



## DISTRIBUTION OF ARSENIC, CADMIUM, LEAD, ZINC, COPPER, MANGANESE, AND IRON CONTAINED IN THE BOTTOM SEDIMENT OF LAKE BIWA\*

Jun KOBAYASHI, Fuji MORII, Shigeki MURAMOTO,  
Susumu NAKASHIMA, Hisayuki TERAOKA and Shoji HORIE\*\*

### INTRODUCTION

Trace metals are one of the greatest causes of the present environmental pollution. Attention has mainly been given to the role of man in polluting the environment with these metals, but it is important also to learn the amounts of such metals deposited by nature. Considerable amounts of these metals must have been carried from their points of origin by water and been deposited in lakes and oceans as their ultimate destination. In other words, if we can correctly estimate the amount of each metal deposited throughout geologic time, we can also estimate the amount added as the result of human activity.

In order to solve this question, we have studied a core sample of lake sediments in which various records of the past are preserved. These substances seem to be terrigenous. Therefore, if a fluctuation in their amounts can be found, this may have some connection with other environmental factors. Only after we have estimated the real quantity of such naturally deposited substances in this extremely long lacustrine core in relation to other environmental factors, we will be able truly to estimate how much their amounts have increased in recent years due to human activity.

The research group of Horie et al. succeeded in obtaining by core boring sediments from the bottom of the central part of Lake Biwa, at a depth of 65.2 m, in 1971. The sediment core is about 200 meters in depth below the surface of the lake bottom and composed mainly of loose homogeneous clay containing some volcanic materials. In the past four years, many investigation—paleomagnetic, paleontological, paleoclimatic, mineralogical, geochemical and so on—have been carried out (1-20) on these materials.

In order to investigate the vertical and horizontal distribution of trace metals contained in the sediment of Lake Biwa, 39 samples from

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\*\* Otsu Hydrobiological Station, Kyoto University.

the vertical core along with other samples from the 4 different volcanic ash strata in the same core, and 20 samples from various points on the surface of the lake bottom were collected; then trace metals such as arsenic, cadmium, lead, zinc, copper, manganese and iron were determined by atomic absorption spectrophotometry.

As a result, several noteworthy facts were discovered. For example, a high concentration of arsenic was detected at several points near the center of the northern part of Lake Biwa where pollution had not been expected. These results will be presented in this paper.

#### MATERIALS AND METHODS

In order to investigate the vertical and horizontal distribution of trace metals contained in the sediments of Lake Biwa, a total of 39 samples were collected from a 200-meter vertical core at every 5-meter interval, and samples of four different volcanic ash layers were collected in various strata of the vertical core; in addition, a total of 20 samples were collected in November 1972 and December 1973 from the surface of various parts of the lake bottom.

The sites of the 200 meter vertical core and of sampling points on the surface sediment at the bottom of Lake Biwa are shown in Fig. 1. The surface sediment was sampled at the mouths of each of the 9 rivers which flow into the lake, at the point where the Seta River flows out of the lake, at 8 central points in the main northern part of the lake, and 2 central points in the smaller southern part of the lake.

These samples were dried and ground into particles small enough to pass through a 100-mesh sieve. In a nickel crucible, 5 g of sodium hydroxide was heated to fuse, and after cooling, 1 g of sample and 0.5 g of sodium peroxide were added and gently heated to fuse again. The contents of the crucible were disintegrated with hot water and transferred into a flask together with 30 ml of hydrochloric acid, and the volume was made up to 80 ml with water. This sample solution was analyzed for arsenic, cadmium, copper, lead, zinc, manganese and iron with atomic absorption spectrophotometry as follows:

a. Arsenic: A portion of the solution was taken into a 50 ml-reaction flask. 5 ml of hydrochloric acid and water were added to make the volume up to 25 ml, and 1 ml of 20 % potassium iodide solution and 0.5 ml of 20 % stannous chloride solution were mixed in. After 15 minutes, 3 g of granulated zinc (arsenic free) was added, and the reaction flask was immediately connected to an arsenic measurement unit (Nippon Jarrell-Ash, Model ASD-1A). By agitating the solution with a magnetic stirrer, the reaction was promoted until the pressure of hydrogen and arsine gas mixture reached 0.5 kg/cm<sup>2</sup>. Then, the stopcock

