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Limnological and Environmental Studies of Elements in the Sediment of Lake Biwa

琵琶湖底泥中の元素に関する陸水学及び環境化学的研究

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Preface from the editor

A lake can be considered to be a natural reaction vessel in which an epitome of the hydrological cycle of elements is demonstrated. Once the riverine (or lesser extent atmospheric) elements have entered a lake, most of them take part in the intricate biological, chemical and physical processes and change their chemical states depending on the individual environment of the lake. Eventually, they are eliminated from lake water as a result of being deposited a sediment at the bottom of the lake, evaporation into the atmosphere, and/or being carried away by the rivers. After deposition, since the chemical states of elements often change as a result of diagenesis, some elements dissolve and move in the sediment pore water and sometimes accumulate in the particular layers (e.g. the uppermost oxidized layer or the layer with maximum reduction) of sediment. Redissolution of the elements into the bottom water from the sediment is also a common case. Therefore, the study on the elemental behavior in a lake associated with lake environment and the chemical properties of elements provides useful limnological information not only for the local interest but also to find mechanisms of the global hydrological cycle of the elements.

Although there are many approaches in which to conduct a study from the above viewpoint, the elemental analysis of the sediment should be a promising way, because the distribution and the chemical states of elements in the sediment often suggest the mechanisms of the large number of reactions in lake water and diagenesis after deposition. A sediment sample also has some analytical advantages. That is, since the sediment has higher coccentration of the elements compared to the other environmental samples, the loss and contamination of the elements during the sample storage and the analytical operation do not give significant errors to the analytical results. The relatively high concentration of elements in the sediment also makes it possible to determine the elements of more than 30 species by the non-destructive analytical techniques such as neutron activation and X-ray fluorescence.

In order to elucidate the behavior of elements on the basis of the elemental analysis of sediment, it is essential to obtain a sample which has not been disturbed by immeasurable factors. The sediment sample from Lake Biwa, particularly from the central region of the northern part of the lake, has not been disturbed appreciably for the following reasons : (1) The depth of the water being more than 70 meters prevents the surface of the sediment from being disturbed by wind. (2) The sediment composition is not influenced directly by the inflow of riverine terrestrial matter due to lake's large size. (3) At the present time, the benthic organisms only sparsely populate on and in the sediment. (4) There is no indication that ground water and volcanic hot springs are flowing out from the bottom of the central basin. In addition, interpretation of the analytical results will be easier to carry out since there has been very little human activity in the catchment area of the northern part of Lake Biwa until recent times.

This report consists of eight chapters and appendixes. Chapter I is of prime importance as it provides fundamental data to be discussed in the following chapters.

October, 1984
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CHAPTER I

General Distribution Profiles of Thirty-six Elements in Sediments and Manganese Concretions of Lake Biwa

T. Takamatsu, M. Kawashima and M. Koyama

ABSTRACT

Thirty sediment cores (30-40cm in length), 47 Ekman dredge sediments, and Mn concretions were collected from Lake Biwa. The concentrations of 36 elements in the samples were determined by instrumental neutron activation, X-ray fluorescence, atomic absorption, and colorimetric analyses. The elements analysed include Mn, P, As, Sb, Fe, Ni, Co, Zn, Cu, Pb, Hg, Cr, Ti, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Hf, La, Ce, Sm, Eu, Yb, Lu, U, Th, Au, Ta, Nd, Br and N. Based on statistical considerations and calculation of the concentration factors of the elements, the features of the elemental distribution in Lake Biwa sediment were determined.

1. INTRODUCTION

From the elemental analysis of lake sediments, important limnological and environmental information was obtained in relation to (1) the removal processes of elements into sediment from a water column (Taylor, 1979), (2) post-depositional transfer and fixation of elements in the sediment (Farmer & Cross, 1979), and (3) environmental change in the lake, including the history of natural and anthropogenic input of elements (Nriagu *et al.*, 1979).

Since Lake Biwa is not only the water resource for 13 million people in Kinki District, but also has a long history of more than a million years, the above information is of great interest to many scientists. However, the analytical data on the sediments available for obtaining this information are limited (Kobayashi *et al.*, 1976 ; Kawashima *et al.*, 1978 ; Kurata, 1978 ; Tatekawa, 1979, 1980 ; Takamatsu *et al.*, 1980b ; Nakashima & Morii, 1982).

The present paper summarizes the data on the concentration and distribution of 36 elements in Lake Biwa sediments along with a brief discussion on the mechanisms governing the distribution of elements.

2. METHODS

Collection and sample preparation : The sediment cores were collected during the period Aug. 1976–Nov. 1977 from 24 sites in the northern lake (N-lake) in addition to six cores from the southern lake (S-lake). The sampling sites are illustrated in Fig. 1.1. A gravity corer equipped with a plastic core liner (3.5cm i.d.) was used to obtain the samples of 30–40cm in length. Most of the retrieved cores showed thin brown oxidized top layers overlying the pale gray reduced sediment. The cores obtained from the nearshore region often contained silt and fine sand. Immediately after sampling, the samples were taken to the laboratory and sliced into 2cm sections. For detailed studies on the distribution and diagenesis of the elements, several representative cores were cut into thinner sections (i.e. 0.2, 0.5 or 1cm length) within the upper 2cm layers. The subsamples were freeze-dried, ground to particles of less than 100 mesh in diameter using an agate mortar, and dried again in an oven at 100°C for 5h.

