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Distribution and fate of biologically formed organoarsenicals in coastal marine sediment

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Marine organisms, including phyto- and zoo-plankton, macroalgae, and animals, concentrate arsenic in various organic forms. However, the distribution and fate of these organoarsenicals in marine environments remains unclear. In this study, the distribution of organoarsenicals in coastal marine sediment in Otsuchi Bay, Japan, has been determined. Methylarsonic acid, dimethylarsinic acid, trimethylarsine oxide, arsenobetaine, arsenocholine and other unidentified arsenic species were detected in marine sediment by high-performance liquid chromatography–inductively coupled plasma mass spectrometry analysis of methanol–water extracts. Arsenobetaine was the dominant organoarsenical at four of the seven stations where tests were carried out, and unidentified species or dimethylarsinic acid dominated at the other stations. Total organoarsenicals (as arsenic) in the surface sediment amounted to 10.6–47.5 μg kg^{-1} dry sediment. Core analysis revealed that concentrations of organoarsenicals decreased with depth, and they are considered to be degraded within 60 years of deposition. These results show that organoarsenicals formed by marine organisms are delivered to the sediment and can be degraded within several decades. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: arsenic; arsenobetaine; organoarsenicals; HPLC–ICP-MS; marine sediment; sedimentation rate

INTRODUCTION

In marine environments, marine organisms concentrate arsenic in various organic forms.[1–5] The recent development of high-performance liquid chromatography (HPLC)–inductively coupled plasma mass spectrometry (ICP-MS)[6] has enabled the accurate analysis of these organoarsenicals in various organisms and environmental samples.[3,7,8] Arsenic is found mainly as arsenosugars in phytoplankton[3] and algae.[9] Marine animals contain arsenic mainly as arsenobetaine (AsB).[4,5,10–14] Total arsenic concentrations in these marine organisms are reported to be <231.0 mg kg^{-1} dry weight for macroalgae[15] and <340.1 mg kg^{-1} wet weight for marine animals.[1] The concentrations of these organoarsenicals in marine organisms are well known. However, with the exception of the study on suspended particles,[16] the fate of organoarsenicals in the marine environment is not well understood. In view of the detection of AsB in suspended particles,[16] we believe it is very likely that organoarsenicals formed by marine organisms are incorporated into the sediment. There have been some reports on methylarsonic acid (MA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO) in marine sediments.[17–19] All of these compounds are known to be the degradation products of other organoarsenicals formed by marine organisms[20–24] or by *in situ* microbial biomethylation in marine sediment.[25] However, all of these studies on marine sediments lack information on important organoarsenicals,

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such as AsB. This study aims to determine the distribution and fate of those organoarsenicals formed by marine organisms in coastal marine sediment.

STUDY AREA AND SAMPLES

Otsuchi Bay is an area located on the Pacific coast of northern Japan, having an indented rias coastline and minimal exposure to human activity (Fig. 1). Sediment and plankton samples were collected from Otsuchi Bay on 25–26 June 2002. Surface sediment was collected by an Ekman Berge sampler from stations 1, 2, 3, 5, 6, and 7 within the bay (Fig. 1). Water depths, water temperature at the sea bottom and sediment facies are shown in Table 1. A sediment core of 5 cm in diameter and of about 60 cm in length was collected with a piston core sampler[26] at station 4 (Fig. 1). Immediately after collection, the sediment core was extruded in 3 cm slices and placed in a sterilized plastic vessel. The outer 1 cm surface was removed using a sterilized spoon, and inner subsamples were placed in sterilized polyethylene bags. A portion of the surface sample from station 4 was used in microbial experiments. All the samples to be used in chemical analyses were stored at −20 °C before lyophilization. Plankton samples were collected by trawling a plankton net vertically at each station. The nets used were GG54 (mesh size 315 μm) and XX13 (mesh size 100 μm). Plankton samples were harvested by centrifugation at 3200 rpm for 12 min and immediately dried at 100 °C overnight. Standard organoarsenicals proved to be stable after this overnight drying (100 °C) treatment. Because of the low amount retrieved, the plankton samples collected at each station were finally mixed together and were treated as a representative plankton sample from Otsuchi Bay.

