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REVIEW

Arsenic in the marine environment

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1 INTRODUCTION

Arsenic is a ubiquitous element in the marine environment. Historically arsenic has been of interest as its compounds are toxic but as well they have been shown to be of therapeutic value.[1] Because of the chemical similarity of arsenic and phosphorus, arsenate (AsO_4^{3-}) may follow the same metabolic pathways in organisms as phosphorus, and interfere in phosphorus metabolism.[2,3] However, it was reported by Chapman[4] in 1926 that arsenic in marine crustaceans and molluscs is non-toxic and it has been suggested recently that arsenic may be an essential element.[5]

Model calculations indicate that the surface waters of the oceans will see a 1% increase in the present arsenic concentration of 2 $\mu g\ dm^{-3}$ by the year 2000AD as a result of anthropogenic inorganic arsenic inputs.[6] Thus it is important to understand the natural biogeochemical cycle of arsenic in order to detect and evaluate changes arising from human activity.

Recent studies have shown that arsenic cycling not only involves arsenate, the major species in seawater, but the formation of reduced and methylated species (Fig. 1). Considerable effort has been directed towards the detection and elucidation of the structure of organoarsenic compounds in marine waters and organisms and to understand the role of biota in speciation changes. The purpose of this review is to give an overview of the biogeochemical cycling of arsenic in the marine environment with particular attention to speciation changes and the biogeochemical controls of arsenic concentration.

2 ARSENIC IN THE WATER COLUMN

2.1 Occurrence and speciation

The concentration of total dissolved arsenic in seawater is normally between 1.0 and 2.0 $\mu g\ dm^{-3}$ (13–27 $nmol\ dm^{-3}$).[7–9] The forms, or species of dissolved arsenic are limited to arsenate [arsenic(V)], arsenite [arsenic(III)], and the organoarsenic compounds, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA).[10,11] The latter three species are derived from biological activity. Arsenic(III) is a thermodynamically unstable oxidation state; the predicted ratio As(III/As(V) under oxic seawater conditions is $10^{-26.5}$.[12] The presence of arsenic(III) in oceanic surface waters is maintained by continual biological reduction of arsenic(V)[13–15] dynamically poised by chemical and biological oxidation of arsenic(III).[16] Both the mono- and di-methylated compounds of arsenic are chemically stable in seawater,[10,11] although they can be demethylated by bacterial assemblages.[17] Using techniques that quantitatively convert all organoarsenic compounds, Andreae has shown that

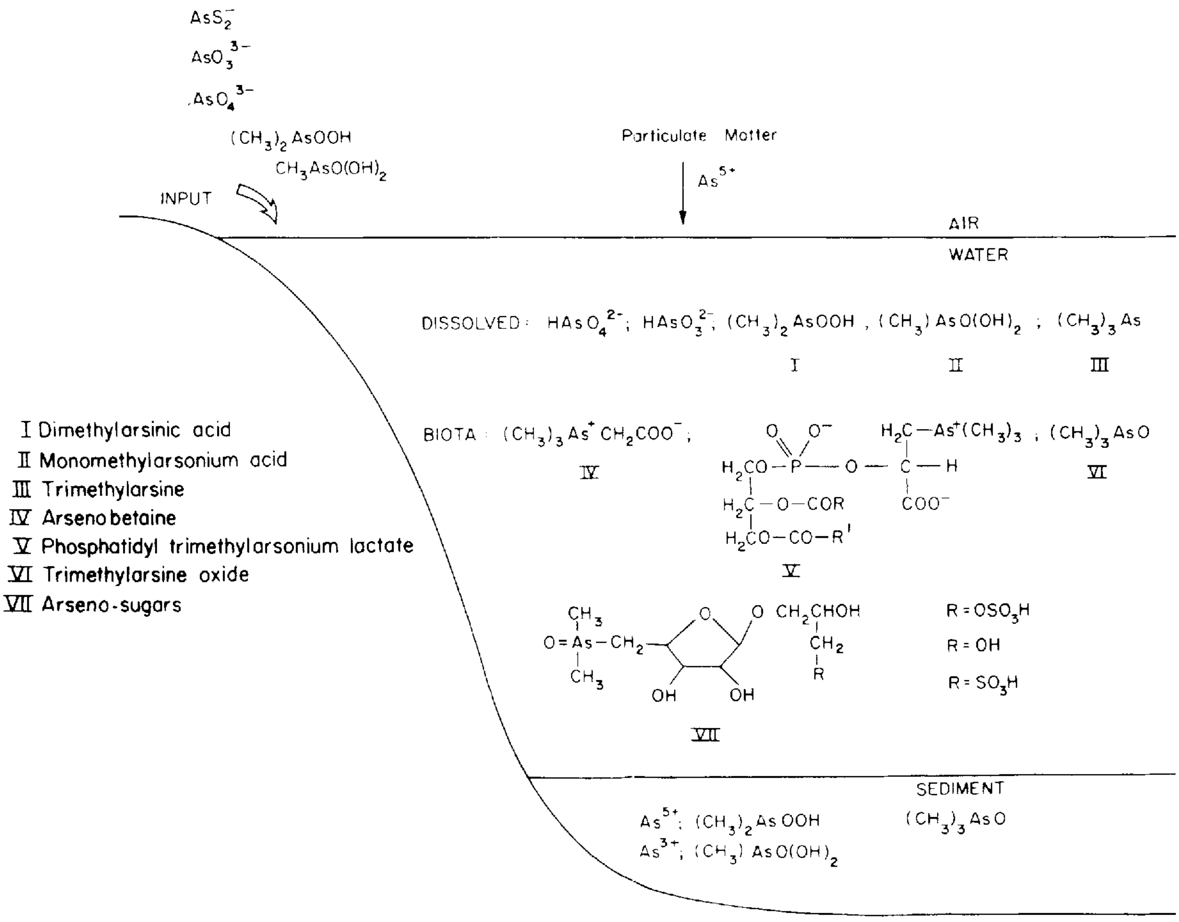

Figure 1 Arsenic species isolated from the marine environment.

methylarsenic acids are the only examples of arsenic–carbon compounds present in measurable amounts in natural seawaters (Fig. 2).[18]

From equilibrium calculations,[19,28] arsenic(III) and arsenic(V) are predicted to exist in the fully hydrolysed state, and in seawater at pH 8.2 the respective species are $HAsO_4^{2-}$ and $As(OH)_3$. A significant fraction of the arsenate is thought to be ion-paired with calcium and magnesium cations.[21] Thermodynamic data are not available to model arsenic–organic ligand complexation.

With the complete, or near complete, removal of oxygen from isolated bodies of seawater, there is a corresponding shift to more reducing conditions. In these instances thermodynamic calculations predict a change in speciation to a distribution favouring arsenic(III). In anoxic basins of Saanich Inlet, British Columbia, Canada, and the Baltic Sea, arsenic(III) was found to be the dominant species consistent with, but not always to the extent of, these thermodynamic predictions.[22,23] In anoxic waters with large quantities of reduced sulphur species it is quite likely that some inorganic arsenic exists as thioarsenite (AsS_2^-) or thioarsenate (AsS_4^{3-}),[19,23,24] formed by abiotic chemical reactions.[25,26] Peterson and Carpenter[22] have discounted the presence of thioarsenite in anoxic waters of Saanich Inlet by calculating equilibrium arsenite/thioarsenite ratios. The presence of DMA or MMA in sulphide-containing seawaters could result in the *in-situ* formation of sulphides of these organoarsenicals, such as cacodyl sulphide $[(CH_3)_2As]_2S$.[27,28] These compounds have not been identified in anoxic waters, although they would, in general, be only slightly soluble. Cullen and co-workers[29] have shown that methylarsenic species

