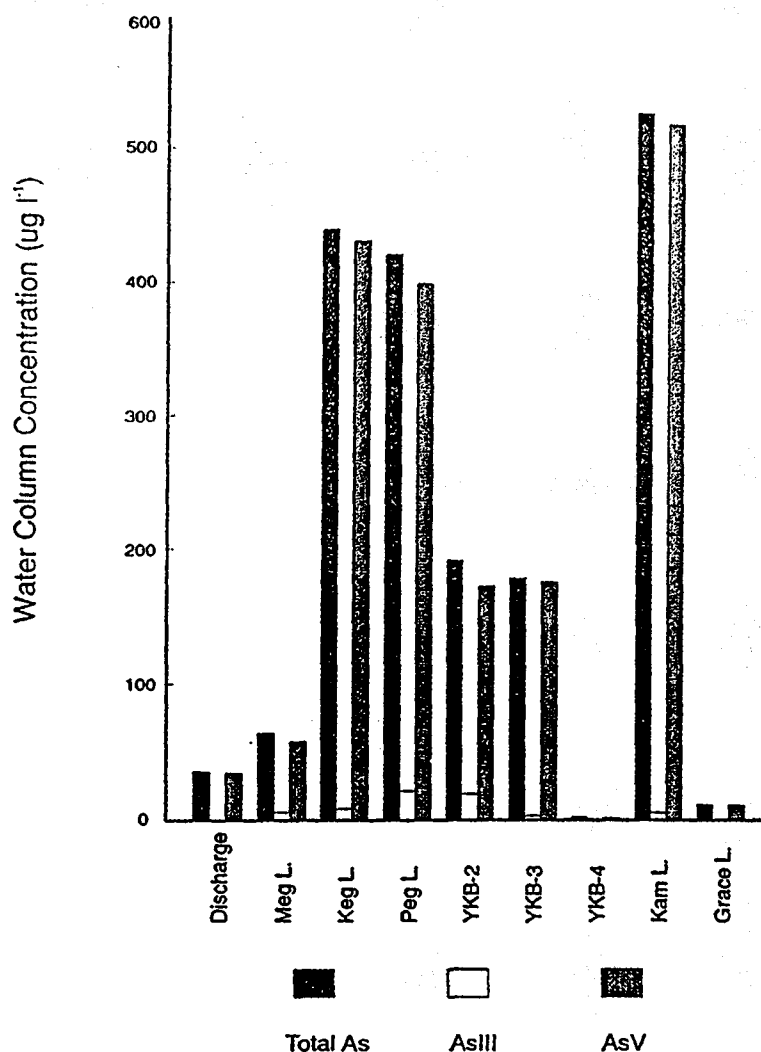


Fig. 4. Water column concentrations ( $\mu\text{g l}^{-1}$ ) of arsenic (total), As(III) and As(V) in lakes downstream of gold mining discharge. Grace Lake is presented as a reference (see text).

