Depth Profiles of Dimethylarsinate, Monomethylarsonate, and Inorganic Arsenic in Sediment from Lake Biwa

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Abstract

Three sediment cores were collected from Lake Biwa, and analysed for their dimethylarsinate (DMA), monomethylarsonate (MMA), and inorganic arsenic (I-As) content. The analytical technique used included solvent extraction, anion-exchange chromatography, and final determination of arsenic by flameless atomic absorption spectrophotometry. The sediment was found to contain trace levels of DMA (undetectable– $24.7 \mu\text{g}\cdot\text{kg}^{-1}$) and MMA (20.8 – $44.1 \mu\text{g}\cdot\text{kg}^{-1}$) in addition to I-As which tended to be present in the greatest amount. The depth profiles of DMA, MMA, and I-As were also analysed in detail.

1. Introduction

Arsenic can be methylated to monomethylarsonate (MMA) and dimethylarsinate (DMA) by common fungi, yeast, bacteria, and algae (CHALLENGER, 1945; McBRIDE and WOLFE, 1971; CULLEN *et al.*, 1979; ANDREAE and KLUMPP, 1979; BAKER *et al.*, 1983). The resulting methylated-arsenic compounds are widely distributed in soils, sediments, water, and organisms of the environment (TAKAMATSU *et al.*, 1982a; BRAMAN and FOREBACK, 1973; SHAIKH and TALLMAN, 1978; IVERSON *et al.*, 1979). Since organic arsenic compounds, particularly DMA, are adsorbed to a much lesser degree than arsenate by soils and sediments (WAUCHOPE, 1975; ANDERSON *et al.*, 1978), they can easily be solubilized and transported in the hydrosphere. In addition, in the microbial methylation cycle of arsenic, they are the precursors of gaseous dimethylarsine and trimethylarsine (COX and ALEXANDER, 1973; McBRIDE and WOLFE, 1971; CULLEN *et al.*, 1979), which may be transported in the atmosphere. Therefore, the measurements of DMA and MMA in the environment may provide useful information on the global cycle of arsenic. Although sediments have been analysed by some authors (IVERSON *et al.*, 1979; MAHER, 1981; TAKAMATSU *et al.*, 1982b), the depth profiles of DMA and MMA have never been described for lake sediments.

2. Materials and methods

Three sediment cores were collected from the central region of Lake Biwa where the accumulation of arsenic on the sediment surface had been observed previously (TAKAMATSU *et al.*, 1980). The sampling sites are illustrated in Fig. 1 with the water depth. A gravity corer, consisting of a plastic core liner (3.5 cm *i.d.*) was used to obtain samples of 30–40 cm in length. The redox conditions in these sediments were essentially similar to those reported by KAWASHIMA *et al.* (1978). The retrieved cores showed thin brown oxidized top layers (*ca.* 0.2 cm in thickness) overlying the pale gray reduced sediment. Immediately after collection, the cores were taken to the laboratory and sliced into 0.5, 1, 2 or 5 cm layers. The subsamples were freeze-dried and homogenized with an agate mortar.

The reagents, apparatus, and analytical operating conditions were identical with those described in the previous reports (TAKAMATSU *et al.*, 1982a, 1982b). The analytical procedures for DMA, MMA, and inorganic arsenic (I-As) determination are therefore only briefly outlined.

The sediment sample (1–5 g) was extracted with a 5-fold volume (5–25 ml) of 10 M HCl by shaking mechanically at 30°C for 1 hr. A desired aliquot (up to 12.5 ml) of extract was taken and 4.15 g of KI, water and HCl were added to prepare a 25 ml solution containing 1 M KI and 5 M HCl. Arsenic compounds

Fig. 1. Sampling sites. Date: A and B 5/28, 1982; C 12/15, 1981. Depth (m): A 97, B 70, C 74.

including DMA, MMA, and I-As were extracted with 10 ml of benzene (twice). Then, arsenic compounds were back-extracted with 5 ml of water containing H_2O_2 (twice). After the aqueous phases were neutralized with NaHCO_3 , the solution was washed with 5 ml of benzene (twice). A portion of this solution was applied to an anion-exchange column (10 mm *i.d.* $\times$ 115 mm, Dowex 1 $\times$ 4, 200–400 mesh, acetate-form). DMA, MMA, and I-As were separated by eluting successively with 0.1% CH_3COOH , 5% CH_3COOH , and 1 M HCl at a flow rate of *ca.* 20 drops min^{-1} and collected in 130-drop fractions. The eluates were subjected to arsenic analysis by flameless atomic absorption spectrophotometry, after adding $\text{Mg}(\text{NO}_3)_2$ to prepare 0.025% of Mg^{2+} solution.