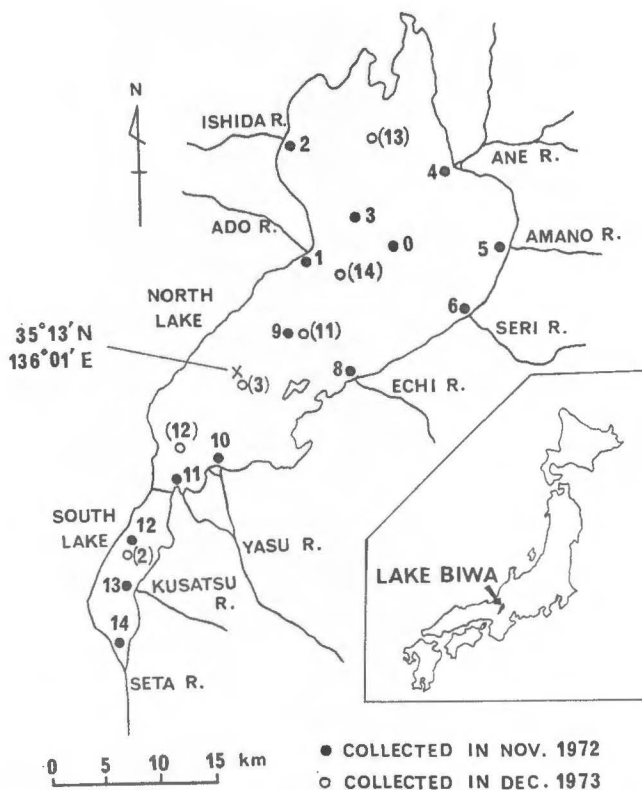


Fig. 1. Sites of the 200 meter vertical core (x) and of sampling points from the surface sediments (•, ○) at the bottom of Lake Biwa.

was opened to send the mixed gas into the hydrogen-argon flame of an atomic absorption apparatus to measure the arsenic content. The stopcock was closed again, and the gas was stored until its pressure came to  $0.5 \text{ kg/cm}^2$ . Thus, the operations were repeated until the reaction of arsenic was completed. The values were summed up and the arsenic content was calculated from the calibration curve and corrected with a blank.

b. Cadmium and lead: A portion of the sample solution was taken into a separating funnel, and 30 % ammonium citrate solution was mixed in. The pH was adjusted to 9.0 with an ammonium hydroxide solution, and cadmium and lead were extracted by shaking with 5 ml of 2 % diethyldithiocarbamate (DDTC) solution and 10 ml of methyl isobutyl ketone (MIBK). The methyl isobutyl ketone layer was separated and cadmium and lead were determined by atomic absorption spectrophotometry with an acetylene-air flame. Standard cadmium and lead solutions and reagent blank solutions were also tested to make calibration curves.

c. Copper, manganese, zinc and iron: These metals were also measured by atomic absorption spectrophotometry with a hydrogen-air

flame, using a portion of the sample solution without any extracting process.

## RESULTS AND DISCUSSION

### A. Vertical distribution of trace metals (core)

The vertical profile of the arsenic, cadmium, lead, zinc, copper and manganese (ppm in air-dried matter) contained in 39 samples collected from the vertical core in Lake Biwa is shown in Table 1. The content of arsenic was in the range of 9-58 ppm with an average of 24 ppm. The lowest value was obtained at a depth of 191 m, and the highest at 166 m. The lowest cadmium content was found to be 0.22 ppm at a depth of 59 m, and the highest 1.36 ppm at 130 m and the average content of cadmium was 0.43 ppm. The lead content varied between 18-43 ppm, showing an average of 27 ppm. The content of zinc ranged from 98 to 160 ppm and was almost uniformly distributed with only slight fluctuations. The lowest value was obtained at a depth of 66 m, and the highest value was obtained at 151 m. The average content of zinc was 132 ppm. The copper content ranged between 34-76 ppm, and the average was 53 ppm. The highest value was found at a depth of 90 m. The lowest manganese content was found to be 620 ppm at a depth of 191 m, and the highest at 130 m. The average was 1,800 ppm.

Thus, the average content of arsenic, cadmium, copper, lead, manganese and zinc in the 200-meter vertical core sample was not found to be so different from that of ordinary soil in unpolluted areas.

Relations between the number of samples from the vertical core and the concentration in each of arsenic, cadmium, lead, zinc, copper and manganese, are shown in Figs. 2, 3, 4, 5, 6 and 7, respectively. As

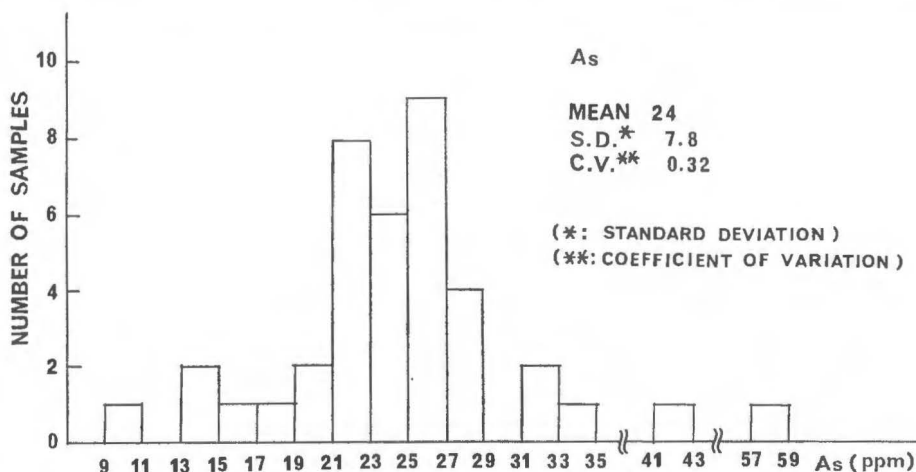


Fig. 2. Relation between the number of samples and concentration of arsenic in samples from the vertical core.