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

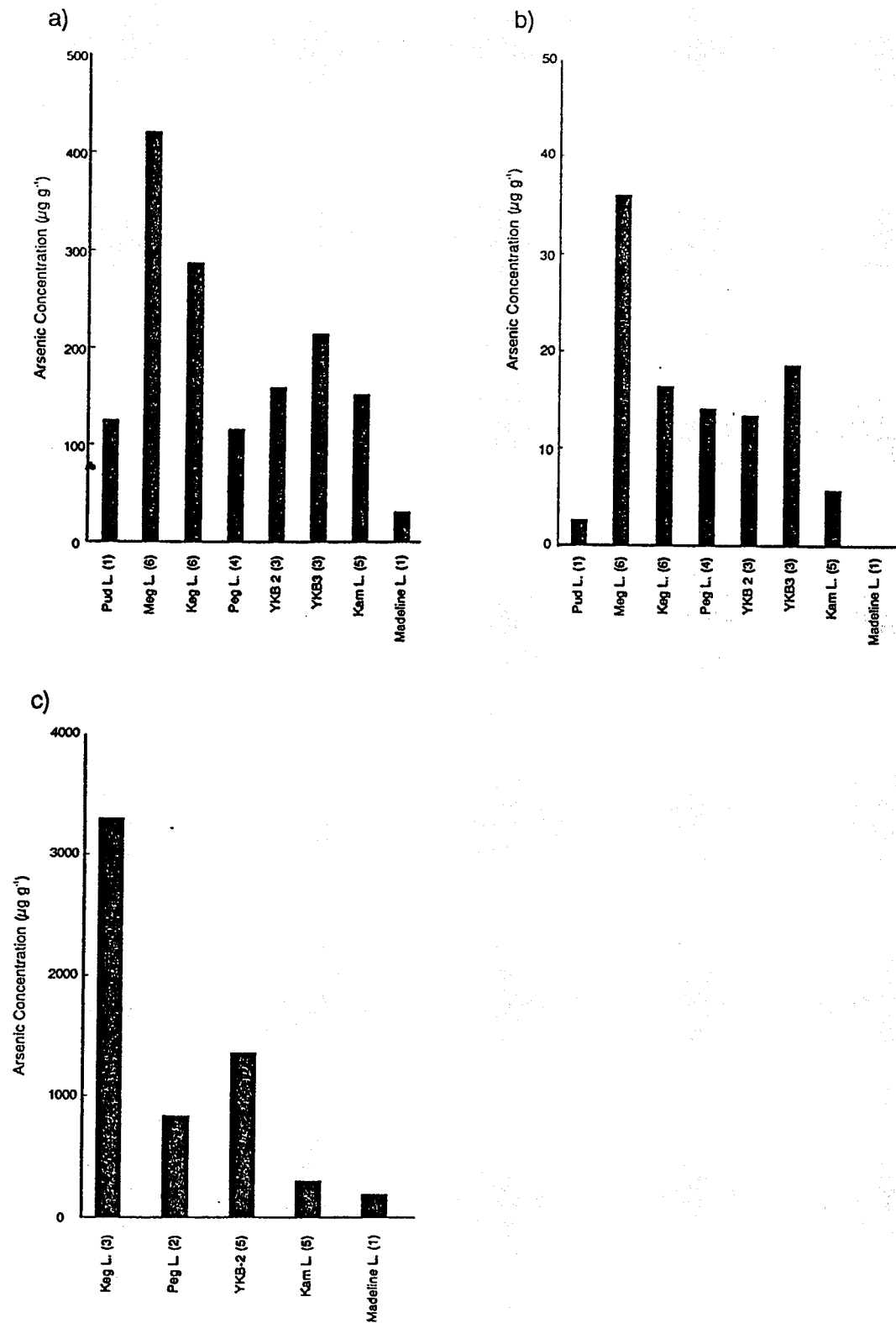


Fig. 5. Concentrations of arsenic ( $\mu\text{g g}^{-1}$ ) in (a) root tissue and (b) shoot tissue of *Typha latifolia*, and (c) whole tissue of *Potamogeton pectinatus* (where sampled) in lakes downstream of gold mining discharge. Madeline Lake is presented as a reference (see text).

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  $\leq 0.05$  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

# Aquatic botany

**Submission of manuscripts:** Manuscripts should be submitted to the Editorial Office of *Aquatic Botany*, P.O. Box 181, 1000 AD Amsterdam, The Netherlands.

All questions arising after acceptance of the manuscript, especially those relating to proofs, should be directed to: Elsevier Editorial Services, Mayfield House, 256 Banbury Road, Oxford, OX2 7DH, UK. Tel: (+44-1865)-3149 00, fax: (+44-1865)-3149 90.

**Electronic manuscripts:** Electronic manuscripts have the advantage that there is no need for the rekeying of text, thereby avoiding the possibility of introducing errors and resulting in reliable and fast delivery of proofs.

For the initial submission of manuscripts for consideration, hardcopies are sufficient. For the processing of *accepted papers*, electronic versions are preferred. After *final acceptance*, your disk plus two, final and exactly matching printed versions should be submitted together. Double density (DD) or high density (HD) diskettes (3.5 or 5.25 inch) are acceptable. It is important that the file saved is in the native format of the wordprocessor program used. Label the disk with the name of the computer and wordprocessing package used, your name, and the name of the file on the disk. Further information may be obtained from the Publisher.

**Authors in Japan please note:** Upon request, Elsevier Science Japan will provide authors with a list of people who can check and improve the English of their paper (*before submission*). Please contact our Tokyo office: Elsevier Science Japan, 20-12 Yushima 3-chome, Bunkyo-ku, Tokyo 113; tel. (03)-3833-3821; fax (03)-3836-3064.