The assignment of chromatographic peaks to DMA, MMA, and I-As has been demonstrated by the authors on the basis of analysis of arsenic compounds spiked in the soil extracts (TAKAMATSU *et al.*, 1982a) and the elution behavior of arsenic compounds as observed in a different chromatography (TAKAMATSU *et al.*, 1983). The good accuracy of analytical results has been also supported by the recoveries (91–103%) of arsenic compounds spiked in the soil extracts (TAKA-

MATSU *et al.*, 1982a).

The total concentration of arsenic (T-As) was determined by X-ray fluorescence analysis according to the method described in the previous report (TAKAMATSU, 1978).

The carbon content was analysed with an elemental analyzer (Carlo Erba Co., Model 1106).

3. Results and Discussion

Figure 2 shows the chromatographic separation of arsenic compounds in the extracts from the uppermost (0–0.5 cm) layers of the cores. The elution patterns consisted of 4 peaks and were quite similar to those of arsenic compounds in the soil and pond sediment extracts (TAKAMATSU *et al.*, 1982a, 1982b). Three peaks were found to correspond to DMA, MMA, and I-As. The other peak (X) was assigned to the new

Fig. 2. Chromatographic separation of arsenic compounds extracted from the 0–0.5 cm layers of the cores. Column: 10 mm *i.d.* $\times$ 115 mm, Dowex 1 $\times$ 4, 200–400 mesh, acetate-form. Eluent: A 0.1% CH_3COOH , B 5% CH_3COOH , C 1 M HCl. Flow rate: 20 drops min^{-1} . Fraction volume: 130 drops/fraction.

Table 1. Concentrations* of arsenic compounds in the sediment cores from Lake Biwa.

Site	Depth (cm)	DMA	MMA	X**	I-As	T-As	Carbon
		$\mu\text{g}\cdot\text{kg}^{-1}$			$\text{mg}\cdot\text{kg}^{-1}$		%
A	0-0.5	16.7	33.3	6.5	87.1	86	2.9
	0.5-1	12.9	31.2	5.0	85.3	94	2.6
	1-2	14.6	30.4	2.5	47.2	55	2.0
	2-3	4.8	38.0	6.3	46.6	50	1.8
	3-4	3.5	44.1	3.5	40.5	38	1.7
	4-6	4.2	39.7	4.0	31.3	35	1.6
	6-8	3.7	35.1	5.1	27.5	30	1.3
	8-10	4.2	33.0	3.2	25.6	28	1.2
	10-15	3.9	33.0	3.9	24.4	26	1.3
	15-20	3.5	34.0	4.9	24.2	31	1.2
	20-25	2.6	34.4	4.9	25.2	26	1.1
	25-30	3.3	34.0	4.7	22.9	27	1.1
	30-35	3.5	29.5	4.2	22.6	21	1.2
		(4.2)†	(33.8)	(4.4)	(28.2)	(31)	(1.3)
B	0-0.5	24.7	37.2	3.5	57.9	68	2.7
	0.5-1	19.1	41.0	4.9	58.1	61	2.7
	1-2	10.1	34.4	4.7	39.4	44	1.9
	2-3	6.0	34.1	5.6	41.8	40	2.0
	3-4	5.1	29.7	3.8	32.7	32	1.7
	4-6	6.3	29.2	4.0	33.2	31	1.7
	6-8	5.3	32.5	6.9	28.3	28	1.2
	8-10	5.4	29.4	5.6	23.6	28	1.2
	10-15	6.5	31.2	4.5	22.7	25	1.3
	15-20	4.9	24.0	3.9	22.9	25	1.2
	20-25	2.4	27.1	4.9	22.2	24	1.1
	25-30	N.D.††	23.6	5.8	22.2	22	1.0
		(4.9)	(28.3)	(5.0)	(26.4)	(27)	(1.3)
C	0-0.5	11.9	31.7	6.9	86.2	89	3.2
	0.5-1	8.7	36.8	5.3	63.4	64	2.5
	1-2	9.7	34.0	7.6	42.0	38	2.1
	2-3	6.3	42.3	7.3	40.7	39	1.9
	3-4	8.3	34.0	N.D.	48.2	44	1.9
	4-6	—	30.9	2.1	40.1	40	1.9
	6-8	6.3	33.3	3.9	35.9	30	1.7
	8-10	4.5	29.9	N.D.	31.1	31	1.4
	10-15	5.6	26.6	1.8	27.3	31	1.3
	15-20	4.7	30.9	N.D.	28.4	28	1.2
	20-25	2.1	20.8	N.D.	25.6	30	1.2
	25-30	4.2	22.2	1.2	26.3	31	1.1
	30-35	3.0	22.2	N.D.	27.5	28	1.0
	35-40	3.2	27.6	N.D.	29.4	26	1.0
		(4.5)	(27.1)	(—)	(31.1)	(32)	(1.3)

