APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 697–705 (1996)

The Distribution of Arsenic Compounds in the Ocean: Biological Activity in the Surface Zone and Removal Processes in the Deep Zone

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The vertical profies of inorganic arsenic [As(III)+As(V)], monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) were investigated at four sampling stations in the Pacific Ocean and a sampling station in the southern Tasman Sea. In addition, the concentrations of those compounds in surface waters of the Pacific Ocean and Tasman Sea have been determined.

The vertical profiles of inorganic arsenic showed the low concentrations in both the surface and deep/bottom zones. The depleted concentrations in the surface zone varied from 1000 to 1700 ng dm^{-3} and that in the deep/bottom zone varied from 1300 to 2050 ng dm^{-3}. The maximum concentrations that varied from 1500 to 2450 ng dm^{-3} were usually observed at a depth of about 2000 m.

Both MMAA and DMAA were observed throughout the water column at sampling stations in the north-western and equatorial regions of the Pacific Ocean. At the sampling station in the central northern Pacific gyre, DMAA was the only methylated arsenic compound observed throughout the water column. On the contrary, at the sampling station in the southern Tasman Sea, the only detected methylated arsenic compound throughout the water column was MMAA. Their vertical profiles showed maximum concentrations in the surface water which abruptly dropped with depth from 0 to 200 m. The concentration in the surface water was close to 10 ng dm^{-3} for MMAA and varied from 27 to 185 ng dm^{-3} for DMAA. At depths greater than 100 m, MMAA and DMAA were at comparable concentrations which varied from 0.7 to 14 ng dm^{-3}.

The low inorganic arsenic concentration in the surface zone was due to biological activity. This activity resulted in the uptake of As(V) and subsequent reduction and methylation to MMAA and DMAA. DMAA was the main predominant arsenic compound resulting from biological activity in surface waters.

The low inorganic arsenic concentrations in the deep and bottom zones were likely to be caused by the adsorption of dissolved inorganic arsenic onto sinking particulates rich in iron and manganese oxides.

Keywords: inorganic arsenic; monomethylarsonic acid (MMAA); dimethylarsinic acid (DMAA); arsenic distribution; Pacific Ocean; Tasman Sea; seawater

INTRODUCTION

In contrast to coastal and estuarine waters, the effects of chemical and biological processes on the distribution and speciation of arsenic in oceanic waters has not been intensively studied. In coastal and estuarine regions, arsenic(V) [As(V)] is usually found as the predominant form of arsenic species in oxygenated water. The other species that are already known to accompany As(V) are arsenic (III) [As(III)], monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). In the oxygenated water, As(III), MMAA and DMAA are thermodynamically unstable species. Thus, their formation is believed not to be mediated by purely chemical processes. The variation of the concentration of those compounds was usually associated with temperature[1–5] and/or salinity[5,6] and, in some cases, the abundance of one of them has been correlated with the occurrence of a particular phytoplankton group.[3,5–7]

In the open ocean, the presence of As(V). As(III), MMAA and DMAA is also well docu-

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CCC 0268–2605/96/090697–09

Received 5 December 1995
Accepted 18 January 1996

mented.[4,8-10] In comparison with coastal regions, the concentration of the methylated arsenic compounds, MMAA and DMAA, in open oceanic waters is generally low. The cause of their lower concentrations in open oceanic waters has been suggested to be the high affinity of ocean phytoplankton communites towards low-nutrient conditions; hence they are able to discriminate better between As(V) and the competing nutrient species (phosphate).[5,10] We found that the variation of inorganic [As(V)+As(III)] and organic [MMAA+DMAA] concentration in the surface water of the ocean seemed to be temperature-dependent.[4,10] Another interesting fact, in the south-west Pacific Ocean, was that methylated arsenic species were found not only in the euphotic zone but also in deeper waters including bottom water.[4,10] Detection of methylated arsenic species throughout the water column may be attributable to employment of the sensitive technique of inductively coupled plasma mass spectrometry (ICP–MS) as a detection technique for our hydride generation (HG) method. The employment of ICP–MS results in a detection limit down to 0.2 and 0.7 ng dm^{-3} for MMAA and DMAA, respectively.

