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Arsenic speciation in marine interstitial water. The occurrence of organoarsenicals

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Abstract. Arsenic speciation data are presented for pore waters squeezed from some native and anthropogenically influenced sediments.

Ten stations were sampled with a box corer (to 20 cm) at two British Columbia coastal sites that are influenced by mine-tailings discharges. These are Rupert Inlet and Alice Arm as well as their associated systems of Quatsino Sound/Holberg Inlet and Hastings Arm respectively.

Total dissolved arsenic concentrations ($\sum As_D$) usually exhibited subsurface maxima at 5–10 cm and were generally related to solid phase arsenic (As_p) levels, but there was also a dependence on the nature of the substrate. Tailings exhibited both the lowest (Rupert Inlet) and the highest (Alice Arm) $\sum As_D$ values. Inorganic arsenicals, arsenate (AsV) and arsenite ($AsIII$) constituted the majority (> 90%) of the dissolved species but *every* sample contained organoarsenicals. This is the first report of mono-, di- and tri-methylated arsenic species in marine interstitial water.

A strong positive correlation between the sum of the methylarsenic compounds ($\sum MeAs$) and the total dissolved arsenic ($\sum As_D$) was found, indicating in situ microbial methylation similar to that observed in non-aquatic systems. Flux values for arsenic at the sediment-water interface suggest that, at present, there is no significant mobilization of arsenic from these mine-derived sediments into the water column.

Introduction

To the general public, arsenic is virtually a synonym for poison (Frost 1984) and this has prompted the measurement of total, *elemental*, arsenic levels in almost every type of substrate. However, recognition that arsenic compounds vary greatly in their toxicities, and the development of analytical techniques capable of determining low concentrations of individual arsenic species, has led to a more realistic appreciation of the impact and fate of both natural and anthropogenically-derived arsenicals (Andreae 1985; Fowler 1983; Lederer & Fensterheim 1983).

Concern about topics such as the use of arsenical herbicides and the arsenic byproducts from smelting and fossil fuel intensive operations, has focused most research on soils, and on the water and sediments of fresh-

water systems. These studies have demonstrated the importance of redox interconversions of the inorganic arsenic compounds, arsenate (*AsV*) and arsenite (*AsIII*), as well as the biomethylation of these species to produce an array of organoarsenic derivatives including: monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsine oxide (TMAO) and their reduced analogues – monomethylarsine (MMA), dimethylarsine (DMA) and trimethylarsine (TMA). A great deal has also been learned about the biochemical pathways of these processes (Challenger 1945; Cullen et al. 1984; Zingaro & Bottino 1983).

Recently there has been considerable interest in the biogeochemical cycling of arsenic in the marine environment (Andreae 1985). Marine bacteria have been found to cause the reduction (Johnson 1972) and oxidation (Scudlark & Johnson 1982) of inorganic arsenic, as well as the demethylation of DMAA (Sanders 1979). The presence of dissolved MMAA and DMAA in association with growing algae in the water column (Andreae 1978, 1979) and in axenic cultures (Andreae & Klumpp 1979; Sanders & Windom 1980) is consistent with biomethylation as a detoxification process. Much less is known about the speciation of arsenic in marine sediments (Maher 1984) – especially in pore waters (Andreae 1979; Peterson & Carpenter 1986; Edenborn et al. 1986).

Our study was predicated on two points. Firstly, the speciation and mobility of arsenic in contaminated freshwater sediments has been the subject of numerous reports (eg. Brannon & Patrick 1987), but little attention has been given to coastal marine areas which have been subjected to severe perturbation from industrial activities. Secondly, no organoarsenicals had been detected in marine interstitial water. None were found in the first study (Andreae 1979) and this has led to the conclusion that such species are not present in marine pore waters (Andreae 1985). This assumption prompted at least one group (Peterson & Carpenter 1986) to not analyze for methylated compounds. These statements are inconsistent with the obvious facile methylation by a diversity of organisms and directly contradicted our own work (Reimer; Thompson, unpublished; Sharon 1983) where sediments incubated in the presence, or absence, of added inorganic arsenic generated a variety of methylated arsenic species. Recently, mono- and di-methylarsenic compounds were extracted from estuarine but not pelagic sediments (Maher 1984) and were detected in estuarine porewaters (Ebdon et al. 1987). However, it was not clear if these organoarsenicals were formed in situ or if they were introduced by riverine input of agricultural chemicals and/or degradation of biological debris.

We describe here the results of a multi-year investigation of the sediments from two anthropogenically influenced British Columbia coastal sites. The

data unequivocally demonstrate the presence of mono-, di-, and tri-methylated arsenic species in marine sediment pore waters.

Study areas

The British Columbia coastline is the site of several mines which discharge mill tailings directly into abutting fjords. Two such fjords are Rupert Inlet and Alice Arm, located on northern Vancouver Island and the northern British Columbia mainland, respectively (Fig. 1).

Rupert/Holberg Inlets, Quatsino Sound

Rupert and Holberg Inlets (Fig. 2) are located near the northern tip of Vancouver Island, British Columbia. Physiography and hydrography have been described recently by Pedersen (1984). The Island Copper Mine is located on the northern shore of Rupert Inlet. The mine, producing copper, molybdenum and some platinum group metals has been in operation since

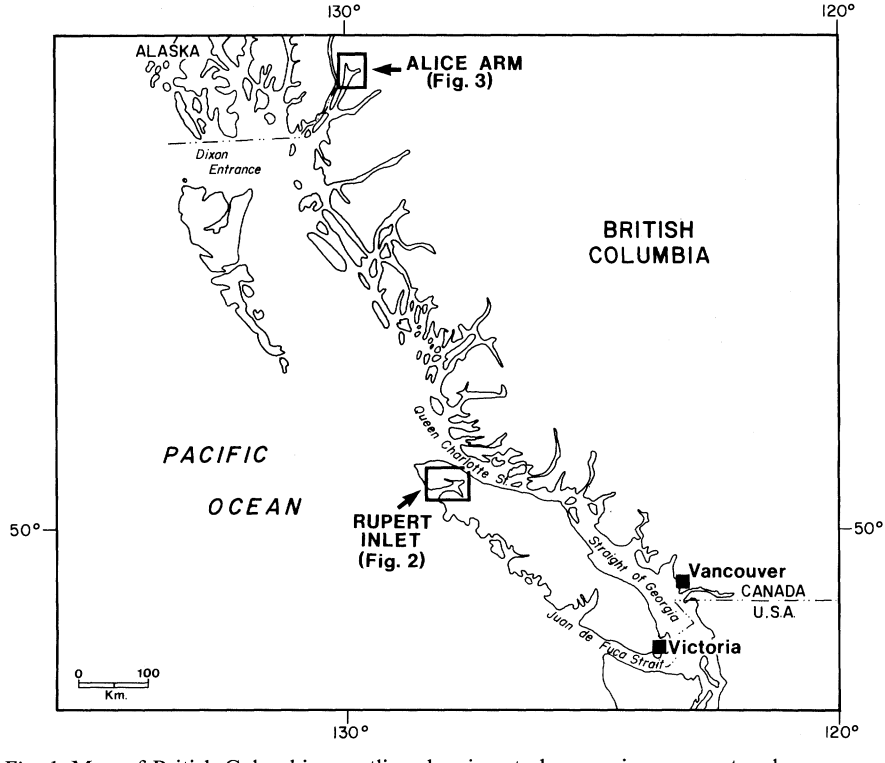

Fig. 1. Map of British Columbia coastline showing study areas in open rectangles.