Table 1. Water depth, water temperature and oxidation–reduction potential (ORP) at the sea bottom, and surface sediment facies at each station

Station	Water depth (m)	Temperature (°C)	Facies	ORP[a] (mV)
1	50.3	11.0	Fine–medium sand	164
2	44.0	11.1	Silty very fine sand	127
3	40.0	11.2	Silt	212
4	36.5	12.0	Clayey silt	ND
5	36.0	11.3	Silt	218
6	24.8	11.5	Silt	209
7	26.5	11.7	Clay	243

[a] ND: not determined.

METHODS

Arsenic speciation analysis

In previous studies, several extractants have been used for arsenic speciation in soil or sediment.[8,27–30] Our preliminary study revealed that amongst the three extractants selected, methanol–water (1 : 1), orthophosphoric acid and diammonium oxalate, the greatest quantity of organoarsenicals were extracted from the surface sediment sample from station 2 with methanol–water. Therefore, methanol–water was used as the extractant for this study. A 2 g portion of the lyophilized sediment was extracted with 15 ml of methanol–water (1 : 1) with ultrasonication for 15 min. The supernatant was collected by centrifugation (5000 rpm, 5 min) and the extraction was repeated twice. The supernatant collected was concentrated by lyophilization and filtered through a 0.2 μm filter. HPLC–ICP-MS (ICPM-8500, Shimadzu, Kyoto, Japan) was used for arsenic speciation analysis. Stock solutions of Na_2HAsO_4, $NaAsO_2$, MA, DMA, TMAO, tetramethylarsonium ion (TEM), AsB, and arsenocholine (AC) in distilled water ([As] = 1000 mg l^{-1}) were prepared as standards. Inorganic arsenicals were obtained from Wako Chemicals (Osaka, Japan). Organoarsenicals were obtained from the Tri Chemical Co. (Yamanashi, Japan). A calibration curve was constructed using [As] = 0–50 μg l^{-1} of each arsenic species. Each peak was identified by comparison with the internal standard. When a compound did not correspond to any of the available standard materials, it was recorded as an unidentified compound. Arsenate, DMA, AsB, TMAO, TEM, and AC were

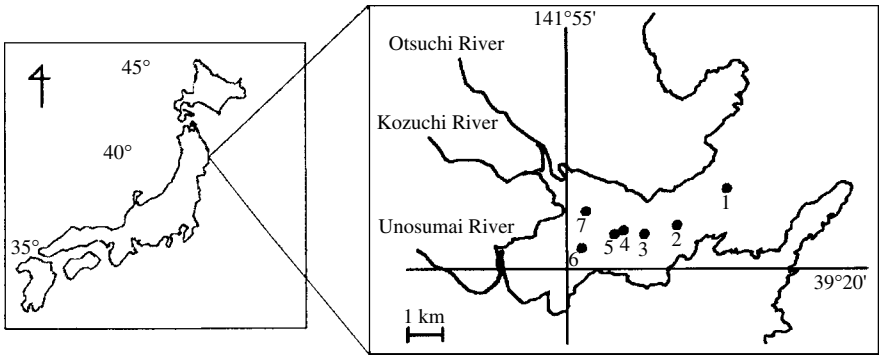

Figure 1. Otsuchi Bay and sampling stations.

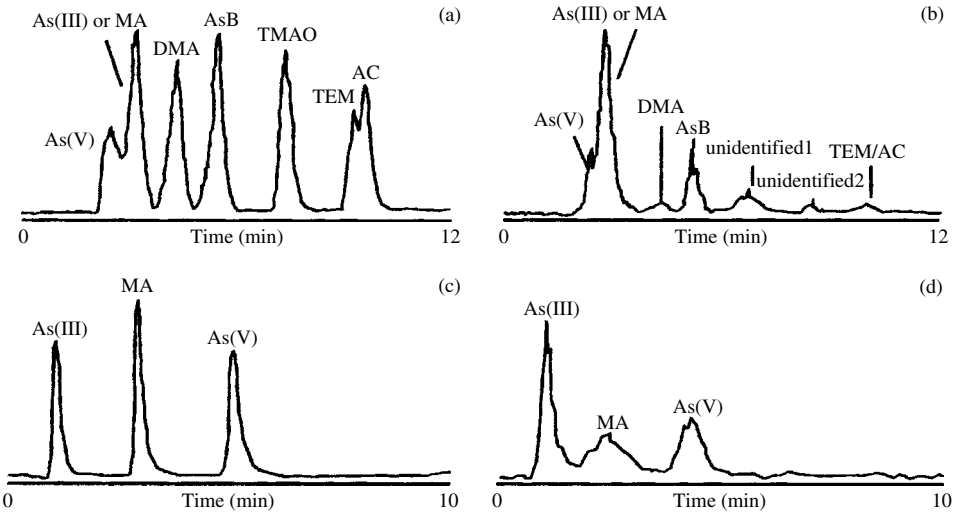

Figure 2. HPLC–ICP-MS chromatogram of standard with (a) CAPCELLPAK C_{18} MG and (c) PRP-X100, and sediment extract (St. 6) with (b) CAPCELLPAK C_{18} MG and (d) PRP-X100.

