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Distribution and Cycle of Arsenic Compounds in the Ocean

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In order to understand the distribution and the cycle of arsenic compounds in the marine environment, the horizontal distributions of arsenic(V) [As(V)], arsenic(III) [As(III)], monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) in the Indian Pacific Oceanic surface waters have been investigated. This took place during cruises of the boat *Shirase* from Tokyo to the Syowa Station (15 November–19 December 1990), of the tanker *Japan Violet* from Sakai to Fujayrah (28 July–17 August 1991) and of the boat *Hakuho-maru* from Tokyo to Auckland (19 September–27 October 1992). Vertical distributions of arsenic in the west Pacific Ocean have also been investigated.

The concentration of As(V) was found to be relatively higher in the Antarctic than in the other areas. Its concentration varied from 340 ng dm^{-3} (China Sea) to 1045 ng dm^{-3} (Antarctic). On the other hand, the concentrations of the biologically produced species, MMAA and DMAA, were extremely low in the Antarctic and southwest Pacific waters. Their concentrations in Antarctic waters were 8 ng dm^{-3} and 22 ng dm^{-3} and those in the southwest Pacific were 12 ng dm^{-3} and 25 ng dm^{-3}. In the other regions the concentration varied from 16 ng dm^{-3} (China Sea) to 36 ng dm^{-3} (north Indian Ocean) for MMAA and from 50 ng dm^{-3} (east Indian Ocean) to 172 ng dm^{-3} (north Indian Ocean) for DMAA. As a result, with the exception of Antarctic and southwest Pacific waters, the percentages of each arsenic species in the surface waters were very similar and varied from 52% (east Indian Ocean) to 63% (northwest Pacific Ocean) for As(V), from 22% (northwest Pacific Ocean) to 27% (east Indian Ocean) for As(III) and from 15% (northwest Pacific Ocean) to 21% (north and east Indian Oceans) for the methylated arsenics (MMAA + DMAA). These percentages in Antarctic waters were 97%, 0.2% and 2.8%, respectively, and those in the southwest Pacific Ocean were 97% for As(V(+ As(III) and 3% for MMAA + DMAA. The very low concentrations of the biologically produced species in Antarctic waters and that of methylated arsenic in southwest Pacific waters indicated that the microorganism communities in these oceans was dominated by microorganisms having a low affinity towards arsenic. Furthermore, microorganism activity in the Antarctic was also limited due to the much lower temperature of the seawater there.

The vertical profile of inorganic arsenic was 1350 ng dm^{-3} in surface waters, 1500 ng dm^{-3} in bottom waters with a maximum value of 1700 ng dm^{-3} at a depth of about 2000 m in west Pacific waters. This fact suggested the uptake of arsenic by microorganisms in the surface waters and the co-precipitation of arsenic with hydrated heavy-metal oxides in bottom waters. The suggested uptake of inorganic arsenic and subsequent methylation was also supported by the profile of DMAA, with a high concentration of about 26 ng dm^{-3} in surface water and a significant decrease to a value of 9 ng dm^{-3} at a depth of 1000 m.

Keywords: Arsenic, As(III), As(V), monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), marine arsenic compounds, arsenic distribution, arsenic cycle

INTRODUCTION

In natural waters, dissolved arsenic exists in both inorganic and organic forms. The predominant inorganic form is arsenic(V) [As(V)], as $H_2AsO_4^-$ in freshwater and $HAsO_4^{2-}$ in ocean waters.[1] Based on thermodynamic equilibrium calculations, As(V) should be the only important dissolved inorganic arsenic in most natural waters.[2,3] However, significant amounts of another dissolved inorganic arsenic species, i.e. arsenic(III) [As(III)], have been found in surface and deep ocean waters.[4,5] On the other hand, As(V) is

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sometimes still present as a major species even under anoxic conditions.[4,5] Therefore, the redox pair As(V)/As(III) in the marine environment seems never to be in thermodynamic equilibrium. In the case of organic forms, some methylated arsenic compounds (arsenobetaine, arsenocholine, arsenoribosides and arsenophospholipids) have been claimed to be the products of bioactivity of marine primary producers and marine animals.[6–12] To date, the methylated arsenic compounds, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA), are the only organoarsenicals that have been found as stable dissolved species in natural waters.[1] In the ocean, these compounds are principally synthesized by primary producers.

Biosynthesis of organoarsenicals by primary producers has been commonly identified during culture experiments.[14–16] Their natural occurrence in the marine environment, especially of MMAA and DMAA, has also been investigated.[1,4,9–12,16] Nevertheless, knowledge of arsenic speciation and distribution and of the arsenic cycle in ocean waters is by no means complete. Much work remains to be done in order to gain a more complete understanding of the distribution of arsenic compounds in marine environments, to elucidate the process of uptake of arsenic by marine microorganisms and finally to assess the arsenic cycle in the marine environment. In this study we attempted to realize the purpose mentioned above by investigating the different forms of arsenic in surface waters of three oceans (west Pacific, north and east Indian, and Antarctic), the China Sea and the Indonesian Archipelago, and also the vertical distribution of those species from a sampling site in the southwest Pacific Ocean.