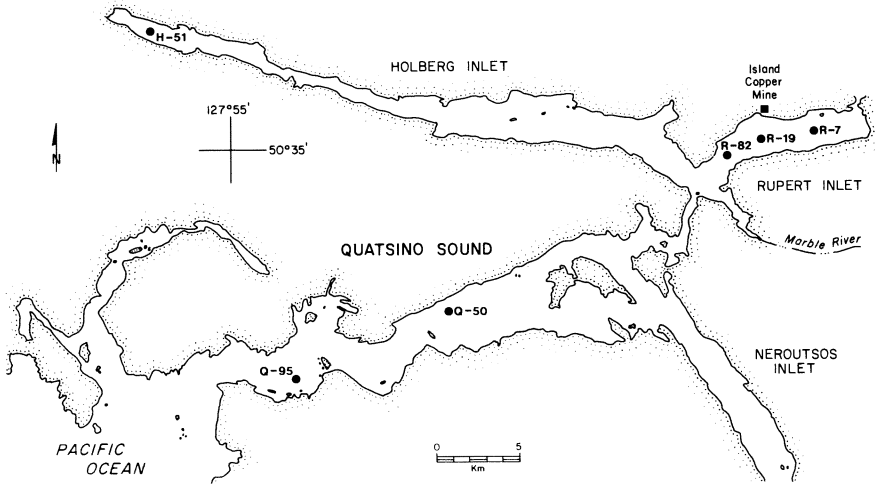

Fig. 2. Map of Rupert–Holberg–Quatsino study area. Core stations are indicated.

1971. Presently, about 4×10^4 t day^{-1} of alkaline tailings (pH 10–11) are discharged into the inlet via a submerged outfall at 50 m. To date, in excess of 200×10^6 tonnes of tailings have been discharged, resulting in accumulations of material tens of metres thick on the inlet floor. Because of vigorous tidal mixing, tailings have been transported about half the length of Holberg Inlet and out into adjoining Quatsino Sound over the 18 m sill in Quatsino Narrows. Tailings consist of silt-sized quartz, felspar, biotite and chlorite particles. Pyrite is found at concentrations of up to 4%. Copper and molybdenum are enriched in the tailings to concentrations of ~ 700 and 40 *mg kg*$^{-1}$ respectively. Arsenic averages 5 *mg kg*$^{-1}$ as arsenopyrite (Poling 1982) while dissolved As in mill effluent has been reported as 37 μgL^{-1} (Pelletier 1977). In addition to mill tailings, overburden, amounting to $\sim 1.2 \times 10^5$ t day^{-1}, from the open pit has been used as fill on the foreshore. This material has been placed to the east of the tailings outfall.

Alice Arm and Hastings Arm

Alice Arm and Hastings Arm (Fig. 3) are the termini of a system of inlets running 110 km inland from the outer Pacific coast on the northern mainland of British Columbia. Alice Arm is the site of the Kitsault molybdenum mine which is located near the head of the inlet on the eastern side.

Alice and Hastings Arms are typical westcoast fjords which are characterized by steep sides and shallow sills created by terminal glacial moraines. A complex of sills is found at the confluence of the two fjords in Observatory

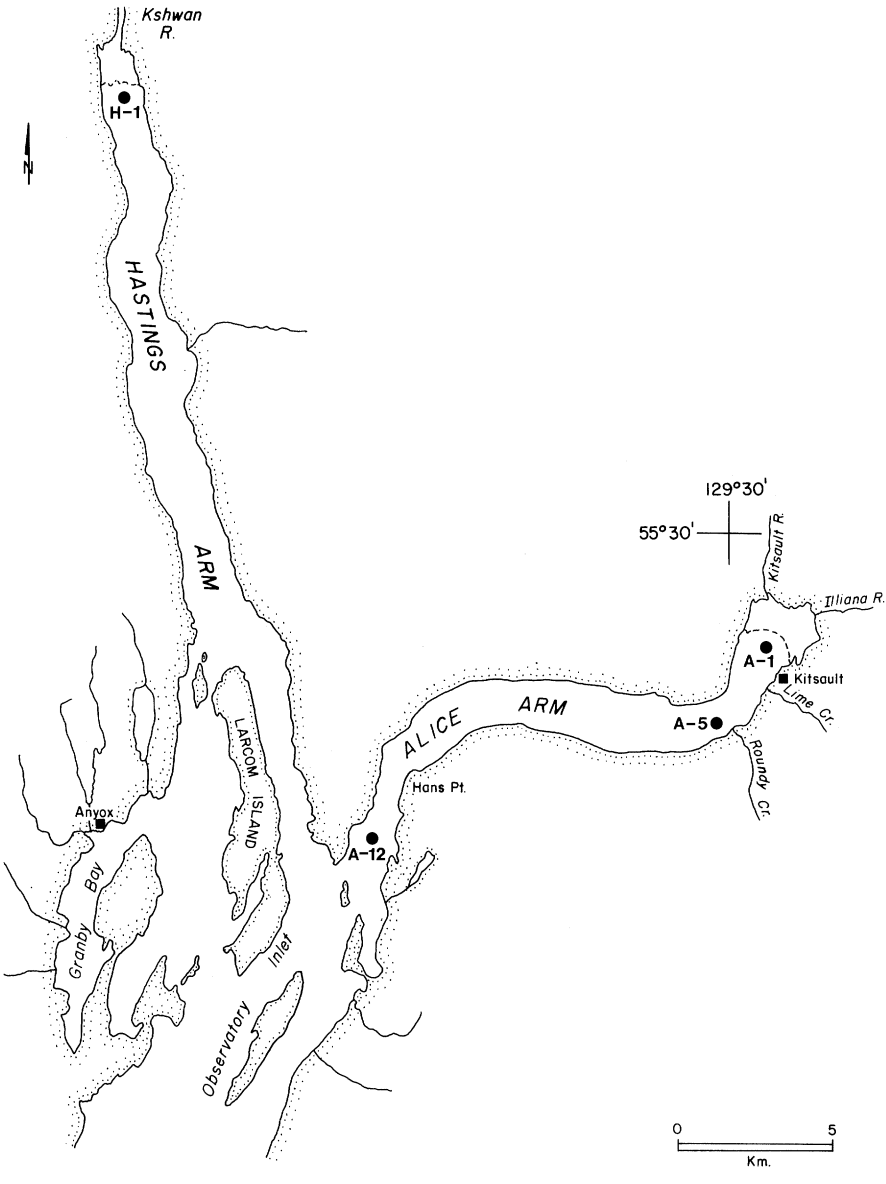

Fig. 3. Map of Alice–Hastings study area. Core stations are indicated.

Inlet (Fig. 3). Hastings Arm is separated from Observatory Inlet by a sill of 51 m depth. Two sills of 42 and 20 m at the mouth of Alice Arm restrict water exchange.

The site at Kitsault was first developed in 1967 and operated as BC Molybdenum for 5 years. During this period mill tailings were discharged

to Alice Arm surface waters via Lime Creek. In April 1981, the redeveloped (Amax) site was put into operation with a throughput of 12×10^3 t of ore day^{-1}. Tailings effluents were discharged via a submarine outfall at 50 m. Operations were terminated in November 1982, owing to a soft market for molybdenum.

The tailings solids are enriched in *Mo*, *Zn*, *Cd* and *Zn* inter alia. The ore body is depleted in As with respect to surrounding formations (Woodcock & Carter 1976). However, arsenic concentrations in tailings have been reported previously to range from 20 to 31 $mg\,kg^{-1}$ (Goyette & Christie 1982) which is slightly lower than values (29–38 $mg\,kg^{-1}$) reported by Burling et al. (1981) for riverine sediment input.

Methods

Sampling

Box cores were collected at stations in Rupert Inlet, Holberg Inlet and Quatsino Sound (Fig. 2) in 1981 and 1983 and in Alice Arm and Hastings Arm in 1983 only (Fig. 3). There was good agreement between the results of the 1981 and 1983 cruises. However, for brevity, only the 1983 results are presented.

The stainless steel box sampler employed was originally supplied by Kahlsico (San Diego). Extensive modifications were made to the box to permit collection of undisturbed cores of up to 50 cm in depth and horizontal subsectioning of the core without extrusion. The latter was accomplished by fitting a face plate through which rows of ports had been cut. The ports were cut to accept plastic 50 cc syringe barrels with the luer tips removed. Prior to each cast, the interior side of the face plate was lined with heavy polyethylene sheet (0.25 mm diameter or greater). Upon core retrieval, the plastic over each port was cut and the syringe barrels carefully inserted across the core. Quadruplicate horizontal subsamples were obtainable at each depth. The spacing between centers was 2 cm and they were arranged so as to permit overlap between core sections (i.e. 0–3, 2–5 cm etc). These overlaps are indicated by the vertical bars in Figs. 4–7.