The surface sediments were collected during the period Nov. 1976–Apr. 1977 with an

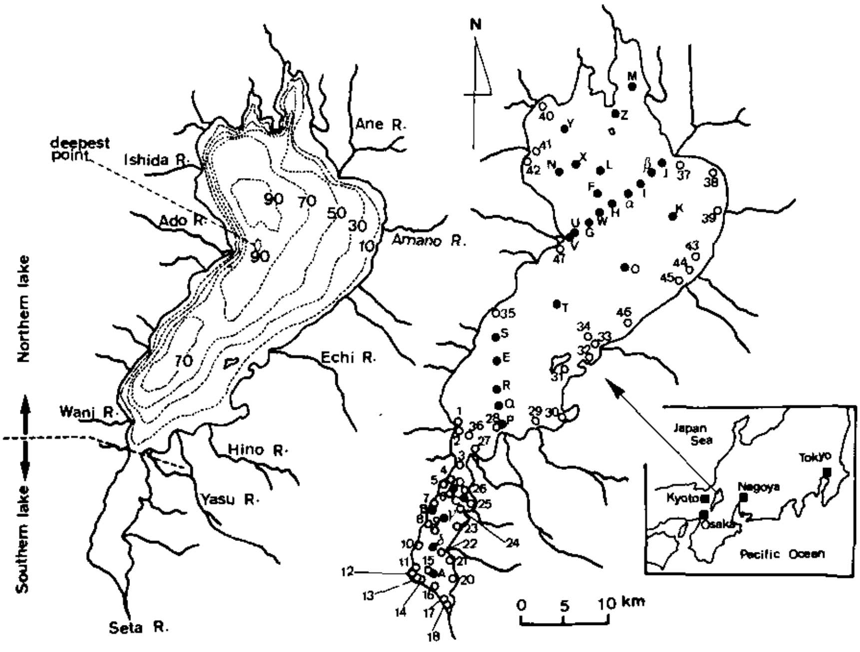

Fig. 1.1 Sampling sites
(●)sediment cores ; (○)Ekman dredge sediments.

Ekman dredge from 47 sites near the shore. After the wet samples were homogenized on the spot, aliquots of the samples were taken to the laboratory and treated in a similar manner to that for the cores before analysis.

Manganese concretions, in the form of irregular friable masses up to 5cm i.d. on the sediment surface at the central sites (G, T, X and H), were picked up with tweezers and treated in a similar manner to that of the cores (photograph of the concretions was shown in Appen. 2).

Analytical procedure : A non-destructive neutron activation analysis was performed by the flux monitor method according to the previous reports (see Appen. 3 ; Koyama & Matsushita, 1980 ; Takamatsu *et al*., 1982b). The elements analysed included Na, K, Rb, Cs, Ba, Mn, Fe, Co, Cr, As, Sb, Br, Sc, La, Ce, Nd, Sm, Eu, Yb, Lu, U, Th, Hf, Ta and Au.

The X-ray fluorescence analysis was performed by the internal standard method according to the previous reports (see Appen. 4 ; Takamatsu, 1978, 1980a). The elements analysed included K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Pb, Rb and Sr.

The atomic absorption analysis for Mn, Na and Mg and the colorimetric analysis for P were performed after acid digestion of the samples with $HClO_4$-HF (Kawashima *et al* ., 1978 ; Murphy & Riley, 1962).

Mercury was determined by a cold vapor technique : after Hg was liberated from the freeze-dried sample by combustion, it was taken up in the $KMnO_4$-H_2SO_4 solution. The Hg was then vaporized again by reduction with $SnCl_2$ before being introduced into the absorption cell of an atomic absorption spectrophotometer.

Nitrogen was determined by the Kjeldahl method (Kawashima *et al*., 1978) and the loss of ignition (I.L.) was determined by combustion of the sample at 550°C for 2h.

3. RESULTS AND DISCUSSION

Average concentrations of the elements in the cores and the Ekman dredge sediments are presented in Table 1.1 along with the maximum and minimum values recorded. The results of the cores include the values for the upper 2cm layers and the lower layers (below 10cm depth) separately. In N-lake, below 10cm from the bottom surface, the elemental concentrations of the sedimentary layers are little affected by human factors in view of the sedimentation rates (Kamiyama *et al*., 1982 ; Matsumoto, 1975) and the early-diagenesis of elements after deposition is practically complete, although the situation in S-lake may be more complicated. Therefore, the values in lower layers of N-lake are considered to be the background levels of the Lake Biwa sediments.