EXPERIMENTAL

Sampling

Surface water samples were collected at various sampling sites (Fig. 1) in the northwest Pacific Ocean, the Indonesian Archipelago and the east Indian and Antarctic Oceans during a cruise of

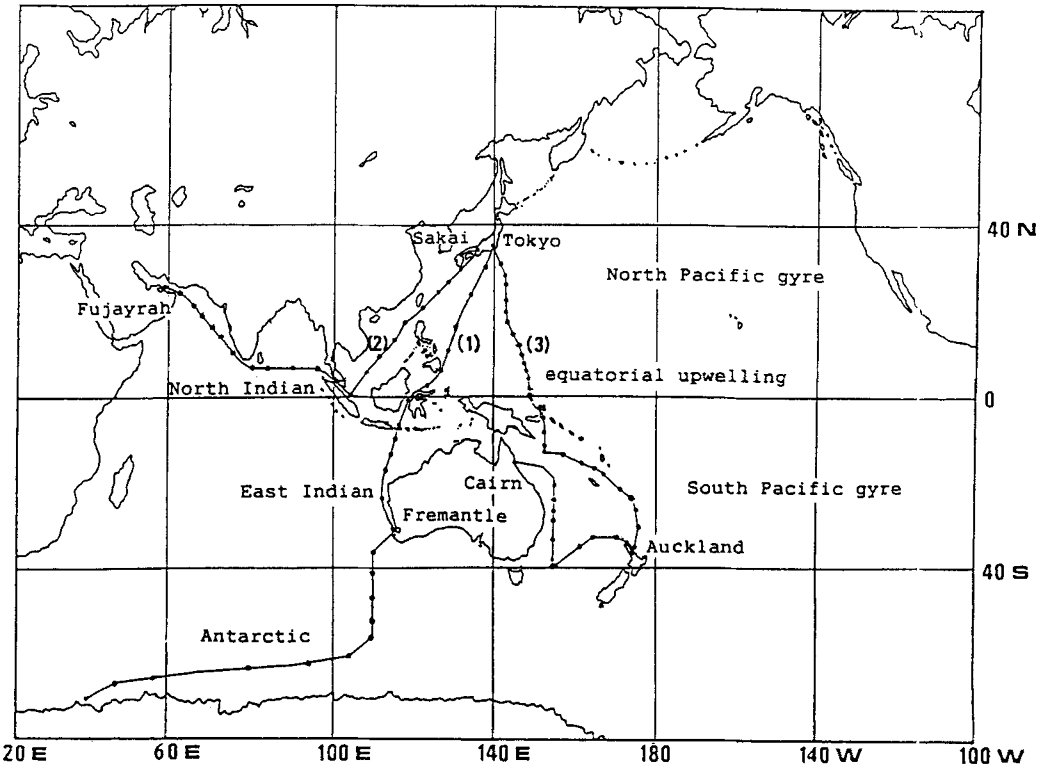

Figure 1 Sampling sites. August conditions are shown for the Indian Ocean. (1) *Shirase* cruise (Tokyo–Antarctic, 15 Nov.–19 Dec. 1990); (2) *Japan Violet* cruise (Sakai–Fujayrah, 28 July–17 Aug. 1991); (3) *Hakuho-maru* cruise (Tokyo–Auckland–Cairns, 19 Sept.–27 Oct. 1992).

Table 1 Analytical conditions for generating arsines from the various arsenic compounds

	As(III)	As(III) + As(V)	MMAA, DMAA
Sample volume			
For combination with AA	100 cm^3	50 cm^3	200 cm^3
For combination with ICP MS	5 cm^3	5 cm^3	5 cm^3
HCl			
For combination with AA	—	6 M, 5 cm^3	6 M, 20 cm^3
For combination with ICP MS	6 M, 0.5 cm^3	6 M, 0.5 cm^3	6 M, 0.5 cm^3
$NaBH_4$ (reducing agent)			
For combination with AA	5%, 1 cm^3	5%, 5 cm^3	10%, 5 cm^3
For combination with ICP MS	5%, 1 cm^3	5%, 5 cm^3	5%, 1 cm^3
Reaction time			
For combination with AA	3 min	3 min	5 min
For combination with ICP MS	3 min	3 min	3 min
Buffer			
Potassium biphthalate, (5%, 2 cm^3) is used for determining As(III) in combination with AA only. For combination with ICP MS, the determination of As(III) was not carried out.			
Masking agent			
Tartaric acid (6 g) + EDTA (0.38 g) per 100 cm^3 of sample			
Carrier gas			
Helium (300 cm^3 min^{-1}) for the combination both with AA and with ICP MS			

the Antarctic observation boat, *Shirase*, from Tokyo to Syowa station (15 November–19 December 1990); in the China Sea, the Indonesian Archipelago and the north Indian Ocean during a cruise of the tanker *Japan Violet* from Sakai to Fujayrah (28 July–17 August 1991); and in the west Pacific Ocean during a cruise of the boat *Hakuho-maru* from Tokyo to Auckland (19 September–27 October 1992). In addition, water samples were taken in the southwest Pacific Ocean from the surface to the bottom (4500 m) at the sampling site 27.16°S, 175.24°E (6 October 1992). Storage of water samples at 0°C in darkness polypropylene bottles was performed after filtering the sample taken from a Niskin sampler using a membrane filter (Millipore filter type HA, pore size 0.45 µm).

Analysis

Analysis of arsenic compounds was performed by hydride generation atomic absorption spectrophotometry (HG AA) using a cold trap of liquid nitrogen for samples collected during the cruise of the boat *Shirase* and the tanker *Japan Violet*, and by hydride generation inductively coupled plasma mass spectrophotometry (HG ICP MS) using a cold trap of liquid nitrogen for samples collected during the cruise of the boat *Hakuho-maru*. The two techniques produced insignificantly different results at the 0.1% level ($P = 0.001$) on a test sample.