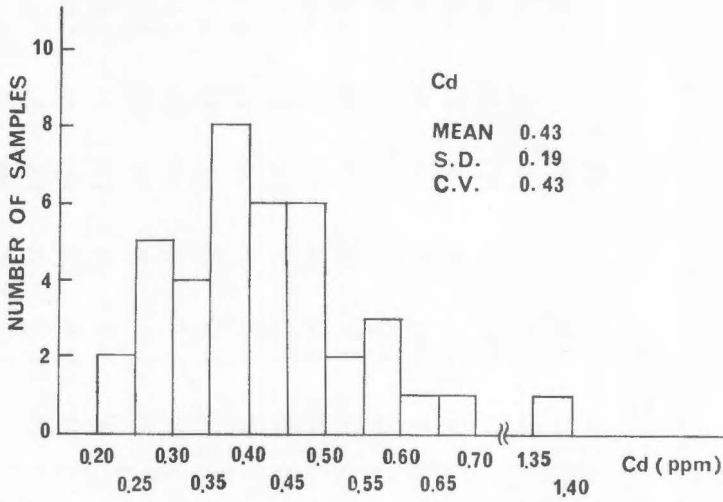


Fig. 3. Relation between the number of samples and concentration of cadmium in samples from the vertical core.

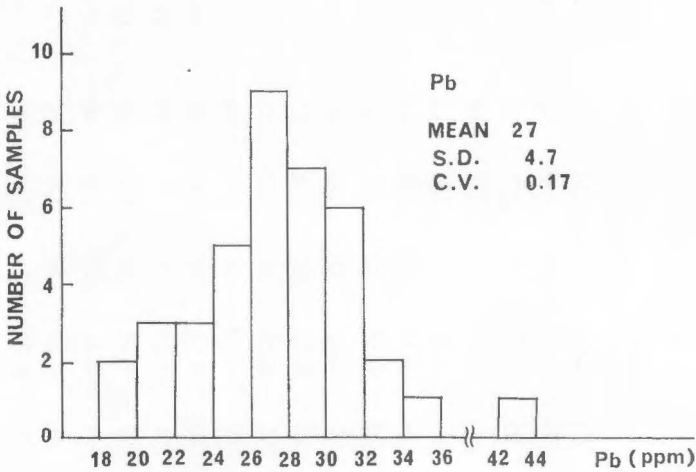


Fig. 4. Relation between the number of samples and concentration of lead in samples from the vertical core.

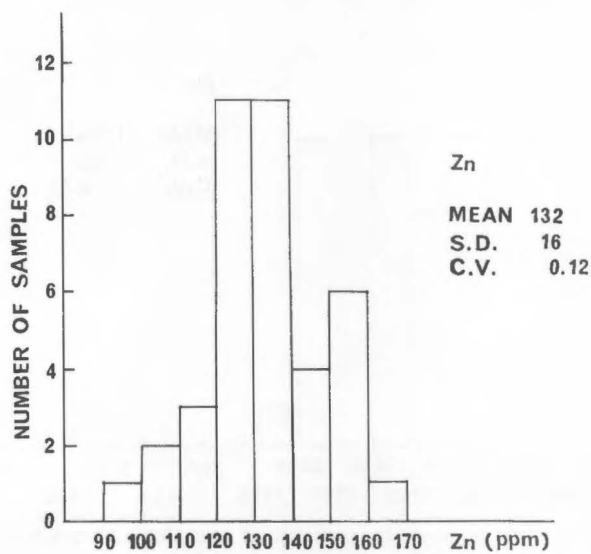


Fig. 5. Relation between the number of samples and concentration of zinc in samples from the vertical core.

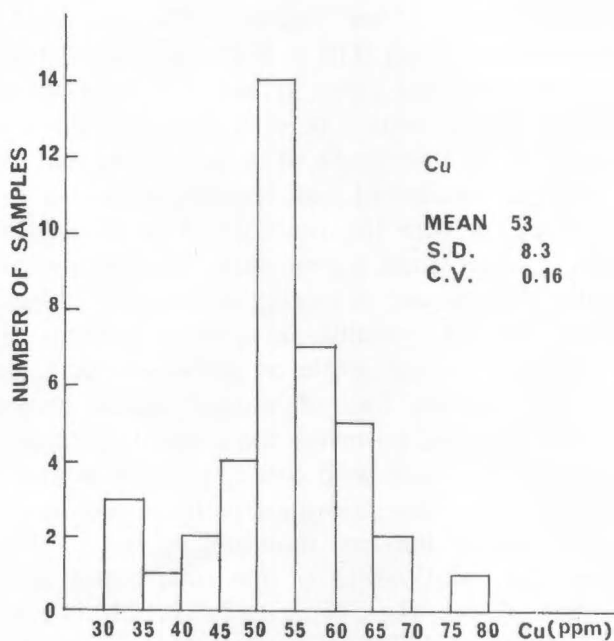


Fig. 6. Relation between the number of samples and concentration of copper in samples from the vertical core.

