July, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *59*, *2273—2278 (1986)*

Vertical Concentration Distributions of Arsenic in a Reservoir and Its Sediment

Yuzo Tamari,* Kimio Nishimura, Haruo Tsuji, and Yuzuru Kusaka
Department of Chemistry, Faculty of Science, Konan University,
Higashinada-ku, Kobe 658

(Received January 24, 1986)

Vertical concentration distributions of arsenite and arsenate in a reservoir (depth, ≈31 m) and its bottom sediment (core depth, ≈18 cm) have been investigated. The concentrations of arsenite and arsenate in the water were determined by a spectrophotometric method, and those in the sediment were also determined by the same method after the following leaching-treatments of the sediment. The leaching of arsenic from the sediment was carried out by using three solutions; (1) 0.1 M† hydrochloric acid (acid-soluble fraction), (2) 1 M sodium hydroxide solution (alkali-soluble fraction), and (3) hydrofluoric and perchloric acid mixture (silicate fraction). It was found that arsenic was rich in the surface layer of the sediment, and most of it existed as arsenite fixed with iron hydroxide. Based on the analytical and leaching results of arsenic, iron, manganese, zinc, copper, and others in the reservoir and in its sediment respectively, the sedimentation process of arsenic from the reservoir and its dissolution process from the sediment have been discussed.

Arsenic is one of the most widely distributed elements in the earth's crust and in the biosphere. Arsenic is commonly considered to be intrinsically toxic to life. However, it has been recognized to be one of the essential trace elements in living organisms since 1975,[1] and has become significant for men and animals as an important element in their nutrition.[2,3] Thus, it is our concern to know the concentration of arsenic contained in drinking water or in its original reservoir.[4]

Arsenic generally exists as the following chemical species; arsine [As(−III)], elemental arsenic [As(0)], arsenite [As(III)], arsenate [As(V)], and organically-complexed arsenic. For the detailed researches of arsenic in natural water, reservoir water, and its bottom sediment, this chemical state analysis of arsenic is important. In this work, a reservoir, which is located in Hyogo Prefecture and has been used for drinking water supplies, was selected as one of the geochemical researches of arsenic. The vertical distributions of arsenite, arsenate, and organic arsenic in the reservoir and its sediment have been investigated. The concentrations of arsenite and arsenate in the water were determined by spectrophotometry.[5] The inorganic and organic arsenic in the sediment were analyzed for the solutions prepared by a chemical leaching method,[6–8] by which arsenic was released from the sediment to a solution.

Experimental

Sediment and Water Samples. A sediment sample was collected from the bottom of the reservoir of a 17.5-cm depth core, using a core sampler (Rigo Co., Ltd., model 2010). The core sample was taken in a plastic cylinder and was immediately cooled in an ice-box. It was then taken back to the laboratory within 1h. The wet core (17.5-cm length) was cut into sections, 1.5-cm in depth, and each of the divided wet core samples was then subjected to a leaching experiment without drying.

Water samples were collected from the surface to a 30.5-m depth of the reservoir. The water samples were collected in a plastic-made sampler (Rigo Co., Ltd., model 22046) and were immediately analyzed for temperature, pH, conductivity, turbidity, dissolved oxygen (D.O.), and oxidation reduction potential (O.R.P.). They were then transferred to a 2000-cm^3 polyethylene bottle after adding 33 cm^3 of 6 M hydrochloric acid to avoid the precipitation of iron (III) hydroxide. However, for the analyses of nitrate, nitrite, and ammonium ions, a part of the water sample in the sampler was transferred to a glass bottle without the addition of 6 M hydrochloric acid.