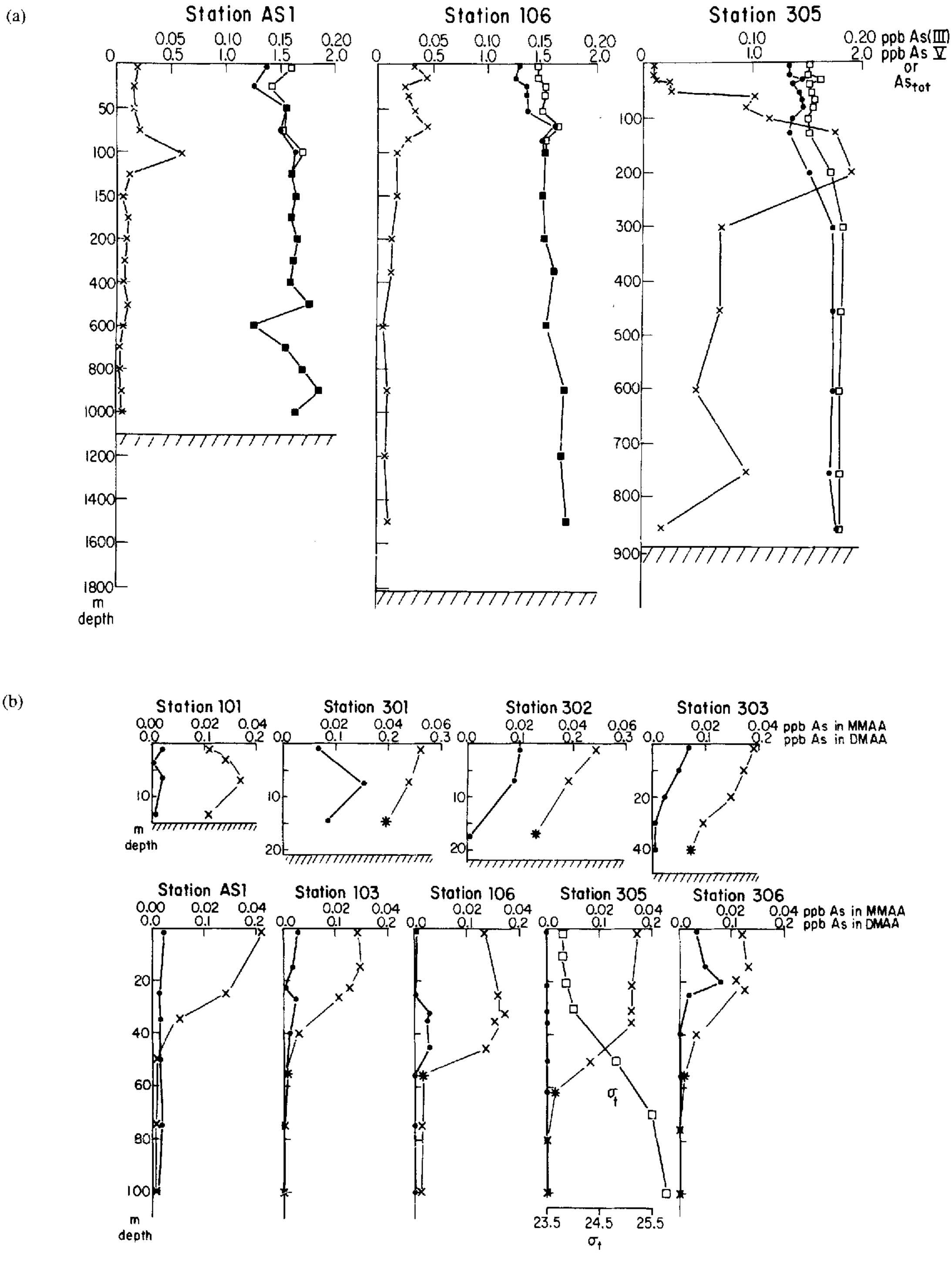

Figure 2 Profiles of arsenic species in the water column.[11] (a) Distribution of arsenite (x), arsenate (•) and total arsenate (□) in the water column. (b) Distribution of methylarsenic acids in the upper waters. X, DMA; •, MMA; *, DMA at the 1% light level. The concentrations are given as ppb As. (Reprinted with permission from M O Andreae, *Deep Sea Res.*, 1978, 25: 391–402, Pergamon Journals Ltd.)

react readily with thiols in aqueous solutions of neutral pH that are stripped of oxygen. The products of these reactions are organosulphur derivatives of arsenic(III). Cullen and his colleagues were interested in these reactions as models for part of a scheme for the biological methylation of arsenic. However, it would appear that these organosulphur compounds of arsenic could also be formed by abiotic processes in anoxic seawaters, where reduced organosulphur species are often found.

Aside from one report of appreciable particulate arsenic in a suite of samples from a coastal sea,[30] arsenic in this phase is negligible in seawater.[11,32,33] Arsenic associated with suspended matter in estuaries[34,35] is either deposited before transport to the open ocean, or its input amounts to a very minor fraction of the oceanic arsenic pool. Whatever its ultimate fate, particulate arsenic in estuarine waters is reputedly non-labile.[34]

In the surface photic zone of the ocean the reduced and methylated species of arsenic account for 5–20% of total dissolved arsenic, with DMA fairly constant at 5–10% of the dissolved species; arsenic(III) is variable, and there is only a trace of MMA.[11,24,35] In exceptional cases, mostly in coastal waters, arsenic(V) becomes a minor fraction of dissolved arsenic species.[37] Arsenic(III) can be the dominant inorganic species in the oligotrophic surface waters of subtropical gyres. Here, the high internal cycling of phosphorus results in the rapid concomitant uptake of arsenic(V) by phytoplankton which rapidly reduce it to arsenic(III), and excrete this form.[18]

A shallow sub-surface maximum of arsenic(III) is often seen and this has been attributed to heterotrophic (bacterioplankton) activity, either in the zone of mixing of surface and intermediate waters,[11] or in a layer below the pycnocline.[24] Additionally, elevated levels of dissolved arsenic(III) and DMA often coincide with near-surface particulate maxima;[38] thus microbial release of arsenic from particulates is probably also occurring.

Arsenic(V) is depleted in surface ocean waters by about 10–30%. Its concentration increases with depth down to 1000 m; below this depth total arsenic content — almost exclusively arsenic(V) — is relatively constant at 1.5–1.8 μg dm^{-3}.[24,39,40]

There is not much information on the variation of arsenic in the horizontal domain, nor on differences between oceans. Early data from Sugawara and colleagues[41] suggested average arsenic levels in the southern Indian Ocean could be seven-fold greater than in the northwest Pacific Ocean. In more recent studies,[11,22,24,33,36,39,40,42–44] arsenic appears to be more uniformally distributed in the world's oceans, with most measurements of total arsenic falling in the interval 1.2–1.8 μg dm^{-3}; and the same patterns appear universal in vertical profiles of arsenic concentration. Burton *et al.*[45] and Sanders[46] have remarked that Pacific Ocean arsenic concentrations seem marginally higher than those in the Atlantic Ocean; this is said to be a lesser manifestation of the irregular phosphorus distribution observed between the two oceans.

From limited data, it would appear that arsenic speciation displays regional differences. Those distinguishing near-shore and offshore waters have already been commented on. In Antarctic coastal waters, DMA was less than 1% of the concentration of total dissolved arsenic, in marked contrast to surface seawaters of the southern Californian Bight, and along the Florida coast where DMA amounted to a 10% or greater fraction.[18] The reported temperature dependence of biological methylation of arsenic[47,48] could mean that higher-latitude waters are characterized by much lower levels of organoarsenic species.

Arsenic has similarities in its distribution and speciation with its neighbouring Group V elements, phosphorus and antimony. Arsenic(V) shows surface depletion and deep-water enrichment in common with phosphate, although the vertical profiles do not correspond in detail[24,45,49] because arsenic appears to be remineralized faster than phosphorus and at a shallower depth. Antimony speciation in seawater parallels that of arsenic, with the thermodynamically favoured antimony(V) predominating and with antimony(III) existing in apparent redox disequilibrium as a result of biological reduction in the photic zone.[50]

2.2 Riverine and atmospheric inputs

Dissolved levels of arsenic in unpolluted rivers are of the same magnitude as in seawater[11,19,34] with a global average concentration suggested to be 1–2 μg dm^{-3}.[51,52] At these concentrations, the annual flux of dissolved arsenic from the rivers to the oceans amounts to 0.001% of the global oceanic pool of dissolved arsenic.[53] Waslenchuk[36] found that dissolved arsenic derived from uncontaminated riverine input into the Georgia Bight, USA, is insignificant compared with arsenic brought on to the shelf by Gulf Stream incursions.

However, the natural riverine input of arsenic may now represent only a historic baseline level, because anthropogenic activity has substantially increased the arsenic content of many estuarine waters.[35,37,52,54,55] The average arsenic concentration in a sampling of European rivers with appreciable industrial and urban regions along their course was 3.5 μg dm^{-3}.[23]

Estuaries can be further contaminated by direct point source inputs.[52]

Doubt exists as to the amount of particulate arsenic of riverine origin injected into the oceans: Mackenzie and co-workers[53] have suggested it may be four times the dissolved load. With recent estimation of the average arsenic content of riverine suspended matter as 5 μg g^{-1},[56] global river transport of arsenic is now thought to be divided equally between dissolved and particulate forms, but with considerable river-to-river variation.[34,55,57] Human activity may disturb this balance as large localized inputs of particulate arsenic are conceivable from estuaries in the vicinity of mining or smelting operations.[58]

Not all of the arsenic in estuarine waters passes into the oceans; physical processes such as flocculation of particulates[59] and adsorption of dissolved arsenic on to freshly precipitated hydrous iron oxides[35,60,61] transfer the element to estuarine sediments. Biological filters, such as fringing marshes, can also remove arsenic from the water column.[62] Should arsenic escape the estuary, its free dispersal into the open ocean can be further restricted by incorporation into coastal and near-shore sediments.[63,64]

The export of arsenic from rivers to the oceans is important in the biogeochemical cycling of the metalloid, but the magnitude of this flux remains uncertian. Estimates from models of the global arsenic cycle are in error since they neglect to consider processes that remove arsenic in its passage from estuary to open ocean.

Conditions that exist in rivers and estuaries have a strong bearing upon arsenic speciation, particularly in near-shore seawaters. Both arsenic(III) and methylated arsenicals occur in fresh waters, with the As(III)/As(V) ratio often greater than that observed in seawaters.[11,65] However, it is in the estuaries where gross changes in arsenic speciation occur; here reduced and methylated species can exceed arsenic(V) concentrations.[37,66] The seasonality of these changes reinforces the premise of biological mediation of arsenic speciation.

Atmospheric arsenic concentrations are extremely variable; background levels may be less than 0.01 μg m^{-3}, but in the vicinity of heavy industrial regions concentrations may exceed 1 μg m^{-3}.[67] Arsenic is found principally in aerosols, with under 10% in the vapour phase.

In biogeochemical models that consider cycling of arsenic through the atmosphere,[68] a net transfer from the land to the ocean is predicted. Mackenzie and co-workers[53] suggest that arsenic release from the ocean in the vapour phase exceeds terrestrial emissions from both natural and anthropogenic sources. Using more recent data, Walsh and others[69] estimate that arsenic emission from the oceans amounts to at most 1% (0.11 $\times$ 10^9 g As year^{-1}) of the total natural arsenic input into the atmosphere. Their estimated removal of atmospheric arsenic by rain and dry deposition over the oceans is 2.76 $\times$ 10^9 g As year^{-1}, which at a minimum gives a net annual arsenic flux from atmosphere to ocean of 2.65 $\times$ 10^9 g.