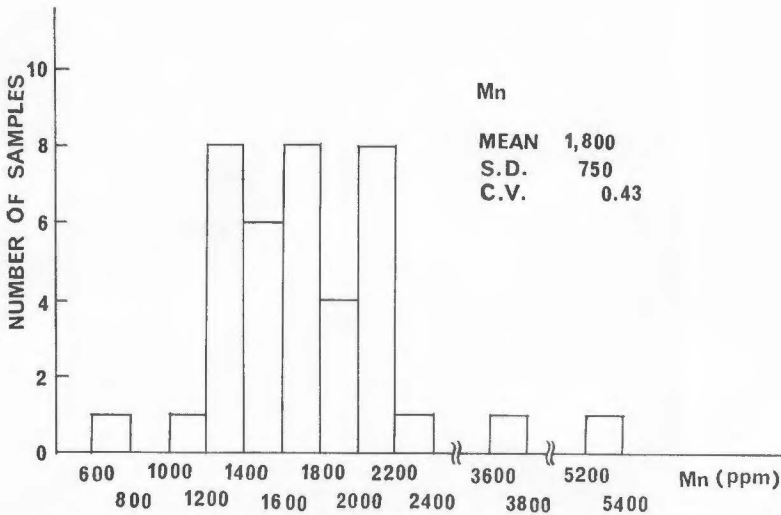


Fig. 7. Relation between the number of samples and concentration of manganese in samples from the vertical core.

shown in these figures, the histograms of these metals show a pattern of almost normal distribution. At the same time, the values of S. D. (standard deviation) and C. V. (coefficient of variation, S. D./mean value) of each metal are shown in these figures. The coefficients of variation of metal contents varied from 0.12 to 0.43 and showed higher values in cadmium and manganese and lower values in zinc, copper and lead.

The variations in the content of each metal in the vertical core are illustrated in Fig. 8. In this figure, it is noticeable that the contents of cadmium and manganese showed their highest peaks at a depth of 130 m, and at this depth in the core the concentrations of cadmium and manganese were about three times higher than the average content of each in the 39 samples. Moreover, according to data of Shigesawa(18), at a core depth of 130 m, the contents of sodium, calcium, silica and iron showed relatively high peaks, while on the other hand, the content of aluminum and the ignition loss of organic matter showed the lowest values. For other samples, however, the content of trace metals investigated did not differ so much with depth, in spite of the fact that the materials from the core are presumed to have been deposited over a period of the past several hundred thousand years.

Fig. 9 shows the relationship of the distribution of cadmium and manganese to that of the  $C_{H_2O_2}/N_{H_2O_2}$  ratio(5,8,12,13,14), to that of the oscillating geomagnetic field(5,8,11), and to that of grain-size distribution(5,8,19) in the vertical core. In this figure, the conspicuous peaks of cadmium and manganese at 130 m in core depth correspond to the peak of the  $C_{H_2O_2}/N_{H_2O_2}$  ratio, to the geomagnetic reversal, and also to the



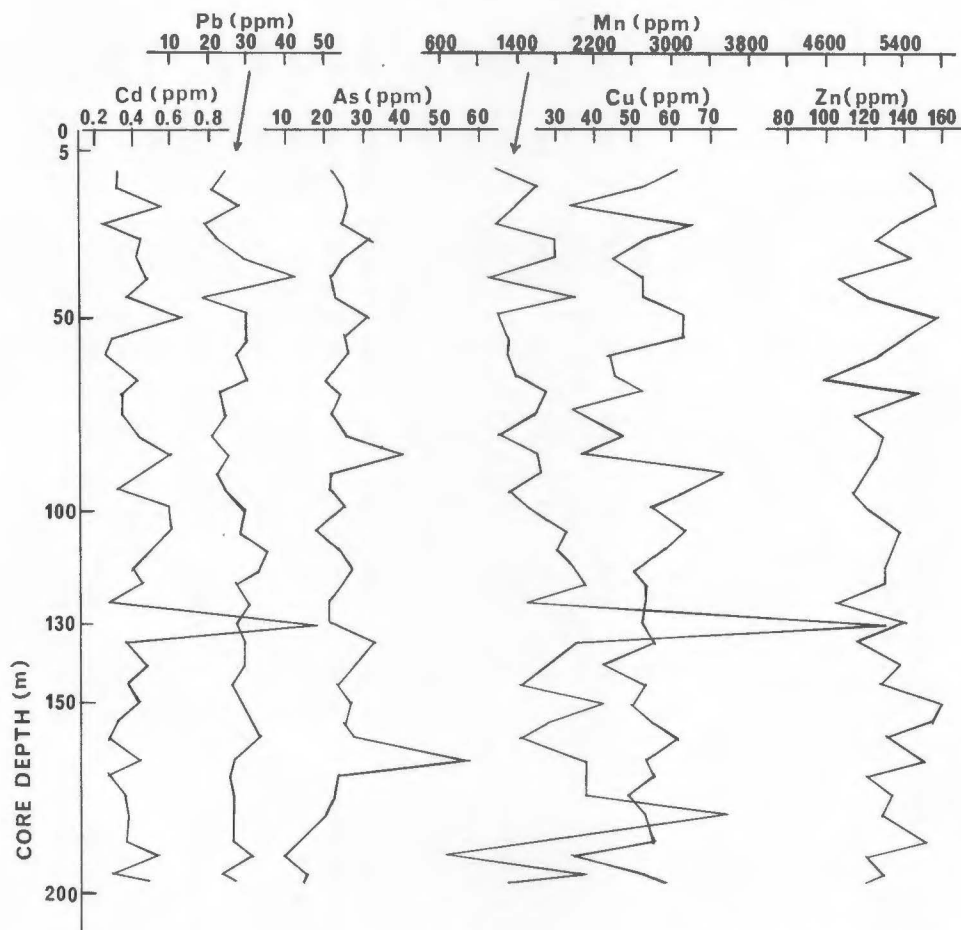


Fig. 8. Vertical distribution of trace metals contained in a 200 meter vertical core from the bottom of Lake Biwa (ppm in air-dried matter).