separated using an ODS column, CAPCELLPAK C_{18} MG (5 μm particle size, 250 mm × 4.6 mm i.d., Shiseido, Tokyo, Japan) (Fig. 2a and b). HPLC conditions were as follows: flow rate 750 μl min^{-1}; column temperature 25 °C; solvent 10 mM 1-butanesulfonic acid sodium salt, 4 mM malonic acid, 4 mM tetramethylammonium hydroxide, 0.05% methanol, pH 3.0. Along with data for arsenic (m/z 75), mass 51 ($^{35}Cl^{16}O^+$) was also monitored as an indicator of potential interference at m/z 75 by $^{40}Ar^{35}Cl$. Using CAPCELLPAK C_{18} MG, interference by chlorine was observed at the arsenate peak. Arsenate, arsenite, and MA were separated on an anion-exchange column PRP-X100 (10 μm particle size, 250 mm × 4.6 mm i.d., Hamilton, NV, USA) with a guard column (Fig. 2c and d).[8] HPLC conditions were as follows: flow rate 1500 μl min^{-1}; column temperature 25 °C; solvent 20 mM $NH_4H_2PO_4$, pH 5.6. Interference by chlorine was observed at the arsenite peak when using PRP-X100. The HPLC system was connected to the ICP nebulizer, Micro Mist Nebulizer (Glass Expansion, Vic, Australia) via a 1/16″ polyether ether ketone tube. For peak area measurements, the coefficient of variation was less than 10% ($n = 5$). Total arsenic concentrations in the methanol–water extract (hereafter total extractable) were separately determined with ICP-MS. In this study, the difference in the concentrations of total extractable arsenic and organoarsenicals was regarded as being due to the concentration of inorganic arsenic in the extract because, as discussed above, in HPLC–ICP-MS analysis inorganic arsenic species may suffer interference due to chlorine.

Total elements

Total concentration of arsenic (hereafter total arsenic) in the sediments was measured by a digestion procedure. 7.5 ml of nitric acid and sulfuric acid were added to 0.2 g of a sediment sample and the resultant suspension was heated on a hot plate until its volume had reduced to half. A further 5 ml of nitric acid was then added and the mixture heated, followed by the addition of 2.5 ml of nitric acid and 1.5 ml of perchloric acid and further heating. Finally, water was added to the samples, bringing their volume to 50 ml, and then filtered through a 0.2 μm filter in preparation for ICP-MS analysis.

Total iron, manganese, aluminium, and silicon concentrations were determined by energy-dispersive X-ray fluorescence (JSX-3220; JEOL, Tokyo, Japan).

Total organic carbon

Total organic carbon (TOC) content in sediment was analyzed using a TOC-5000A connected to an SSM-5000A (Shimadzu, Kyoto, Japan).

Ability of the sediment microbes to degrade AsB

The potential ability of surface sediment bacteria at station 4 to degrade AsB was examined. 20 g of sediment was suspended in 60 ml of sterilized seawater and sonicated for 1 min. In a microwell plate, 0.1 ml of the suspension was inoculated into 0.9 ml of a nitrate mineral salts liquid medium[31] to which had been added 25 g l^{-1} of NaCl, 2.0 g l^{-1} of $MgSO_4 \cdot 7H_2O$, and 1 mg l^{-1} of AsB. The experiment was performed in triplicate. The microwell plate was incubated under dark aerobic conditions at room temperature for 30 days. After incubation, each sample was filtered and used in HPLC–ICP-MS analysis. A control was prepared without inoculation.