In contrast with the other studies for the open ocean, our previous reports revealed that the low concentration of inorganic arsenic [As(V)+As (III)] occurred not only in the surface zone but also in the bottom zone.[4,10] Low concentration in the surface zone may be an indication of biological activity, as suggested by other researchers. However, the low concentration in the bottom zone has not been observed before. In this study, further work on the presence of methylated arsenic species throughout the water column and the decrease of inorganic arsenic in the bottom zone (as has been found in the south-western Pacific Ocean) is continued for the other oceanic areas in the Pacific Ocean and the Tasman Sea. In addition, the temperature dependence on the distribution of the methylated arsenic compound (as has been found in Indian and Antarctic Ocean surface waters[4,10]) will also be further investigated for the Pacific Ocean.

EXPERIMENTAL

Sampling sites

Surface water samples were collected at the various locations shown in Fig. 1 using a Niskin

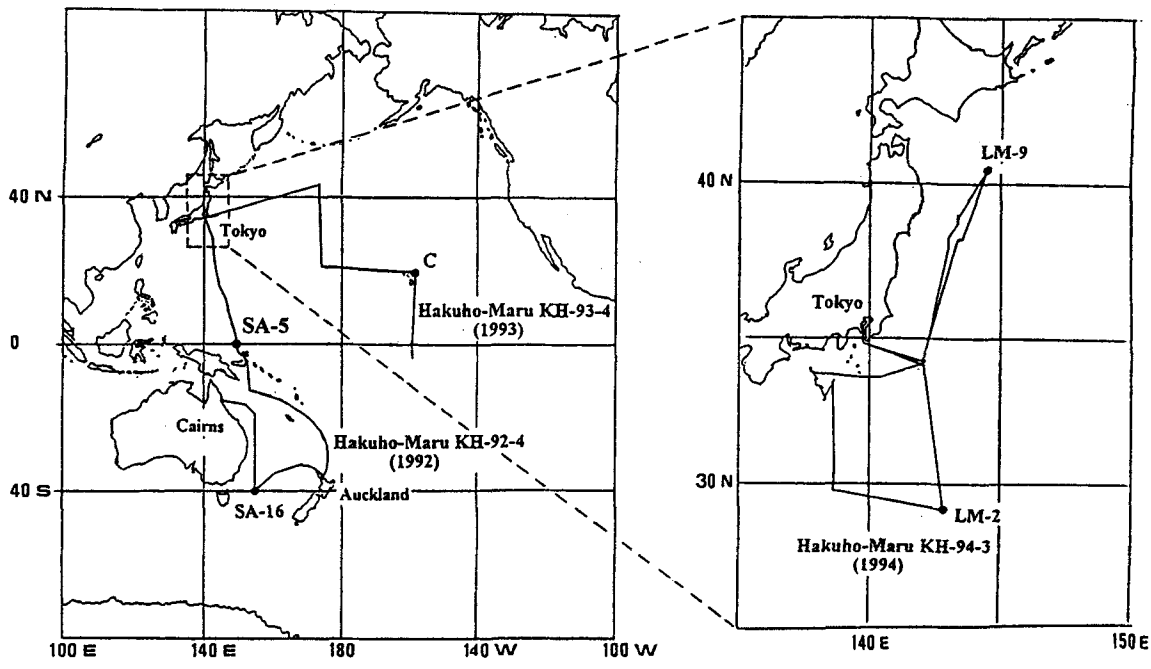

Figure 1 Sampling locations. Full lines depict the routes of three separate cruises; solid circles depict vertical profile stations.