Arsines were generated in a reaction vessel after injecting sodium tetrahydroborate solution, and then trapped in a U-tube containing a column packing of OV-3 15% Chromosorb WAW DMCS 60/80-mesh, immersed in liquid nitrogen. The arsines were volatilized in order of their boiling points from the trap, transferred to a quartz cell and atomized by an air–hydrogen flame (for HG AA) or an argon plasma (for HG ICP MS) using a helium carrier gas at a flowrate of 300 cm^3 min^{-1}. For determinations using HG AA, the flow rate of hydrogen and air were each 300 cm^3 min^{-1}. A Hitachi 180-70 atomic absorption spectrometer was used. The analytical conditionse for generating the arsines are given in Table 1 and the details of the cold-trap HG AA method were described in a previous paper.[17] In the case of HG ICP MS, an ICP-MS model PMS 2000 (Yokogawa Analytical Systems) was used and its operating conditions, along with the operating conditions for AA, are shown in Table 2. Under these conditions it is taken that the natural analyte species are the methyl arsenic acids or inorganic arsenic, respectively.

Table 2 Operating conditions for AA and ICP MS for determining the various arsenic compounds

AA	
Analytical wavelength	193.7 nm
Lamp current	18.0 mA
Slit setting	2.6 nm
H_2 flow rate	300 cm^3 min^{-1}
Air flow rate	300 cm^3 min^{-1}
ICP MS	
Forward RF power	1.3 kW
Argon gas flow rate	
Coolant	14 dm^3 min^{-1}
Auxiliary	1.3 dm^3 min^{-1}
Carrier	0.7 dm^3 min^{-1}
Counting condition	
Dwell time	20 ms
Number of scans	2
Monitoring ion (m/z)	^{75}As

RESULTS AND DISCUSSION

Horizontal distribution of arsenic compounds in surface waters

East Indian and Antarctic Oceans

The distribution of the dissolved arsenic compounds, inorganic arsenic [As(V) + As(III)] and organic arsenic [MMAA + DMAA], and chlorophyll *a* in the surface waters of the east Indian and Antarctic Oceans from 00.88°S to 65.85°S (Fig. 2) was investigated during the cruise of the *Shirase* from Japan to the Antarctic Ocean (15 November–19 December 1990). The first two data points were obtained from samples taken in the Strait of Ujung Pandang and the Strait of Lombok (Indonesian Archipelago), the third data set at 11.70°S to the seventh data set at 31.88°S were considered to be obtained from east Indian samples and the rest (between 32.35°S and 67.45°S) were considered to be obtained from Antarctic samples.

It is seen clearly that the distribution of arsenic compounds in the surface waters of the east Indian Ocean was significantly different from that in the Antarctic Ocean. In the surface water of the east Indian Ocean, the average concentration of dissolved inorganic arsenic was 785 ng dm^{-3}. This value was significantly lower than that in the surface waters of the Antarctic Oceans, which was as high as 1048 ng dm^{-3}. On the other hand, a very different pattern compared with that of dissolved inorganic arsenic was displayed by methylated arsenic compounds (MMAA + DMAA). Relatively high concentration levels in the east Indian Ocean and extremely low concentration levels in Antarctic waters were revealed. A calculation of average concentrations gave values as high as 82 ng dm^{-3} and 30 ng dm^{-3}, respectively, for east Indian and Antarctic Oceans. When the inorganic and methylated arsenic species were each considered, average concentrations in surface waters of the east Indian Ocean were 452 ng dm^{-3}, 232 ng dm^{-3}, 50 ng dm^{-3} and 32 ng dm^{-3}, respectively for As(V), As(III), DMAA and MMAA. In the surface waters of the Antarctic, their average concentrations were 1045 ng dm^{-3}, 3 ng dm^{-3}, 23 ng dm^{-3} and 7 ng dm^{-3}, respectively. Therefore, based on these average concentrations, As(V) is always found as the predominant species. Its concentration in east Indian and Antarctic waters was 52% and 97%, respectively. For As(III), the concentration in those regions was 27% and 0.2%. In the case of MMAA and DMAA, the concentrations were 4% and 17% in east Indian and 0.8% and 2% in Antarctic waters.

It has been frequently reported that As(III) and the methylated arsenic species are not chemi-

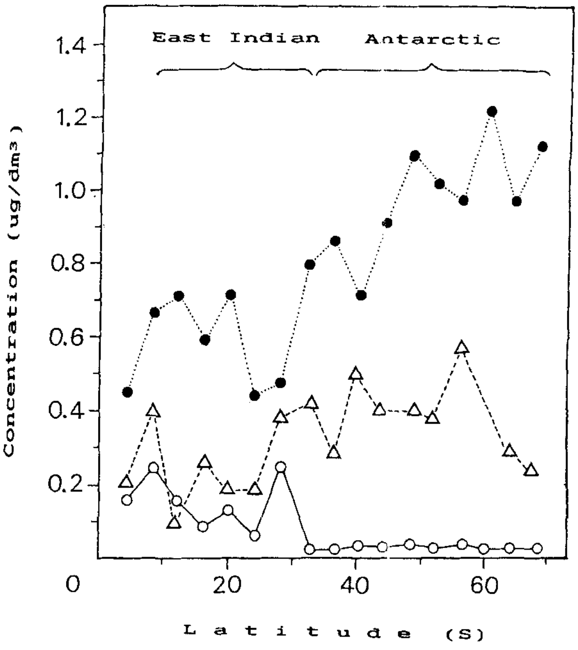

Figure 2 Distribution of dissolved inorganic arsenic [As(V) + As(III)], organic arsenic [MMAA + DMAA] and chlorophyll *a* in the surface waters of the east Indian and Antarctic Oceans from 0.08° to 67.45°S (*Shirase*; 15 Nov.–19 Dec. 1990). ●, [As(V) + As(III)]; ○, [MMAA + DMAA]; △, Chlorophyll *a*.