* Values are based on the freeze-dried materials, and show the averages of two runs.

† Weighted average values. †† Undetectable ($<1 \mu\text{g}\cdot\text{kg}^{-1}$).** New arsenic compound whose tentative structure has been proposed previously (TAKAMATSU *et al.*, 1982a).

arsenic compound whose tentative structure ($C_5H_7AsO_3H_2$) has been proposed previously (TAKAMATSU *et al.*, 1982a). Another peak appearing in the second fraction prior to the elution of DMA, was often observed in the lower sediment extracts.

The analytical data are presented in Table 1. Although a greater part of arsenic in the sediment corresponded to I-As, DMA and MMA could also be detected in most of the samples. The low levels of these organic arsenic compounds, comparable to *ca.* 0.1% of I-As, were similar to those observed in the arsenic-polluted soils (TAKAMATSU *et al.*, 1982a). The Lake Biwa and pond sediments (TAKAMATSU *et al.*, 1982b) appeared to have higher concentrations of MMA ($20.8\text{--}44.1\text{ }\mu\text{g}\cdot\text{kg}^{-1}$) than DMA (undetectable– $24.7\text{ }\mu\text{g}\cdot\text{kg}^{-1}$).

Typical arsenic profiles were observed in the core from site A (Fig. 3). The profiles of the carbon content (a large portion of the carbon is organic carbon) and redox potential (KAWASHIMA *et al.*, 1978) are also illustrated in the figure for reference. I-As (and T-As) were present at high concentrations in the upper layer of the core and these profiles were quite consistent with those reported in our previous survey (TAKAMATSU *et al.*, 1980). The accumulation of I-As at the sediment surface should result from a dissolution-deposition cycle of arsenic within the sedimentary column associated with

the redox cycle of manganese, although the detailed mechanism is described elsewhere. The profiles of DMA and MMA are here described for the first time; that is, DMA was present in a greater amount in the surface (0–2 cm) layers, whereas MMA tended to decrease somewhat in the surface but increase in the lower layers where DMA was noted to decrease.

Two possible processes may be responsible for the configuration of these profiles. (1) The mechanisms for the biological reduction and methylation of arsenic are not known in detail (WONG *et al.*, 1977; WOOLSON, 1983), but two models have been proposed. The first (M-1) is based on a study of anaerobic bacteria and involves the transfer of methyl carbanions (CH_3^-) from methylcobalamine (McBRIDE and WOLFE, 1971; WOOD, 1974). The second model (M-2) is based on a study of aerobic fungi and involves the transfer of carbonium ions (CH_3^+) from S-adenosylmethionine (CHALLENGER, 1945; CULLEN *et al.*, 1977). In either model, the pathway from MMA to DMA includes a reduction step with the gain of two electrons, *i.e.*, $CH_3As^{3+}O(OH)_2 \rightarrow (CH_3)_2As^{+}O(OH)$ in M-1 or $CH_3As^{5+}O(OH)_2 \rightarrow CH_3As^{3+}O(OH)_2$ in M-2. Therefore, the pathway from MMA to DMA might be relatively accelerated in sediment layers at a depth of 0.2–2 cm where the lowest redox potential was recorded although the production of MMA and DMA by microorganisms may be

Fig. 3. Depth profiles of arsenic compounds in the core from site A.
*: base concentrations (averages in 10–35 cm layers).

promoted by the large amount of carbon in the surface sediment (TAKAMATSU *et al.*, 1982a, 1983).