Analytical Methods. Arsenite and arsenate were determined by spectrophotometry with silver diethyldithiocarbamate, after converting the arsenic into arsine with sodium tetrahydroborate.[5] Calcium, magnesium, iron, manganese, copper, and zinc were determined by atomic absorption spectrometry. Sodium and potassium were determined by flamephotometry. Sulfide was determined by iodatimetry after converting the sulfur into hydrogen sulfide with hydrochloric acid. The other chemical species dissolved in water samples were determined by ordinary spectrophotometry and other conventional methods.[9]

Chemical Leaching Methods. The following solutions were used for fractionation into acid-soluble, alkali-soluble, and silicate fractions: (1) 0.1 M Hydrochloric acid solution[7,10,11] to dissolve sulfide, hydroxide, and some ions loosely adsorbed with sediments, but not to dissolve both lithogeneous materials derived from rocks and organically-complexed ions such as copper. (2) 1 M Sodium hydroxide solution[8] to leach some organically-bound elements or organic compounds such as humic acids. (3) Hydrofluoric and perchloric acid mixture[11,12] to decompose residual silicates and their lattice constituent elements. The preparing procedure of each fraction was as follows.

Acid-soluble fraction: Accurately weighed 2—3 g of a wet core-sediment (e.g., 2.17 g corresponds to 1.00 g of the sediment on dry basis) was placed in a 50-cm^3 centrifugal tube. Into the tube, 25 cm^3 of 0.1 M hydrochloric acid was added. The tube was then set in a hot water-bath thermostatically controlled at 40 °C, and ultrasonic waves were irradiated into the bath in order to mix and suspend the sediment particles into the acid solution. The

---

† 1 M=1 mol dm^{-3}.

irradiation time was for 20 min. After centrifuging the tube, the supernatant solution was filtered (filter pore size: 0.45 µm). This filtrate was saved for later analyses. Another aliquot (25 cm^3) of the fresh hydrochloric acid was then added to the residue in the tube. The mixture was again subjected to ultrasonic irradiations. This procedure was repeated five times to perfectly dissolve arsenic and other ions from the sediment.6)

Alkali-soluble fraction: The alkali-soluble fraction was collected in a similar manner to the acid-soluble fraction. This fractionation procedure was carried out on the residue after the acid leaching.

Silicate fraction: Finally, the residue, after the alkali leaching, was transferred to a Teflon beaker, and decomposed with the mixture of 10 cm^3 of 46% hydrofluoric acid and 2 cm^3 of 60% perchloric acid. The resulting mixture was concentrated under heating until white fumes of the perchloric acid appeared. To decompose some organic compounds in the mixture, 4 cm^3 of 61% nitric acid and 2 cm^3 of 60% perchloric acid were also added, and the new mixture was again concentrated in a similar manner. The resultant solution was diluted to 50 cm^3 with 0.1 M hydrochloric acid.

Results and Discussion

Effect of Leaching Numbers on the Dissolution of Arsenic from Sediments. Figure 1 shows one of the leaching patterns of arsenic by acid- and alkali-leaching. Each shape of the patterns was a log-normal distribution, and so were those of calcium, magnesium, iron, and zinc. Therefore, it was found that these elements were effectively dissolved in the leaching solutions up to No.5.

Vertical Distribution Profiles of Several Sedimental Elements in Acid-Soluble, Alkali-Soluble, and Silicate Fractions. Table 1 summarizes the amount of each element leached out from one gram of dry sediments in each fraction. The value in parentheses represents a dissolved percentage of the element in the sediment (see the calculation formula in the footnotes in Table 1). It is noted in Table 1 that about 63—73% of total calcium went into the acid-soluble fraction throughout the entire core depth, whereas the other alkaline earth metal magnesium, alkali metals sodium and potassium (from other measurements) were poorly dissolved, e.g., 4—7% for magnesium, 0—3% for sodium and potassium. The much dissolution of calcium from the sediment can be explained from a result that the sediment is derived from detritus of rhyolite rocks which surround the reservoir of interest, because the dissolved percentages of calcium and the other elements by acid leaching of the rocks were almost same as those of the sediment.