Lead and caesium radioactivity measurement

In order to determine the sedimentation rate, radioactivity measurements of ^{210}Pb and ^{137}Cs were taken from the sediment core sample (station 4). About 1 g of sediment sample was placed in a tube with a cap and the tube was sealed. After 1 month, the activities of ^{210}Pb (peak energy: 46.5 keV), ^{214}Pb (352 keV), ^{137}Cs (661.6 keV) and ^{40}K

(1461 keV) were measured by gamma-ray spectrometry using well-type germanium detectors (GWL-120230-S, ORTEC, TN, USA).[32] The activity of excess ^{210}Pb was calculated by subtracting that of ^{214}Pb from that of ^{210}Pb, as it is assumed that the supported ^{210}Pb is in equilibrium with ^{226}Ra and ^{214}Pb. The sedimentation rate was calculated by the profile of excess ^{210}Pb and the peak of ^{137}Cs.[33]

RESULTS

Spatial distribution

Owing to the fact that a clear discrimination between TEM and AC proved difficult, TEM or AC are referred to as TEM/AC. HPLC–ICP-MS analysis detected MA, DMA, AsB, TMAO, and TEM/AC together with some other unidentified arsenic species (Fig. 2). Unidentified arsenicals were also quantified using the standard curve for known arsenic species. Any unidentified arsenicals were summed together and are presented as unidentified. The concentrations of each arsenic species and their proportions of the total extractable arsenic concentration in sediments and planktons are shown in Table 2. Total concentration of organoarsenicals calculated as the sum of each organoarsenical ranged from [As] = 10.6 to 47.5 μg kg^{-1} dry sediment. Total organoarsenical accounted for 21.5–74.3% of the total extractable arsenic in the sediment. AsB was the dominant organoarsenical in the surface sediment at stations 1, 2, 5, and 6. Organoarsenicals accounted for 80.5% and 97.3% of total extractable arsenic in the >315 μm and >100 μm plankton fractions respectively. AsB was the dominant organoarsenical in both plankton samples, but plankton fraction >315 μm contained higher percentages of AsB than plankton fraction >100 μm.

Total arsenic concentrations in surface sediments ranged from 1.9 to 23.1 mg kg^{-1} dry sediment, with the highest at station 6 and the lowest at station 1 (Table 3). TOC in surface sediments was also highest at station 6 (Table 3). TOC and total iron were higher at stations 5, 6, and 7 than at the other stations (Table 3).

Vertical profile

The vertical profile of the concentration of organoarsenicals in the sediment core from station 4 was determined. AsB, TEM/AC and the unidentified organoarsenicals disappeared

Table 3. Total concentrations of elements and TOC in surface sediment[a]

Station	[As] (mg kg^{-1})	Fe (wt%)	Al (wt%)	Mn (wt%)	Si (wt%)	TOC (%)
1	1.9 (1.1)	1.6	15.1	0.1	67.2	1.4
2	6.5 (1.5)	4.3	21.4	0.1	56.4	2.1
3	9.9 (1.0)	5.9	20.5	0.1	56.7	3.1
4	9.9 (2.0)	5.9	22.0	0.1	54.1	2.2
5	9.7 (0.8)	6.2	21.5	0.1	54.9	3.4
6	23.1 (2.9)	6.4	23.6	0.1	51.7	5.0
7	7.8 (1.1)	6.8	20.8	0.1	55.5	3.9

[a] Values in parentheses show standard deviation of triplicates.

Table 2. Concentrations ([As]/μg kg^{-1}) and percentages of total extractable arsenic (in parentheses) of each arsenic species in sediments and planktons[a]

Station	TI-As[b]	TO-As[c]	MA	DMA	AsB	TEM/AC	TMAO	Unidentifieds
1	8.6	10.6	ND	1.2	6.8	ND	ND	2.6
	(44.6)	(55.4)		(6.2)	(35.5)			(13.8)
2	32.8	34.9	ND	4.8	14.3	3.4	ND	12.4
	(48.5)	(51.5)		(7.1)	(21.1)	(5.0)		(18.3)
3	60.5	30.5	6.75	1.7	5.1	2.9	ND	13.9
	(66.5)	(33.5)	(7.4)	(1.9)	(5.6)	(3.2)		(15.3)
4	85.5	23.5	8.7	9.9	1.6	0.8	ND	2.6
	(78.5)	(21.5)	(8.0)	(9.1)	(1.4)	(0.7)		(2.4)
5	16.6	33.6	9.84	3.4	8.6	4.5	ND	7.2
	(33.1)	(66.9)	(19.6)	(6.8)	(17.2)	(8.9)		(14.4)
6	16.4	47.5	12.1	2.8	15.5	3.9	ND	13.2
	(25.7)	(74.3)	(18.9)	(4.4)	(24.2)	(6.1)		(20.7)
7	25.2	29.3	13	9.0	2.2	1.4	2.9	0.8
	(46.2)	(53.8)	(23.9)	(16.4)	(4.0)	(2.6)	(5.4)	(1.5)
>100 μm plankton	343.3	1306.0	108	350.7	535.5	81.7	ND	338.0
	(19.5)	(80.5)	(6.1)	(20.0)	(30.5)	(4.6)		(19.2)
>350 μm plankton	115.5	3961.4	242	716.3	2272.5	188.0	ND	784.6
	(2.7)	(97.3)	(21.3)	(16.6)	(52.6)	(4.4)		(18.2)