Waslenchuk[36] has estimated that an annual atmospheric contribution of 2.5 $\times$ 10^4 g arsenic occurs to Georgia Bight (USA) waters, mainly from continental aerosols. This flux was comparable with riverine arsenic input in the same region. Where there are localized sources of arsenic from large industrial or urban centres, aerosol deposition of the metalloid may exceed the input derived from terrestrial run-off.[70]

Arsenic(V) and DMA have been detected in rain water.[71] The only arsenic species detected in airborne particulates over temperate near-shore waters has been inorganic arsenic(V).[36] However, recent work has shown that almost 10% of air particulate arsenic may be methylarsenic.[72] Organoarsenic species in the atmosphere are most likely derived from biomethylation of arsenic,[73,74] releasing to the atmosphere gaseous di- and tri-methylarsine, that are in turn oxidized by abiotic processes to DMA and trimethylarsine oxide.[75] The latter compounds are apparently stable in the atmosphere, because no decomposition has been found in air with their exposure to sunlight.[76]

Studies with urban dust (a model for atmospheric particulates) have shown that on dissolution in seawater half the arsenic content of dust is released.[70] Thus it is expected that solubilization of atmospheric particulates containing mostly arsenic(V) will result in the release of arsenic in this form to seawater and the impact on arsenic speciation will be negligible.

2.3 Processes influencing concentration and speciation

Since seawater is considerably undersaturated with respect to most solid phases, adsorption on to particulate matter is the physical process most likely to limit dissolved concentrations for most elements.[77,78] It had been suggested that barium in natural waters could control the arsenic concentration by way of the very insoluble solid, $Ba_3(AsO_4)_2$.[79] However, more recently Crecelius *et al.*[80] rebutted this proposal on the grounds of erroneous solubility product data and the fact that there was no evidence of a barium arsenate phase in sediments. Aside from compounds of arsenic with sulphide, all other arsenic solids likely in natural waters have solubilities greater than 0.05 mg dm^{-3}.[81]

Experiments using a range of model substrates have shown that arsenate is strongly adsorbed by hydrous oxide phases, as expected from analogy to the isostructural, and intensively studied, phosphate anion. On diverse solid phases, adsorption of either arsenic(III) or arsenic(V) is a function of pH. With the latter oxidation state, maximal removal is observed at about pH 4 with amorphous ferric hydroxide [am-$Fe(OH)_3$],[82] alumina,[81] and the clay minerals, kaolinite and montmorillonite.[83] It is the monovalent $H_2AsO_4^-$ anion, predominant around pH 4, that is adsorbed better than the neutral molecule, or divalent and trivalent anions. Arsenic(III) usually shows a shallower adsorption peak at neutral or slightly alkaline pH, and this is a result of uncharged $As(OH)_3$ being the form of arsenic(III) most strongly bound.

The ability of ferric hydroxide to adsorb arsenic species has been exploited to collect the element quantitatively from seawater for analysis.[84] Pierce and Moore[82] found that adsorption of arsenic(III) and arsenic(V) on to amorphous $Fe(OH)_3$ at near-natural concentrations fitted Langmuir isotherms. It is concluded that the surface binding mechanism is not one of electrostatic interaction, but is either a specific adsorption process[85] or by formation of a chemical bond. Studies with natural suspended particulates[86–88] show that arsenic is strongly associated with iron or iron–manganese phases. The diminished binding of arsenic by some of these natural particulates is attributed to their coating with organic matter.[87] Recent work by Aggett and Roberts[88] has demonstrated that much of the arsenic in a freshwater sediment was incorporated by co-precipitation at the time of formation of the hydrous iron oxides. Along with adsorption on to existing surfaces, such a process could also apply to marine waters.

Alumina is another hydrous oxide phase which strongly removes arsenic from seawater.[81] Arsenic(III), primarily as $As(OH)_3$, appears to be adsorbed on to alumina by a different mechanism from the one that applies to arsenic(V), because removal of the former, unlike the latter, is affected by its initial solution concentration and the presence of dissolved silicate. Hydrated manganese(IV) oxide, $MnO_2.nH_2O$, as a pure phase is a much less effective adsorbent of arsenic than amorphous $Fe(OH)_3$ or alumina. Although it may have little affect upon total dissolved arsenic concentration, manganese(IV) oxide in aqueous systems can rapidly oxidize arsenic(III) to arsenic(V), and thus have an impact on dissolved arsenic speciation.[89–91]

Thanabalasingham and Pickering[92] have demonstrated that humic acids are capable of removing both arsenic(V) and arsenic(III) from solution. They suggest that calcium and polyvalent cations associated with humic acids can be involved in arsenic adsorption. Their use of terrestrial humic acids makes it difficult to assess how relevant this work is to marine waters.

To this stage, adsorption of inorganic arsenic alone has been considered. Nevertheless, Holm *et al.*[93] have observed that along with inorganic arsenic, both MMA and DMA are removed by anaerobic river sediments. The degree of adsorption decreases in the following order:

$$\text{arsenate} > \text{MMA} > \text{arsenite} > \text{DMA}.$$

Whether this order applies more generally to other particulate phases remains to be ascertained.

Despite the proven capacity of particulates to adsorb arsenic, an 'equilibrium' value of only 5–6% arsenic is calculated[87] to be bound to iron/manganese oxides at seawater concentrations of dissolved arsenic (1.6–2.0 $\mu g\ dm^{-3}$) and with suspended particulates at 3 $mg\ dm^{-3}$ (typical of estuaries). Much less arsenic is associated with all other particulate phases. This result corroborates observations in marine waters that particulate arsenic is a minor fraction of total arsenic. However, under specific conditions, particulates might strongly influence arsenic mobility. For example, at redox boundaries (the interfaces in aqueous environments between reducing and oxidizing zones), freshly formed precipitates of hydrous iron and manganese oxides can strongly impede diffusion of arsenic that is released by remineralization and solubilization processes within the reducing zone.[19,94] Manganese dioxide would promote oxidation of arsenic(III) to arsenic(V), which in turn would be efficiently scavenged by $Fe(OH)_3$.

Biological activity affects arsenic speciation in the oceans, but the extent depends upon factors such as temperature, phytoplankton populations, and pre-existing arsenic speciation. Arsenic(V), and to a lesser degree, arsenic(III) are bioactive, but MMA and DMA are intractable to all but certain bacteria.[95] Many of the reactions of arsenic that are influenced by marine biota arise because of the chemical similarities between arsenic(V), arsenate, and the nutrient phosphate. To avoid the toxic effects of inorganic arsenic, phytoplankton actively discriminate against arsenic when assimilating phosphate,[96,97] or detoxify it by forming methylarsenic compounds[98] (see Section 3, Arsenic in marine biota). Whatever the strategy for avoiding arsenic toxicity, the phytoplankton incorporate little of the metalloid; the less toxic methylarsenic species, MMA and DMA, are rapidly excreted when formed intracellularly.

Laboratory studies using cultures of a wide range of marine phytoplankton[14,99–101] demonstrate that phytoplankton can mediate arsenic speciation under such conditions. Arsenic(V) was taken up — and subsequently released in varying proportions as arsenic(III), MMA and DMA — depending upon the phytoplankton species.

Investigations of planktonic blooms in coastal waters[102,103] have confirmed observations in the laboratory. Sanders[37] reported strong positive correlations of phytoplankton densities with arsenic in reduced and methylated forms. In particular he noted *Chroomonas* spp. abundance was highly correlated with the presence of MMA.

In the water column of a controlled experimental enclosure (CEE), Apte and co-workers[97] observed that although phosphate was greatly depleted in a spring phytoplankton bloom, there was little effect on the concentration and speciation of arsenic. Only at the base of the CEE bag was there change. More than half the inorganic arsenic was converted to DMA, but since total dissolved arsenic levels remained unchanged, microbial methylation of dissolved arsenic was inferred. The authors acknowledged that the results of this investigation could not be extrapolated to all marine ecosystems, because of limited phytoplankton diversity and water temperatures of only 6–7°C. They had previously noted distinct seasonal variation in arsenic speciation in estuarine waters, with reduced and methylated species evident only at about 12°C.[47] In another CEE investigation of the biogeochemical behaviour of arsenic, it was found that the biota were capable of producing arsenic(III) and DMA in an arsenic(V)-enriched ($5\ \mu g\ dm^{-3}$) enclosure.[104] In an eclosure enriched to the same level with arsenic(III), rapid oxidation of this species to arsenic(V) was noted. Water column temperature was not reported, although the experiments were begun in mid-summer in Saanich Inlet (Canada).

Phytoplankton in different ecosystems — coastal as against oceanic, temperate as against tropical — appear to have different strategies for dealing with arsenic.[95,105] These idiosyncrasies could partly explain variations in distribution of reduced and methylated arsenic species.

Many marine organisms, other than phytoplankton, are reported to influence arsenic speciation. However, most of these studies are again based upon laboratory culturing, and therefore their relevance to the marine biogeochemistry of arsenic is unknown. Bacteria have been implicated in all aspects of arsenic species interconversion: reduction of arsenic(V) to arsenic(III),[13,106] oxidation of arsenic(III) to arsenic(V),[16] methylation,[106,107] and demethylation[17] reactions, as well as formation of volatile arsines.[73] Likewise, macroalgae and their epiphytes can influence inorganic arsenic speciation,[108] and are thought to release DMA and, to a lesser extent,[48] MMA. A scleractinian coral has been shown to reduce arsenate to arsenite,[15] and a marine yeast is capable of not only arsenic(V) reduction, but also the production of MMA, DMA, and volatile organarsines.[106] Ingestion of arsenic by marine animals at higher trophic levels is likely to lead to limited excretion of arsenic(III), and the simple methylated species, MMA and DMA — since it appears that there is biodiminution of arsenic up marine food chains.[18]

To summarize the influence of marine biota upon arsenic in the water column, it would seem that biological mediation can alter arsenic speciation, particularly in surface waters under the right conditions as demonstrated by the close positive correlation of DMA with phytoplankton activity (^{14}C assimilation rate) and to a lesser extent chlorophyll concentration.[24] However, as for other biointermediate trace elements, the biota do not significantly affect the total arsenic concentration.