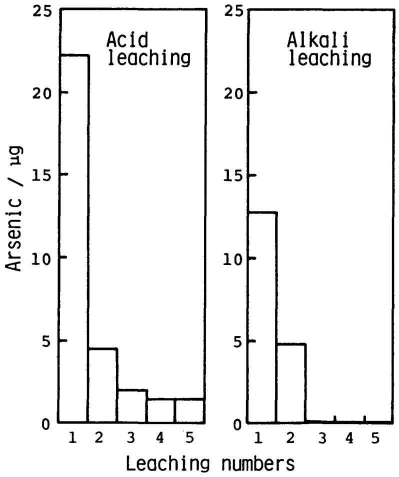

Fig. 1. Leaching patterns of arsenic by acid- and alkali-leaching treatments.
Amounts of arsenic (arsenite+arsenate) indicate to be leached from one gram of dry sediments (the core depth: 1.5—3.5 cm from sediment surface).

Figure 2 is drawn from the data of Table 1, and shows the depth distribution pofiles of typical elements, arsenic and metal ions, in the core sediment. It is worth noting that arsenic, copper, zinc, and iron dissolved by the acid leaching were rich in the surface layer of the sediment and were poor in the deeper layers. A similar tendency was found in sulfide content of the sediment (this data is listed in Appendix 1).

Alkali-soluble fractions occupied considerable portions of dissolved percentages of total arsenic, copper, and zinc in the sediment. The percentages for each element were nearly constant for the entire core depth, e.g., at 11—19 µg for arsenic, 11—20 µg for copper, and 10—20 µg for zinc. It is pointed out that arsenic in the alkali-soluble fraction could not be volatilized directly as arsine from the acidified determining solution of the fraction by the addition of tetrahydroborate. Accordingly, the arsenic was determined after wet-ashing with nitric and perchloric acid mixture (see the procedure in silicate fraction of this paper). Thus the arsenic leached in the alkaline solution is probably in some form of organically-complexed arsenic, but not a simple inorganic arsenic.

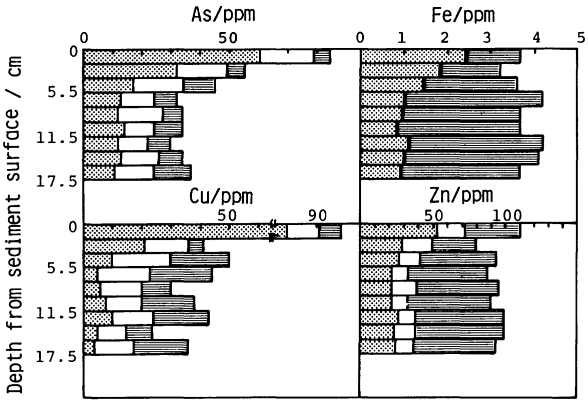

Fig. 2. Vertical distributions of concentrations of arsenic and several elements in sediments.
▨ : Acid-soluble fraction, □: Alkali-soluble fraction, ▤ : Silicate fraction.
Concentrations of elements in dry sediments.

In silicate fractions, the dissolved percentages of calcium and magnesium were almost constant regardless of the core depth, while those of arsenic, copper, zinc, iron, and manganese increased with the core depth.

Chemical Oxidation State of Arsenic in the Sediment. Figure 3 shows the vertical concentration distributions of arsenate and arsenite in the acid-

Table 1. Arsenic and Several Elements Dissolved in Acid-Soluble, Alkali-Soluble, and Silicate Fractions from One Gram of Dry Sediments