Filled syringes were placed into plastic sleeves, sealed and immediately removed to the pore water sampling assembly or to a cooler (4 °C). The assembly was a custom-designed nitrogen-pressure system patterned after that reported by Reeburgh (1967). Our assembly consisted of three pressure cells constructed entirely of milled polypropylene stock. Each cell containing up to 100 mL of sediment was fitted with a polyethylene filter support

(Millipore), over which was placed an acid-washed 0.45 μm cellulose acetate membrane filter (Millipore). The sediment was extruded from the syringe into the cell and was covered with acid-washed latex dental dam cut to the outer diameter of the cell. Each entire cell assembly was held in place in a modified "C" clamp. The clamped cells were contained in a modified fiberglass glove box (Labconco Model 50004). All manipulations with sediment and pore waters were made in the glove box under a continuous flow nitrogen atmosphere. Nitrogen pressure applied directly to the cells varied between 138 and 207 kPa.

In some cases, the sediment was taken from the box sampler by syringe and expelled directly into a whirl-pack bag. This intact sediment was then frozen on dry ice, stored at −20 °C, and returned to the RRMC laboratory. Shortly before analysis, each sample was thawed, taking care to keep the temperature below 10 °C and the pore water was extracted as described above. We have found (Reimer, unpublished) that, depending on the substrate, this procedure yields results that are identical to those obtained for samples that were squeezed on board.

Expressed pore water from each cell was collected in a polyethylene bottle which had been pre-cleaned by repeated washings in hydrochloric acid and doubly-deionized water (Milli-Q). Sample bottles were sealed under nitrogen. Pore water samples for As speciation were frozen without addition of any preservative.

Analysis

Interstitial water arsenic speciation

Arsenate and arsenite, MMAA, DMAA and TMAO were converted to AsH_3 and the corresponding methylarsines and determined by a procedure modified from Andreae (1977) and Braman et al. (1977).

Interstitial water aliquots were introduced into a rigorously pre-silanized (dimethyldichlorosilane, Sigma) reaction vessel and buffered with Tris-HCl to pH 6. Slow addition of 4% KBH_4 released AsH_3 from *AsIII* only. After the liberated AsH_3 was analyzed by the system described below, the water sample was acidified to pH 1 by the addition of 4 M *HCl*. Further addition of KBH_4 reduced *AsV* and the methylarsenic acids to AsH_3, MMA, DMA and TMA. These were swept from the reaction vessel by a helium flow, through a −78 °C water trap, and collected in a U-tube immersed in liquid nitrogen. This U-tube was partly filled with 15% OV-3 on Chromosorb W AW/DMCS 60/80 mesh and was wrapped with a coil of nichrome wire that was attached to a temperature programmer. When the trapping period was over, the liquid nitrogen was removed, a gas sampling valve was switched,

and the temperature program initiated. This resulted in the arsenicals being sequentially released via a boiling point separation. They were swept by a second helium flow to an Instrumentation Laboratories 351 Atomic Absorption spectrophotometer where they were combusted in a hydrogen-air flame in a quartz curvette. The signal was monitored at 193.7 nm and processed by a Hewlett Packard 3390 A integrator.

The detection limits (Long & Winefordner 1983), were found to be: *AsIII*, 0.12 ng; *AsV*, 0.25 ng; MMAA, DMAA, TMAO, 0.25 ng. Due to the large difference in the inorganic- and organo-arsenic concentrations, these were usually determined using two separate aliquots of 2–5 ml and 30 ml respectively. Concentrations of individual arsenic species are reliable to $\pm 5\%$.

Some caveats are worth stressing. We, and others (Anderson et al. 1986), have found that DMAA detection is very pH dependent and we have noted that this species is easily lost if excess water is not carefully removed from the system. Also, reports of TMAO in any environmental substrate are few. This may be due in part to the employment of techniques primarily designed for the detection of mono- and di-methylated species (Ebdon et al. 1987) or to inattention to the special requirements needed for this compound. When these requirements have been satisfied, TMAO has been found in samples where it has previously been overlooked (Odanaka et al. 1983). In the case of the hydride generation procedure used here, the evolved TMA was not observed as a distinct peak unless the chromatographic packing was heated to at least 150 °C. Reagent blanks and standard curves were run continuously to ensure the quality of the data. It is unlikely, but possible that other dissolved arsenic species could produce identical volatile arsenicals. However, in the absence of such information we elected to report our results in terms of As V, As III, MMAA, DMAA and TMAO only.

Solid phase arsenic

Arsenic compounds not dissolved in pore water were defined as solid phase arsenic and determined by hydride generation and atomic absorption detection of samples obtained by aqua regia digestion (Government of Canada, 1979). A marine sediment standard (NRC MESS−1) was included with each set of sediments and results are considered valid to $\pm 10\%$.

Results

Rupert/Holberg/Quatsino

Porewater profiles for total dissolved arsenic ($\sum As_D$), *AsV* and the total of the methylarsenic species concentrations ($\sum MeAs$) in four shallow box cores

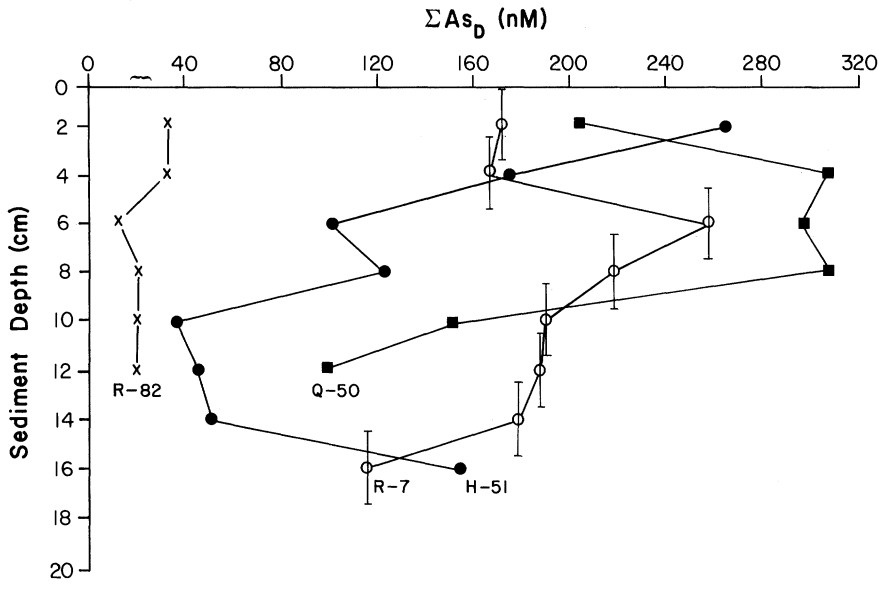

Fig. 4. Total dissolved *As* ($\sum As_D$) profiles for pore waters from Rupert–Holberg–Quatsino study. Curved bracket on concentration axis denotes range of interfacial *As* concentrations.

are displayed in Figs. 4, 5 and 6, respectively. As can be seen from Fig. 2, stations R-7 and R-82 were most directly affected by mine discharges. At R-7 the non-detrital material consisted of an overburden removed to expose the ore body and of tailings material, whereas R-82 samples were comprised exclusively of tailings material in a zone of rapid deposition. The lack of a major riverine influence together with little water exchange over the shallow sill, resulted in station H-51 sediments being largely anoxic. Station Q-50, in Quatsino Sound, was representative of coastal oceanic conditions.