The photochemistry of arsenic in natural waters is an area that has tended to be overlooked. It is well established that photoinduced radicals can reduce chemical species in natural waters (e.g. Fe(III)/Fe(II), Mn(IV)/Mn(II).[109] Thus the speciation of arsenic in surface waters may be modified by physical processes such as photoreduction as well as by biota.

3 ARSENIC IN MARINE BIOTA

3.1 Bioaccumulation and elimination

Marine organisms in general accumulate more arsenic than fresh-water organisms.[110] High arsenic levels in some marine organisms can be related to prevailing high environmental arsenic levels.[54,63,111,112] However, dissolved arsenic concentrations are normally low ($1–2\ \mu g\ dm^{-3}$)[11,24] and marine organisms have the ability to concentrate arsenic (Table 1). Symbiotic relationships between organisms may result in arsenic accumulation in some organisms. For example, zooanthellae enhance the accumulation of arsenic ($> 1000\ \mu g\ g^{-1}$ dry wt) in the giant clam *Tridacna maxima*.[113]

Experimental studies have shown that arsenic can be accumulated from water, food or sediment. Algae,[100,101,102,114,116] seaweed,[115] molluscs[116–118] and crustaceans[116] can accumulate arsenate from seawater. Arsenate uptake is either proportional to the arsenate concentration until a threshold value is reached, after

Table 1 Arsenic in the South Australian marine environment (Refs *a*, *b*, *c*)

		Arsenic ($\mu g\ g^{-1}$)	
Source[a]	Range	*n*[b]	Mean ± S.D.
Macroalgae	6.3–179	41	37 ± 37
Pisces (M)	0.8–13.8	12	7 ± 3
(D)	0.6–22.8	12	9 ± 7
Mollusca (M)	3.9–47	24	19 ± 15
(V)	23.3–72	20	42 ± 23
Crustaceans (M)	7.1–91	24	27 ± 20
(S+D)	22.3–58	8	39 ± 3
Seawater	$(1.1–1.61) \times 10^{-3}$	16	$(1.3 \pm 0.1) \times 10^{-3}$

[a] M, muscle tissue; D, digestive system; V, viscera; S, soft parts. [b] *n*, number of samples.

REFERENCES TO TABLE 1

a. Maher, W A and Clarke, S M *Mar. Pollut. Bull.*, 1984, 15: 111
b. Maher, W A *Mar. Pollut. Bull.*, 1983, 14: 308
c. Maher, W A *Wat. Res.*, 1985, 19: 933

which arsenate uptake is inhibited[100,112] or independent of arsenate concentration.[100,115,117] This suggests that at high external arsenic concentration, regulation of internal arsenic concentration is occurring, or uptake sites have become saturated. Threshold values vary depending on the organism.[100,117] Uptake of arsenic into some species of mussels has been found to be not proportional to or independent of arsenate concentration,[112,118] probably because mussels decrease their filtering rate in response to increased external metal concentrations.[119] Physical processes such as surface adsorption play a minor role in uptake.

Arsenic uptake may also be a function of salinity,[117,118,120] temperature,[115,117,118] light[115,121] and exposure.[54] Increased salinity has been shown to have no effect or to cause a reduction in arsenate uptake whilst temperature increases result in increases in arsenate uptake. Contradictory results have been reported for the effect of light. Bottino *et al.*[121] found that arsenic uptake into the marine alga *Tetraselmis chui* is light-dependent, more light causes greater arsenate uptake suggesting arsenate adsorption is an endergonic process that may compete with cell growth for available photosynthetic energy. Klumpp[115] in contrast, found that for the macroalga *Fucus spiralis*, arsenic uptake in the dark or in the presence of photosynthetic inhibitors is greater than in the light, and he postulated that the energy required for uptake is derived from respiration. Maximum arsenic concentrations have been found in the basal parts of the macroalgae *Ascophyllum nodosum, Fucus serratus* and *Fucus vesiculosus*,[54] implying that the duration of exposure influences arsenic concentration.

Dissolved arsenic may be taken up by biota because arsenate is similar to phosphate in size, geometry and its ability to enter into biochemical reactions. Studies of the accumulation of arsenic in marine algal cultures[99,100] and macroalgae experiments[117] show arsenic uptake is related to the prevailing phosphate concentration. Phosphate present at low levels often does not influence arsenate uptake.[117] Arsenic uptake increases as phosphate uptake increases until a threshold value is reached and arsenic uptake is inhibited.[99,100,117] The increased uptake of arsenic as phosphate uptake increases at low phosphate concentrations is attributed to increasing phosphate metabolism and indiscriminate arsenate uptake. Arsenate may enter cells by transport mechanisms unable to discriminate between phosphate and arsenate. Under phosphate stress arsenic is concentrated, converted to non-toxic products and excreted.[99,100]

Field measurements have revealed that in an estuary with abnormally high concentrations of phosphorus the uptake and retention of arsenic was low during algal blooms compared with estuaries with high As/P ratios.[103] During a CEE experiment[97] in which the change in arsenate and phosphate concentrations during a phytoplankton bloom was monitored there was no evidence of arsenic uptake at low phosphorus concentrations, suggesting that organisms may have the ability to discriminate between arsenic and phosphorus.

A major route of arsenic accumulation in organisms is via diet. Falconer *et al.*[122] have measured concentrations of arsenic in fish and shellfish from the North Sea. They found that differences in arsenic concentrations between species may be directly related to their diet (food source) and this may account for differences in arsenic levels in the same species from different sampling areas. Studies of arsenic in marine organisms from the Pacific Coast of Canada[123] and Greenland[124] have revealed similar relationships of arsenic concentrations in organisms and their dietary intake.

It has been demonstrated in many studies that arsenic is preferentially accumulated when taken up in food[118,125,126] rather than dissolved in water and that, in general, carnivores contain higher arsenic concentrations.[125] It also appears that the amount of ingested arsenic assimilated is dependent on the chemical form of arsenic present in the food,[126] organic arsenic being preferentially retained relative to inorganic arsenic. Strong correlations of the concentration of arsenic in tissues of benthic organisms and in sediments has demonstrated the ability of organisms to use a fraction of particulate bound arsenic.[111,112] Transplant experiments in which bivalves were removed from areas of high sediment-arsenic concentration to areas of low sediment-arsenic concentration (and reverse) confirm sediments as a source of arsenic.[112] Arsenic in these sediments was also correlated with iron hydroxide concentration; arsenic uptake may have been the result of an increase in available arsenic due to the release of dissolved or particulate arsenic under prevailing physicochemical conditions rather than the direct usage of sediment arsenic by bivalves. The high arsenic concentrations found in the bivalves' digestive glands are however consistent with the assimilation of arsenic from ingested particles. No consistent pattern for uptake of arsenic from sediments by organisms has been established.

Little is also known about the loss mechanisms of arsenic from organisms. Culture studies[14,99,100,102] have shown that phytoplankton species release arsenite or methylated arsenicals to the surrounding environment. The products released vary within a particular species and all algal species may not contain the necessary enzymes required for methylation.[95] The amount of arsenic eliminated by marine animals appears to be dependent on the chemical form of arsenic in food.[126] For example, the crab *Carcinus maenas* has been shown to excrete arsenite more readily than organic arsenic.[126] The effective excretion of inorganic arsenic forms would shift the proportion of arsenic in marine organisms towards organoarsenic forms.

Arsenic elimination appears to be a function of temperature,[118] while salinity may also be important.[118]

3.2 Biomagnification

Biomagnification, the process whereby higher organisms in a food chain have higher element levels, appears not to occur for arsenic. Marine macroalgae at the bottom of the food chain often contain the greatest concentrations of arsenic.[54,127,128]

Penrose[129] reviewed the work of several authors and classified specimens according to their position in the food web. He concluded that as one ascends the trophic levels the concentration of arsenic decreases. However, since samples have been collected from different areas and could not all have come from comparable environments, concentrations may only reflect the environmental availability of arsenic. It is not certain in some reports whether whole organisms or selected tissue components were analysed.

Klumpp and Peterson[54] collected organisms from Restronguet Creek, southwest England. Although evidence of accumulation of arsenic occurs at all trophic levels, biomagnification does not appear to occur up the food chain. For example, *Patella vulgata* (33.5–41.0 μg As g^{-1}) and *Littorina obtusata* (48.5–59.8 μg As g^{-1}) graze on macrophytes (59.1–189 μg As g^{-1}) yet show no biomagnification on an entire-animal basis. Shiomi *et al.*[125] measured the arsenic content of shellfish collected from coastal waters of south Japan. The arsenic content of herbivorous gastropods which feed on marine algae containing high amounts of arsenic was low compared with the arsenic levels in carnivorous gastropods.

Andreae[18] suggested that the As/P ratio in different marine organisms should be used for evaluation of biomagnification. His analysis of other authors' data shows that the As/P ratio continuously decreases up the marine food chain and concludes that this represents a progressive purification of the phosphate pool and elimination of arsenic.

Indirect evidence also indicates that arsenic is not biomagnified. Penrose *et al.*[129] have reported that arsenic consumed by sea urchins through ingesting algae is not accumulated, but is excreted in a soluble organic form. Boothe and Knauer[130] have found that arsenic is concentrated in the faeces of the kelp-grazing crab *Pugettia producta*: thus elimination of arsenic occurs.

3.3 Biochemical associations and speciation

Lipid-soluble, water- or methanol-soluble, and residual unextractable arsenic compounds have been isolated from marine biota. The relative proportions of each vary with chosen organisms.[99,111,131,132] The route of accumulation of arsenic may determine the biochemical associations of arsenic. Gorgy *et al.*[133] placed sea anemones in aquaria and added arsentate; 1% of arsenic was accumulated in the lipid fraction and 90% in the protein fraction. The study by Wrench *et al.*[116] of arsenic accumulation in a phytoplankton–zooplankton–shrimp food chain found that if arsenic was accumulated through water intake only, phytoplankton (not zooplankton) synthesized lipid-soluble organoarsenic compounds to a major extent (i.e. 91% compared with 2.7–2.3% for the zooplankton). If the accumulation of arsenic was from food, the zooplankton and shrimp contained 66 and 79% of accumulated arsenic, respectively, in the lipid phase. They concluded that the organic component is synthesized by the primary producer and passed along the food chain.