Core depth of sediment (cm from surface)	Ca/mg Fraction			Mg/mg Fraction			Fe/mg Fraction			Mn/mg Fraction		
	Acid	Alk.	Sil.	Acid	Alk.	Sil.	Acid	Alk.	Sil.	Acid	Alk.	Sil.
0— 1.5	0.91	0.11	0.33	0.20	0.020	2.4	24	0.38	13	1.3	0.006	0.11
	(67)	(9)	(24)	(7)	(1)	(92)	(64)	(1)	(35)	(92)	(1)	(7)
1.5— 3.5	0.71	0.064	0.31	0.12	0.012	2.0	18	0.36	14	0.91	0.013	0.10
	(66)	(5)	(29)	(5)	(1)	(94)	(56)	(1)	(43)	(89)	(1)	(10)
3.5— 5.5	0.85	0.062	0.42	0.18	0.011	3.8	14	0.24	22	0.67	0.015	0.18
	(64)	(4)	(32)	(4)	(1)	(95)	(39)	(1)	(60)	(77)	(2)	(21)
5.5— 7.5	0.96	0.029	0.40	0.27	0.014	4.4	10	0.14	33	0.60	0.008	0.20
	(69)	(2)	(29)	(5)	(1)	(94)	(23)	(1)	(76)	(74)	(1)	(25)
7.5— 9.5	0.89	0.058	0.51	0.24	0.011	4.0	9.8	0.24	27	0.49	0.012	0.16
	(61)	(4)	(35)	(5)	(1)	(94)	(26)	(1)	(73)	(74)	(2)	(24)
9.5—11.5	0.89	0.036	0.49	0.18	0.009	3.8	8.2	0.22	29	0.58	0.010	0.24
	(63)	(2)	(35)	(4)	(1)	(95)	(22)	(1)	(77)	(70)	(1)	(29)
11.5—13.5	1.3	0.033	0.44	0.31	0.009	4.2	11	0.22	31	0.89	0.012	0.19
	(73)	(2)	(25)	(6)	(1)	(93)	(26)	(1)	(73)	(82)	(1)	(17)
13.5—15.5	1.1	0.044	0.51	0.27	0.008	4.6	9.8	0.16	31	0.84	0.007	0.18
	(67)	(2)	(31)	(5)	(1)	(94)	(24)	(1)	(75)	(82)	(1)	(17)
15.5—17.5	1.1	0.042	0.38	0.27	0.016	4.0	9.3	0.16	27	0.73	0.009	0.17
	(72)	(3)	(25)	(6)	(1)	(93)	(25)	(1)	(74)	(80)	(1)	(19)

Core depth of sediment (cm from surface)	Cu/μg Fraction			Zn/μg Fraction			As(III+V)/μg Fraction		
	Acid	Alk.	Sil.	Acid	Alk.	Sil.	Acid	Alk.	Sil.
0— 1.5	80	11	7.8	53	20	40	60	19	6.0
	(81)	(11)	(8)	(47)	(18)	(35)	(71)	(22)	(7)
1.5— 3.5	21	15	4.7	29	20	31	33	18	5.3
	(52)	(36)	(12)	(36)	(25)	(39)	(58)	(32)	(10)
3.5— 5.5	9.8	20	20	27	14	53	18	17	11
	(20)	(40)	(40)	(29)	(15)	(56)	(38)	(38)	(24)
5.5— 7.5	4.7	18	21	22	9.6	56	13	11	8.0
	(11)	(41)	(48)	(25)	(11)	(64)	(41)	(34)	(25)
7.5— 9.5	5.8	14	10	22	17	56	12	16	6.4
	(19)	(47)	(34)	(23)	(18)	(59)	(35)	(46)	(19)
9.5—11.5	8.2	12	18	22	10	58	14	10	10
	(21)	(32)	(47)	(24)	(12)	(64)	(42)	(29)	(29)
11.5—13.5	9.6	14	19	27	12	64	12	9.6	8.7
	(23)	(32)	(45)	(26)	(12)	(62)	(40)	(32)	(28)
13.5—15.5	5.3	9.8	8.9	24	16	62	13	14	7.8
	(22)	(41)	(37)	(24)	(15)	(61)	(36)	(41)	(23)
15.5—17.7	3.8	13	19	24	13	56	11	13	10
	(11)	(36)	(53)	(26)	(14)	(60)	(38)	(35)	(27)

Acid: 0.1 M Hydrochloric acid.
Alk. : 1 M Sodium hydroxide solution.
Sil. : Conc. Hydrofluoric and perchloric acid mixture.
Values in parentheses: Dissolved percentages $\left(\frac{\text{amounts of an element dissolved from 1 g of sediments}\times 100}{\text{total amounts of an element in 1 g of sediments}}\right)$.