Total dissolved arsenic concentrations were the highest at R-7 and Q-50. The $\sum As_D$ and *AsV* profiles were also similar, displaying maxima of 265–318 nM and ~140 nM respectively, at a depth of ~6 cm. In contrast, at R-82 dissolved arsenic and arsenate were invariant and consistently below 40 nM. At H-51 the surficial $\sum As_D$ maximum of 268 nM decreased to 38 nM at a depth of ~10 cm. The increase in *AsV* at the base of the core is not consistent with the decreasing redox potential expected for this station, and may be a result of post-sampling oxidation of arsenite.

Methylarsenic profiles (Fig. 6) represent the sum of the quantities of mono-, di- and tri-methylated species (Table 1). Maxima at the 6–8 cm depths in cores R-7 and Q-50 were coincident with those observed for $\sum As_D$ and *AsV*, but the values were much lower – 10 and 14 nM respectively. The $\sum MeAs$ concentrations were well below 4 nM at H-51 and R-82 but the

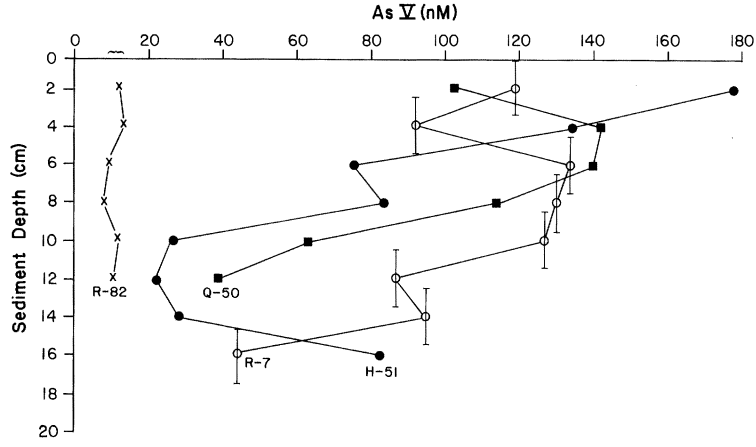

Fig. 5. Arsenic *V* profiles for pore waters from Rupert–Holberg–Quatsino study. Curved bracket on concentration axis denotes range of interfacial *As* concentrations.

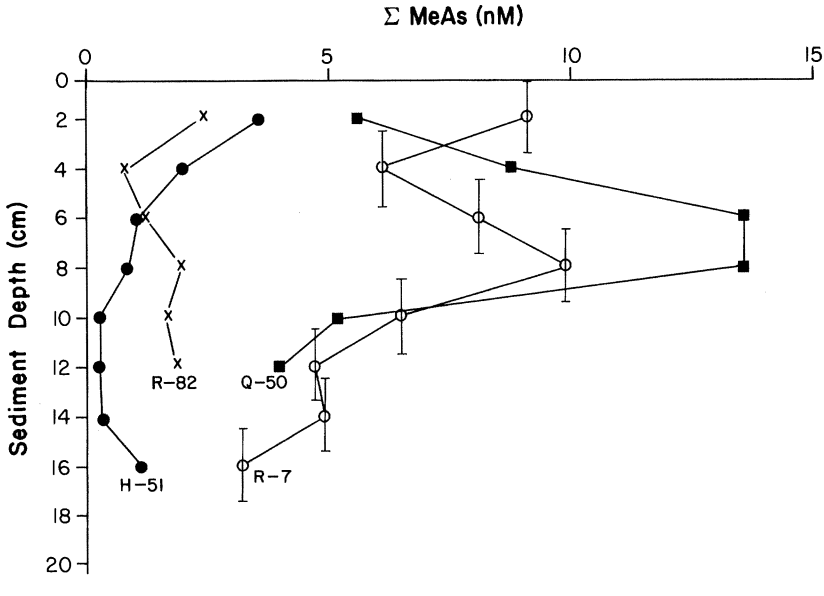

Fig. 6. Total methylarsenical ($\sum MeAs$) profiles for pore waters from Rupert–Holberg–Quatsino study.

Table 1. Methylarsenic[a] speciation: Rupert–Holberg–Quatsino.

Station/Depth (cm)	Concentration (nM)		
	MMAA	DMAA	TMAO
R-7			
0–3	4.5	1.9	2.7
2–5	2.7	2.3	1.2
4–7	4.1	1.5	2.5
6–9	3.3	3.2	3.3
8–11	2.7	2.3	1.6
10–13	1.9	1.9	0.9_3
12–15	2.1	1.7	1.1
14–17	1.2	1.5	0.5_3
H-51			
0–3	< 0.1	< 0.1	3.6
2–5	< 0.1	< 0.1	2.0
4–7	< 0.1	< 0.1	1.1
6–9	< 0.1	0.5_3	0.9_3
8–11	< 0.1	< 0.1	0.2_7
10–13	< 0.1	< 0.1	0.2_7
12–15	< 0.1	< 0.1	0.4_0
14–17	< 0.1	< 0.1	1.2
R-82			
0–3	0.3_6	0.5_3	1.5
2–5	0.2_7	0.1_3	0.4_0
4–7	0.5_3	0.4_0	0.2_7
6–9	0.8_0	0.8_0	0.4_0
8–11	1.1	0.4_0	0.2_7
10–13	0.8_0	0.6_7	0.4_0
Q-50			
0–3	1.3	< 0.1	4.3
2–5	1.5	1.2	7.1
4–7	1.7	2.5	9.3
6–9	2.4	2.9	8.2
8–11	0.1_3	< 0.1	5.1
10–13	0.2_7	0.5_3	3.2

[a] MMAA = monomethylarsonic acid; DMAA = dimethylarsinic acid; TMAO = trimethylarsine oxide.

profiles generally followed those for $\sum As_D$. Concentrations of the individual methylarsenicals are given in Table 1.

Alice Arm/Hastings Arm

Shorter cores were obtained in this area. Accordingly, the data are presented in Table 2 and only representative profiles are plotted as Fig. 7. Sediments