Studies on the relationships of feeding habits to the chemical form of arsenic in marine animals[125] have shown that arsenic in carnivores is different from that in planktonic feeders and herbivores. Carnivores, in general, contain higher arsenic contents and more methanol-soluble than lipid-soluble arsenic.

Lunde[114,131,134] has shown that the lipid-soluble organic arsenic compounds in marine oils are present as polar compounds and that they can be separated from neutral lipids by chromatographic means. Further fractionation of the polar fraction has revealed that at least two lipid-soluble arsenic compounds are present. The pattern of arsenic compounds isolated in the polar fraction varies and they may be artefacts of the isolation and separation procedures. The compounds resemble phospholipids but differ from them in behaviour in that they do not appear to be bound to cell membranes in the same way as phospholipids.

Vaskovsky *et al.*[132] in their study of arsenic in the lipids of marine mussels, shrimps and snails also found several lipid-soluble arsenic compounds. The properties of the arsenic compounds resembled those of saponifiable lipids with one arsenic compound in *Dunaliella nippon* corresponding in behaviour to phosphatidylcholine. Bottino *et al.*[121] have isolated a compound from the alga *Tetralsemis chui* which was chromatographically similar to phosphatidylarsenocholine but only contained 0.5% as compared with the expected 8.8% of arsenic.

The chromatographic behaviour of lipid-soluble arsenic compounds in general suggests them to be arseno-containing phospholipids in which the nitrogen atom of the choline group has been replaced by arsenic. The work of Wrench and Addison[101] and Benson[105] suggests other arsenolipid compounds may be present. Wrench and Addison[101] isolated an arsenolipid from *Dunaliella tertiolecta* identical to a complex between phosphatidylinositol and arsenite. Benson[105] has shown that the product obtained by the enzymatic cleavage of the arsenolipid found in the diatom *Chaetoceros* sp. is identical to an arsenosugar. The structure of arsenolipids awaits further elucidation.

Lunde has also shown that lipid-soluble arsenic in marine plants[114] and animals[137] can be converted to water-soluble arsenic compounds by boiling with hydrochloric acid. Comparisons of water-soluble extracts boiled with hydrochloric acid have indicated the presence of only one arsenic compound.

The chromatographic properties of the water-soluble arsenic compound is identical in all organisms except seaweed.[137] When extracts of fish were fractioned by gel chromatography, arsenic eluted before the amino acids (MW 300–400) and was not bound to high-molecular-weight proteins or polypeptides.[138] Radioactive arsenic uptake experiments have indicated that up to ten water-soluble arsenic compounds are produced by algae,[99,136] while molluscs only produce one water-soluble arsenic compound.[136] The physiological significance and relationship (interconvertibility) of water-soluble and lipid-soluble arsenic compounds still needs to be determined.

Accumulated evidence indicates that arsenic in marine animals occurs mainly as non-toxic organoarsenic compounds with only small amounts of the more toxic inorganic arsenic species present.[139–144,167]

Chapman[142] showed that the arsenic compound(s) in a lobster had to be decomposed by nitric and sulphuric acids before determination as inorganic arsenic. Sadolin[143] concentrated an arsenic compound isolated from cod liver oil by various distillation procedures and achieved an extract containing 0.1% of arsenic, but could not chemically define the arsenic compound. Lunde[131] demonstrated that most of the arsenic in several samples of fish extracts exhibited ion-exchange behaviour that differed from that of arsenite and arsenate. Lunde[144] and Flanjak[167] found that fractionation of arsenic in marine raw materials, by distillation from 6.6 mol dm^{-3} hydrochloric acid as arsenic trichloride, removed only a small proportion of the total arsenic present; Reinke *et al.*[140] Maher[139] and Shinagawa *et al.*[141] using selective extraction procedures for inorganic arsenic, have reported that the concentrations of inorganic arsenic in a large number of fish, crustaceans and molluscs are insignificant when compared with total arsenic concentrations.

Marine macroalgae however can contain an appreciable quantity of inorganic arsenic[127,141a,152,170] with edible seaweeds containing up to 50% of arsenic in the inorganic form. Challenger[145] suspected that marine organisms form methylated arsenic compounds since oysters were observed to have the characteristic odour of trimethylarsine. With the development of suitable analytical methodology[146] it was shown that the organic arsenic compounds present in molluscs,[147–150,168] crustaceans[147,148,168] and algae[148–150,171] could be partially degraded to monomethyl-, dimethyl- or trimethyl-arsenic moieties by alkaline hydrolysis. Arseno-sugars containing the dimethylarsenoso group (Fig. 1) have been isolated from the seaweeds *Ecklonia radiata*[151] and *Hizikia Fusiforme*,[152] the diatom *Chaetoceros gracilis*[153] and the kidney of the giant clam *Tridacna maxima*.[154] An arsonium phospholipid, *O*-phosphatidyl trimethylarsonium lactic acid, was reported to have been isolated from the alga *Chaetoceros concavicorris*[156] but is now thought also to be an arsenoriboside of phosphatidylglycerol.[153,158] Arseno-sugars hydrolyse under basic conditions to dimethylarsenic species.[151]

Arsenobetaine ($(CH_3)_3As^+CH_2COO^-$) appears to be widely distributed in marine animals at different trophic levels (Table 2) and is probably the end-product of arsenic metabolism in the marine ecosystem. Alkaline hydrolysis of arsenobetaine forms trimethylarsine and dimethylarsine.[147] Thus previous reports of dimethyl- and trimethyl-arsenic produced by the alkaline hydrolysis of marine animals are likely to be due to the breakdown of arsenobetaine. Other organoarsenic compounds have also been found in marine organisms (Table 3).

3.4 Metabolism

Because of the low concentrations of methylated arsenic compounds found in the water column it would seem likely that methylation occurs *in situ*. Wong *et al.*[107] have shown that *in-situ* methylation is possible by demonstrating that bacteria from freshwater fish intestines are able to methylate arsenic. Possible pathways for the production of organoarsenic species in marine ecosystems that have been postulated are shown in Fig. 3.

Although it is not possible to assign methylation activity to specific groups of organisms (bacterial, microbial, planktonic), algae,[14,99,100,159] macrophytes[14] and coral[166] have been shown to take up arsenate in cultures and to produce arsenite and methylated arsenic species which are excreted. As arsenate and phosphate are likely to be adsorbed indiscriminately by the same uptake mechanism, methylation may be a means of detoxifying arsenic. Not all algae produce and release the same arsenic compounds,[99,100] and pathways of reduction and methylation are probably related to the enzymes occurring in particular algae.[159] Benson *et al.*[160] have suggested that the incorporation and metabolism of arsenic in algae depends on the prevailing As/P ratio. At low As/P ratios marine algae adsorb arsenic which is bound to —SH proteins and is solvent-unextractable. At high As/P ratios arsenic is not bound to proteins but is converted to water- or lipid-soluble intermediates. The mechanisms of reduction of arsenic and the formation of methylated arsenic compounds are still unknown. Challenger[161] suggests that arsenate is methylated using *S*-adenosylmethionine as a source of methyl groups. Knowles and Benson[158] have postulated that the reduction is the result of the reaction of arsenic groups with sulphydryl groups. Cullen *et al.*[162] have shown that thiols can reduce methylated arsenic compounds and also proposed that biological sulphydryl groups may reduce arsenic moieties. However, the identity of methyl donors (i.e. *S*-adenosylmethionine, folate, B_{12}, etc.) and reduction mechanisms (e.g. source of electrons) still has not been elucidated.

Arseno-sugars found in marine organisms may be formed as intermediates during the methylation process. Phillips and Depledge[163] have postulated that arsenic forms an analogue of ethanolamine, $NH_2CH_2CH_2OH$ with As replacing N and that during the synthesis of arsenophosphatidylcholine from arsenophosphatidylethanolamine (Fig. 3) by *S*-adenosylmethionine, two methylations occur, but steric hindrance then causes the $S^+—CH_2$ bond to be preferentially attacked and a lipid intermediate (Fig. 3A) with a structure similar to the arseno-sugars to be produced. It has been found that the enzymatic cleavage of the arsenolipid found in the diatom *Chaetoceros* sp. produced an arseno-sugar.[105] Arseno-containing sugars may be a general response of algae to arsenate and may be a precursor for arsenobetaine. Edmonds *et al.*[164] have outlined a metabolic pathway for the formation of arsenobetaine and arsenocholine from arseno-sugars by anaerobic fermentation. The demonstration that inorganic arsenic orally administered to fish was converted to trimethylarsine oxide but not to arsenobetaine[157] lends further evidence that arsenobetaine is not synthesized *de novo* by fish but is passed to fish via the food chain. Phillips and Depledge[163] have suggested an alternative pathway by which marine organisms can produce arsenocholine by the breakdown of arsenophosphatidylcholine by phospholipases (salvage pathway,