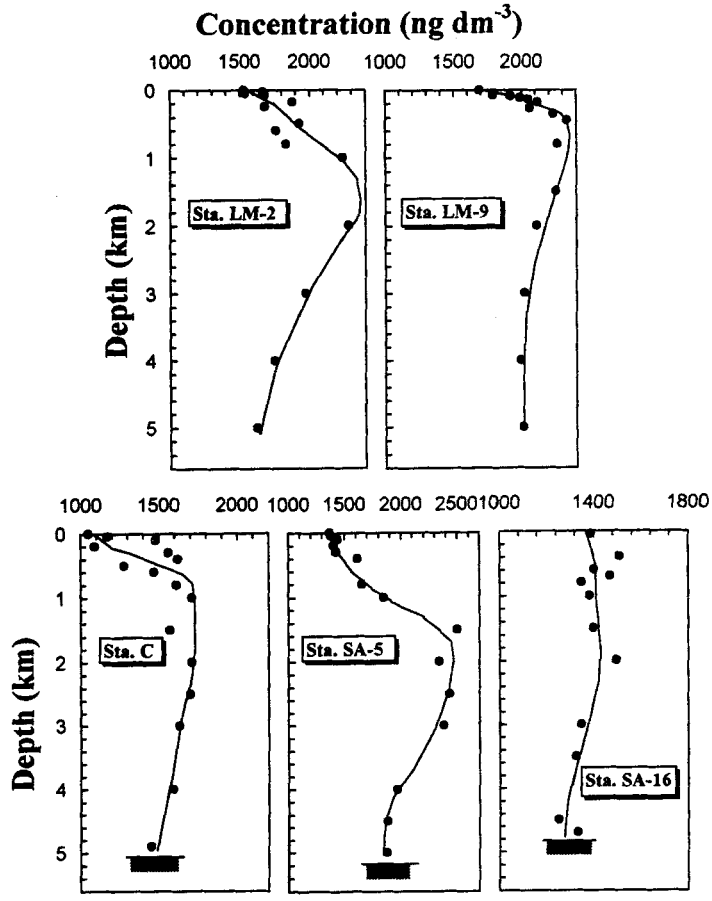

Figure 2 Vertical profiles of dissolved inorganic arsenic [As(V)+As(III)] at various stations in the Pacific Ocean (Sta. LM-2, LM-9, C and SA-5) and at a station in the southern Tasman Sea (Sta. SA-16).

Table 1 Temperature and average concentrations of arsenic compounds and nutrients in the surface zone (< 100 m) of four sampling stations in the Pacific Ocean and one in the southern Tasman Sea

Sampling station	Seawater temp. (°C)	Nutrient (μmol dm^{-3})			Arsenic compounds (ng dm^{-3})			MMAA/DMAA ratio
		Phosphate	Nitrite+Nitrate	Silicate	Inorg. As	MMAA	DMAA	
LM-2 (northwest Pacific)	25.9	0.03	0.11	1.38	1580	10.5	59.3	0.18
LM-9 (northwest Pacific)	13.6	0.96	3.81	8.4	1528	11.1	53.7	0.21
C (central north Pacific gyre)	25.7	<0.02	<0.09	1.2	1110	15.9	184.5	0.09
SA-5 (West Pacific equatorial region)	28.8	0.08	2.34	1	1400	8.7	26.7	0.33
SA-16 (southern Tasman Sea)	11.4	0.32	3.98	<0.30	1389	7.7	< 0.7	—

bottle. In addition, vertical profile samples down to 5000 m were collected at stations LM-2 (29°04.75′ N, 142°50.94′ E) and LM-9 (40°26.00′ N, 144°29.00′ E) in the north-western Pacific Ocean, respectively, on 4 October 1994 and 15 October 1994, and other vertical profile samples down to the bottom were collected at stations C (22°45.83′N, 158°06′ W) in the central north Pacific gyre, SA-5 (0°, 149°56.00′ E) in the equatorial region of the west Pacific Ocean and SA-16 (40°02.16′ S., 155°08.36′ E) in the southern Tasman Sea on 31 October 1993, 24 September 1992 and 17 October 1992, respectively. The water samples were immediately filtered through a Millipore filter (pore size 0.45 μm) and stored in polypropylene bottles at 0 °C in darkness. Analysis was performed at our laboratory within three months of sampling. During storage, it was confirmed that no change in the arsenic species had occurred.

Method of analysis

Analysis of the arsenic compounds by inductively coupled plasma mass spectrometry (ICP–MS) was performed using a model PMS 2000 instrument (Yokogawa Analytical Systems) after generating their hydrides from the sample using $NaBH_4$. The hydrides were trapped in a U-tube packed with OV-3 15% Chromosorb WAW DMCS 60/80-mesh, and cooled with liquid nitrogen; the arsines were then successively volatilized and transferred to ICP–MS using helium as a carrier gas. The details of the method were exactly as given in a previous report.[10] Detection limits were 9.2 ng dm^{-3} for As(V)+As(III) and 0.2 and 0.7 ng dm^{-3} for MMAA and DMAA, respectively. Precision was