Appendix 1. Total Concentrations of Arsenic and Several Elements Dissolved in Sum of Acid-Soluble, Alkali-Soluble, and Silicate Fractions

Core depth of a sediment (cm)	Na %	K %	Ca %	Mg %	Fe %	Mn %	Cu ppm	Zn ppm	S[a] ppm	As[b] ppm
0— 1.5	0.33	2.0	0.14	0.26	3.7	0.14	99	110	190	85
1.5— 3.5	0.38	2.2	0.11	0.21	3.2	0.10	41	80	110	56
3.5— 5.5	0.37	2.1	0.13	0.40	3.6	0.087	50	94	70	46
5.5— 7.5	0.35	1.8	0.14	0.47	4.3	0.081	44	88	38	32
7.5— 9.5	0.39	1.9	0.15	0.43	3.7	0.066	30	95	39	34
9.5—11.5	0.33	1.8	0.14	0.40	3.7	0.083	38	90	51	34
11.5—13.5	0.39	1.9	0.18	0.45	4.2	0.11	43	100	25	30
13.5—15.5	0.32	2.0	0.17	0.49	4.1	0.10	24	100	70	35
15.5—17.5	0.27	1.9	0.15	0.43	3.7	0.091	36	93	—	34

a) Sulfide. b) Total of As(III) and As(V). All values are on dry basis.

Appendix 2. Arsenite and Arsenate Leached in Acid-Soluble Fraction from One Gram of Dry Sediments

Core depth of sediment (cm from surface)	As(III) μg	As(V) μg	As(III+V) μg	As(III)/As(V) ratio
0— 1.5	55.1	5.1	60.2	10.8
1.5— 3.5	28.0	4.7	32.7	6.0
3.5— 5.5	11.1	6.7	17.8	1.7
5.5— 7.5	8.4	4.4	12.8	1.9
7.5— 9.5	7.3	4.4	11.8	1.7
9.5—11.5	6.9	6.7	13.6	1.0
11.5—13.5	7.1	5.3	12.4	1.3
13.5—15.5	6.7	5.8	12.5	1.1
15.5—17.7	6.2	5.1	11.3	1.2

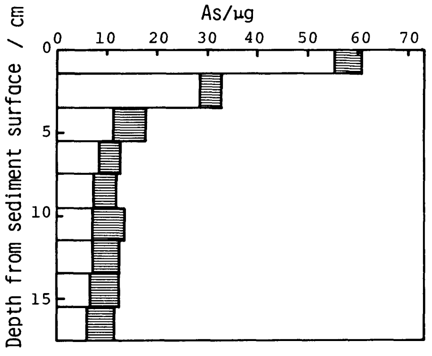

Fig. 3. Vertical distributions of concentrations of arsenite and arsenate in acid-soluble fractions leached from one gram of dry sediments.
□: Arsenite, ▤: Arsenate.

soluble fraction of the core sediment. Original data are tabulated in Appendix 2. As shown in Fig. 3, arsenite exists predominantly in the surface layer of the sediment, whereas the amounts of arsenate was almost constant throughout the entire core depth.

Table 2. Coefficients of Correlations between Arsenic and Other Elements in Sediments

	Total As (Acid-soluble fraction)	As(III) (Acid-soluble fraction)	As(V) (Acid-soluble fraction)	Total As (Alkali-soluble fraction)	Total As (Silicate fraction)
Ca	−0.40	−0.39	0.007	0.86	0.33
Mg	−0.49	−0.46	−0.23	0.46	0.022
Fe	0.97	0.97	−0.15	0.73	0.48
Mn	0.45	0.84	−0.09	0.11	0.74
Cu	0.97	0.97	−0.11	0.042	0.85
Zn	0.97	0.96	−0.06	0.04	0.86
S[a]	0.97	0.96	−0.06		

a) Sulfide determined as hydrogen sulfide from the sediment.

Table 2 presents the correlations between arsenic and the other elements in the sediment. In the acid-soluble fraction, good correlations were found for arsenite but not for arsenate. For example, the coefficients of correlation are 0.96—0.97 for Fe/As(III), Cu/As(III), and S/As(III). From these results the following discussions are made on the chemical oxidation state of arsenic in sediment.