[a] ND: not detected.
[b] TI-As: total inorganic arsenicals.
[c] TO-As: total organic arsenicals.

below 12–15 cm, whereas MA and DMA were detected at greater depths (Fig. 3). Total arsenic concentrations ranged from 9.9 to 44.7 mg kg^{-1} dry sediment, with the peak concentration found at a depth of 12–15 cm (Fig. 4).

To determine the rate of sedimentation rate at this station, lyophilized sediments were used for ^{210}Pb and ^{137}Cs radioactivity measurements. The vertical profile of ^{210}Pb suggests mixing in the upper 3 to 6 cm due to bioturbation (Fig. 5a). The ^{137}Cs peak was detected at a depth of 6–9 cm (Fig. 5b), the depositional date of which is estimated to be 1963.[33] From the vertical profile of excess ^{210}Pb and ^{137}Cs, the sedimentation rate at this station was calculated to be 0.10 g cm^{-2} $year^{-1}$(0.18 cm $year^{-1}$).

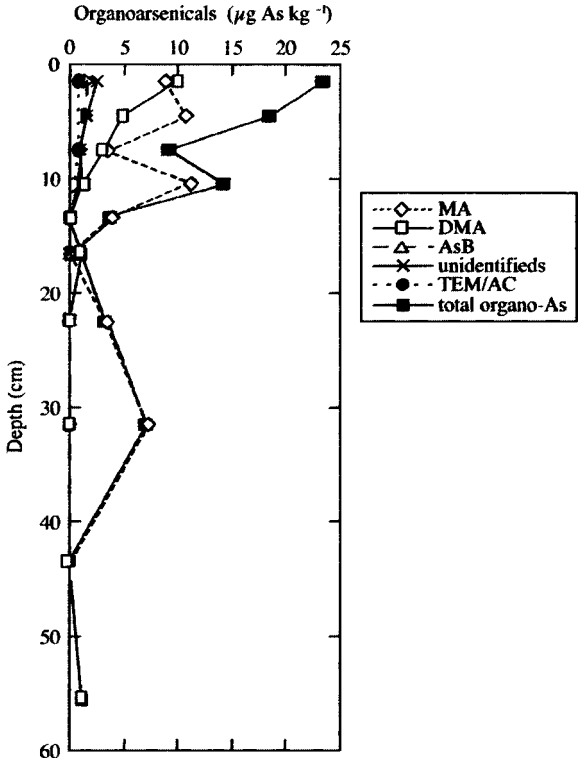

Figure 3. Vertical profile of organoarsenicals at station 4 ([As]/μg kg^{-1} dry sediment).

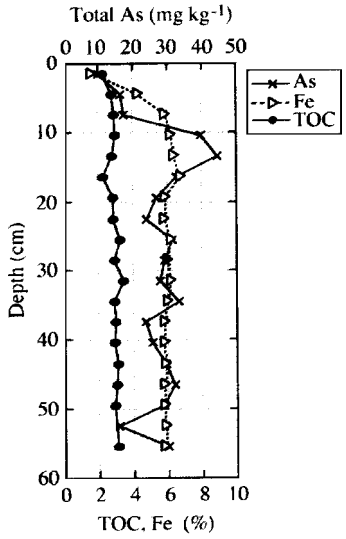

Figure 4. Vertical profile of total arsenic (mg kg^{-1} dry weight), Fe (wt%), and TOC (%) concentrations at station 4.