peak in the quantity of coarse grains. This phenomenon is suggestive of the possibility that some environmental changes may have accompanied the geomagnetic reversal which is roughly estimated to have occurred about 300,000 years ago; some environmental changes may have taken place.

#### B. Content of trace metals in volcanic ash (core)

Studies on the content of trace metals in volcanic ash have been fewer than those on gases contained in such ash. We determined the concentrations of arsenic, cadmium, copper, lead, zinc, manganese and iron in the four different volcanic ash layers that were found in various strata of the vertical core. The analytical result is tabulated in Table 2. As for stratum No. 153, obtained at a depth of 62.2 m from the top of the core, four samples including those from its volcanic ash layer

TABLE 2  
Concentrations of trace metals in four volcanic ash strata in the vertical core  
in the bottom sediment of Lake Biwa (collected in 1971).

No.	Stratum Depth from the top of the core	Thickness of volcanic ash	Portion of sampling	ppm (air dry)							Fe/Mn
				As	Cd	Pb	Zn	Cu	Mn	Fe	
153	62.2 m	2 cm	a. Clay just above the volcanic ash	21	0.24	18	120	69	1,200	52,400	43.7
			b. Volcanic ash layer	6	<0.02	3	40	43	670	20,600	30.7
			c. Clay just below the ash	26	0.06	22	120	47	1,200	51,200	42.7
			d. Clay 5 cm below the ash	29	0.34	18	140	56	980	41,400	42.2
207	88 m	7 cm	a. Clay 1.5 cm above the ash	15	0.36	14	110	62	1,000	31,600	31.6
			b. Upper part of the ash layer	12	0.04	<3	100	52	1,300	33,000	25.4
			c. Lower part of the ash layer	17	0.02	<3	60	40	1,300	38,400	29.5
			d. Clay 2 cm below the ash	23	0.26	16	60	59	1,700	57,600	33.9
265	110 m	80 cm or more	a. Upper part of the ash layer	12	0.58	6	60	36	5,000	48,800	9.8
			b. Lower part of the ash layer	12	0.19	14	50	44	8,000	68,600	8.6
			c. Lowest part of the ash layer	14	0.22	—	90	39	9,600	84,600	8.8
			d. Clay 3 cm below the ash	24	0.42	33	130	75	2,100	60,000	28.6
395	157.3 m	3 cm	a. Clay 3 cm above the ash	27	0.30	19	130	68	1,300	43,800	33.7
			b. Clay just above the ash	25	0.25	21	130	67	950	35,600	37.5
			c. Volcanic ash layer	48	—	—	70	29	1,500	53,200	35.5
			d. Clay 2 cm below the ash	30	0.19	32	140	68	1,100	39,000	35.5
			e. Clay 4 cm below the ash	44	0.34	36	150	61	1,100	50,000	45.5

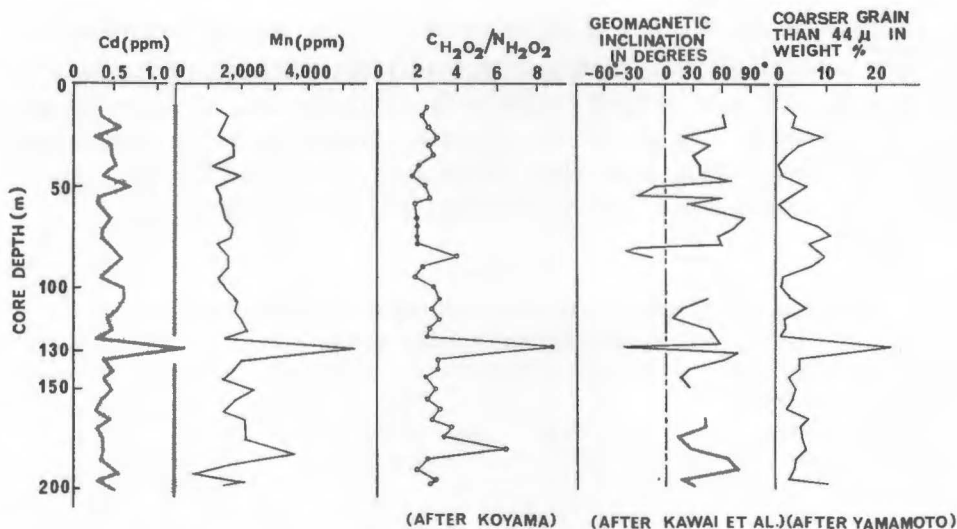


Fig. 9. Relationship of the vertical distribution of cadmium and manganese to the  $C_{H_2O_2}/N_{H_2O_2}$  ratio, to the oscillating geomagnetic field, and to grain-size distribution in a 200 m core from the bottom of Lake Biwa.