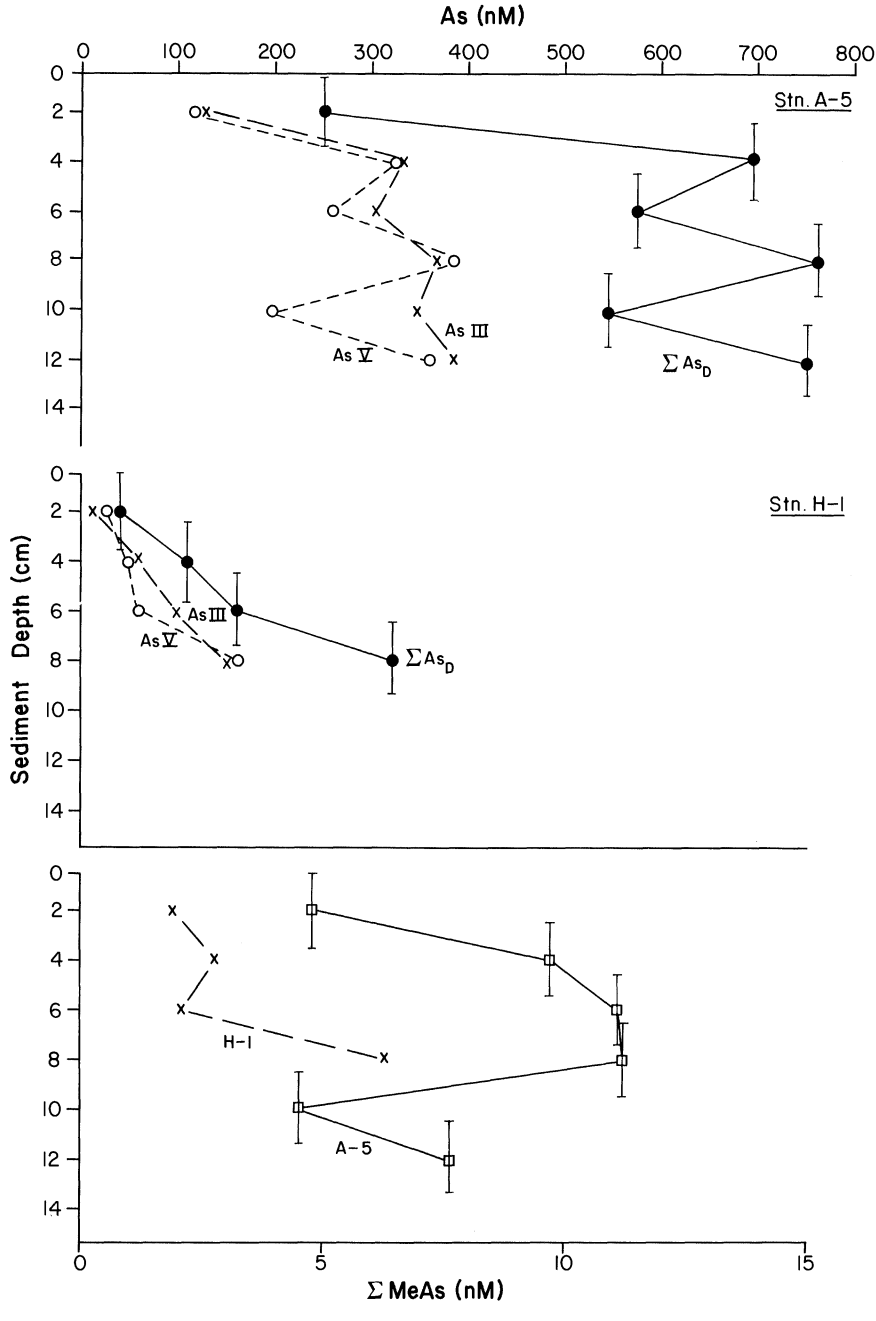

Fig. 7. Inorganic arsenic species profiles (top, middle) and total methylarsenical profiles (bottom) for stations A-5 and H-1 in the Alice-Hastings study.

Table 2. Concentrations (nM) of arsenic species[a]: Alice–Hastings.

Station/Depth (cm)	As V	As III	MMAA	DMAA	TMAO
H-1					
0–3	26.7	10.7	0.1_3	1.7	< 0.1
2–5	49.3	58.7	0.4_0	1.2	1.2
4–7	60.0	100.0	0.2_7	1.2	0.6_7
6–9	161.3	153.3	0.2_7	3.1	2.9
A-12					
0–3	117.3	38.7	0.5_3	1.1	1.3
2–5	141.3	72.0	0.8	2.3	1.7
4–7	61.3	62.7	1.1	2.5	0.9_3
A-1					
0–3	30.7	45.3	0.5_3	1.1	0.6_7
2–5	68.0	54.7	0.4_0	1.2	0.6_7
4–7	44.0	40.0	0.2_7	1.1	0.5_3
A-5					
0–3	120.0	126.7	2.7	1.1	1.1
2–5	353.3	330.7	6.3	0.8_0	2.7
4–7	261.3	304.0	5.3	0.8_0	4.4
6–9	384.0	366.7	4.7	1.1	5.5
8–11	196.0	345.3	0.8_0	1.5	2.3
10–13	358.7	384.0	3.4	1.3	2.8

[a] As V = arsenate; As III = Arsenite; MMAA = monomethylarsonic acid; DMAA = dimethylarsinic acid; TMAO = trimethylarsine oxide.

collected at station A-5 consisted almost entirely of tailings due to the proximity of the submarine outfall. Station A-1 and H-1 were both near river estuaries and A-12 was located to the seaward side of the sill in Alice Arm (Fig. 3); these three stations should therefore be representative of different, but nevertheless natural sedimentary environments.

In core A-5 the $\sum As_D$ concentrations increased rapidly from 247 nM to ~ 684 nM in the first 4 cm, and then fluctuated between 546 and 762 nM to the bottom of the core. These fluctuations were due primarily to similar changes in *AsV* concentrations, as the *AsIII* increase was more linear. Arsenic concentrations in this core were the highest of the entire study.

In contrast to A-5, $\sum As_D$ in core H-1 increased smoothly from 39 to 321 nM at the bottom of the core (8 cm). A-1 and A-12 appeared to display dissolved arsenic maxima of 125 and 218 nM at 2–5 cm depth.

At A-5, the $\sum MeAs$ profile displayed a maximum of ~ 11 nM at 6–8 cm. Although this was coincident with the elevated $\sum As_D$ values, $\sum MeAs$ and not $\sum As_D$ decreased at 10 cm. Methylarsenic species at H-1 were found at concentrations ranging from 1.8 to 6.3 nM and the profile paralleled the

inorganic arsenic values. If sediment of similar depth (7 cm) is compared, the overall methylarsenic concentrations decreased in the order: A-5 > A-12 > A-1 ≈ H-1.

Discussion

Organoarsenic compounds

The signal feature of this study is the detection of three methylated arsenicals in the interstitial waters of sediments, native and anthropogenic, from Pacific coastal waters. Quantities of mono-, di- and tri-methylated arsenicals up to 5.5 nM were found in two British Columbia inlets.

The profiles of the overall concentrations of these species ($\sum MeAs$) with depth (Figs. 6, 7), consistently displayed maxima at 3 to 8 cm – coincident with the maximum concentrations of total dissolved and inorganic arsenic. Furthermore, reduced major axis log-log plots of $\sum MeAs$ versus $\sum As_D$ at all depths (Figs. 8, 9) indicate for both study areas, a strong positive correlation between these parameters.

In the Rupert/Holberg/Quatsino study two different regimes can be noted (Fig. 9). Data for three cores (R-7, R-82 and Q-50) lie along one line ($y = 0.20x^{0.68}$; $r = 0.94$) which is comparable in slope to the line for the Alice Arm data (Fig. 8). The second line in fig. 9, representing only the core from

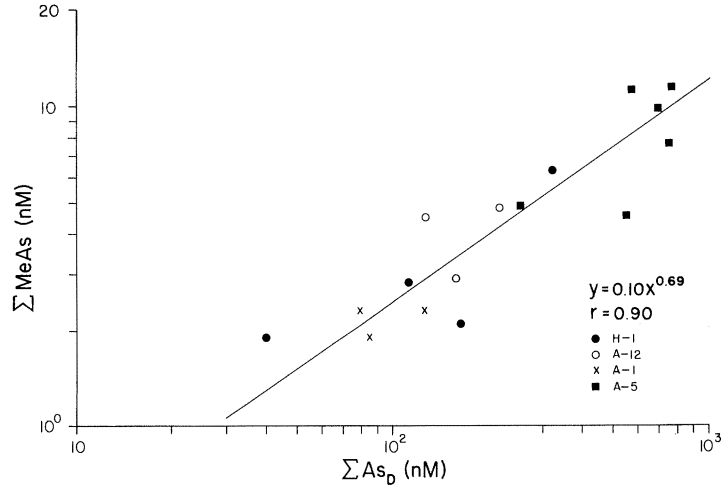

Fig. 8. Log-Log relationship between pore water concentrations of methylarsenicals ($\sum MeAs$) and total dissolved arsenic ($\sum As_D$) in the Alice–Hastings study.