**Advertising information:** advertising orders and enquiries may be sent to: Elsevier Science B.V., Advertising Department, P.O. Box 211, 1000 AE Amsterdam, The Netherlands, tel. (+31-20)4853796, fax (+31-20)4853810. Courier shipments to street address, Molenwerf 1, 1014 AG Amsterdam, The Netherlands. In the UK: TG Scott & Son Ltd., attn. Vanessa Bird, Portland House, 21 Narborough Rd., Cosby, Leicestershire, LE9 5TA, UK, tel. (0116)2750-521/2753-333, fax (0116)2750-522. In the USA and Canada: Weston Media Associates, attn. Daniel Lipner, P.O. Box 1110, Greens Farms, CT 06436-1110, USA, tel. (203)2612500, fax (203)2610101.

For a full and complete Guide for Authors please refer to *Aquatic Botany*,  
Vol. 48, No. 1, pp. 93-98

© 1995, Elsevier Science B.V. All Rights Reserved

0304-3770/95/\$09.50

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the Publisher, Elsevier Science, B.V., Copyright and Permissions Department, P.O. Box 521, 1000 AM Amsterdam, The Netherlands.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

Although all advertising material is expected to conform to ethical (medical) standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality or value of such product or of the claims made of it by its manufacturer.

∞ The paper used in this publication meets the requirements of ANSI/NISO 239.48-1992 (Permanence of Paper).

Printed in The Netherlands

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.

### Acknowledgements

Many thanks are due to Bill Coedy and the Water Resources Laboratory, Department of Indian and Northern and Development (DIAND) in Yellowknife, for their assistance in co-ordinating and facilitating the field study and providing laboratory space. The valuable assistance provided by the 1990 sampling team (Catherine Vardy and Bernard Lakowski) and the team in 1991 (Matt Dodd, Olivia Whitwell, Gary Hewitt and John Nelson) is also gratefully acknowledged. We thank John Poland and the ASU of Queen's University for chemical analysis, and Patricia M. Fortin for logistic support. This project has been jointly funded by DIAND and a Department of National Defence Academic Research Programme Allocation (3705-624 FUHHG).

### References

- Andreae, M.O., 1978. Distribution and speciation of arsenic in natural waters and some marine algae. *Deep Sea Res.*, 74: 391–402.
- Barko, J.W., Gunnison, D. and Carpenter, S.R., 1991. Sediment interactions with submersed macrophyte growth and community dynamics. *Aquat. Bot.*, 41: 41–65.
- Braman, R.S., Johnson, D.L., Forback, Ammons, J.M. and Bricker, J.L., 1977. Separation and determination of nanogram amounts of inorganic arsenic and methylarsenic compounds. *Anal. Chem.*, 49: 621–625.
- Bright, D.A., Coedy, B., Dushenko, W.T. and Reimer, K.J., 1994. Arsenic transport in a watershed receiving gold mine effluent near Yellowknife, Northwest Territories, Canada. *Sci. Total Environ.*, 155: 237–252.
- Campbell, P.G.C., Lewis, A.G., Chapman, P.M., Crowder, A.A., Fletcher, W.K., Imber, B., Luoma, S.N., Stokes, P.M. and Winfrey, M., 1988. Biologically available metals in sediments. *Nat. Res. Counc. Can.*, 27694, 298 pp.
- Crowder, A.A. and Macfie, S.M., 1986. Seasonal deposition of ferric hydroxide plaque on roots of wetland plants. *Can. J. Bot.*, 64: 2120–2124.
- Cullen, W.R. and Reimer, K.J., 1989. Arsenic speciation in the environment. *Chem. Rev.*, 89: 713–764.
- Guilizzoni, P., 1991. The role of heavy metals and toxic materials in the physiological ecology of submersed macrophytes. *Aquat. Bot.*, 41: 87–109.
- Horowitz, A.J. and Elrick, K.A., 1990. Arsenopyrite in the bank deposits of the Whitewood Creek–Bell Fourche–Cheyenne River–Lake Oahe system, South Dakota, U.S.A. *Sci. Total Environ.*, 97–98: 219–233.
- Jackson, L.J. and Kalff, J., 1993. Patterns in metal content of submerged aquatic macrophytes: the role of plant growth form. *Freshwater Biol.*, 29: 351–359.
- Jackson, L.J., Rasmussen, J.B., Peters, R.H. and Kalff, J., 1991. Empirical relationships between elemental composition of aquatic macrophytes and their underlying sediments. *Biogeochemistry*, 12: 71–86.
- Kabata-Pendias, A. and Pendias, H., 1992. *Trace Elements in Soils and Plants*, 2nd edn. CRC Press, Boca Raton, FL, 365 pp.
- Lee, C.K., Low, K.S. and Hew, N.S., 1991. Accumulation of arsenic by aquatic plants. *Sci. Total Environ.*, 103: 215–227.
- Mok, W.M. and Wai, C.M., 1989. Distribution and mobilization of arsenic species in the creeks around the Blackbird Mining District, Idaho. *Wat. Res.*, 23: 7–13.
- Moore, J.W., Sutherland, D., Beaubien, V.A. and Wheeler, S.J., 1979. The effects of metal mines on aquatic systems in the Northwest Territories. III. Cominco Ltd., Con Mine, Yellowknife, N.W.T., Rep. EPS-5-NW-79-5.