(1) Arsenic exists rich in the surface of the sediment mainly as an arsenite species. This trace arsenite is considered to be fixed with large amounts of iron hydroxide from the following experimental results. (I) There was a good correlation between trace arsenite and large amounts of iron (see Table 2). (II) The vertical distribution curve of arsenite in the acid-soluble fraction was nearly same as that of iron (see Figs. 2 and 3). (III) Arsenite and iron were easily dissolved in the acid-soluble fraction (see Table 1). (IV) Trace arsenite is usually coprecipitated from a neutral solution with iron (III) hydroxide but not with manganese hydroxide. All the manganese in the reservoir was in the form of soluble species and not in colloidal ones such as manganese hydroxide, because the concentration of manganese determined in the water with the addition of hydrochloric acid was equal to that in the same water sample without

Appendix 3. Concentrations of Major and Minor Species in the Reservoir (Sampling Date: Nov. 1983)

Water depth	Temp.	pH	Cond. at 18 °C	O.R.P. vs. N.H.E.	D.O.	Turb.	E.R.	Ca	Mg	Na	K	HCO_3	Cl	SO_4
m	°C		μs/cm	mV	ppm									
0	14.6	6.6	66	137	8.2	6	80.8	7.1	1.1	4.0	1.5	22	6.0	3.0
5	13.7	6.5	64	145	8.5	10	73.1	7.1	1.1	5.0	1.5	22	6.3	3.0
10	13.6	6.5	61	139	9.2	10	85.8	7.0	1.0	4.0	1.5	22	5.0	N.D.
15	13.2	6.6	61	142	8.3	10	80.5	7.3	1.1	4.0	1.4	24	4.4	N.D.
20	12.8	6.6	62	135	3.1	10	86.5	7.4	1.1	4.0	1.4	24	4.5	N.D.
25	9.0	6.4	96	121	2.3	10	114	11	1.6	5.5	1.5	54	5.6	N.D.
27	7.6	6.2	195	80	3.2	10	191	15	2.1	6.0	2.3	120	5.8	N.D.
29	7.7	6.3	327	72	4.4	24	160	17	2.6	6.5	2.8	200	6.5	N.D.
30	7.4	6.5	438	52	3.8		168	19	2.9	6.5	2.9	240	7.1	N.D.

Water depth	PO_4	SiO_2	C.O.D.	NO_3-N	NO_2-N	NH_4-N	Fe	Mn	Cu	Zn	Al	As(III)	As(V)
m	ppm				ppb								
0	N.D.	10	1.1	2.0	26	300	72	70	4.0	6.6	66	N.D.	0.7
5	N.D.	8.4	1.2	12	16	220	78	97	3.2	16	63	N.D.	0.7
10	N.D.	9.7	1.3	11	14	220	72	92	4.4	11	46	N.D.	0.7
15	N.D.	11	1.4	1.0	23	440	94	280	2.4	6.6	100	N.D.	0.7
20	N.D.	9.4	1.3	0.5	23	390	130	410	2.8	7.6	58	N.D.	0.9
25	N.D.	9.4	1.3	0.4	N.D.	1400	130	3700	3.4	10	58	N.D.	0.7
27	N.D.	11	5.7	1.3	N.D.	4300	15000	9000	4.4	14	97	9.9	5.0
29	N.D.	21	5.4	0.4	N.D.	13000	56000	11000	4.8	19	150	100	15
30	N.D.	40	13	0.4	N.D.	14000	88000	14000	19	40	810	240	28

Temp: Temperature. Cond: Conductivity. O.R.P.: Oxidation reduction potential. D.O.: Dissolved oxygen. Turb.: Turbidity. E.R.: Evaporated residue. C.O.D.: Chemical oxygen demand.

the additin of the acid. (V) It is not expected that the trace arsenic is coprecipitated by the formation of aluminum hydroxide, because the concentration of aluminum in the reservoir was extremely lower than that of iron (see Appendix 3).

(2) In deep layers of the sediment, arsenite fixed with iron (III) hydroxide is released from the iron by the reductive dissolution reaction of iron (III) to iron (II). This reaction is considered from the data of a good correlation between arsenite and iron dissolved from the core sediment, shown in Table 2. Similar idea on the dissolution of arsenic from lake sediments has been reported by Nakashima et al.[11] With the dissolution of the iron hydroxide, arsenite will be released from the deeper layer of the sediment to an aqueous phase, and diffuse up to the surface layer of the sediment.