Table 1.1 Elemental concentrations in the sediments from Lake Biwa

	Northern lake			Southern lake		
	below 10 cm*	0-2 cm**	surface***	below 10 cm	0-2 cm	surface
W.D.	5-97(66)m	5-97(66)m	1.2-23(8.2)m	2.5-4(3.4)m	2.5-4(3.4)m	1.2-8(2.8)m
I.L.	3.4-11.4(7.7)%	5.6-11.7(9.5)%	0.9-9.8(4.4)%	9.1-10.0(9.6)%	9.1-11.0(10.1)%	6.2-14.8(9.7)%
	%	%	%	%	%	%
Fe	2.36-5.11(4.57)	3.33-5.18(4.53)	0.91-4.24(3.22)	3.94-4.66(4.29)	4.04-4.38(4.21)	2.72-4.75(3.64)
K	2.25-3.53(2.49)	2.03-2.85(2.40)	1.89-4.38(2.68)	2.25-2.45(2.35)	2.15-2.38(2.29)	1.47-2.79(2.19)
Na	0.58-1.48(0.86)	0.59-1.94(0.93)		(0.90)	(1.07)	
Mg	0.38-1.26(0.96)	0.74-1.20(0.97)		(0.84)	(0.83)	
Ti	0.23-0.64(0.50)	0.35-0.60(0.45)	0.01-0.60(0.37)	0.42-0.52(0.47)	0.36-0.51(0.43)	0.26-0.50(0.39)
Ca	0.24-0.63(0.34)	0.21-0.74(0.37)	0.13-0.94(0.46)	0.28-0.36(0.33)	0.36-0.45(0.40)	0.21-1.04(0.47)
	mg·kg^{-1}	mg·kg^{-1}	mg·kg^{-1}	mg·kg^{-1}	mg·kg^{-1}	mg·kg^{-1}
N	1230-2100(1900)	1410-4200(3020)	200-3430(1179)	2520-2660(2590)	2670-5460(3780)	1750-5150(3370)
P	320-1180(830)	560-1710(1150)	92-1750(650)	330-570(420)	590-750(680)	460-2980(1130)
Mn	690-3180(1860)	690-13900(3760)	180-1500(710)	800-1020(880)	1460-1630(1540)	480-1830(1060)
Ni	*6-42(30)*	*19-49(33)*	*N.D.-28(12)*	*19-26(23)*	*22-45(30)*	2-38(18)
Cu	13-88(52)	42-99(76)	N.D.-69(31)	41-45(42)	50-79(60)	9-154(68)
Zn	84-187(135)	112-346(203)	17-287(126)	150-194(164)	254-426(336)	110-899(366)
Pb	16-52(32)	19-76(51)	10-64(30)	38-53(47)	52-76(65)	30-311(100)
C*o*	*14.4-20.7(17.8)*	*13.3-21.8(17.6)*		(15.7)	(12.8)	
Cr	60-75(70)	46-84(67)		(70)	(52)	
As	6-41(23)	7-130(55)	1-40(13)	7-8(8)	15-28(20)	N.D. -16(5)
Sb	1.4-2.4(1.9)	1.7-3.7(3.2)				
Sc	11.5-16.2(14.5)	10.6-14.9(13.4)		(13.9)	(12.3)	
Rb	108-161(139)	115-153(131)	77-215(126)	145-155(150)	140-149(143)	85-161(128)
Cs	9.3-12.7(10.8)	7.7-13.4(10.4)		(6.1)	(6.3)	
Sr	62-114(76)	56-110(72)	42-149(90)	64-83(76)	65-94(82)	50-233(101)
Ba	570-740(680)	500-820(690)				
Sm	7.7-8.8(8.3)	6.9-8.5(7.8)				
Ce	79-94(84)	76-92(81)				
Yb	2.7-3.6(3.1)	2.7-3.7(3.2)				
Lu	0.40-0.56(0.50)	0.41-0.55(0.49)				
Hf	3.6-6.9(5.2)	3.0-6.9(4.8)				
Eu	1.0-1.2(1.1)	0.9-1.2(1.1)				
La	36.1-52.0(43.9)	35.3-44.9(40.0)		(54.5)	(46.5)	
Nd	36-67(49)	46-61(54)				
Br	4-12(7)	5-13(9)				
U	2.5-4.4(3.4)	2.8-4.3(3.5)				
Th	14.4-18.8(16.6)	14.4-17.0(15.5)				
Hg	0.10-0.13(0.12)	0.16-0.21(0.19)	0.02-0.07(0.05)	0.11-0.13(0.12)	0.18-0.24(0.20)	0.10-1.42(0.49)
Ta	1.1-1.3(1.2)	0.8-1.4(1.1)				
Au	0.011-0.032(0.018)	(0.014)				

minimum-maximum (average).

N.D. : not detectable ; W.D. : water depth ; I.L.: ignition loss.

* lower layers (below 10 cm depth) of the sediment cores.

* * upper 2 cm layers of the sediment cores.

* * * surface sediments collected with an Ekman dredge from the area near the shore.

When compared with the typical elemental composition of the earth's crust (Taylor, 1964), shale (Turekian & Wedepohl, 1961), and abyssal clay (Sugimura, 1972), it is apparent that the Lake Biwa sediments have much higher concentrations of As, Sb and Cs, and lower concentrations of alkaline earth metals except for Ba. The concentrations of U and Th are also much higher than those in abyssal clay (see Appens. 5–7).

The content of the elements of the Mn concretions sampled at site G are presented in Table 1.2. Although the concretions usually contained lower levels of trace elements than the abyssal concretions (Dean & Ghosh, 1978), high concentrations of Mn(16.7%), As ($721 mg \cdot kg^{-1}$) and Ni($340 mg \cdot kg^{-1}$) are evident. A comparison with the elemental composition of the lake concretions previously reported for Lake Michigan (Edgington & Callender, 1970), Lake Ontario (Cronan & Thomas, 1972), and Lake Oneida (Dean & Greeson, 1979) shows the Lake Biwa concretions to be similar to those of Lake Michigan, and the content of U and Th to be considerably higher. In addition, the high As content is

Table 1.2 Elemental concentrations of Mn concretions from the sediment surface at site G

Element	Concn., $mg \cdot kg^{-1}$	Element	Concn., %
Rb	70	Na	0.86
Cs	5.0	K	1.32
Sr	103	Mg	1.01
Ba	1380	Ca	0.43
Cr	37.2	Ti	0.29
Co	23.8	Mn	16.7
Ni	340	Fe	3.1
Cu	60	Al	4.9
Zn	189	Si	27.3
Pb	26		
P	2700		
As	721		
Sb	5.5		
Br	14.3		
Sc	7.5		
La	21.5		
Ce	39.6		
Nd	28		
Sm	4.6		
Yb	2.0		
Lu	0.27		
U	4.9		
Th	9.2		
Hf	1.9		
Ta	0.8		

Values are based on freeze-dried materials.

comparable to that of Green Bay in Lake Michigan, and the high Ba content is comparable to that of freshwater lakes at large (Edgington & Callender, 1970 ; Moore *et al.*, 1980).

3.1 Vertical distribution of elements

The profiles of elements in the core sites G and D are shown in Figs. 1.2 and 1.3, respectively. The profiles of the elements at site G represent the profiles of the offshore sediments of N-lake, while those at site D represent the profiles of S-lake. Although the profiles are influenced by the chemical properties of the elements and environmental factors affecting the sediments, the elements can be classified into some groups as a result of a statistical comparison of their depth distribution, as shown in Fig. 1.4.