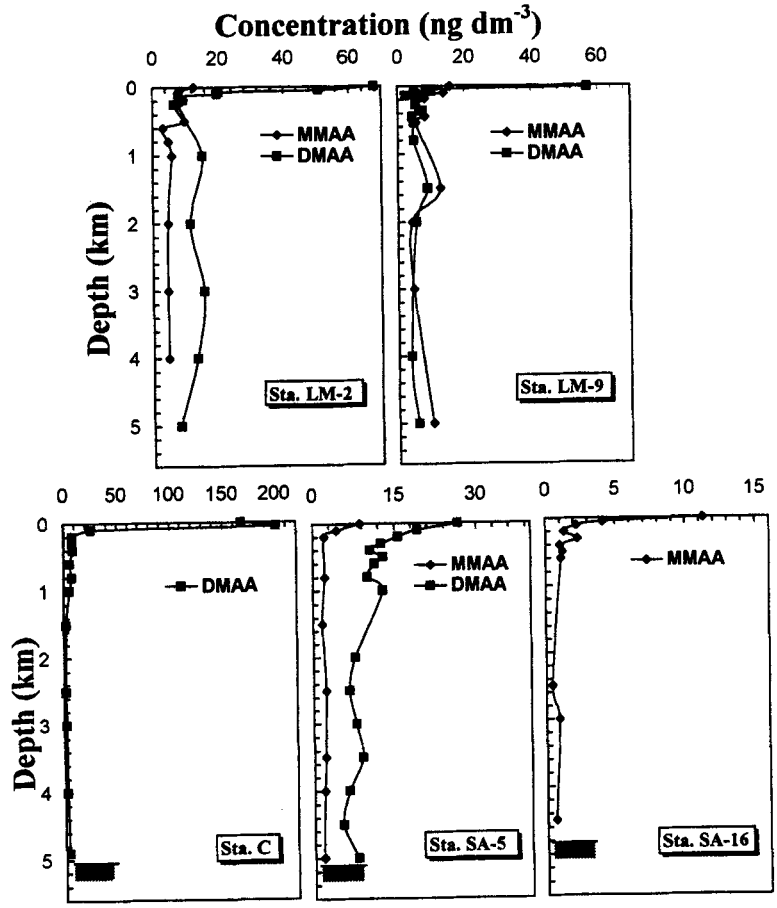

Figure 3 Vertical profiles of dissolved organic arsenic (MMAA and DMAA) at various stations in the Pacific Ocean (Sta. LM)2, LM-9, C and SA-5) and at a station in the southern Tasman Sea (Sta. SA-16).

estimated to be 7% for As(III)+As(V), 6% for MMAA and 6% for DMAA.

RESULTS AND DISCUSSION

Vertical distribution of arsenic compounds

The vertical profiles of dissolved inorganic arsenic at five sampling stations (Fig. 2) displayed a consistent decrease in concentration from the mid-depth zone to both the surface and deep/bottom zones. The concentrations in the surface water ranged from 1100 (Station C) to 1700 ng dm^{-3} (Station LM-9) and those in the deep/bottom zone ranged from 1300 (Station SA-16) to 2050 ng dm^{-3} (Station LM-9). The maximum concentrations, which varied from 1500 (Station SA-16) to 2450 ng dm^{-3} (Station SA-5), usually occurred at a depth of 2000 m.

Station C was located in the central north Pacific gyre where the surface water contained less phosphate and total nitrite and nitrate than Stations LM-2 and LM-9 in the north-western Pacific Ocean, Station SA-5 in the western Pacific equatorial region and Station SA-16 in the sourthern Tasman Sea (Table 1). The low phosphate concentration in the surface water of Station C may indicate that the most intensive uptake of phosphate has occcurred. Considering a similar incorporation pathway between the predominant inorganic arsenic species of As(V) and nutrients, especially phosphate, in marine algae,[11–13] the intensive uptake of phosphate in the surface water of Station C must result in the high uptake and subsequent reduction and methylation of As(V). Indeed, the concentration of the methylated arsenic compound in the surface water of Station C was the highest.

At Stations LM-2, LM-9 and SA-5, both MMAA and DMAA were detected throughout the water column (Fig. 3). At Station C, although MMAA displayed a significantly high concentration in the surface zone (Table 1), its concentration in deeper waters was generally lower than the detection limit of the method and hence DMAA was the only methylated arsenic compound detected throughout the water column (Fig. 3). On the other hand, the only detected methylated arsenic compound throughout the water column of Station SA-16 was MMAA.