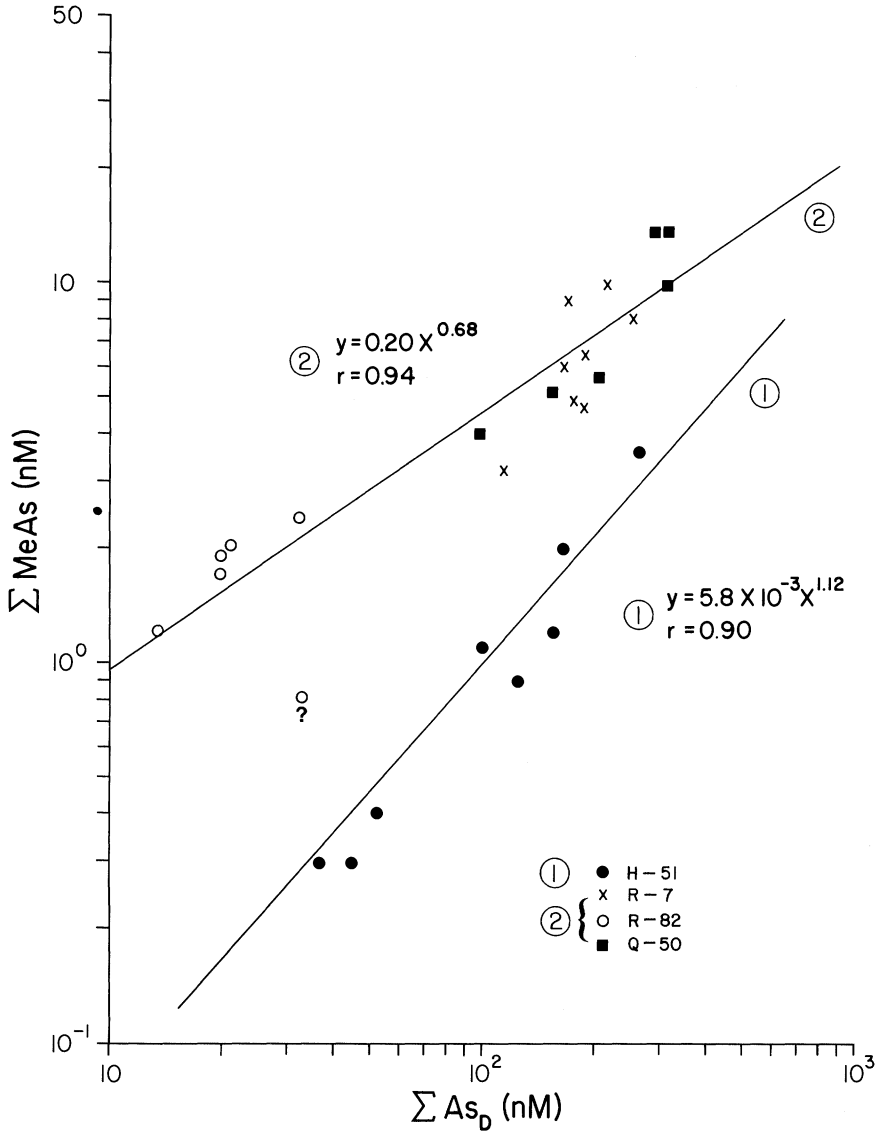

Fig. 9. Log-log relationship between pore water concentrations of methylarsenicals, ($\sum MeAs$) and total dissolved arsenic ($\sum As_D$) in the Rupert–Holberg–Quatsino study. Question mark indicates outlier.

station H-51 has a different slope and intercept ($y = 5.8 \times 10^{-3}x^{1.12}$; $r = 0.90$). A comparison of the slopes of the two lines indicated that they were statistically dissimilar at $p < 0.001$. These data clearly indicate that methylation was dependent upon the amount of dissolved arsenic in interstitial waters.

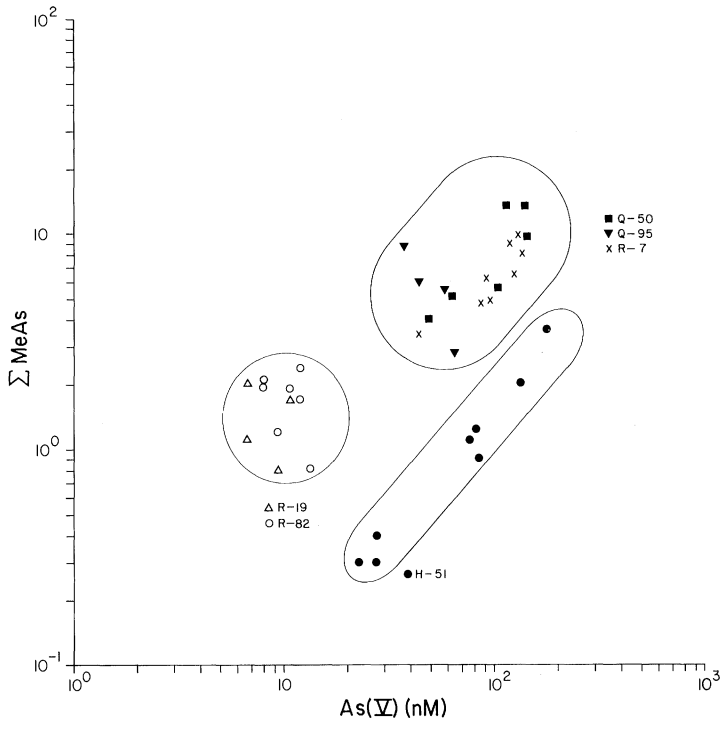

Fig. 10. Log-log relationship between methylarsenicals ($\sum MeAs$) and AsV showing clustering of data for similar sediment types in Rupert–Holberg–Quatsino area.

Fig. 10 represents a similar comparison of the pattern of methylation, but in this case to the AsV concentrations instead of to $\sum As_D$. As might be expected, a good correlation was found as the arsenate profiles themselves (Fig. 5) paralleled those for $\sum As_D$ (Fig. 4). Also, in this plot the data are clustered with respect to the type of sediments involved. The core from station R-82 was removed from an area where rapid sedimentation of fresh tailings was occurring; core Q-50 from near open coastal sediments; and R-7 from mine over-burden deposits mixed with light tailings and detrital material. Two additional stations, R-19 and Q-95, which, for brevity, have been omitted from the rest of this report are also included. Reference to Fig. 2 shows their geographical similarities to R-82 and Q-50 respectively, and these similarities were mimicked by their arsenic speciation. Lastly, core H-51 was taken from an area where anoxia is prevalent. In view of the observed clustering, we conclude that $\sum As_D$, and thus $\sum MeAs$, are determined by the characteristics of the sediments.

The sediment type also appears to affect the distribution of individual methylarsenic species (Table 3). Tailings (R-82, A-5) and tailings-influenced

Table 3. Relative (%) amounts[a] of methylarsenicals[b].

Station	MMAA	DMAA	TMAO
Rupert–Holberg–Quatsino			
R-7	43	30	27
R-82	39	29	32
H-51	n.d.[c]	n.d.	~100
Q-50	14	14	72
Alice–Hastings			
A-1	19	52	29
A-5	57	11	32
A-12	19	48	33
H-1	12	61	27

[a] Expressed as percent of total methylarsenicals in cores of comparable depth.
[b] MMAA = monomethylarsonic acid; DMAA = dimethylarsinic acid; TMAO = trimethylarsine oxide.
[c] n.d. indicates below limit of detection.

sediments (R-7) from both study areas contained higher relative concentrations of MMAA whereas this form was the least abundant in native sediments. The dimethyl and trimethyl moieties displayed no obvious pattern, except that at H-51 essentially only the trimethyl species was found.

To our knowledge, there are only two reports (excluding soils – e.g. Haswell et al. 1985) of possible arsenic methylation in pore waters. Crecelius (1975) noted higher concentrations of DMAA in Lake Washington sediments than in the overlying waters, but it has been suggested (Andreae 1985) that this may have been due to the decomposition of deposited algal material. Ebdon et al. (1987) found mono- and di-methyl arsenic compounds in an estuary but, once again, their formation from biological debris could not be excluded. In contrast, we conclude that the organoarsenicals observed in our study are due to in situ microbial methylation. We base this conclusion on two points:

- there is a strong correlation between $\sum MeAs$ and $\sum As_D$. It is unlikely that the decomposition of organic matter will directly parallel the release of inorganic arsenic to pore water.
- There is no relationship between $\sum MeAs$ and the organic carbon concentrations of 0.5% that have been found for tailings in Rupert Inlet (Pedersen 1985) and Alice Arm (Losher 1985) or those for natural sediments that are generally 1–2% (Losher 1985) or 7% in Holberg Inlet (Pedersen 1985).