(3) There is another arsenic species leached in alkali-soluble fractions. The color of the alkaline solution was light-brown, and the maximum wavelength in the absorption and fluorescence of the solution were measured respectively to be 470 and 540 nm, which correspond to probably humic acids or derivatives of chlorophylls. The arsenic was not vollatilized directly as arsine from the acidified alkaline solution, as already mentioned above. It can be, therefore, pointed out that the arsenic in the alkaline solution is chemically stable, and is probably organically-complexed or -bonded with

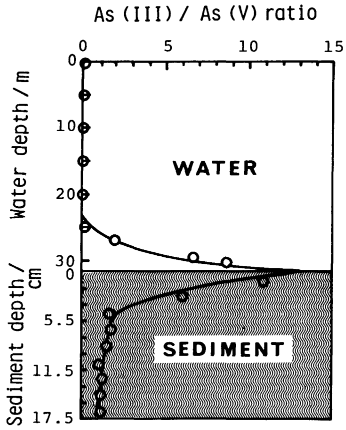

Fig. 4. Concentration ratios of arsenite to arsenate in the reservoir and its bottom sediment.
Data for sedimental arsenic are obtained from acid-soluble fractions.

humic acids and their further decompositional products. It is worth noting that a considerable 30—40% of total arsenic content was leached out from the sediment by the alkali leaching.

Arsenite to Arsenate Ratio in Reservoir Water and Its Sediment. Figure 4 shows the ratio of As(III)/As(V) in the reservoir water and its bottom sediment. The concentrations of arsenite and arsenate in the water were quoted from Appendix 3, and those in the sediment were from the acid-soluble fraction shown in Appendix 2. As is seen in Fig. 4, the As(III)/As(V) ratio increased from the water depth of 25 m toward the bottom, which is in line with the decreasing O. R. P. values (see Appendix 3). The As(III)/As(V) in the water and in the sediment indicate a common feature that they reached maxima in the boundary layers between the two phases. On the other hand, the concentration ratio of Fe/As(III) in the bottom water, 370, was nearly equal to that in the surface sediment by acid leaching, 440. It is, therefore, considered that the formation and dissolution of the iron hydroxide coprecipitating arsenite are taking place repeatedly at the boundary layer between the water and the sediment.

References

1) S. Maeda, *Kagaku No Ryoiki.* **37**, 606 (1983).

2) M. Anke, "Trace Element-Analytical Chemistry in Medicine and Biology," Walter de Gruyter & Co. (1984), Vol. 3, p. 421.

3) S. Toda and A. Yamasaki, *Kagaku To Kogyo,* **38**, 324 (1985).

4) S. D. Faust and O. M. Aly, "Chemistry of Natural Waters," Ann Arbor Science Publishers Inc., (1981), p. 320.

5) H. Tsuji, K. Nishimura, Y. Tamari, and Y. Kusaka, *Bunseki Kagaku,* **33**, 43 (1984).

6) Y. Tamari, Y. Inoue, H. Tsuji, and Y. Kusaka, *Bunseki Kagaku,* **31**, E409 (1982).

7) Y. Tamari, Y. Inoue, H. Tsuji, and Y. Kusaka, *Bull. Chem. Soc. Jpn.,* **55**, 3760 (1982).

8) Y. Tamari, K. Hiraki, and Y. Nishikawa, *Chikyu Kagaku,* **12**, 37 (1978).

9) Nihon Bunseki Kagakukai Hokkaidoshibu, "Mizu no Bunseki," Kagakudozin Co. Ltd., (1985), p. 173.

10) D. Z. Piper, *Geochim. Cosmochim. Acta,* **35**, 531 (1971).

11) S. Nakashima and F. Morii, *Nogaku Kenkyu,* **59**, 189 (1982).

12) Y. Kitano and R. Fujiyoshi, *Geochem. J.,* **14**, 113 (1980).