- Mudroch, A. and Capobianco, J.A., 1979. Effects of mine effluents on uptake of Co, Ni, Cu, As, Zn, Cd, Cr and Pb by aquatic macrophytes. *Hydrobiologia*, 64: 223-231.
- Olsen, S.R. and Dean, L.A., 1965. Phosphorus. In: C.A. Black (Editor), *Phosphorus, Methods of Soil Analysis*. Part 2. Agron. No. 9, Am. Soc. Agron., Madison, WI, pp. 1035-1049.
- Otte, M.L., Rozema, J., Beek, M.A., Kater, B.J. and Broekman, R.A., 1990. Uptake of arsenic by estuarine plants and interactions with phosphate, in the field (Rhine Estuary) and under outdoor experimental conditions. *Sci. Total Environ.*, 97-98: 839-854.
- Raven, P.H., Evert, R.F. and Curtis, H., 1976. *Biology of Plants*, 2nd edn. Worth, New York, 685 pp.
- Reay, P.F., 1972. The accumulation of arsenic from arsenic-rich natural waters by aquatic plants. *J. Appl. Ecol.*, 9: 557-565.
- Reimer, K.J., 1989. The methylation of arsenic in marine sediments. *Appl. Organomet. Chem.*, 3: 475-490.
- Reuther, R., 1992. Arsenic introduced into a littoral freshwater model ecosystem. *Sci. Total Environ.*, 115: 219-237.
- Sanders, J.G., 1985. Arsenic geochemistry in Chesapeake Bay: dependence upon anthropogenic inputs and phytoplankton species composition. *Mar. Chem.*, 17: 329-340.
- Sanders, J.G. and Windom, H.L., 1980. The uptake and reduction of arsenic species by marine algae. *Estuarine Coastal Mar. Sci.*, 10: 555-567.
- St. Cyr, L., 1989. Iron plaque of *Phragmites australis* (Cav) Trin. ex. Stuedel and bioavailability of iron, manganese, copper, zinc and nickel. Ph.D. Thesis, Department of Biology, Queen's University at Kingston, Ont., 212 pp.
- Wagemann, R., Snow, N.B., Rosenberg, D.M. and Lutz, A., 1978. Arsenic in sediments, water and aquatic biota from lakes in the vicinity of Yellowknife, Northwest Territories, Canada. *Arch. Environ. Contam. Toxicol.*, 7: 169-191.
- Wallace, R.R. and Hardin, M.J., 1975. Chemical and biological characteristics of seepages from tailings areas at Cominco Coastline into Kam Lake, Northwest Territories, 1974. Reports EPS 5-NW-75-3.
- Wallace, A., Mueller, R.T. and Wood, R.A., 1980. Arsenic phytotoxicity and interactions in bush bean plants grown in solution culture. *J. Plant Nutr.*, 2: 111.
- Van Wijck, C., de Groot, C.J. and Grillas, P., 1992. The effect of anaerobic sediment on the growth of *Potamogeton pectinatus* L.: the role of organic matter, sulphide and ferrous iron. *Aquat. Bot.*, 44: 31-49.