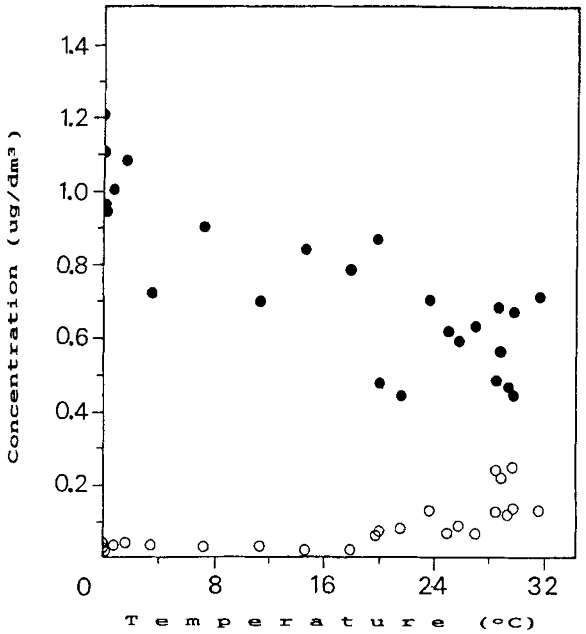

Figure 3 The relationship between surface water temperature and concentration of inorganic arsenic [As(V) + As(III)] and organic arsenic [MMAA + DMAA] in the east Indian and Antarctic Oceans (*Shirase*; 15 Nov.–19 Dec. 1990). ●, [As(V) + As(III)]; ○, [MMAA + DMAA].
Points not arranged in order of elapsed time of cruise—hence not joined.

cally produced under the oxidizing conditions found in ocean surface waters. The presence of both species in surface waters is due to a biologically mediated process. Therefore, their amounts are usually associated with the productivity of the surface ocean waters. Compared with east Indian waters, the surface waters of the Antarctic Ocean contained more chlorophyll *a* as an indicator of productivity. Contrariwise, the amounts and the percentages of the biologically produced species, i.e. As(III), MMAA and DMAA, in Antarctic waters were much lower than those in east Indian Ocean waters. Therefore, other parameters should also be taken into account in order to understand this fact.

An examination of the relationship between the temperature of the surface waters and the concentrations of arsenic compounds during the *Shirase* cruise (Fig. 3) showed that the concentration of methylated arsenic increased with increasing temperature of the surface waters. On the other hand, inorganic arsenic showed an opposite trend. For that reason, the low percentages of the biologically produced arsenic species in the Antarctic Ocean could be caused by limitation of the activity of microorganisms due to the much lower temperature of the surface water. The amount of the microorganism is, therefore, not the only parameter determining the productivity of the surface ocean water, especially for distinct regions such as Antarctica.

North Indian Ocean

Investigation of the horizontal distribution of arsenic compounds in the surface waters of the north Indian Ocean was based on sampling from the *Japan Violet* cruise to the Persian Gulf. During the cruise from Singapore to the Fujayrah, the horizontal distribution of the methylated arsenic species showed low concentrations in the western section (Fig. 4). The significant increase occurred from 80 ng dm^{-3} at longitude 64.78°E to 334 ng dm^{-3} at 68.20°E; then the level was relatively constant from 334 ng dm^{-3} at 68.20°E to 318 ng dm^{-3} at 99.62°E. From 99.62°E eastwards (Strait of Malacca), a slight increase to 510 ng dm^{-3} occurred. A different profile was displayed by inorganic arsenic with a significant decrease from 980 ng dm^{-3} at longitude 56.47°E (near Fujayrah) to 590 ng dm^{-3} at 79.12°E and

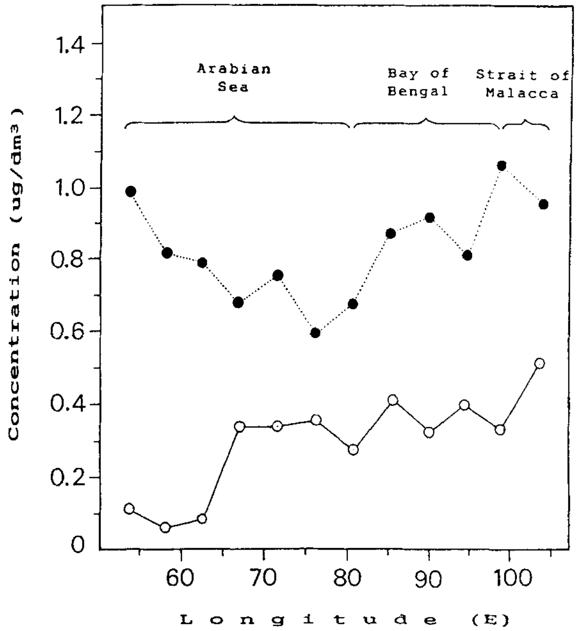

Figure 4 Distribution of dissolved inorganic arsenic [As(V) + As(III)] and organic arsenic [MMAA + DMAA] in surface waters of the north Indian Ocean during the *Japan Violet* cruise from Singapore to Fujayrah (6–8 Aug. 1991). ●, [As(V) + As(III)]; ○, [MMAA + DMAA].