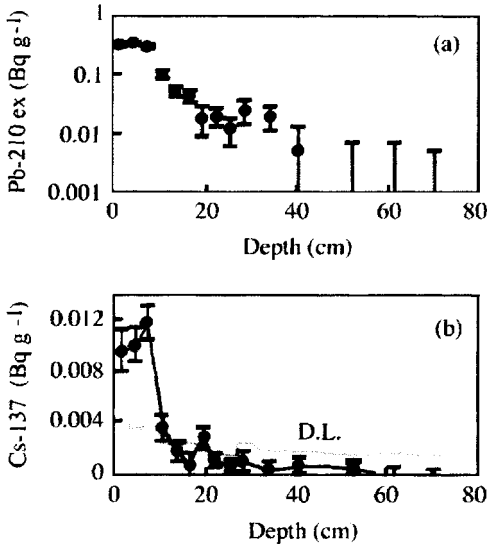

Figure 5. Radioactivities of (a) excess ^{210}Pb and (b) ^{137}Cs in the core sample from station 4. D.L. means detection limit.

AsB, one of the predominant organoarsenicals that is primarily formed by marine animals, is known to be degraded by marine bacteria.[20–24] The potential biodegradability of AsB by microorganisms in surface sediment at station 4 was confirmed. Sediment samples were incubated with 1 mg l^{-1} of AsB. After incubation, inorganic arsenic, MA, DMA, and TMAO were detected in every sample. No degradation products were detected in the control sample.

DISCUSSION

Organoarsenicals in surface sediments

To date, there has been no information on the distribution of biologically concentrated organoarsenicals, such as AsB, in marine sediments. Using HPLC–ICP-MS analysis, several organoarsenic species, including AsB, have been detected in coastal marine sediment. The total concentration of organoarsenicals in the surface sediment was [As] = 10.6–47.5 μg kg^{-1} dry sediment. In Otsuchi Bay, $\delta^{13}C$ analysis revealed that more than 50% of the organic matter in sediment in the inner bay is land-derived.[34] However, the majority of organoarsenicals in marine sediments are likely to be derived from marine organisms, because only small amounts of arsenic can be methylated in freshwater organisms.[35,36] One or two unidentified organoarsenicals have been found in sediments, and three or four such species in plankton samples were thought to include arsenosugars, which are the major form of arsenic in macroalgae[9,37] and phytoplanktons.[3]

Unfortunately, the present experiments could not confirm this because standard materials were not commercially available.

Reimer and Thompson[19] considered organoarsenicals in marine sediment to be mainly those produced by *in situ* microbial methylation. However, they determined the presence of only MA, DMA and TMAO, all of which can be formed by microbial methylation. In our study, not only these methylated arsenicals were found, but also AsB, TEM/AC and probably arsenosugars. The latter three compounds accounted for more than 50% of the total organoarsenicals in marine sediment at five of the seven stations. Our findings strongly suggest that, at least in coastal areas, the majority of organoarsenicals in marine sediment are formed by marine organisms such as planktons and animals, or are the degradation products of such organoarsenicals, and are not formed by microbial methylation.

DMA is a minor arsenic species in marine organisms,[3] but it is known to be a degradation product of AsB.[21–24] At stations 4 and 7, the ratios of DMA to total organoarsenicals were higher (30.6–42.4%) than at the other stations (5.7–13.8%), suggesting that AsB is being degraded in the sediment at these stations. At stations 1 and 2, the ratios of AsB to total organoarsenicals were 64.0% and 40.9% respectively. These levels were similar to those in the >100 μm and >315 μm plankton fractions (37.9% and 54.1% respectively), indicating that AsB does not undergo microbial degradation in these sediments. This may be because of the slightly lower water temperatures and ORP at the sea bottom, which would suppress aerobic microbial degradation (Table 1).

Undaria pinnatifida (wakame) is one of the main natural populations in Otsuchi Bay, and is also commercially cultured there. From its carbon content (24.1–31.5%[38]) and arsenic concentration (33.8 μg g^{-1} dry weight[9]), which is relatively high among marine organisms,[2] the C : As ratio in *U. pinnatifida* is calculated to be approximately 10 000 : 1. Some 83–97% of the arsenic in *U. pinnatifida*[39] is in an organic form. Considering the finding that 30% of TOC in the sediment near station 6, where TOC concentration was the highest, is of marine origin,[34] then, if marine-originated organic matter is derived from the debris of organisms such as *U. pinnatifida*, [C] = 12 mg g^{-1} sediment would be of marine origin and the total organic arsenic concentration would be around [As] = 1 μg g^{-1} dry weight. However, the observed concentration of organoarsenicals was 47.5 ng g^{-1} sediment. This suggests that organoarsenicals are relatively more easily degraded than other organic materials.