Table 2 Arsonobetaine in marine organisms

Common name[a]	Species	Reference
Pisces		
Haddock (M)		*t*
Halibut (M)		*t*
Cod		*t*
Herring (M)		*t*
Mackerel (M)		*t*
Sole (M)		*t*
Sole (M)	*Solea solea*	*i*
Blue pointer shark (M)	*Isurus oxyrhincus*	*q*
White tip shark (M)	*Carcarhinus longimanus*	*q*
Round nose flounder (M)	*Eopsetta grigorjewi*	*p*
Flat fish (M)	*Limanda herzensteini*	*j*
Lemon sole (M)	*Microstomus kitt*	*i*
Flounder (M)	*Platichthys flesus*	*i*
Dab (M)	*Limanda limanda*	*i*
Blue shark (M,L)	*Prionace glaucus*	*d*
Pelagic shark (M)	*Carcharodon carcharias*	*m*
Starspotted shark (M,L)	*Mustelus manazo*	*n,o*
Dusky shark (M)	*Carcharinus obscurus*	*c*
Plaice	*Pleuronectes platessa*	*g*
Spotted whiting (M)	*Sillaginodes punctatus*	*l*
Estuary catfish (W)	*Cnidoglanis macrocephalus*	*r*
Shortnose dogfish (M,L)	*Squalus brevirostris*	*n,o*
School whiting (M)	*Sillago bassensis*	*f,r*
Mollusca		
Clam (M,V)	*Meretrix lusoria*	*s*
Scallop (M)	*Pecten alba*	*l*
Squid (M)	*Sepioteuthis australis*	*l*
Octopus (M)	*Paroctopus dofleini*	*k*
Scallops (M)		*t*
Crustaceans		
Alaskan king crab (M)	*Paralithodes camtschatica*	*a*
Alaskan snowcrab (M)	*Chionoecetes bairdii*	*a*
Dungeness crab (M)	*Cancer magister*	*a*
Crab (M)	*Cancer cancer*	*i*
Norwegian shrimp (M)	*Nephrops norvegicus*	*h,i*
Prawn (M)	*Penaeus latisulcatus*	*l*
Lobster (M)		*t*
Lobster (M)	*Panulirus cygnus*	*b*
American lobster (M)	*Homarus americanus*	*e*
Lobster (M)	*Jasus novaehollandiae*	*l*
Shrimp		t
Other		
Echinodermata		
Sea cucumber (M)	*Stichopus japonicus*	*j*

[a] M, muscle; L, liver; V, viscera; W, whole. If not specified, tissue analysed unknown.

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Fig. 3). Arsenocholine could then be oxidized to arsenobetaine.[165]

Arsenobetaine has been found in marine organisms from different trophic levels (Table 2). It remains to be established if arsenobetaine is formed from arsenosugars via the dimethyloxyarsylethanol intermediate and passed up the food chain or if organisms at different trophic levels have the ability to synthesize arsenobetaine.

4 ARSENIC IN SEDIMENTS

4.1 Occurrence and mineral associations

The sediments are the largest geochemical reservoir of arsenic, containing in excess of 99.9% of the element. Residence time for arsenic in sediments is close to 100 000 000 years; next in duration is the residence time of dissolved arsenic in seawater, but this in comparison is just 9400 years.[53]

Arsenic concentrations in near-shore unpolluted marine sediments are normally between 0.1 and 50 μg g^{-1}.[172–175] In sediments subject to anthropogenic inputs, especially from mines and smelters, the arsenic content can exceed 1000 μg g^{-1}.[58,176] Anthropogenic influence on sediments with elevated arsenic has been discerned in the lack of accompanying high manganese levels.[175] The capacity of marine sediments to bind up large quantities of arsenic derived from human activities is noteworthy; the very limited dispersion of arsenic about effluent sources is proof.[63,177,178]

Deep-sea sediments have arsenic levels comparable with uncontaminated near-shore sediments. Localized enrichment of arsenic occurs in the vicinity of mid-ocean ridges, where hydrothermal activity is a likely source of this and other elements.[179,180] Neal and coworkers[181] contend that arsenic may not be derived from hydrothermal contribution, but instead freshly precipitated hydrous iron oxides from hydrothermal solutions can be far more efficient scavengers of arsenic in seawater than other iron phases. Other anomalously high arsenic values in deep-sea sediments are ascribed to volcanic emanations.[182,183]

In common with arsenic in suspended particulates, sedimentary arsenic is principally associated with sesquioxide material, mostly hydrous iron oxide phases.[111,174,181,184] Significant enrichment of arsenic is observed in ferromanganese nodules,[185] so elevated arsenic levels in sediments result not only from the settling of iron-rich particulates, but also from direct adsorption on to the sediment surface. Although iron may be crucial in the binding of arsenic to sediments, there is a strong correlation between solid-phase arsenic and manganese[175] possibly because the two elements have similar geochemical mobilities.[186]

Sediment fractionation studies reveal that in addition to sesquioxides, arsenic is associated with organic and carbonate phases.[174] However, the latter two phases bind a very minor portion of sedimentary arsenic, aside from an estuarine sediment where 25% of the metalloid was found with organics. However, it is not possible to differentiate iron and organic phases in organic-rich sediments,[187] and organic arsenic in estuarine sediments may be overestimated. Solid-phase

Table 3 Organoarsenic compounds in marine organisms

Compound	Common name	Species	Reference
2-hydroxy-3-sulphopropyl-5-deoxy-5-(dimethylarsenoso) furanoside	Brown kelp	*Ecklonia radiata*	*f*
2,3-dihydroxypropyl-5-deoxy-5-(dimethylarsenoso) furanoside	Brown kelp	*Ecklonia radiata*	*f*
Arsenic-containing ribofuranosides	Edible seaweed	*Hizikia fusiforme*	*g*
Dimethyloxyarsylethanol	Brown kept (decomposing)	*Ecklonia radiata*	*e*
(2*S*)-3-[5-Deoxy-5-(dimethylarsinoyl)-β-D-ribofuranosyloxyl]-2-hydroxypropyl hydrogen sulphate	Giant clam (kidney)	*Tridacna maxima*	*j*
5-trimethylarsonium ribosylglycerol sulphate	Diatom	*Chaetoceros gracilis*	*k*
Arsenocholine	Shrimps	—	*a,b*
	Shrimp	*Pandalus borealis*	*i*
Trimethylarsine oxide	Estuary catfish	*Cnidoglanis macrocephalus*	*c*
	Baltic herring	*Clupea harengus*	*n*
	Fourhorn sculpin	*Myoxocephalus quadricornis*	*n*
	Perch	*Perca fluviatilis*	*n*
	Plaice	*Pleuronectes platessa*	*n*
Tetramethylarsonium salt	Clam (gill)	*Meretrix lusoria*	*d*
Trimethylarsine	Prawns	*Hymenopenaeus sibogae*	*h*
		Plesionika sp	*h*
		Aristeomorpha foliacea	*h*
		Metapenaeus endeavouri	*h*
		Metapenaeus macleayi	*h*
		Penaeus longistylus	*h*
	Lobsters	*Ibacus peronii*	*h*
		Thenus orientalis	*h*
Not identified	Sea squirt	*Halocynthia roretzi*	*l*
Not identified	Shrimp	*Sergestes lucens*	*m*

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arsenic levels in anoxic sediments are similar to those in oxic sediments,[175,185] but it is almost certain that arsenic is associated with quite different mineral phases in these two environments. Belzile and Lebel[188] have recently suggested that in suboxic sediments arsenic is 'captured' by pyrite.

4.2 Speciation

In early studies only arsenate and not arsenite or methylated species of arsenic were detected in sediments[24,189] except in such cases as contamination of estuarine sediments by arsenic based pesticides.[174] However, very recently Reimer and co-workers[190,191] have found MMA, DMA and trimethylarsine oxide in natural and anthropogenically perturbed sediments. It has not been determined if these arsenic species are excretion products of organisms or are synthesized by micro-organisms within the sediments.

4.3 Sediment–water exchange

Diagenesis of sedimentary material liberates arsenic to the sediment porewaters; thus the arsenic concentration of these interstitial waters reflects solid-phase arsenic levels, although their arsenic content always remains a minor fraction of total sedimentary levels.[24,175] Other factors affecting the concentration and distribution of arsenic in the porewaters are redox potential, hydrous oxide mineral phases, bioturbation and other surface mixing processes.

The prime mechanism for the release of arsenic into porewaters is the dissolution of hydrous oxide phases to which the metalloid is adsorbed. Dissolution occurs by the reduction of iron(III) and manganese(IV) to their soluble lower oxidation states, iron(II) and manganese(II). From laboratory experiments, it is evident that arsenic is bound to iron rather than manganese oxides.[192] Release of arsenic from the decomposition of organic matter in sediments has not been demonstrated, even in an anoxic sediment where ammonia and phosphate concentrations increased markedly with depth.[175]

Both arsenic(V) and arsenic(III) are found in the interstitial waters of sediments. The redox potential at which iron(III) is reduced to iron(II) still favours arsenic(V) over arsenic(III) at $pH > 7$, and it is this fact that might explain As(III)/As(V) ratios of less than unity observed in some coastal sediment porewaters that are reducing in character.[24,175] In most instances of porewaters at reducing potentials, it is arsenic(III) that predominates.[192] Bacterial reduction may mediate the redox chemistry of arsenic in sediments.