The concentrations of methylated arsenic compounds in the surface zone were close to 10 ng dm^{-3} for MMAA and ranged from 27 to 185 ng dm^{-3} for DMAA, and those in deeper waters (>100 m) were in the range 0.7–14 ng dm^{-3} for both MMAA and DMAA.

As(V), having entered the algal cell, is transformed rapidly to MMAA and DMAA, but these make up only a minor fraction of the organic arsenic in algae.[14,15] On the other hand, it is known that DMAA and MMAA are the only metabolites found in culture media of algae.[16] Therefore, MMAA and DMAA were suggested as intermediates in the formation of more complex organoarsenic compounds in algae and their presence in culture media could be the result of the excretion of these compounds either immediately after their biosyntheses or following breakdown of larger organoarsenic compounds.

If the breakdown of larger organoarsenic compounds was purely a chemically mediated process and the only major process that leads to the presence of MMAA and DMAA in the open ocean, the MMAA/DMAA ratio in the surface zone of stations at the same water temperature should be comparable. As summarized in Table 1, the MMAA/DMAA ratio at Station C was much lower than that at Stations LM-2 and Sa-5, although the water temperatures of those stations were little different. Moreover, the MMAA/DMAA ratio at Station C was also much lower than that at Station LM-9, which displayed a significantly lower water temperature. On the other hand, MMAA was the only methylated arsenic compound detected at Station SA-16. Therefore, instead of being the breakdown product of larger organoarsenic compounds, direct excretion from the algal cell immediately after biosynthesis is more likely to be the predominant source of MMAA and DMAA in oceanic surface waters.

The dominant phytoplankton species that live successfully in the extremely limited phosphate, nitrate and nitrite zones, in the surface water of Station C are likely to be different from those in the surface waters of other stations in the northwest and equatorial regions of the western Pacific Ocean. The successful phytoplanktons at Station C may excrete DMAA predominantly rather than MMAA. In the case of Station SA-16, the relatively high content of phosphate, nitrate and nitrite was not balanced with the extremely low silicate content. This nutrient composition may induce specific phytoplankton species different from that in northern Pacific waters to thrive. Because MMAA was the only detected

methylated arsenic compound, the successful phytoplankton species at Station SA-16 were suggested to excrete only, or mainly, MMAA.

In estuarine and coastal regions, effects of the chemical composition of water (especially phosphate content and salinity) on the composition of the phytoplankton community are well documented.[3,5-7] In turn, phytoplankton species compositions greatly influence arsenic speciation in the surrounding water. As an example, abundances of MMAA and DMAA have been found to correlate with cryptophyte-dominated phytoplankton communities[5] and the dinoflagellate *Katodinium rotundatum*,[7] respectively. Unfortunately, the effect of chemical constituents (other than phosphate and salinity) on the composition of the phytoplankton community has rarely been studied in estuarine, coastal and open oceanic regions. Therefore, the dominant phytoplankton species in the ocean region (displaying a specific nutrient composition as found in Stations C and Sa-16) has not been observed yet.

Arsenic scavenging in deep waters

The decrease of inorganic arsenic concentration in bottom zones has only been reported in our previous study for a sampling site in the southwestern Pacific Ocean.[4,10] Now, it becomes clearly apparent that the decrease in bottom zones consistently occurs in the bottom and deep zones of the other oceanic areas as shown in Fig. 2. On the other hand, Statham *et al.*[17] have shown that the vertical distribution of dissolved inorganic arsenic at six stations in the Cape Basin shows no, or only slight, depletion of its concentration in the bottom zone. A similar vertical profile to that shown in the Cape Basin was also found for As(V) in the northern Atlantic Ocean.[18] Regardless of this discrepancy, we tried to elucidate the processes responsible for the decrease in the bottom and deep zones (Fig. 2).

The association of arsenic with hydrated heavy-metal oxides through adsorption and/or coprecipitation was observed not only in laboratory experiments[19-21] but also in natural environments such as lake,[22-24] estuary[25] and marine sediments.[24-29] Among the hydrated heavy-metal oxides, those of iron and manganese are the oxides most responsible for scavenging arsenic.