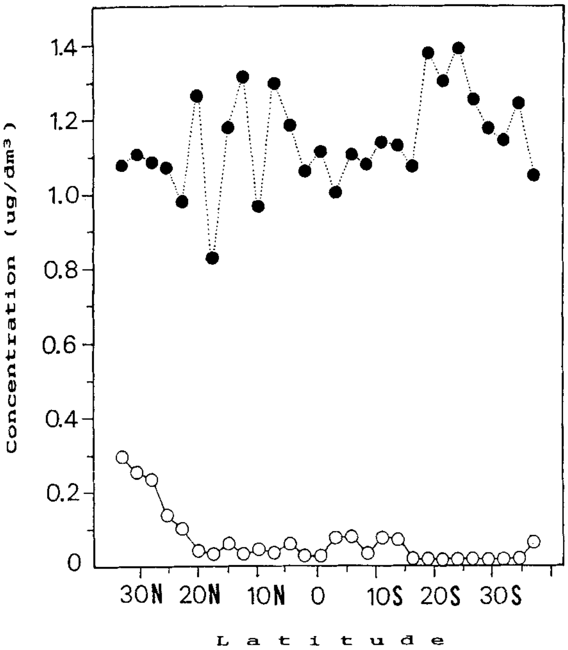

Figure 5 Distribution of dissolved inorganic arsenic [As(V) + As(III)] and organic arsenic [MMAA + DMAA] in surface waters of the west Pacific Ocean from Tokyo to Auckland (*Hakuho-maru*; 17 Sept.–8 Oct. 1992). ●, [As(V) + As(III)]; ○, [MMAA + DMAA].

then a significant increase from this longitude to 950 ng dm^{-3} at 104.60°E (near Singapore).

A calculation of the average concentration of each arsenic species resulted in values as high as 470 ng dm^{-3}, 196 ng dm^{-3}, 176 ng dm^{-3} and 33 ng dm^{-3} for As(V), As(III), DMAA and MMAA, respectively. Based on these average concentrations, the percentages of those species in the north Indian Ocean were 56%, 23%, 17% and 4%, respectively.

West Pacific Ocean

The horizontal distribution of inorganic arsenic [As(V) + As(III)] and methylated arsenic (MMAA + DMAA) in the surface waters of the west Pacific Ocean from Tokyo to Auckland during the cruise of the *Hakuho-maru* KH-92-4 from 17 September to 27 October 1992 is given in Fig. 5. By contrast with the first five data points from Tokyo, the distribution of dissolved methylated arsenic showed a relatively uniform pattern throughout the surface waters of the west Pacific Ocean, with the average concentration as high as 38.3 ng dm^{-3}. For the first five data points, the highest concentration, 295 ng dm^{-3}, was found from the sampling site nearest Tokyo. From this sampling site to the fifth sampling site, a great decrease to 100 ng dm^{-3} was found. These high amounts of methylated arsenic may be caused by the activity of coastal marine organisms in that area. Compared with methylated arsenic, dissolved inorganic arsenic displayed a greater fluctuation in distribution. Although its distribution was more varied, the average concentration in the north and south Pacific, however, was almost the same, i.e. as high as 1115 ng dm^{-3} and 1167 ng dm^{-3}, respectively. The percentage of methylated arsenic with respect to total arsenic in the south Pacific (which was as high as 3%) was found to be significantly lower than that in the north Pacific (which was as high as 8.5%).

China Sea and Indonesian Archipelago

The distribution of arsenic compounds in the surface waters of the China Sea was investigated during the cruise of the *Japan Violet* before entering the Indonesian Archipelago. In addition to the samples taken during the cruise of the *Japan Violet*, the distribution of arsenic compounds in the surface waters of the Indonesian Archipelago was also based on samples taken during the cruise of the *Shirase* before entering the Indian Ocean.

In the China Sea, the average concentrations of As(V), As(III), MMAA and DMAA were 340 ng dm^{-3}, 172 ng dm^{-3}, 16 ng dm^{-3} and 85 ng dm^{-3}, respectively. In the Indonesian Archipelago, the average concentrations of those species were 418 ng dm^{-3}, 175 ng dm^{-3}, 33 ng dm^{-3} and 89 ng dm^{-3}. As a result, the percentage of each arsenic compound in the China Sea and the Indonesian Archipelago was very similar to that in the northwest Pacific and the east and north Indian Oceans, i.e. 53%, 27%, 3% and 17% respectively for As(V), As(III), MMAA and DMAA in the China Sea and 59%, 25%, 5% and 11% for these in the Indonesian Archipelago. Compared with the values shown in the northwest Pacific, higher percentages were shown in the China Sea for biologically produced arsenic compounds.

It is generally known that areas close to the mainland are nutrient-rich environments. Therefore, by considering the point of view of the competitive mechanism between the assimilation of phosphate and arsenate by marine phytoplankton,[18] it was surprising that in areas close to the mainland high production of biologically produced arsenic was found. Similar evidence was also found in Chesapeake Bay,[19] in Charlotte Harbor (Florida)[20] and in the northwest

Pacific Ocean near Tokyo (as shown above). For that reason, a difference in the strategies of primary producers in coastal seas and open ocean waters towards available nutrients is the most reasonable interpretation of this evidence. As has been proposed by Sanders,[19] in the ocean phytoplankton communities are likely to be dominated by species with a high affinity towards low-nutrient conditions and may be able to discriminate better between phosphate and As(V). On the other hand, in coastal seas (i.e. nutrient-rich environments) species with a low ability for discriminating between phosphate and As(V) may thrive. As a result, in nutrient-rich environments such as coastal seas, uptake of As(V) and subsequently reductions to As(III) and methylation to MMAA and DMAA was a biologically unprohibited process.