In common with dissolved arsenic in the water column, the presence of reduced sulphur species under anoxic conditions could favour the formation of inorganic and organic thioarsenic species. Up to now there has been no indisputable evidence to indicate the occurrence of such compounds in sediments. Nevertheless, the decrease in total arsenic concentration of porewaters with depth in strongly reducing porewaters has been attributed to formation of an insoluble arsenic–sulphur compound or the adsorption of arsenic to a metal–sulphidic solid phase.[175] A recent review by Salomons and others[193] suggests that arsenic does not form sulphide compounds, and that it is bound to sediments exclusively by adsorption processes — such as observed by Belzile and Lebel.[188]

The occurrence of organoarsenic species in sediment porewaters is consistent with Wood's (1974) postulated biological cycle[194] for arsenic where bio-reduction and -methylation by bacteria in sediments can produce MMA, DMA, and organoarsines. Whether organoarsenic compounds are mobile in sediments, or rapidly and irreversibly bound, is not known, although the latter condition may explain why such compounds were not identified in earlier porewater analyses. Furthermore, their lifetime in sediments may be quite short, because demethylation of MMA and DMA has been reported for incubation of anaerobic sediments.[93]

Compaction of sediments forces porewaters upwards. Arsenic(III) released into porewaters at reducing redox potentials will also diffuse upwards along concentration gradients. If this reduced arsenic species encounters oxidizing conditions, it is oxidized

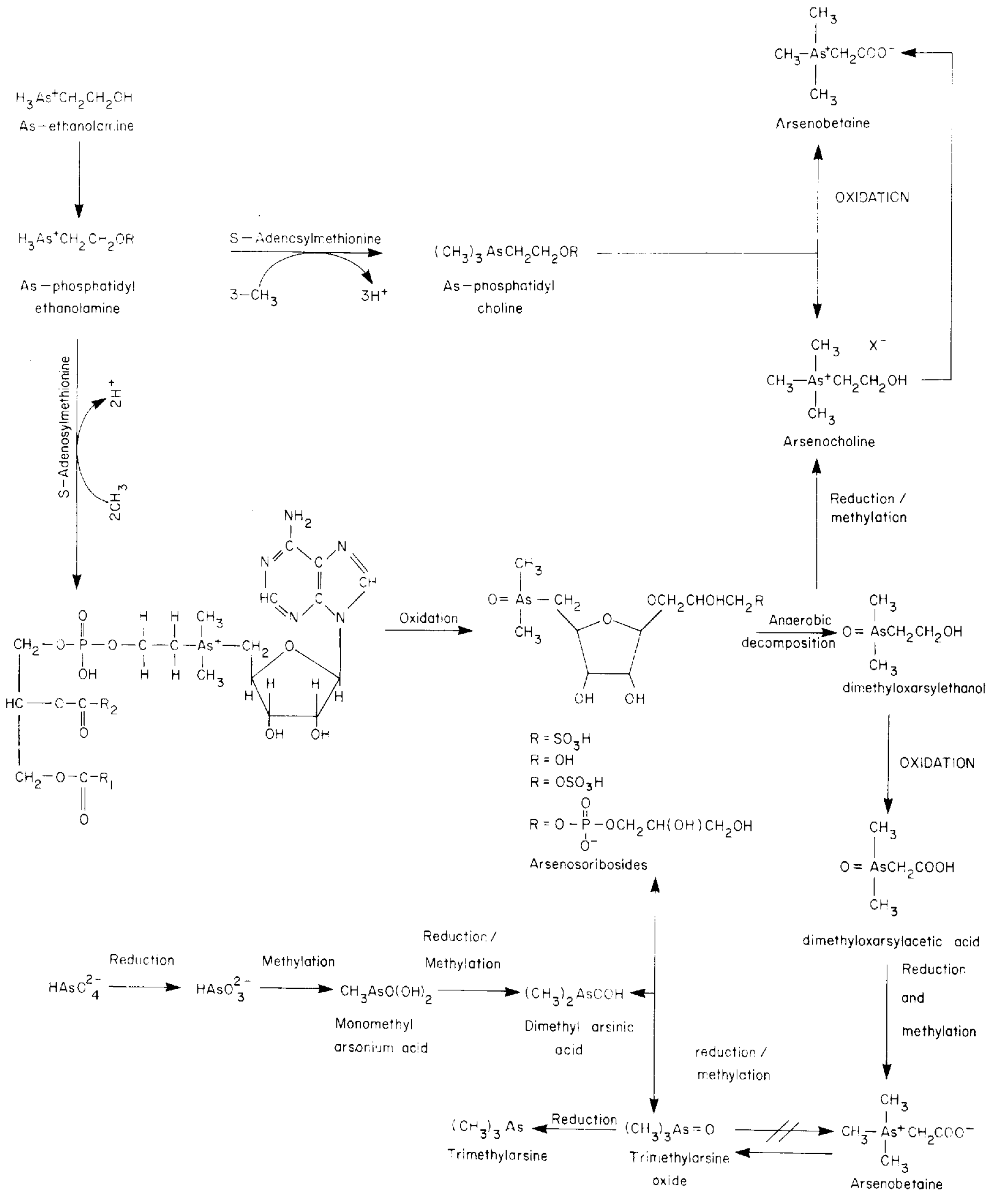

Figure 3 Postulated biotransformations of arsenic.

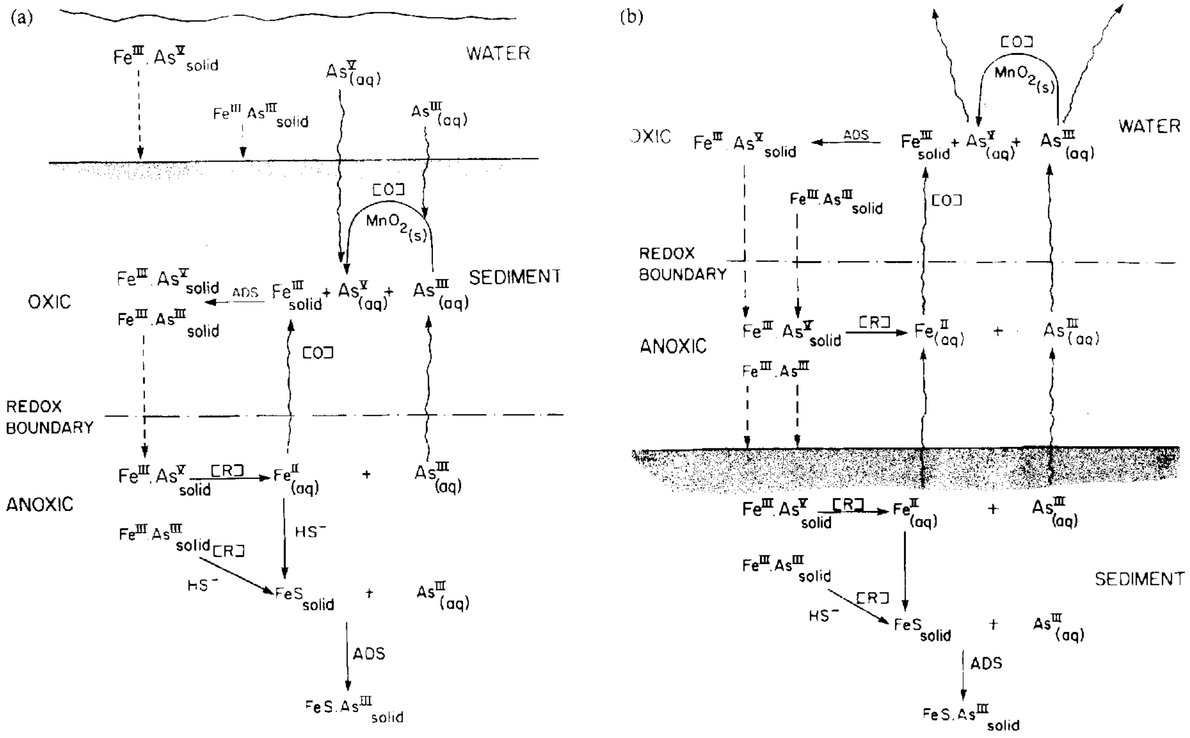

Figure 4 Arsenic transformations in sediment. [O] = oxidized; [R] = reduced; ADS = adsorbed.

to arsenic(V) and readily adsorbed by freshly precipitated am-Fe(OH)$_3$ arising from the oxidation of iron(II), which too has diffused from the deeper reducing zone.[19,192] A redox boundary within the sediment column means that arsenic released by diagenesis is confined to sedimentary cycling (Fig. 4a). However, this barrier can be overcome if the surface oxic layer is too thin to fully trap the upwardly diffusing arsenic, or physical processes such as surficial mixing occur. In a study of bioturbation, Waslenchuk and coworkers[189] observed that burrow venting greatly enhanced the flux of some elements from sediment porewaters to the overlying water column, but arsenic was not one of them. Nevertheless As(III)/As(V) ratios in burrow waters were greater than in the bottom waters overlying the sediment, and so the venting process could alter arsenic speciation of bottom water. In contrast, Riedel *et al.*[195] have observed that the presence of burrowing organisms in contaminated sediments increased the outward flux of arsenic several-fold with greater relative fluxes of reduced and methylated arsenic compounds. It appears that the impact of organisms will specifically depend on the nature of their activity in the sediment. Benthic organisms therefore may play an important role in arsenic geochemistry.

If the redox boundary is not in the sediments but in the overlying waters, there is no constraint on the efflux of arsenic and other elements from the sediment porewaters (Fig. 4b). The diffusion of arsenic into oxygen-deficient or anoxic marine waters has been recorded in estuarine, coastal and shelf environments.[24,196]

5 ARSENIC CYCLING

Mackenzie *et al.*[53] have predicted that the arsenic concentration in surface waters of the ocean will increase by approximately 2% by the year 2000. Examination of the biogeochemical cycling model of arsenic used[53] revealed that the role of particulates in transporting arsenic to the sediment (Fig. 5) may have been underestimated. Recalculation of the particulate-to-sediment flux (Table 4) using available sedimentation rates from sediment trap experiments[196] and deep-sea sediment arsenic concentrations away from active ridges[197–201] suggests that *in-situ* adsorption of arsenic to particulate matter could remove incoming dissolved arsenic from anthropogenic sources. More reliable data on sedimentation rates and the arsenic

Table 4 Arsenic fluxes in the marine environment (calculated from Ref. *a*.)