Biological methylation of metals and metalloids is common in nature (Thayer & Brinckman 1982) and the biosynthesis of organoarsenic compounds from inorganic arsenic has been observed for a wide range of microroganisms (bacteria, fungi, algae), invertebrates and vertebrates – including man (Andreae 1985). The first example of arsenic methylation was the production of garlic smelling gas by moulds growing on wallpaper treated with arsenate-derived pigments. This gas was identified as trimethylarsine by Challenger (1945) who also proposed a pathway that has been largely confirmed (Cullen et al. 1984). This process involves successive reduction/oxidative methylation as follows (ignoring the degree of protonation):

$$As0_4^{3-}(AsV) \rightarrow As0_3^{3-}(AsIII) \rightarrow (CH_3)As0_3^{2-}(MMAA) \rightarrow (CH_3)_2As0_2^{-}(DMAA)$$

$$\rightarrow (CH_3)_3As0(TMAO) \rightarrow (CH_3)_3As(TMA)$$

Depending on the organism, this process can stop at the methylarsenic oxy acids (MMAA, DMAA) as it does for man, or produce additional volatile species such as AsH_3, $(CH_3)AsH_2$, $(CH_3)_2AsH$ as has been observed for the mixed microbial communities in soils (Andreae, 1985). It seems reasonable that these pathways should be available to marine organisms. However to date, only a few of the compounds have been reported.

Arsenic is incorporated intracellularly by algae, marine invertebrates and fish as more complex organo species (including arsenobetaine and arsenocholine), but MMAA and DMAA are excreted in the euphotic zone. The formation of methylarsenicals in sedimentary pore waters has been discounted by Andreae (1979, 1985) as they were not found in pore waters of sediments collected off the California coast, nor were they produced by methanogenic bacteria in laboratory cultured marine mud (McBride et al. 1978). However, Wong et al. (1977) have shown the production of MMAA, DMAA, TMAO, DMA and TMA in culture experiments with freshwater sediments. These experiments were conducted at elevated arsenic concentrations, and it has been suggested (Andreae 1985) that this is a bacterial response to extreme arsenic stress. However, we (Reimer unpublished) have confirmed Wong's results with sediments collected from the study areas described in this report; the absence of methylation when sediments were autoclaved providing additional evidence of microbial methylation at normal arsenic levels.

We were therefore not surprised to find the organoarsenicals reported

here; in fact, we were only surprised that they comprised such a low overall percentage ($< 10\%$) of the total dissolved arsenic content. Similarly small amounts (1–4%) were found in estuarine porewaters (Ebdon et al. 1987) and it seems likely that methylarsenic distributions are governed, as methyl mercury concentrations are (Spangler et al. 1973), by a balance between methylating and demethylating bacteria and by adsorption phenomena (Holm et al. 1980). It is also possible that a significant portion of the marine pore water organoarsenic budget is comprised of more volatile species (like MMA, DMA and TMA) which were lost during sampling. These compounds were found in our culture studies and were detected, albeit qualitatively, during our analysis of the water samples described here. Most of the sediments in this study were oxic. However, H_2S even at low concentrations could have lowered the apparent arsenical concentrations by producing thioarsenic compounds (e.g. $(CH_3)_3AsO \rightarrow (CH_3)_3AsS$; Cullen et al., 1984) which may not be detected by the procedure employed here. These factors probably influenced the H-51 arsenic profiles.

Total dissolved and inorganic arsenic

The dissolved arsenic concentrations presented here (40–700 nM) are similar to those (160–750 nM) reported by Peterson & Carpenter (1986) for other fjord sediments, and are greater than those found ($\leqslant 20$ nM) for oxic and anoxic deep ocean sediments (Andreae 1979). The deep ocean sediments' $\sum As_D$ profiles were essentially featureless with only slight increases with depth (to 85 cm) that were attributed to the release of arsenic from organic matter. In contrast, the fjord sediments exhibited narrow (2–3 cm) subsurface $\sum As_D$ maxima, in the upper 10 cm of the cores, that were most closely associated with dissolved Fe^{2+} profiles. Edenborn et al. (1986) made similar observations concerning coastal marine sediments and adapted a model (Aggett & O'Brien 1985) that proposes that arsenic is released to pore waters at the same time as iron. Surficial $\sum As_D$ profiles are then controlled by the upward diffusion of this material, followed by release to the overlying water column and/or co-precipitation with Mn and Fe oxides.

The cores were shorter in the study reported here but subsurface $\sum As_D$ maxima were apparent at 3–6 cm in most cases. The flat profile found at R-82 is consistent with the non-equilibrium conditions expected for these rapidly deposited tailings. At H-51, the maximum was located at the surface, similar to the behavior of arsenic in anoxic pore waters collected from Saanich Inlet (Peterson & Carpenter 1986). The most unusual behavior was noted for Alice Arm tailings (A-5) which displayed a rapid increase, at 4 cm, to fluctuating but high values of $\sum A_{s_D}$. The AsV profile paralleled these

Table 4. Arsenic III/V ratios in porewaters.

A. Rupert–Holberg–Quatsino Depth/Core (cm)	Q-50	R-82	R-7	H-51
0–3	0.9_4	1.6_7	0.3_7	0.4_7
2–5	1.1_1	1.4_0	0.7_4	0.3_0
4–7	1.0_2	0.4_3[a]	0.8_7	0.3_2
6–9	1.5_9	1.5_0	0.6_1	0.4_4
8–11	1.3_4	0.5_6	0.4_4	0.4_0
10–13	1.4_5	0.7_5	1.1_2	0.7_9
12–15	–	–	0.8_3	0.8_6
14–17	–	–	1.5_8	0.8_5
B. Alice–Hastings				
	A-1	A-5	A-12	H-1
0–3	1.4_8	1.0_6	0.3_2	0.4_0
2–5	0.8_0	0.9_4	0.5_1	1.1_9
4–7	0.9_1	1.1_6	1.0_2	1.6_7
6–9	–	0.9_5	–	0.9_5
8–1	–	1.7_6	–	–
10–13	–	1.0_7	–	–

[a] Possible outlier.

fluctuations, suggesting that it is a substrate-dependent phenomenon. This is supported by the smooth increase in *AsIII* which is more reflective of a redox gradient.

Relative quantities of *AsIII* and *AsV* were used by Peterson & Carpenter (1986) to evaluate redox conditions in the sediment column. In their study, *AsIII*/*AsV* ratios in some cores from the Washington coast were < 1.0, consistent with the dominance of *AsV* to depths of 40 cm. Two highly anoxic cores were devoid of *AsV* in all but three consecutive sections from one core – a result that was attributed to penetration of oxic overlying waters into the sediment. For more anthropogenically influenced Puget Sound cores the ratios were usually 1.0–4.0; these varied with the station and interestingly, values < 1.0 were found at the greatest depths. Consistent with these variations, the authors demonstrated that the arsenite-arsenate equilibrium is delicately poised, requiring in their study, a change in *pe* of only 0.6 to reverse the dominance of one or the other *As* species.

In the current study, *AsIII*/*AsV* ratios ranged from 0.30 to 1.8 (Table 4). For natural sediments the *AsIII*/*AsV* values were generally high at the surface and either increased with depth or remained essentially static through the length of the core. *AsIII* was also greater than, or equal to, *AsV* in the tailings material. Surprisingly, the *AsIII*/*AsV* ratio was < 1.0 at H-51,

Table 5. Solid phase arsenic (As_p) concentrations[a].

Rupert–Holberg–Quatsino Depth (cm)	R-7	R-82	H-51	Q-50
0–3	16.3(1.6)	14.9(3.7)	29.4(3.5)	13.5(2.1)
2–5	20.9(1.7)	16.3(3.6)	23.0(2.0)	14.2(2.3)
4–7	n.a.[b]	18.4(3.4)	n.a.	n.a.
6–9	n.a.	17.6(1.6)	25.6(3.2)	n.a.
8–11	15.5(1.2)	21.9(4.4)	19.2(0.4)	n.a.
10–13	n.a.	n.a.	25.2(4.3)	n.a.
12–15	n.a.	n.a.	20.0(1.0)	n.a.
14–17	17.0(0.8)	16.8(3.4)	28.2(3.4)	n.a.
Alice-Hastings Arm				
	A-5	A-12	H-1	A-1
0–3	34.1(1.3)	9.9(0.9)	16.6(0.3)	33.6(1.1)
2–5	n.a.	n.a.	n.a.	32.6(3.8)
4–7	33.7(1.8)	n.a.	n.a.	n.a.
6–9	29.9(5.9)	n.a.	n.a.	n.a.
8–11	32.5(2.4)	n.a.	n.a.	n.a.
10–13	29.6(0.3)	n.a.	n.a.	n.a.