Recent measurements on the vertical profile of iron and manganese in Pacific Ocean waters showed that their dissolved forms were generally of a maximum in the minimum oxygen zone, and tended to decrease with increasing depth.[30] On the other hand, amorphous hydrated iron oxide and manganese oxide particles, and those adsorbed onto other particle surfaces, tended to increase with increasing depth from the minimum oxygen zone.

Amorphous hydrated iron and manganese oxides have been found to have a high capacity for the adsorption of arsenic.[20] Through an adsorption and/or coprecipitation process, insoluble hydrated amorphous iron and manganese oxides in deep ocean waters were suggested to be responsible for the decrease of inorganic arsenic in the deep waters as shown in Fig. 2.

According to Maher,[25] and references therein, hydrated iron(III) oxides have a positive surface charge under the ranges of pH found in seawater, and As(V) is adsorbed onto these hydrated oxide surfaces by a ligand exchange mechanism. In the case of As(III), the report of Peterson and Carpenter,[28] and references therein, imply that the adsorption of As(III) occurs after the oxidation of As(III) to As(V). For the oxidation of As(III) to As(V), manganese(IV) oxide was found to be more reactive than iron(III) oxide. Accordingly, the adsorption of inorganic arsenic onto hydrated iron(III) oxide can be summarized and simplified as shown in Eqns [1]–[3].

(a) *Hydrated iron(III) oxide formation*

$$Fe_2O_{3(p)} + nH_2O \rightarrow (\mathbf{H_2O^+})_n Fe_2^{n-/2}O_{3(p)} \quad [1]$$

(b) *Adsorption of As(V) onto hydrated iron(III) oxide through a ligand exchange mechanism*
All H_2O groups bonded to iron oxide are assumed to be replaced by As(V).

$$[(O)(OH)As(O^-)(O^-)_{(aq)}]_n + (\mathbf{H_2O^+})_n Fe_2^{n-/2}O_{3(p)} \rightarrow [(OH)_3(O^-)As(O)]_n Fe_2^{n-/2}O_{3(p)} \quad [2]$$

(c) *Oxidation of As(III) before adsorption onto hydrated iron(III) oxide*

$$MnO_{2(p)} + H_3AsO_{3(aq)} \rightarrow Mn^{2+}_{(aq)} + (O)(OH)As(O^-)(O^-)_{(aq)} + H_2O \quad [3]$$

The evidence of the association of arsenic with iron and manganese oxides has been confirmed in both estuarine and pelagic sediments.[25] Using the sequential extraction procedure proposed by Tessler *et al.*[31] for the speciation of particulate trace metals, the majority of extractable arsenic in pelagic sediments off the coast of Africa was found be be associated with the iron–manganese

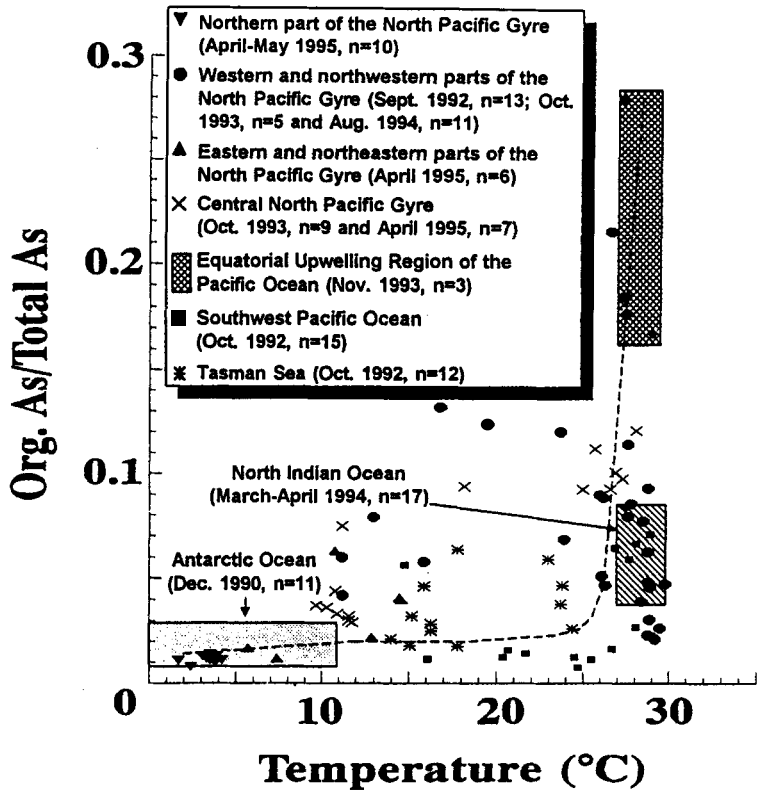

Figure 4 Variation of the (MMAA+DMAA)/[As(V)+As(III)+MMAA+DMAA] ratio relative to temperature in Pacific surface waters. The variation of this ratio in Antarctic and North Indian Ocean surface waters is given for comparison.