Manganese, As, and to a lesser extent Ni showed extremely high concentrations in the uppermost thin layers and sharply decreased concentrations within a few centimeters. Below 10cm from the tops of the cores, the concentrations of the elements remained almost constant. In the offshore sediments of N-lake, the profiles of Zn, Sb and P resembled those of Mn and As.

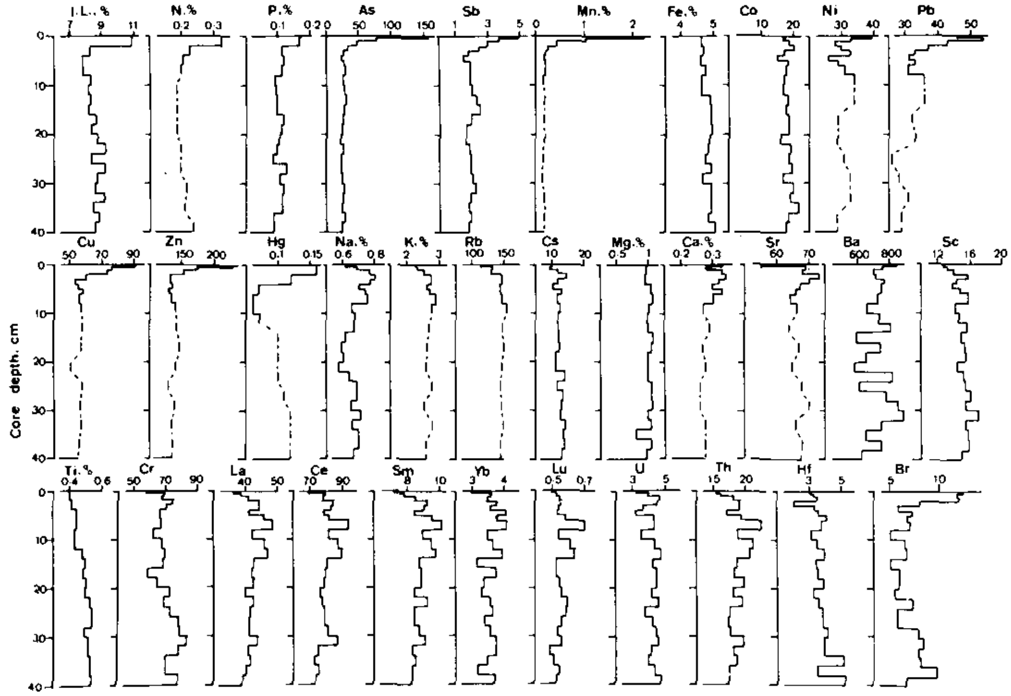

Fig. 1.2 Distribution of elements in the sediment core from site G
One concentration unit, other than %, is mg·kg^{-1}.

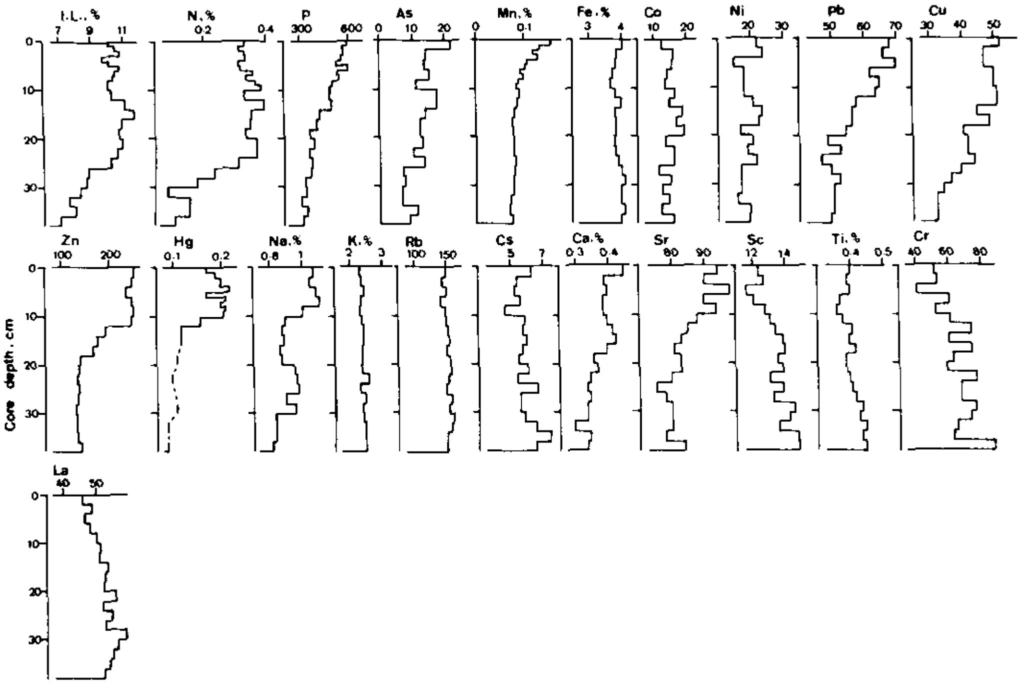

Fig. 1.3 Distribution of elements in the sediment core from site D
One concentration unit, other than %, is mg·kg^{-1}.

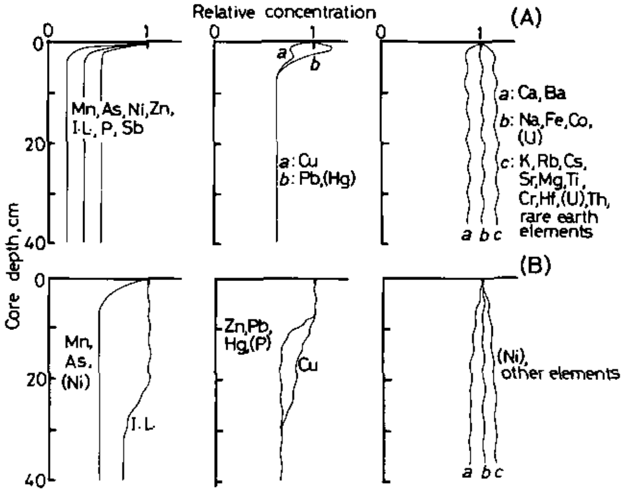

Fig. 1.4 Vertical distribution patterns of elements in the sediment
(A) offshore region of N-lake ; (B) S-lake.