[a] In units of $mg\,kg^{-1}$ ($\pm 1\,s$), dry weight.
[b] Not analyzed.

although it increased at depths ($\approx 17cm$) which were reported by Pedersen (1984) to coincide with the onset of sulfate reduction.

Considering the sensitivity of the $AsIII/AsV$ ratio, it might be anticipated that slight errors in the manipulation of the samples could result in large changes in the relative concentrations of these species (Peterson & Carpenter 1986). However, it seems most likely that such changes would favor the formation of AsV, and thereby result in consistently smaller $AsIII/AsV$ values than reported here. Further work is needed to evaluate the balance between heterogeneous redox reactions (Huang et al. 1982) and possible microbial transformations (Ehrlich 1981).

Solid phase arsenic concentrations (As_p) are often used as an indicator of the extent of arsenic impact in contaminated areas. It might be expected that dissolved arsenic levels would be a better measure of bioavailability, but in one report (Peterson & Carpenter 1986) it was noted that there was a statistically significant correlation between these parameters for marine, but not lacustrine, sediments. No such relationship ($r = 0.39$) is apparent between As_p (Table 5) and $\sum As_D$ if *all* of the stations investigated in this study are included. Anomalous behavior is apparent for two stations: R-82 and A-1. For example, the As_p values for R-7 and R-82 are comparable but $\sum As_D$

is 4–6 times larger at R-7 (Fig. 4). This might be expected for R-82 in view of the non-equilibrium conditions in freshly deposited tailings. It is less obvious why A-1 is non-conforming. Both of the estuarine sediments at A-1 and the tailings at A-5 give similar As_p, but vastly different $\sum As_D$ levels. If R-82 and A-1 are excluded from the comparison, a reasonable correlation is obtained ($r = 0.82$; *slope* = 16.4; *intercept* = 21.5). This correlation is further enhanced if H-51, where the presence of H_2S may suppress $\sum As_D$, is also excluded ($r = 0.96$; *slope* = 19.6; *intercept* = 4.4). Subsequent work in the same study areas (Reimer, unpublished) also supports this relationship, but in our more recent work we have also observed increased concentrations of dissolved arsenic at A-5. Collectively these data suggest that it may be dangerous to assume that $\sum As_D$ will always be proportional to As_p – especially for anthropogenically modified sediments. Factors other than the total concentration of arsenic in the solid phase may determine the dissolved arsenic levels. It is instructive to note that both the lowest and highest values of $\sum As_D$ (and $\sum MeAs$) were for tailings material (see Figs. 9, 10).

Mine tailings discharges

From an environmental perspective it is important to assess the role played by mine tailing discharges on the distribution of elements within the hydrogeosphere. Regardless of *As* concentrations in the tailings relative to the natural sediments, differences in the physico-chemical properties (e.g. particle size, freshly exposed surfaces, process chemicals) of these materials determine the extent of the diagenesis of arsenic, and may thereby modify release rates to the water column.

Fluxes between the sediment and the water column were estimated using Fick's first law (Table 6) with diffusion coefficients for tortuosity (Ullman & Aller 1982), temperature (Li & Gregory 1974) and also the consideration of porosity differences between natural sediments and sedimented tailings (Pedersen, pers. comm.).

Natural sediments (cores H-51 and Q-50 in Holberg-Quatsino; H-1 in Hastings) exhibited fluxes ranging from -0.10 up to $-0.53 \mu g\, cm^{-2} yr^{-1}$ for H-51. This suggests supply to the overlying waters, assuming no co-precipitation in the oxidized surface layer. Values reported by Peterson & Carpenter (1986) for two stations in the anoxic Saanich Inlet were slightly higher at -0.79 and $-0.85 \mu g\, cm^{-2} yr^{-1}$, and data for two stations in Puget Sound where total dissolved *As* was higher were very comparable to the fluxes reported here. However, a value of -2.4 was reported for a particularly contaminated area of Puget Sound.

Table 6. Fluxes of dissolved arsenic at the sediment–water interface.

	Core	$\frac{\delta \cdot [As]^a}{\delta z}$ ($\mu g\, cm^{-4}$)	J^b ($\mu g\, cm^{-2}\, yr^{-1}$)
Natural sediment	H-51	8.0×10^{-3}	−0.53
	Q-50	2.9×10^{-3}	−0.19
	H-1	1.5×10^{-3}	−0.10
Tailings	R-82	-0.083×10^{-3}	0.003
	R-7	1.6×10^{-3}	−0.09
	A-5	3.8×10^{-3}	−0.13

[a] Concentration gradient in sediment to $\delta[As]$ is difference between $[As]$ at maximum and bottom water. δz is depth of concentration maximum.

[b] Calculated from $J = -\phi(\delta[As]/\partial z)D_s$ (Fick's First Law) where $\phi \simeq 0.8$ (estimated average porosity for natural sediments) and $\simeq 0.6$ (for tailings); D_s is the bulk diffusion coefficient for $H_2AsO_4^-$ at 5 ° (Li & Gregory 1974) and corrected for tortuosity according to Ullman and Aller (1982). For tailings $D_s \simeq 57\, cm^2\, yr^{-1}$; for natural sediments $\simeq 80\, cm^2\, yr^{-1}$.

For the active tailings deposition in Rupert Inlet (cores: R-82 in Table 6 and R-19 where $J = 0.001\ \mu g\, cm^{-2}\, yr^{-1}$) fluxes between tailings and overlying waters are very weak, and these regions may serve as arsenic sinks. In contrast, the flux at R-7 is slightly negative. Based on these data, *present* conditions in Rupert Inlet are such that recently deposited mine tailings containing arsenic do not represent an immediate source of the element so as to result in an elevation of environmental concentrations. Within ten years it is expected that the ore body will be depleted and the operation will shut down. Once quiescence at the sediment-water interface occurs and surficial sediments become detrital in nature, conditions may become more reducing and more favorable to arsenic release. Any release, however, will be countered by the strong tidal flushing which occurs in the inlet and which would serve to dilute arsenic so introduced into the water column.

In the Alice Arm area, flushing rates within the fjord are considerably slower but partial or complete replacement of bottom water does occur annually (Rambold & Stucchi 1983; Stucchi pers. comm.). Tailings from the molybdenum mine here contain arsenic in greater quantities that those in Rupert Inlet which may be reflected in the higher dissolved *As* concentrations and the slightly greater flux (Table 6). Here the flux is very close to that for natural sediments at the head of Hastings Arm (core H-1) and again it would suggest that there would be an appreciable contribution of *As* to overlying waters.

Conclusions

In this study we have established that at least three methyarsenic species exist in coastal marine sediment pore waters. The quantities of these species bear a strong correlation to dissolved inorganic arsenic, which is in turn dependent on the sediment type. Approximate flux values for arsenic at the sediment water interface suggest that the mine-derived sediments investigated here do not represent an inordinate source of this element. However, in consideration of the finding that methylarsenic compounds represent up to 10% of total dissolved quantities, contributions to fluxes by these compounds may require further consideration.

Further work is required to identify the factors that influence the distribution of individual organoarsenicals with depth and the type of sediments. All of the available evidence suggests that these compounds are formed by in situ microbial methylation, but the involvement of exocellular biogenic metabolites cannot be completely excluded (Brinckman et al. 1985). The quantitative detection of MMAA, DMAA and TMAO, as well as the qualitative observation of the corresponding methylarsines, suggests that Challenger's reduction/oxidative methylation pathway may be more common in the aquatic environment than previously thought.

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