Riverine input *Assumption*: suspended load is precipitated in estuary and does not reach the ocean. Total yearly run-off i.e. 3.6×10^{16} dm^{3} yr^{-1} (Ref. *b*)	× mean arsenic concentration × 1.5 μg As dm^{-3}		$= 540 \times 10^{8}$ g yr^{-1}
Atmospheric input Arsenic removal i.e. $(22 + 5.6) \times 10^{8}$ g yr^{-1} (Ref. *c*)	- arsenic release from ocean $- 1.1 \times 10^{8}$ g yr^{-1} (Ref. *c*)		$= 26.5 \times 10^{8}$ g yr^{-1}
Dissolved-to-biota phase Uptake into organic matter Rate of carbon fixation i.e. 2.5×10^{16} g C yr^{-1} (Ref. *d*)	× As/C ratio $\times 1.62 \times 10^{-6}$ g As/C (Ref. *e*)		$= 405 \times 10^{8}$ g yr^{-1}
Uptake into skeletal matter SiO_2 uptake in photic zone i.e. 250×10^{14} g yr^{-1} (Ref. *f*)	+ $CaCo_3$ uptake in photic zone $+ 94.5 \times 10^{14}$ g yr^{-1} (Ref. *g*)	× Mean [As] of skeletal matter $\times 1 \times 10^{-6}$ g As g^{-1} (Ref. *h*)	$= 344.1 \times 10^{8}$ g yr^{-1}
Biota-to-dissolved phase Release from organic matter Rate of fixation by biota i.e. 405×10^{8} g As yr^{-1}	- biota to particulate matter $- 14.5 \times 10^{8}$		$= 390.5 \times 10^{8}$ g yr^{-1}
Release from skeletal matter Dissolved to skeletal flux i.e. 344.1×10^{8} g yr^{-1}	- skeletal to particulates $- 29.4 \times 10^{8}$		$= 315.1 \times 10^{8}$ g yr^{-1}
Biota-to-particulate phase (not further degraded) In organic matter Sedimentation of organic carbon Oceanic C − oceanic C fixation oxidation i.e. $(250 \times 10^{14} - 241 \times 10^{14})$g yr^{-1} (Refs *d,i*)	× As/C ratio (phytoplankton) $\times 1.62 \times 10^{-6}$ (Ref. *e*)		$= 14.5 \times 10^{8}$ g yr^{-1}
In skeletal material Total mass of SiO_2 skeletons in sediment i.e. 10.5×10^{14} g yr^{-1} (Ref. *j*)	+ total mass of $CaCo_3$ skeletons in sediment $+ 18.9 \times 10^{14}$ g yr^{-1} (Ref. *g*)	× mean skeletal As $\times 1 \times 10^{-6}$ g^{-1} (Ref. *h*)	$= 29.4 \times 10^{8}$ g yr^{-1}
Particulate to sediment Sedimentation rate i.e. 1.68 mg cm^{-2} yr^{-1} (Ref. *k*)	× area of ocean $\times 360 \times 10^{12}$ m^{2}	× median [As] of cretaceous shelf sediments (Ref. *l*)	$= 725 \times 10^{8}$ g As yr^{-1}
Sediment to particulate by diffusion i.e. 4.8×10^{6} g yr^{-1} (Ref. *m*)			$= 0.05 \times 10^{8}$ g yr^{-1}

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content of settling particulate material are needed to confirm this hypothesis.

Given the imprecise nature of the flux calculations it appears that biota only play a small role in removing arsenic from the water column. Arsenic removed in biogenic particulate material could not be replenished by diffusion from sediments to conserve dissolved arsenic in the water column.

6 SUMMARY AND CONCLUSIONS

The dissolved forms of arsenic in the water column are limited to arsenate, arsenite, MMA and DMA. MMA and DMA are the only examples of arsenic–carbon compounds present in the aqueous marine environment, with the possible exception of traces of alkylarsines in sediments. Other species [AsS_2^-, AsS_4^{3-}, $[(CH_3)_2As]_2S$] predicted to occur in anoxic waters have not been identified.

Arsenic appears to be uniformly distributed in the world oceans, and exhibits similar patterns with depth world-wide. Anthropogenic inputs to rivers and estuaries can substantially increase arsenic concentrations in inshore areas. Atmospheric sources of arsenic are normally negligible but in some localized areas can be comparable with riverine inputs.

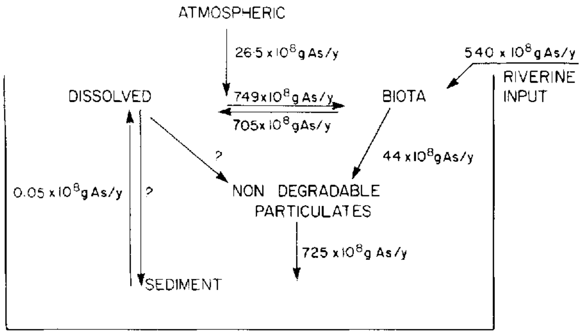

Figure 5 Arsenic fluxes in the marine environment.

Since seawater is undersaturated with respect to most solid phases, adsorption on to particulate matter is the physical process most likely to limit dissolved arsenic concentrations. Arsenate is strongly adsorbed to hydrous oxide phases and clays, whilst arsenite and methylated arsenicals have been shown to be adsorbed to river particulates. The role of humic acids has not been determined.

Biological activity can alter arsenic speciation in surface waters away from the thermodynamically favoured arsenic species, but negligibly changing the total arsenic concentration, and suggesting no volatile arsenic compounds are produced. Close correlations between biological activity in the euphotic zone and the presence of arsenite and methylated arsenic species have been found. The influence of biological activity on arsenic speciation will thus depend on the prevailing water temperature and the presence of phytoplankton, bacteria and other biota, and will be seasonal. Arsenate is likely to be taken up by phytoplankton during growth because of its chemical similarity to the nutrient, phosphate. To avoid the toxic effects of inorganic arsenic, arsenic is detoxified by the formation and excretion of arsenite, MMA and DMA. Phytoplankton in different marine ecosystems (coastal/oceanic, temperate/tropical) appear to have different strategies for dealing with arsenic uptake, which could explain the variations found in the distribution of arsenite and methylated arsenic species in marine waters.

Marine organisms accumulate arsenic from water and food. Arsenic uptake from water is usually proportional to arsenate concentration until a threshold value is reached after which arsenate uptake is inhibited or becomes independent of arsenate concentration. When arsenic is accumulated through food, differences in arsenic concentration between species and in the same species can be directly related to diet. Arsenic uptake via food appears to be more efficient; ingested organic arsenic is retained in preference to inorganic arsenic. It has not been established if direct accumulation of arsenic through ingestion of sediment particles is possible. Little is known about the elimination of arsenic from organisms. Inorganic arsenic is eliminated more readily than organic arsenic forms and this observation would account for the observed shift in the proportion of arsenic in marine organisms towards organoarsenic forms. Biomagnification of arsenic up food chains does not appear to occur. Most evidence points towards biodiminution of arsenic up marine food chains.

Lipid-soluble and methanol- or water-soluble organoarsenic compounds have been isolated from marine biota. The relative proportions vary with organisms and may be a function of diet. Carnivores generally contain more methanol-soluble arsenic in relation to lipid-soluble arsenic than planktonic feeders and herbivores. The chromotographic behaviour of lipid-soluble arsenic compounds suggests them to be arseno-containing phospholipids. Lipid-soluble arsenic compounds can be converted to water- (or methanol?) soluble arsenic compounds by boiling. The physiological significance of, and the relationship and interconvertibility of, lipid- and water-soluble arsenic compounds still need to be determined.

Arsenic occurs in marine organisms mainly as non-toxic organic arsenic compounds with only small amounts of the inorganic arsenic species present. Arseno-sugars, arsenobetaine, arsenocholine trimethylarsenic oxide and other unidentified organic arsenic compounds containing $(CH_3)_4\ As^+$—; $(CH_3)_3As^+$— and $(CH_3)_2As$— have been isolated from marine organisms. Arsenobetaine is widely distributed in marine animals at different trophic levels and is probably the end-product of arsenic metabolism in marine food chains. It remains to be established if arsenobetaine is synthesized from other arsenic compounds (e.g. plant arseno-sugars) and passed up the food chain, or if organisms at different trophic levels have the ability to synthesize arsenobetaine.

Sediments provide the largest reservoir of arsenic and have the capacity to bind up arsenic introduced from human activities, thus limiting the dispersion of arsenic in the marine environment. Arsenic is principally associated with sesquioxide phases, whilst organic and carbonate phases may be of importance in estuarine sediments. Arsenate is the predominant species in sediments and it is only recently that methylated arsenic species have been isolated from non-anthropogenically perturbed sediments.

Diagenesis of sedimentary material liberates arsenic to water through dissolution of hydrous oxide phases under reducing conditions. Both arsenic(V) and arsenic(III) are found in pore water with mostly the latter as the major species. There is no evidence for the formation of thioarsenic species in marine sediments.

When present in sediments, the redox boundary at the oxidized/reduced interface should normally act as a barrier to upward diffusion of arsenic. The freshly precipitated hydrous oxides will rapidly readsorb arsenic species. However, in the absence of a sedimentary redox boundary, as for example in oxygen-depleted marine basins, elevated bottom-water arsenic concentrations can arise from the efflux of arsenic from the sediments.

From an examination of available arsenic data, arsenic concentrations can become elevated in some estuaries and near-shore waters adjacent to heavy industrial or mining and mineral-processing areas. The possibility of long-term elevation of arsenic concentrations and the altering of the biogeochemical arsenic cycle requires better estimates of riverine and atmospheric inputs, especially the remobilization of arsenic from particulates and research into sections of the biogeochemical cycle which are still not fully understood, e.g. adsorption processes, the role of microbes and particulate arsenic fluxes to ocean sediments. Biota only play a small role in removing arsenic from the water column but influence arsenic speciation. Abiotic processes do not appear to produce or degrade methylated arsenic species to a significant extent. The methylated arsenic compounds produced by biota are non-toxic. It is not known whether arsenic is taken up because it is chemically similar to phosphorus and organisms have no way of discriminating between arsenate and phosphate, or if the methylated arsenic compounds have a specific biochemical role. For example, arsenobetaine may act as an osmotic regulator in a similar way to betaine.

The continued measurement of arsenic in the marine environment is important not only as a method of addressing these questions but because arsenic measurements are useful as markers for anthropogenic inputs into oceans, especially for mining and processing activities. Arsenic also has potential as an oceanic tracer coupled with a suite of other elements (e.g. chromium(VI), selenium, etc.) to provide characteristic ratios for water masses (e.g. As/Se) as suggested by Rahn and Lowenthal[202] for air masses.

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