The concentrations of Cu, Pb and Hg were also high in the upper layers of the sediments but their unique profiles indicated that the elements belonged to a group different from that of Mn and As. Zinc and P also had profiles similar to those of Pb and Hg in S-lake. The increased levels of the above elements compared with the background levels reached to a depth of 4-5cm in the offshore sediments of N-lake, while those in the S-lake sediments reached to a depth of 15-25cm.

Concentrations of the other elements did not vary significantly in the cores.

For a more precise determination of the concentrations of elements in the upper 2cm layers of the cores, concentration factors (F) were calculated as follows. $F = (C_x - C_r)/C_r$, where C_x and C_r refer to the elemental concentrations in the upper 2cm layer and in the lower layer (below 10cm depth), respectively. In Table 1.3, the elements were arranged in order of decreasing F. Although the effects of I.L. were not considered, it was found that the concentrations of 17 elements increased and those of 18 elements decreased in the upper 2cm layer of the N-lake sediment.

Furthermore, F was also calculated in the same way for the surface thinner (i.e. 0-1, 0-0.5 and 0-0.2cm) layers of the cores and Mn concretions. In the calculation, the concentrations of elements in the lower layers of the core from site G were used as base levels for the Mn concretions. The averaged F is listed in Fig. 1.5. It is evident that As, Ni, Sb, P, U and alkaline earth metals (particularly Ba and Sr) are enriched in Mn concretions, whereas Zn, Cu, Pb, Fe, Ti, K, Cr, Cs, Rb, Th, Hf and rare earth elements are depleted compared to the underlying sediment.

Brief discussion on several elements is given in the following.

Mn, As, Sb and Ni : Because the distribution profiles of components such as Mn, As, possibly Sb and Eh value (Kawashima *et al.*, 1978) are very much alike, early-diagenesis associated with redox processes should take place within the top several cm layer.

The cycling of Mn within the sedimentary column is well known in connection with the redox conditions of sediments (Robbins & Callender, 1975 ; Förstner, 1983). That is, Mn precipitates primarily within inorganic and organic particles on the lake floor, and after being burried, a part of Mn is reduced to Mn^{2+} and solubilized in the pore water. The Mn^{2+}, after diffusing out of the reduced layer, is immobilized again by catalytic reoxidation (Delfino & Lee, 1968 ; Sung & Morgan, 1981 ; Uren & Leeper, 1978) and by adsorption onto oxides (Morgan & Stumm, 1964 ; Murray, 1975a ; Takematsu, 1979) at the oxidized sediment surface and/or in the bottom water.

The bottom surface of N-lake is mostly covered with a oxidized layer throughout the

Table 1.3 Concentration factors* of elements in the upper 2 cm layers of the sediment cores from Lake Biwa

	Northern lake	Southern lake	Total
As	0.25-3.64(1.34)	1.14-2.50(1.62)	0.25-3.64(1.39)
Mn	(−)0.03-4.54(0.93)	0.60-0.97(0.77)	(−)0.03-4.54(0.90)
Sb	0.21-1.18(0.66)		
Hg	0.45-1.10(0.65)	0.38-1.00(0.67)	0.38-1.10(0.66)
Pb	0.00-1.59(0.60)	0.16-0.71(0.41)	0.00-1.59(0.57)
Zn	0.09-1.40(0.45)	0.59-1.70(1.08)	0.09-1.70(0.55)
N	0.15-1.01(0.56)	0.06-1.10(0.46)	0.06-1.10(0.53)
Br	(−)0.42-1.50(0.44)		
P	(−)0.10-1.15(0.36)	0.32-1.15(0.66)	(−)0.10-1.15(0.41)
Cu	(−)0.14-0.68(0.40)	0.11-0.93(0.42)	(−)0.14-0.93(0.40)
I.L.	(−)0.20-0.45(0.20)	0.00-0.10(0.05)	(−)0.20-0.45(0.18)
Au	(0.17)		
Ca	(−)0.32-0.25(0.10)	(−)0.06-0.29(0.21)	(−)0.32-0.29(0.12)
Ni	(−)0.41-0.48(0.04)	(−)0.08-0.73(0.26)	(−)0.41-0.73(0.07)
Yb	(−)0.03-0.12(0.05)		
U	(−)0.15-0.24(0.04)		
Ba	(−)0.13-0.34(0.02)		
Na	(−)0.22-0.21(0.01)	(0.19)	
Lu	(−)0.06-0.10(0.00)		
K	(−)0.18-0.09(−0.01)	(−)0.05-0.00(−0.03)	(−)0.18-0.09(−0.02)
Fe	(−)0.11-0.06(−0.02)	(−)0.08-0.03(−0.02)	(−)0.11-0.06(−0.02)
Sr	(−)0.27-0.12(−0.04)	(−)0.12-0.16(0.08)	(−)0.27-0.16(−0.02)
Cs	(−)0.17-0.14(−0.02)	(0.03)	
Ce	(−)0.11-0.05(−0.02)		
Mg	(−)0.12-0.11(−0.03)	(−0.01)	
Co	(−)0.13-0.05(−0.01)	(−0.18)	
Eu	(−)0.25-0.10(−0.04)		
Sm	(−)0.10-0.04(−0.05)		
Rb	(−)0.19-0.19(−0.06)	(−)0.07-(−)0.03(−0.05)	(−)0.19-0.19(−0.06)
Ta	(−)0.27-0.08(−0.06)		
Cr	(−)0.23-0.14(−0.06)	(−0.26)	
Sc	(−)0.15-0.07(−0.08)	(−0.12)	
Th	(−)0.22-0.00(−0.08)		
Hf	(−)0.19-0.08(−0.09)		
La	(−)0.29-0.07(−0.08)	(−0.15)	
Nd	(−0.11)		
Ti	(−)0.22-0.07(−0.12)	(−)0.17-0.00(−0.09)	(−)0.22-0.07(−0.12)

minimum-maximum (average).