The production rate of MMA from arsenite may proceed steadily without acceleration by lowering the redox potential since this step in M-1, *i.e.*, $\text{As}^{3+}\text{O}(\text{OH}) \rightarrow \text{CH}_3\text{As}^{3+}\text{O}(\text{OH})_2$, involves no redox process and that in M-2, *i.e.*, $\text{As}^{3+}(\text{OH})_3 \rightarrow \text{CH}_3\text{As}^{5+}\text{O}(\text{OH})_2$, is an oxidation process with respect to arsenic atoms. In addition, since the concentration of arsenite (reactant of the above process) detected in the reduced sediment, *e.g.*, $7.9 \text{ mg} \cdot \text{kg}^{-1}$ As in the 0.5–2 cm layer and $4.3 \text{ mg} \cdot \text{kg}^{-1}$ As in the 2–4 cm layer (TAKAMATSU *et al.*, 1979), is much higher than that of MMA (product), the production rate of MMA from arsenite should be held approximately constant regardless of a little change of arsenite concentration. Therefore, the enhanced transformation of MMA to DMA, which occurs in the sediment with maximum reduction immediately below the uppermost thin (*ca.* 0.2 cm) oxidized layer, should result in depletion of MMA in the upper 2 cm sediment. This is consistent with the variations in the DMA/MMA ratio corresponding to changes in the redox potential in the arsenic-polluted paddy soils (TAKAMATSU *et al.*, 1982a).

(2) The methylated-arsenic compounds were found only in the euphotic zone of marine environment and planktonic algae were suggested to be the most important producers of these compounds (ANDREAE, 1978, 1979). In addition, recent studies showed that freshwater green algae as well as marine algae are highly capable of methylating arsenic, and the resulting DMA and MMA are contained in these algal cells (ANDREAE and KLUMPP, 1979; BAKER *et al.*, 1983). Plankton is generally recognized as an important source of sedimentary organic matter (JACKSON, 1975; ISHIWATARI, 1977). It is thus likely that the biological debris rich in DMA and MMA settle on the lake floor, and then upon burial, DMA decomposes to MMA and subsequently to I-As with increasing depth. The difference in the decomposition rates of DMA and MMA (the rate: $\text{DMA} > \text{MMA}$) may account for the configuration of the profiles.

The inflow of agricultural chemicals may be another conceivable source of methylated-arsenic compounds. In order to prevent the incidence

of sheath blight of rice, derivatives of MMA, *i.e.*, iron and calcium salts of MMA and bis-(dithiocarbamate)methanearsine have been occasionally used in the paddy fields of the watershed since 1957, though DMA was not used at all. The agricultural use of such arsenicals was begun at most 25 years ago before sampling of the cores, and this period corresponds to the sediment depth of 3–3.5 cm because the sedimentation rates at the lake bottom near site A are $1.2\text{--}1.4 \text{ mm} \cdot \text{yr}^{-1}$ (KAMIYAMA *et al.*, 1982). However, the increased concentrations of MMA above its base levels are extending to the deeper zone (*ca.* 8 cm depth) of the core and the upper 2 cm sediments which deposited within the recent *ca.* 15 years contain less amounts of MMA compared to the deeper sediments. Therefore, it was concluded that the influence of agricultural chemicals is negligible in this case.

Although at this time it is difficult to say which of the above processes, (1) and (2), is predominant in this lake, the higher levels of DMA and MMA detected within the upper 10 cm sediment may play a significant role in determining the behavior of arsenic in bottom water and sediment.

摘 要

琵琶湖の湖心部から3本の底泥柱状試料(30~40 cm)を採取した。試料は0.5, 1, 2および5 cmの厚さに分割し、凍結乾燥した後、ジメチルアルシン酸(DMA)、モノメチルアルソン酸(MMA)および無機ヒ素(I-As)の濃度を次の方法で分析した。まずヒ素化合物を試料から10M HClで浸出した後、ベンゼンに抽出して分離、濃縮した。次にアニオン交換樹脂カラムを用いたクロマトグラフィーでDMA, MMAおよびI-Asを分離し、最後にフレイムレス原子吸光度法でヒ素を定量した。

その結果、琵琶湖の底泥中のヒ素は大部分がI-Asであったが、DMAやMMAもほとんどの試料で検出され、その濃度はDMAで検出されないものから $24.7 \mu\text{g} \cdot \text{kg}^{-1}$ の範囲を、MMAで20.8から $44.1 \mu\text{g} \cdot \text{kg}^{-1}$ の範囲を示した。底泥はI-Asのはば0.1%に相当するメチル化ヒ素化合物を含んでいた。またDMAとMMAの詳細な深度分布をはじめて明らかにした。

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