Open ocean areas

As shown above, the closer the sampling site to the mainland, the higher is the production of biologically produced arsenic. As shown in Fig. 6, the percentage of biologically produced arsenic in the northwest Pacific Ocean, the north and east Indian Ocean, the China Sea and the Indonesian Archipelago varied from 22% (northwest Pacific Ocean) to 27% (east Indian Ocean and China Sea) for As(III), from 3% (northwest Pacific Ocean and China Sea) to 5% (Indonesian Archipelago) for MMAA and from 11% (Indonesian Archipelago) to 17% (China Sea and north and east Indian Ocean) for DMAA. In the southwest Pacific and Antarctic areas, the percentage was 0.2% (only determined for the Antarctic) for As(III), 1% and 0.8% for MMAA and 2% for DMAA. This fact, of course, leads to the result that there is a higher percentage of As(V) in both the southwest Pacific and Antarctic regions than in other areas.

Examination of data on the total concentrations of the arsenic compounds results in average values as high as 948 ng dm^{-3}, 640 ng dm^{-3}, 715 ng dm^{-3}, 849 ng dm^{-3}, 867 ng dm^{-3}, 1167 ng dm^{-3} and 1078 ng dm^{-3}, respectively, in the northwest Pacific, China Sea, Indonesian Archipelago, north Indian, east Indian, southwest Pacific and Antarctic areas. The concentrations of total arsenic compounds in the surface waters of these seas and oceans, except for the southwest Pacific and Antarctic, were relatively low (Fig. 6). This evidence may indicate that arsenic incorporated in biogenous matter in those regions is higher than that in the southwest Pacific and Antarctic oceans.

Vertical distribution of arsenic compounds

The vertical distribution of dissolved inorganic arsenic and DMAA at 27.16°S, 175.24°E in comparison with those of the nutrients is presented in Fig. 7. At this sampling site, variation in concentration of inorganic arsenic with depth was small.

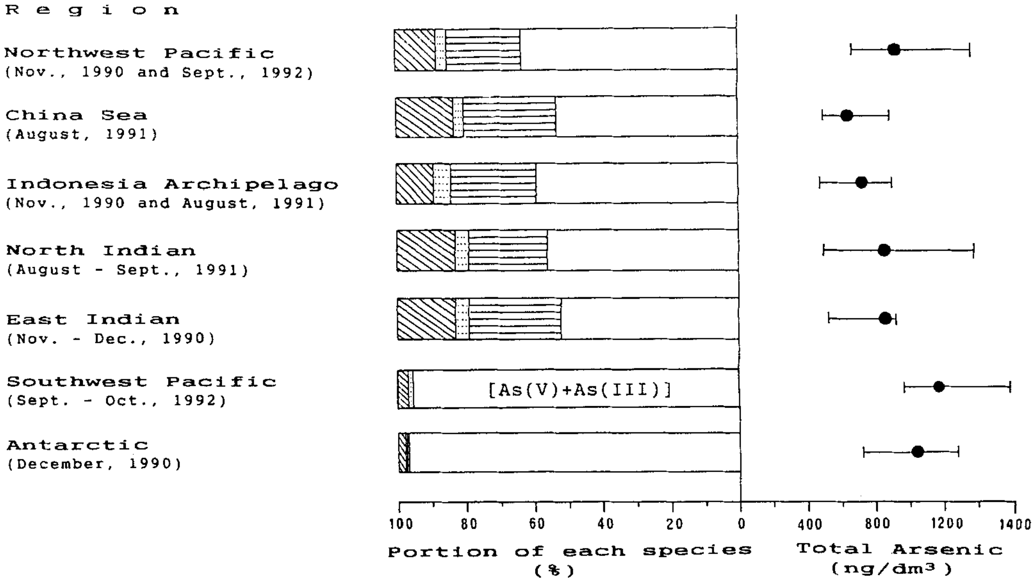

Figure 6 Total dissolved arsenic and the percentage of each species in a variety of ocean surface waters. □: Arsenic(V), ⊟: Arsenic(III), ▦: MMAA, ▧: DMAA.