*$F = (C_x - C_r)/C_r$, C_x : elemental concentration in the upper 2 cm layer of the sediment core, C_r : elemental concentration in the lower layer (below 10 cm depth) of the sediment core.

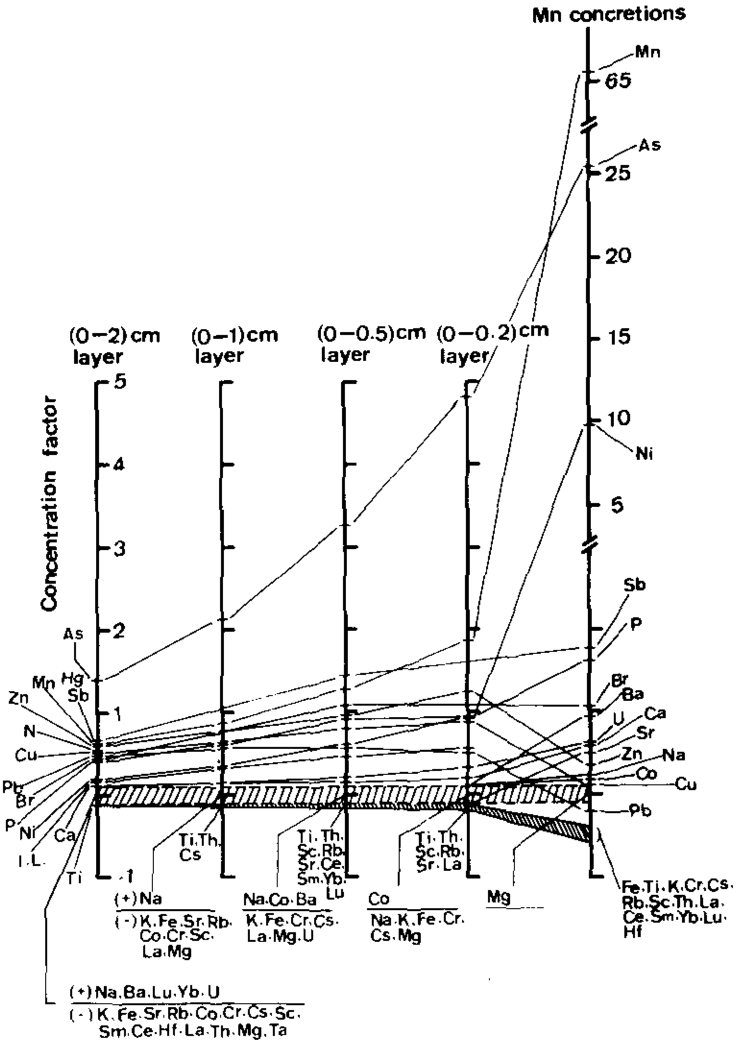

Fig. 1.5 Average concentration factors of elements in the upper thin layers of the sediment cores and Mn concretions

year because the bottom water contains DO of ca. 4mg$\cdot$kg^{-1} even at the end of the summer stratification (Naka, 1973 ; Kawashima *et al*., 1978). The cores retrieved from the central region of N-lake always showed thin (ca. 0.2cm) brown oxidized top layers. The redox potential (70–100mV) observed in the reduced sediment (below 0.5cm depth) of N-lake (Kawashima *et al*., 1978) is low enough for Mn reduction (ca. 600mV at pH 6 ; Hem, 1972). In addition, microorganisms in the lake water can rapidly oxidize Mn^{2+} to Mn oxide under aerobic conditions (Chap. VI). Therefore, the above mechanism can accout for the profiles of Mn in the sediment of Lake Biwa.

Arsenic has accumulated to high concentrations in the thin surface layers (0–0.2 and 0–0.5 cm depth), particularly in the central region of N–lake and the depth profiles of As is quite similar to those of Mn, as supported by the high distribution correlations between both elements (e.g. correlation coefficients, $r=0.986$, 0.930, 0.998 at sites T, X and G respectively). The Mn concretions also contained high concentrations of As up to $721 mg\cdot kg^{-1}$. These facts suggest that the surface accumulation of As may result from a dissolution–deposition cycle within the sedimentary column associated with that previously described for Mn. Since the redox conditions (70–100mV) of the reduced layers (Kawashima *et al.*, 1978) approximate the boundary potential of arsenate-arsenite interconversion, i.e. 83mV at pH 6 (the author's calculation based on the data compiled by Sillén and Martell, 1964), arsenic should partly be reduced to mobile arsenite in the reduced sediment though arsenate is more difficult to be reduced than Mn oxide (Peterson & Carpenter, 1983). In fact, Takamatsu *et al.* (1979a) have found As present entirely as arsenate at the sediment surface but the ratio of arsenite to arsenate increased to 0.76 with depth. In addition, Mn oxide is known to be a powerful oxidant of arsenite (Oscarson *et al.*, 1981) and Mn^{2+}–rich Mn oxide found in the oxidized sediment surface (see Fig. 2.3 in Chap. II ; Kawashima *et al.*, 1978) is an effective scavenger of arsenate (see Fig. 2.2 in Chap. II). Therefore, the profiles of As may result from post-depositional migration of arsenite in the sediment pore water followed by oxidation to arsenate at the sediment surface and adsorption onto Mn^{2+}–rich Mn oxide (the detailed mechanism is discussed in Chap. II).