and three other adjacent layers were taken for analysis, and the results were as follows on an air-dried matter basis: arsenic 6-29 ppm, cadmium <0.02-0.34 ppm, copper 43-69 ppm, lead 3-22 ppm, zinc 40-140 ppm, manganese 670-1,200 ppm and iron 20,600-52,400 ppm. Among the four different layers of stratum No. 153 the four metals, cadmium, lead, arsenic and zinc, were found in very much smaller quantities in the lava ash than in the three layers of clay. This difference in quantity was greatest in the case of cadmium—that mineral which we would expect most readily to be lost by volatilization—, second greatest in the case of lead, and so on, in the order mentioned.

Thus, throughout these four different volcanic ash strata, No. 153 ( $1.1 \times 10^5$  years ago), No. 207 ( $1.8 \times 10^5$  years ago), No. 265 ( $2.7 \times 10^5$  years ago) and No. 395 ( $4.0 \times 10^5$  years ago)(16), it was found that the content of those metals with lower boiling points—cadmium, arsenic, zinc and lead—was lower in the volcanic ash layers than in other geologic formation from the same core. This was considered to have been caused by volatilization of these metals through volcanic activities before they fell into the lake. Furthermore, the fact that a large amount of manganese was found in one of the four layers of volcanic ash (that in stratum No. 265 from a depth of 110 m below to the bottom of the lake) and that the iron-to-manganese ratio in that sample was much lower than in other layers of volcanic ash as shown in Table 2, indicated that this layer had a different origin from the other three.

*C. Horizontal distribution of trace metals (bottom surface sediments)*

The content of trace metals in the surface sediments at the bottom of Lake Biwa is summarized in Table 3. The amounts of trace metals contained were as follows on an air-dried matter basis: arsenic 9-450 ppm, cadmium 0.24-26 ppm, lead 10-259 ppm, zinc 114-736 ppm, copper 40-111 ppm, manganese 560-17,300 ppm, iron 43,000-58,000 ppm.

TABLE 3  
Horizontal distribution of trace metals from the surface sediments  
at the bottom of Lake Biwa.

Site No.	Collected date	ppm (air dry)						
		As	Cd	Pb	Zn	Cu	Mn	Fe
0	Nov. 7-9, 1972	174	0.56	42	152	71	11,800	
1	"	20	0.27	27	138	69	1,700	
2	"	27	0.32	27	120	85	1,100	
3	"	450	0.80	35	197	79	17,300	
4	"	25	0.34	24	114	82	1,200	
5	"	21	0.59	19	128	55	1,300	
6	"	34	0.24	10	195	111	1,800	
8	"	28	0.53	30	149	63	1,300	
9	"	126	0.80	43	158	74	8,300	
10	"	17	0.59	30	202	61	1,100	
11	"	13	0.53	35	129	45	980	
12	"	43	0.75	47	320	69	1,100	
13	"	9	0.56	36	174	40	560	
14	"	18	26	259	736	79	730	
(2)	Dec. 4, 1973	39	0.90	44	280	50	1,200	47,200
(3)	Dec. 6, 1973	89	0.52	52	180	101	3,800	54,600
(11)	Dec. 10, 1973	206	0.56	26	150	77	8,600	56,600
(12)	"	71	0.64	44	190	78	1,500	43,000
(13)	Dec. 11, 1973	248	0.66	62	160	103	10,000	54,700
(14)	"	147	0.48	30	170	69	6,900	58,000

The horizontal distribution of arsenic and manganese contained in the top surfaces of the bottom sediments of Lake Biwa is given in Figs. 10 and 11, respectively. A remarkable accumulation of arsenic (126-450 ppm) and manganese (6,900-17,300 ppm) was observed at 6 central points (Nos. 0, 3, 9, (11), (13) and (14), where the water depths were more than 68 meters) at the main northern part of the lake where pollution had not been expected. The content of arsenic and manganese at these

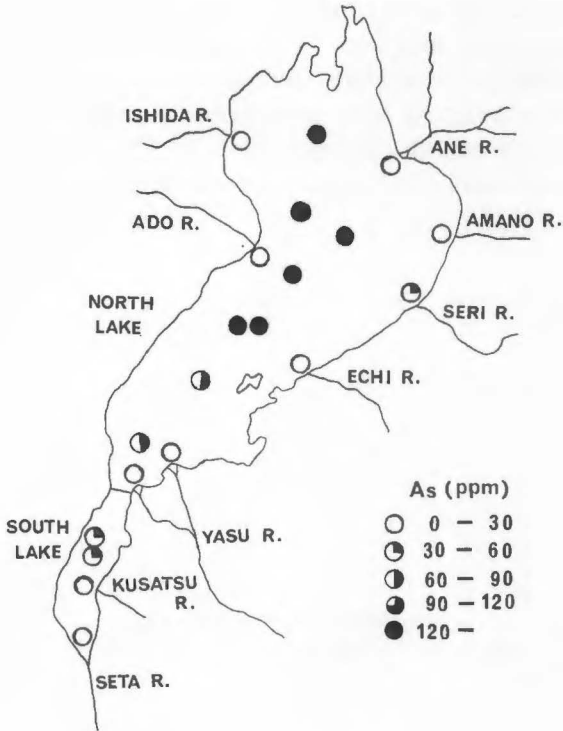


Fig. 10. Horizontal distribution of arsenic contained in the upper part of the surface sediments from the bottom of Lake Biwa (collected in Nov. 1972 and Dec. 1973).