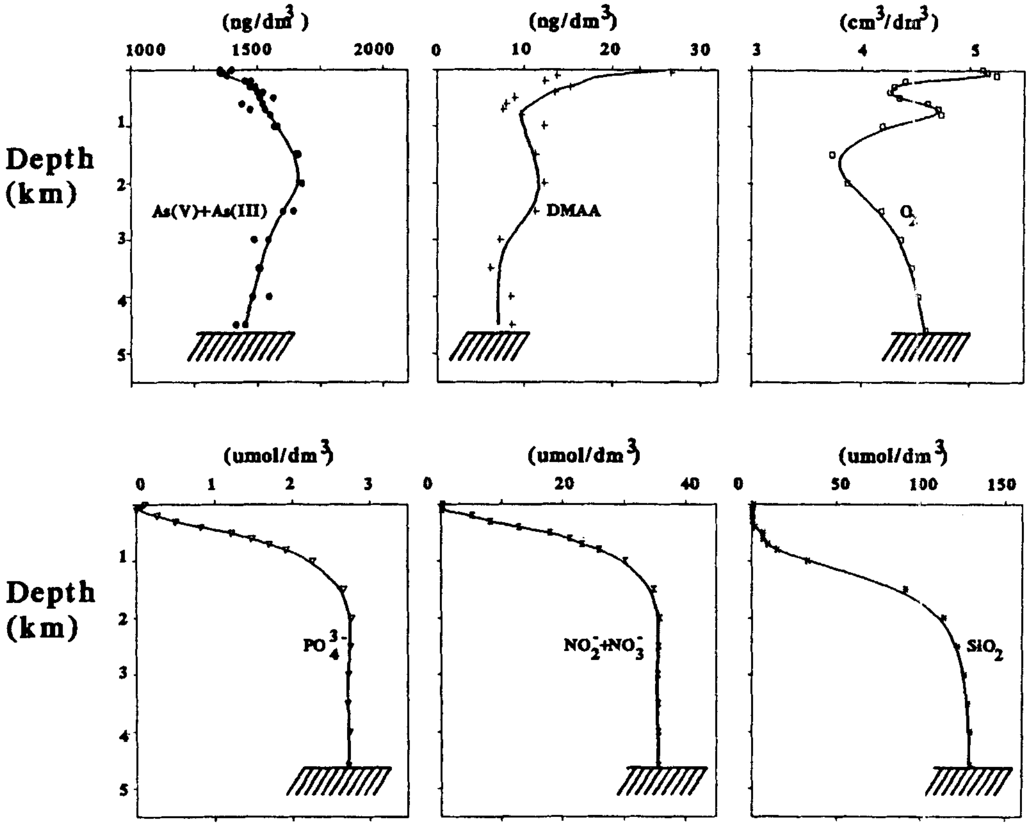

Figure 7 Vertical profiles of inorganic arsenic [As(V) + As(III)], DMAA, phosphate, total nitrite and nitrate, and silicate at 27.16°S, 175.24°E (6 october, 1992).

A depleted concentration of 1350 ng dm^{-3} in the surface and 1500 ng dm^{-3} at the bottom, and a maximum concentration of 1700 ng dm^{-3} at a depth of about 2000 m, was shown. In the case of DMAA, the high concentration of 26 ng dm^{-3} and a significant decrease to a concentration of about 9 ng dm^{-3} at a depth of 1000 m was detected. A small increase in concentration to about 13 ng dm^{-3} occurred at a depth of 2000 m, and from this depth to the bottom there was again a gradual decrease to a concentration of about 9 ng dm^{-3}.

Reduction of As(V) and subsequent methylation by algae (and the role of temperature) has been reported not only in culture experiments but also in ocean and river waters.[21-23] Therefore, the depletion of the concentration of inorganic arsenic in the surface water as shown in Fig. 7 could be an indication of uptake of As(V) by microorganisms.

The evidence for the reduction of As(V) and subsequent methylation is also supported by the data on DMAA. The high concentration of DMAA in the euphotic zone should be a result of bioactivity. The inability to deplete As(V) totally in surface water may also be caused by the fact that the reduced and methylated arsenic species are readily reconverted to As(V) by other bioactivity processes.[24,25] Bioactivity resulted not only in the cycling of arsenic between the different chemical forms in the euphotic zone but also in the incorporation of arsenic into biogenous matter.

The significant increase of inorganic arsenic to the maximum value at a depth of 2000 m, the small increase of DMAA concentration at a depth of 2000 m and the presence of DMAA in bottom water may be caused by regeneration of arsenic species due to degradation of biogenous matter entering those zones via sinking. Support for this evidence was obtained from the results of a regression analysis ($n = 19$) as shown in Eqns [1]-[3].

$$\mathrm{DMAA} = -0.008(\mathrm{NO_2} + \mathrm{NO_3}) + 0.370 \quad [1]$$

$$(r=0.793,\ P<0.001)$$

$$\mathrm{DMAA}=-0.097\mathrm{PO}_4+0.360 \qquad [2]$$
$$(r=0.772,\ P<0.001)$$

$$\mathrm{DMAA}=-0.001(\mathrm{SiO}_2)+0.261 \qquad [3]$$
$$(r=0.521,\ P<0.05)$$

(Unit is nmol dm^{-3} for DMAA and μmol dm^{-3} for the others.)

As shown above, the correlations between DMAA and total nitrogen (nitrite + nitrate) and between DMAA and phosphate were much higher than that between DMAA and silicate. The significance of the relationship with total nitrogen (nitrite + nitrate) and phosphate indicated that the production of DMAA in the euphotic zone was a function of uptake of nitrogen and phosphate, and that the distribution to deeper water was the result of degradation of soft tissue by microbial process.

The depletion of inorganic arsenic occurred not only in surface waters but also in bottom waters. In general, the ocean bottom water layer is well oxygenated due to a relatively high oxygen content. These conditions are suitable for co-precipitation of arsenic with hydrated heavy-metal oxides.[3] The insignificant difference in inorganic arsenic concentrations between bottom and surface waters indicated that the co-precipitation process in bottom water is as intensive as bioactivity in the surface water.

Bioactivity factors

The bioconcentration factor (BCF), i.e. the comparison between the arsenic content in a microorganism and its content in the seawater surrounding the microorganism, is usually used for the purpose of clarifying the evidence for arsenic depletion in surface waters. In this study, however, a bioactivity factor (BAF), instead of the bioconcentration factor, was used for the same purpose. Calculation of the bioactivity factor (BAF) of arsenic was based on Eqn [4].

$$\mathrm{BAF}=\frac{\text{arsenic uptake by microorganism}}{\text{arsenic content in ocean surface water}}=\frac{\text{ideal content} - \text{arsenic content in ocean surface water}}{\text{arsenic content in ocean surface water}} \qquad [4]$$

where the ideal content is the content of arsenic in ocean surface water exhibiting no bioactivity.