ORGANOARSENICALS IN PLANKTON FRACTIONS

The main arsenic species found in phytoplankton (*Chaetoceros*) and copepods are arsenosugars, whereas Antarctic krill and amphipods contain mainly AsB.[3] It was expected that the >100 μm plankton fraction would mainly contain phytoplanktons, and the >315 μm plankton fraction would mainly contain zooplankton such as copepods, amphipods, barnacle larvae, and fish larvae. However, AsB accounted for 30.5% of the total extractable arsenic in the >100 μm plankton fraction, although this was less than the level of AsB in the >315 μm plankton fraction (52.6%). The AsB in the >100 μm plankton fraction is probably from small debris of animals containing AsB. Arsenosugars, which are typically found in diatoms,[3] would be detected as unidentified species in this study. Unidentified species in the >100 μm fraction were not significantly more abundant than in the >315 μm fraction. The possibility that some of the arsenosugars had been decomposed into DMA after the drying of plankton samples at 100 °C cannot be ruled out. However, because AsB comprised 30.5% of the total extractable arsenic in the >100 μm fraction, phytoplanktons containing mainly arsenosugars were not considered to be the dominant component.

Total arsenic in surface sediments

Three rivers flow into Otsuchi Bay, namely the Rivers Otsuchi, Kozuchi, and Unosumai (Fig. 1). The River Unosumai has the greatest flow.[40] Total arsenic concentration was highest at station 6 (Table 3). The observation of the highest value of arsenic at station 6 may be related to the flow of the River Unosumai. Gomez-Ariza *et al*.[41] reported that 60–78% of arsenic is bound to the Fe–Mn oxide phase in intertidal sediment. Iron, a good coprecipitator of arsenic, has been known to be removed from the water column at river mouths as iron oxide–organic matter colloids with increasing salinity of the river water.[42] Arsenic is expected to be trapped and sedimented near the mouth of the river with iron oxide–organic matter colloids. Higher concentrations of TOC and total iron at station 6 (Table 3) may support this hypothesis.

It should be noted that Mukuromi Contact Metasomatic Gold Deposits exist in the upper stream of the River Unosumai. Gold has been found there along with loellingite ($FeAs_2$).[43] Although the mine has been closed since 1943, the transportation of small particles of loellingite may be occurring through the River Unosumai.

Organoarsenicals consisted of less than 1% of total arsenic in the surface sediments. Although the sedimentation and degradation rates must be determined and considered, the contribution of organoarsenicals to the total arsenic in marine sediment may be low.

Vertical distribution

Core analysis at station 4 revealed a decrease in organoarsenicals with depth (Fig. 3). Small amounts of DMA and MA were found below 12–15 cm, but AsB, TEM/AC and the unidentified species were not detected below 12–15 cm. The sedimentation rate at this station was calculated to be 0.18 cm $year^{-1}$. AsB could have been degraded by surface sediment microbes at station 4. Assuming that organoarsenicals such as AsB, TEM/AC and arsenosugars were constantly supplied to the sediment, these could have been almost completely degraded

over approximately 60 years. *In situ* anaerobic biomethylation of inorganic arsenic into MA and DMA has been reported in both lake sediment[44] and marine sediment.[25] The MA and DMA detected at greater depths may be the product of the *in situ* microbial methylation of arsenic. Similar increases in arsenic and iron in the upper 10 cm showed that the distribution of arsenic in marine sediment is related to that of iron (Fig. 4). The peak of total arsenic concentration was observed at depths of 12–15 cm and at an average depth of 13.5 cm. The sediment at this depth is calculated to have been deposited 66 years ago, i.e. in 1936. Mukuromi Mine was under operation from 1935 to 1943.[43] This suggests that, during the mining era, there was an active transportation of loellingite through the river to Otsuchi Bay.

In conclusion, organoarsenicals, such as AsB, formed by marine organisms were found to have been delivered to the marine sediment. They were detected at [As] = 10.6–47.5 μg kg^{-1} and comprised up to 74.3% of total extractable arsenic in the surface sediment. In the core sample, organoarsenicals were not present below 13.5 cm. Once organoarsenicals have been sedimented, they can be degraded by microorganisms and disappear within several decades, approximately 60 years.

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