Antimony has also accumulated in the surface sediment and Mn concretions (see Fig. 1.5). Since the redox potential of antimonate–antimonite interconversion, i.e. 133mV at pH 6 (the author's calculation) is somewhat higher than that of the As couple and Mn^{2+}–rich Mn oxide can adsorb antimonate appreciably in a pH range of 6 to 7 (Takamatsu *et al.*, unpublished), the redox cycle of Sb, similar to that of As, may contribute to the profiles of Sb.

The most extreme instance of the above mechanisms was shown by the formation of As (and Sb)–rich Mn concretions on the bottom surface.

As for Ni which is also concentrated in the Mn concretions, definite profiles such as Mn and As cannot be seen sometimes when analysing bulk sediments. One reason for this is that the average concentrations of Ni in clay minerals are high enough to shade the accumulation of Ni in the Mn–rich layers within experimental error.

Zn, Cu, Pb and Hg : The high concentration levels of these metals continue to deeper parts of the cores beneath the Eh-minimums which have been recorded at a 0.5-2cm depth of the core in the offshore part of N-lake and at a 6-8cm depth in S-lake (Kawashima *et al.*, 1978). In view of the sedimentation rates of 1.2-1.6mm/y for N-lake and 2.4mm/y for S-lake (Kamiyama *et al.*, 1982), the start of accumulation of the elements should go back 30-40 years ago in N-lake, while in S-lake, it goes back more than 60 years. Because the watershed of S-lake was land-developed, populated, and industrialized much more earlier and densely than that of N-lake, pollution by human activity should be the most important factor for the increased levels of these metals (Kurata, 1978 ; Tatekawa, 1979, 1980).

Although the fine depth profiles of the elements are distinct from one another in the metal-rich upper sediments, the increased concentrations of Cu always reach to the deeper zone than those of Zn. A process can be proposed relating to such differences in the profiles of Cu and Zn.

Phytoplankton (dominant species : *Staurastrum*) collected with a net (NXX 25) from Lake Biwa contained considerably higher concentrations of Zn (225mg·kg^{-1}) and Cu (155mg·kg^{-1}) and lower concentrations of other 25 elements (see Table 4.1 in Chap. IV) compared to those (see Table 1.1) of sediments, in contrast to the fact that very high concentrations and concentration factors (these factors are based on the concentrations of dissolved elements in lake water) of 11 elements including Zn, Cu and Pb have been reported with respect to phytoplankton (Kurata, 1982). Phytoplankton is recognized as a major source of sedimentary organic matter (Ishiwatari, 1973 ; Jackson, 1975 ; Cranwell, 1976) and the deposition of metal-rich planktonic debris has been suggested as a significant removal process of metals from the water column (Kemp *et al.*, 1976 ; Lund, 1957 ; Taylor, 1979). Thus, also in Lake Biwa, large fractions of Zn and Cu may settle on the lake bottom in association with planktonic debris. During the course of the early-degradation of the debris and subsequent slower humification, copper, which binds strongly to humic materials (Takamatsu *et al.*, 1983b , 1983c) may remain in a greater amount in sediments than Zn. High Cu concentrations, often detected in humic materials of sediments (Nriagu & Coker, 1980), tends to support this process (the detailed mechanism is discussed in Chap. IV).

As for Pb and probably Hg, another inorganic process perhaps should be considered since the concentration of Pb was low in the plankton.

Other elements : The other elements showed nearly constant concentrations throughout the cores, indicating that they were not mobilized to any significant extent after deposition. As for Fe, Co, U and Cr, redox reactions did not appear to take place to cause appreciable mobilization. Cobalt, U and certain alkaline earth metals abundant in Mn concretions sometimes showed slightly high concentrations on the sediment surface. Elements such as Cr, Ti, Hf, Th, some alkali metals and rare earth elements, scarce in the Mn concretions or the plankton and mostly deposited as the principal components in clay minerals, showed a slight decline in concentration toward the surface, along with a negative correlation with I.L.

3.2 Horizontal and local distribution of elements

To obtaining information on the horizontal profiles of the elements, variation in their relative concentrations along the transect from Ado River to Ane River (from sites U to J) is given in Fig. 1.6. Although many elements showed slightly higher concentrations in the nearshore sediments along the eastern margin compared to the western (Tatekawa, 1979), the concentrations of some elements clearly increased from the shore to the central region, while others showed an inverse pattern. The elements could be arranged in the order of enrichment in the central region as follows : Hf (most depleted in the central region) < Na, K ≦ Rb, Ca, Sr, Cr, Ti, lanthanides except for Lu and Yb(nearly constant over the entire region) ≦ Yb, Lu ≦ Cs, Fe, Co, Ni, Sc, U, Th ≦ Sb, Br, P, Pb, Zn, Cu, I.L. < Mn, As(most enriched in the central region). This order is roughly similar to that of elements on the sediment surface (see Table 1.3).

Brief discussion on some elements is prsented as follows.

Mn, As, and probably Sb : The accumulation of these elements in the central deeper region should result from the same chemical properties of elements and mechanisms as those responsible for the vertical distribution of the elements. That is, the repeated dissolution-deposition cycles within the sedimentary column and bottom water must have carried the elements to the deeper part.

Zn, Cu and Pb : These elements also showed high concentrations in the offshore sediments although this was more pronounced for Pb in the upper 2cm layer. Among the elements, Zn and Cu exhibited similar horizontal profiles to that of I.L., especially in the upper layer, reflecting good correlation coefficients along the transect from sites U to J (Zn : 0.910, Cu : 0.948). Thus, the role of planktonic debris rich in these metals should also be emphasized in this case.

Alkali metals : The order of increasing concentration of alkali metals in the sediment from the central region compared with the nearshore sediment was identical to the order of increasing atomic numbers from Na to Cs ; that is, the concentration of Cs increased from the shore to the central region, while Na and, to a lesser extent, K showed an inverse pattern.