oxide phase.[25]

In the case of methylated arsenic species, their presence in deep and especially bottom waters (Fig. 3) is not likely to be caused by diffusion process from the sediments. This is because the methylated arsenic compounds have never been found in pelagic sediment.[25] This also implies that the methylated arsenic compound is not likely to be subject to scavenging. Moreover, the affinity of the methylated arsenic compound for metal oxides is commonly known to be much lower than that of inorganic arsenic. Instead of diffusion from the sediment to the water column, advective and diffusive mixing of seawater must be the most likely reason for the presence of methylated arsenic compounds in deep and bottom waters. Advective and diffusive mixing should distribute the methylated arsenic compounds from their high concentrations in the surface zone to the deeper zones. This advective and diffusive mixing of seawater can supply a significant amount of methylated arsenic compounds to deep and bottom waters only when the methylated arsenic is sufficiently stable over the time of water mixing. Indeed, MMAA and DMAA have been found to be stable with respect to demethylation and oxidation by purely chemical means.[9] To date, only bacterial in the estuarine water are known to have the ability to demethylate and subsequently oxidize DMAA to As(V).[32]

Temperature dependence on the horizontal distribution of arsenic

A temperature dependence of the distribution of arsenic, especially methylated arsenic compounds, has been found in north Indian and Antarctic Ocean surface waters.[4,10] Now, the temperature dependence of the distribution of arsenic has also been confirmed in the Pacific Ocean. As can be seen in Fig. 4, the ratio of organic As (org.As/total As (tot.As) increased with increasing water temperature [org.As is the sum of MMAA and DMAA; and tot.As is the sum of As(V), As(III), MMAA and DMAA].

Below a water temperature of 25 °C, increasing the water temperature only resulted in a small increase in the org.As/tot.As rato. Above 25 °C, however, this ratio was greatly increased with increasing water temperature. The org.As/tot.As ratio seemed to be influenced not only by the water temperature but also by the local variability of the biological activity. The equatorial upwelling region of the Pacific Ocean, which is commonly known to contain more nutrients than the surrounding areas, displays a greater org.As/tot.As ratio than other areas with similar water temperatures. The high nutrient values in the upwelling area may promote biological activity so that concentrations of the biologically produced arsenic compounds are also high.

CONCLUSIONS

Low inorganic arsenic concentrations were consistently obseved in both surface and deep zones. The low concentration in the surface zone was due to biological activity and resulted from arsenic cycling between the different chemical forms. DMAA was the commonly predominant arsenic compound resulting from biological activity in the surface waters of the ocean which usually contained phosphate at extremely low concentations. On the other hand, in surface waters that contained silicate at extremely low concentrations, biological activity resulted in MMAA as the predominant species. Therefore, the nutrient composition of the surface water, which was suggested to affect the composition of the phytoplankton community, will greatly influence arsenic speciation. In addition to nutrient composition, water temperature was also the important parameter determining production of methylated arsenic compounds. The concentration of methylated arsenic compounds in the surface waters seemed to increase with increasing water temperature.

The low inorganic arsenic concentrations in deep zones is probably caused by adsorption onto sinking particulates rich in iron and manganese oxides, rather than by intrusion of water mass containing low inorganic arsenic concentrations.

Advective and diffusive mixing of seawater was the most likely reason for the presence of the methylated arsenic compounds in the deep and bottom waters. Advective and diffusive mixing distributed the methylated arsenic compounds, from their production zones in surface water, and in the minimum oxygen zone, to deeper waters.

Acknowledgement We thank the captain and crew of the R/V Hakuho-Maru for assistance during the sampling. We also gratefully acknowledge the Hitachi Scholarship Foundation for supporting the work of the first author (S.J.S.) and the Monbusho Scientific Research Program, Japan, for providing reasearch support.

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