It is impossible to determine the ideal content directly. Therefore, it should be found indirectly by using a reference species, i.e. a species which resists the microorganism. Antimony has shown to be an element displaying high resistance towards microorganisms.[26,27] On the other hand, as mentioned above, As(V) is significantly depleted in ocean surface waters by microorganisms. In order to discover the ideal amount of As(V) in

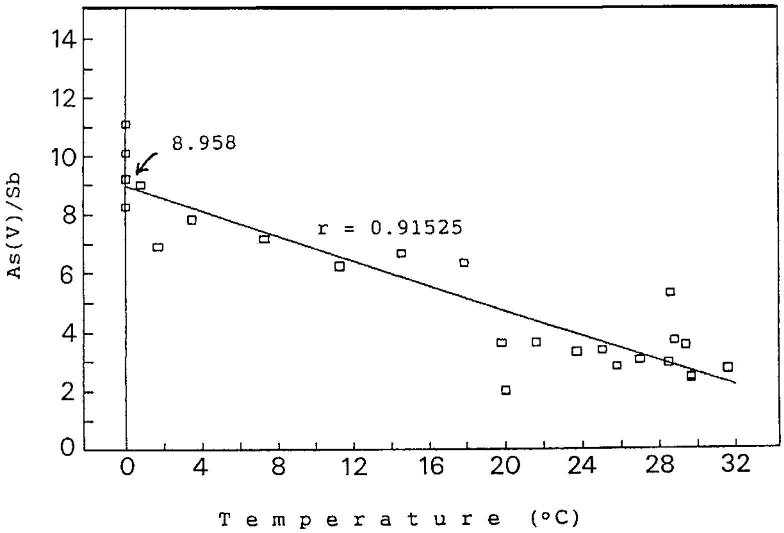

Figure 8 Relationship between the concentration fraction of arsenic(V) with respect to antimony and the temperature of the ocean surface water (*Shirase*; 15 Nov.–19 Dec. 1990).

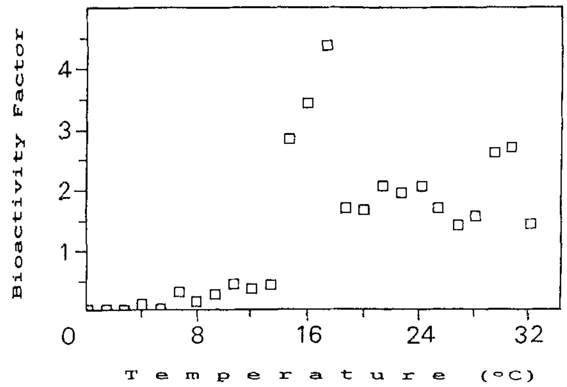

Figure 9 Relationship between the surface water temperature and the bioactivity factor of arsenic(V) (*Shirase*; 15 Nov.–19 Dec. 1990).
Points not arranged in order of elapsed time of cruise—hence not joined.

ocean surface waters, therefore, antimony was used as a reference element. The relationship between the concentration fraction of As(V) with respect to antimony and the temperature of the ocean surface water is displayed graphically in Fig. 8. As can be seen, the concentration fraction of As(V) with respect to antimony increases with decreasing temperature of the ocean surface water. At a temperature of 0 °C, the temperature of ocean surface waters near the Antarctic continent, the concentration fraction of As(V) with respect to antimony reached a value of 8.958. At a temperature of 0 °C, the activity of marine microorganisms towards As(V) was predicted to be very limited. The value of 8.958, therefore, should be seen as a reflection of the concentration fraction between As(V) and antimony in the ocean surface water if microorganism activity was absent. The ideal amount of As(V) in certain ocean surface waters was then determined by multiplication of the concentration of antimony in that region by 8.958. As a result, the bioactivity factor of As(V) was calculated using Eqn [5]:

$$\text{BAF of As(V)} = \frac{8.958\,[\text{Sb}]_{\text{seawater}} - [\text{As(V)}]_{\text{seawater}}}{[\text{As(V)}]_{\text{seawater}}} \qquad [5]$$

The bioactivity factor of As(V) as a function of the temperature of the ocean surface water is shown in Fig. 9. Although a very high bioactivity factor was found at a temperature of about 16 °C, in general it was clearly apparent that the bioactivity factor of As(V) becomes higher with increasing temperature of the ocean surface water. The arsenic uptake by microorganisms will exceed the amount of arsenic in the seawater surrounding them when the temperature of the seawater is higher than 15 °C. At seawater temperatures between 7 and 15 °C, the arsenic uptake by microorganisms was about half of the amount in the seawater surrounding them. At a seawater temperature lower than 7 °C, the arsenic uptake by marine microorganisms was negligible.

In a specific volume of the surface water of ocean, the amount of arsenic uptake by microorganism living in that volume of water is larger than the amount of arsenic remaining in the surface water when the temperature of the sea water is higher than 15 °C.

CONCLUSIONS

It became apparent that the presence of methylated arsenic [MMAA and DMAA] and reduced species [As(III)] in surface seawaters was due to bioactivity, while the predominant species of arsenic in seawater was As(V). Nevertheless, the cycle of arsenic in the ocean was not only limited to these species. Bioactivity also caused the incorporation of arsenic in biogenous matter. The amount of arsenic incorporated in biogenous matter was generally higher than that contained in seawater surrounding the matter. This amount became negligible only for ocean waters with a low temperature at the surface (such as Antarctic waters).

Degradation of biogenous matter reaching deep water via sinking leads to regeneration of arsenic species in that zone. Increase in concentration of both the dissolved inorganic arsenic and MMAA in deep waters and also the presence of significant amounts of DMAA in bottom waters should be the result of that process.

The evidence for co-precipitation of arsenic with hydrated heavy-metal oxides in well-oxygenated ocean bottom waters should also be considered as a part of the arsenic cycle in ocean environments. This co-precipitation process was likely to be as intensive as the bioactivity in the ocean surface water.

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