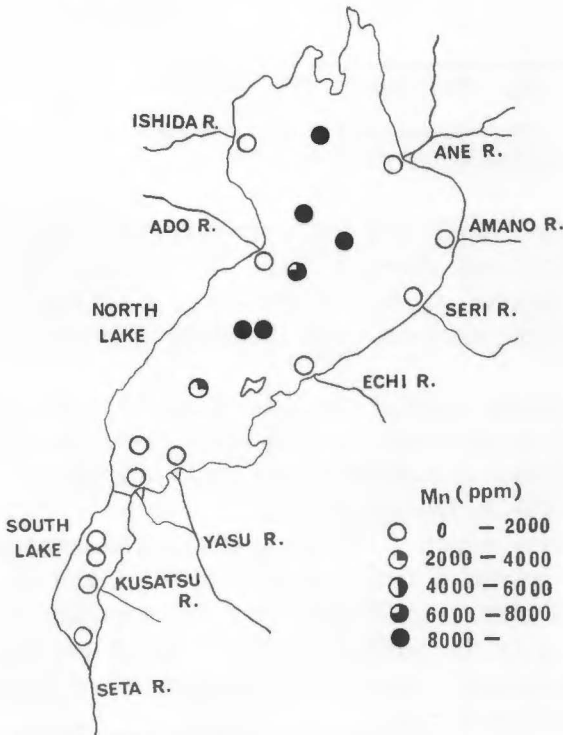


Fig. 11. Horizontal distribution of manganese contained in the upper part of the surface sediments from the bottom of Lake Biwa (collected in Nov. 1972 and Dec. 1973).

points was respectively 5-19 times and 4-10 times as much as the average content of each of the vertical core samples. The correlation between manganese and arsenic contained in the surface sediments at the bottom is shown in Fig. 12. A close correlation was recognized between these two metals, as shown by the equation of the regression line  $\log [\text{Mn}] = 0.90 \log [\text{As}] + 1.84$  ([ ]: ppm) with the correlation coefficient  $r = 0.95$  (significant at the level of  $P < 0.01$ ).

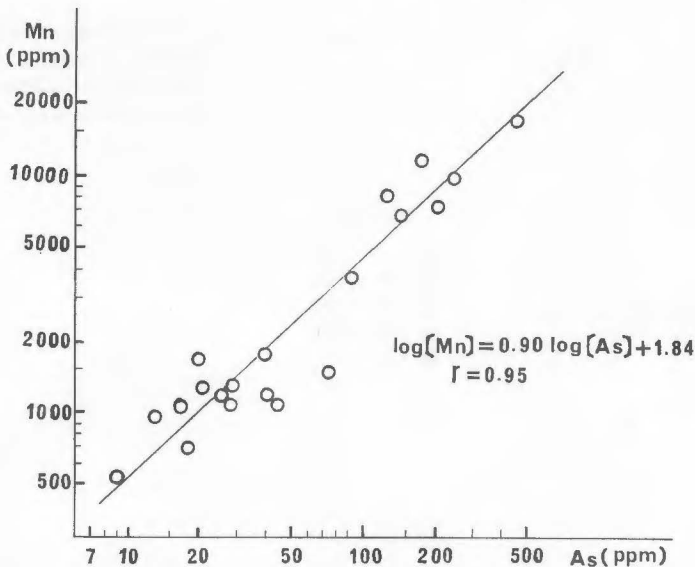


Fig. 12. Correlation between manganese and arsenic contained in the surface sediments from the bottom of Lake Biwa.

Relations between the water depth and the arsenic and manganese content in the surface sediments are shown in Figs. 13 and 14, respectively. As shown in both figures, it was found that the content of arsenic and manganese correlates positively with the water depth of the sampling points.

Furthermore, in the southern part of the lake, it was found that the surface sediment near the point where the Seta River flows out was remarkably polluted by cadmium and other metals (cadmium 26 ppm, lead 259 ppm, zinc 736 ppm) due to human activity.

At the mouths of the rivers which flow into the lake, the content of trace metals (average of 9 points, Nos. 1, 2, 4, 5, 6, 8, 10, 11 and 13: arsenic 22 ppm, cadmium 0.44 ppm, lead 26 ppm, zinc 150 ppm, copper 68 ppm, manganese 1,200 ppm) in the surface sediment was much the same as that found in the 200-meter vertical core samples taken from below the level of recent pollution by man.

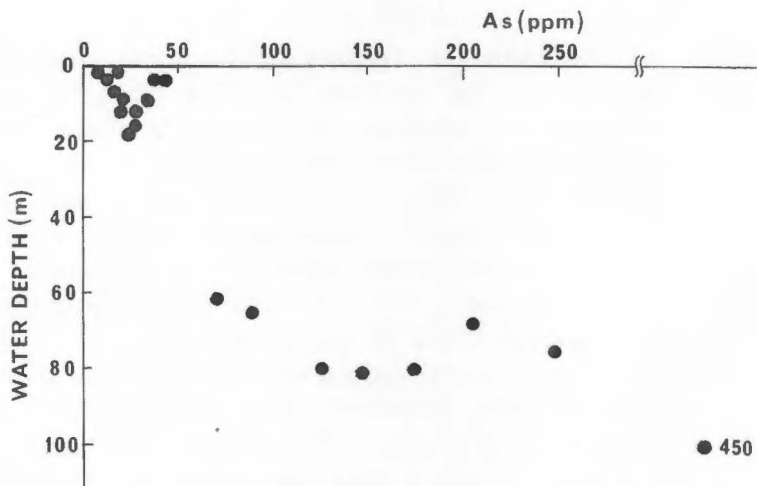


Fig. 13. Relation between water depth and arsenic content in the surface sediments from the bottom of Lake Biwa.

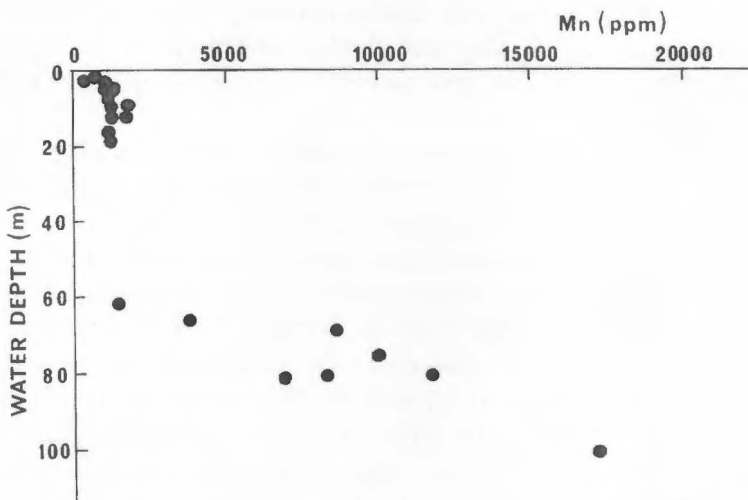


Fig. 14. Relation between water depth and manganese content in the surface sediments from the bottom of Lake Biwa.

Thus, it is striking that high concentrations of arsenic and manganese were observed at several points near the center of the main northern part of the lake, and that a higher content of cadmium, lead and zinc was found at the southern end from which the lake water flows out into the Seta River. Such unusually high accumulations of trace metals in the surface sediment indicate that even the biggest lake in Japan has begun to be affected and polluted by present-day human activities.

## ABSTRACT

In order to investigate the vertical and horizontal distribution of trace metals contained in the sediment of Lake Biwa, a total of 76 samples were collected and analyzed for arsenic, cadmium, lead, zinc, copper, manganese and iron by atomic absorption spectrophotometry. Of these samples, 20 were taken from various points on the surface of the bottom sediments, 39 were taken at intervals of about every 5 meters from a vertical core to a depth of 200 meters below the surface of the lake bottom, and 17 were taken from four different volcanic ash layers that were found in various strata of the vertical core.

The average of metals in the vertical core was found on an air-dried matter basis to be as follows: arsenic 24 ppm, cadmium 0.43 ppm, lead 27 ppm, zinc 132 ppm, copper 53 ppm and manganese 1,800 ppm. It was noticed that the highest values of both manganese and cadmium were found in the same sample from a depth of 130 m, and it may be supposed that some great environmental changes took place during the period in which it was deposited, which is estimated to be roughly 300,000 years ago. It was found that the conspicuous peaks of cadmium and manganese at 130 m of the core depth correspond to the peak of the  $C_{H_2O_2}/N_{H_2O_2}$  ratio and to the geomagnetic reversal and also to the peak of coarse grains.

As for the volcanic ash, it was found that the four kinds of metal, cadmium, lead, arsenic and zinc were found in much smaller quantities in the lava ash than in the neighboring layers of clay.

As concerns the horizontal distribution of trace metals in the surface sediment deposited in modern ages, a remarkable accumulation of arsenic (126-450 ppm) and manganese (8,300-17,300 ppm) was observed at several points near the center of the northern main part of the lake basin, where pollution had not been expected. Furthermore, in the southern part of the lake, it was found that the surface sediment near the Seta River which flows out of the lake was remarkably polluted by cadmium and other metals (cadmium 26 ppm, lead 259 ppm, zinc 736 ppm).

At other points investigated, the content of trace metals in the bottom surface sediment was much the same as that in the vertical core samples from below the level polluted by man.

Thus, the high concentration of trace metals detected in the surface sediment at some points indicated that the natural process of accumulation of trace metals which had gone on throughout the past several hundred thousand years has begun to be disrupted by recent human activity.

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