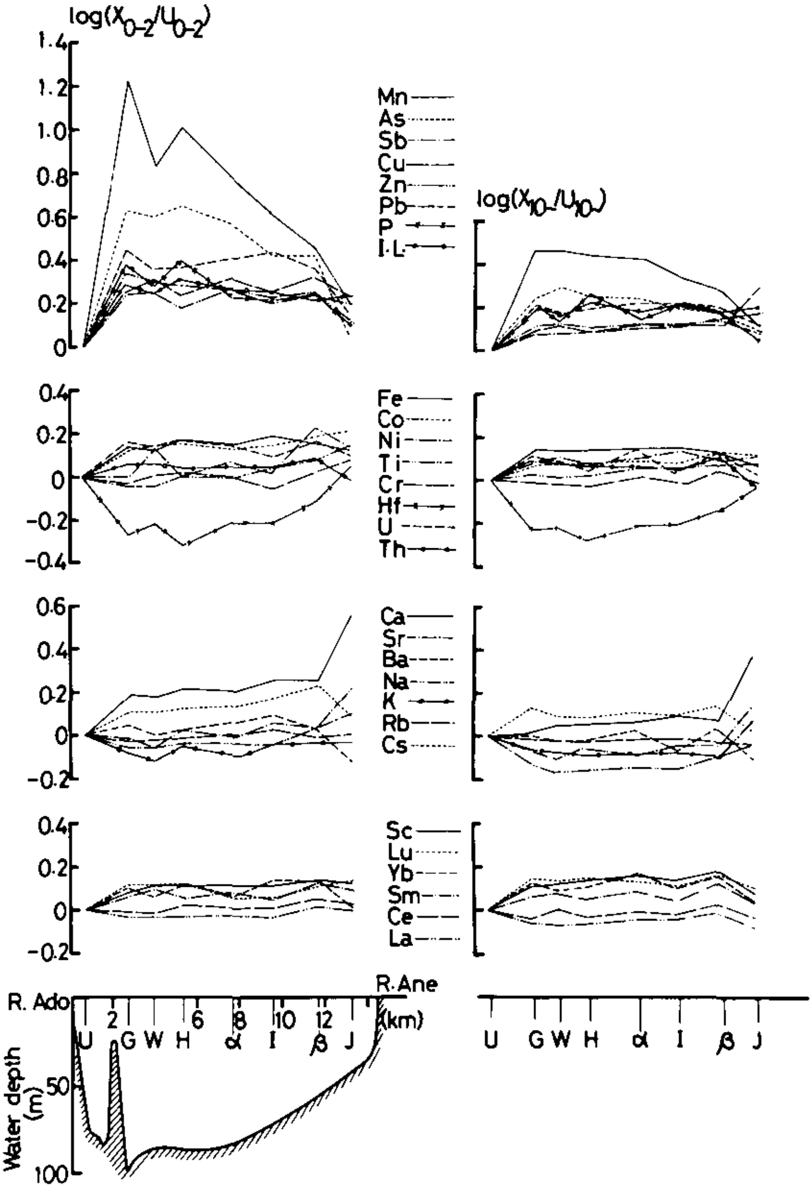

Fig. 1.6 Horizontal distribution of elements in the sediments along the transect from Ado River to Ane River

X_{0-2} and U_{0-2} show the elemental concentrations in the upper 2cm layers at each site and U, respectively. X_{10-} and U_{10-} show the elemental concentrations in the lower layers (below 10cm depth) at each site and U, respectively.

This order reflects the dissolution tendency of alkali metal ions from clay minerals and also the affinity for these ions to be incorporated into the sediment components from the water column. These processes may be controlled by ion-exchange processes because the decrease in the ionic radii of hydrated metals is recognized to induce a higher affinity of the metals for an ion-exchanger (Kakihana, 1970).

Lanthanides : The sediment from the central region showed an appreciable increase in the concentration of heavier lanthanides compared with the nearshore sediment ; namely, there was an increase in the ratio of the heavier lanthanides to the lighter ones from the shore to the central region. The ratio of soluble lanthanides vs. particulate ones is known to increase perceptibly from La to Lu in a river, although this ratio has the same low order (ca. 1.4%) for all the elements (Martin *et al.*, 1976). Therefore, it is likely that the particles deprived of heavier lanthanides settle near the shore and that the soluble fraction rich in heavier lanthanides remains longer in solution and is transported to the offshore before deposition. This process may be reflected by the higher (Yb+Lu)/(La+Ce) ratios observed in the plankton (0.036 ; see Table 4.1 in Chap. IV) and the Mn concretions (0.037) compared with those (0.028) in the bulk sediment (see Tables 1.1 and 1.2).

Hf : The Hf concentration decreased greatly from the shore to the central region, showing a high inverse correlation with Mn and the depth of the water. Hafnium shows a very low solubility of hydroxide ($K_{sp}=10^{-53.4}$; Sillén & Martell, 1964 ; see Appens. 18 and 19) and is insoluble in water (the maximum solubility is ca. 7.1×10^{-8}pg·kg^{-1} at pH 6). Also, this element cannot be reduced to a lower valence state in a natural environment. Therefore, most of this element should be deposited as a component of terrestrial clay minerals, as is supported by the fact that the ratio of elemental concentration in the Mn concretions or the plankton to that in the bulk sediment is lowest for Hf (0.36, 0.20 for the Mn concretions and plankton respectively ; cf. (Ti)0.58, (Th)0.55, (La)0.49 for the Mn concretions ; (Th) 0.26, (La)0.25 for the plankton). The Hf content in the sediment may be a promising indicator of the deposited amount of allochthonous matter.

The concentrations of 16 components in the upper 2cm layers of cores and the Ekman dredge sediments are illustrated on the map of Lake Biwa (Figs. 1.7 to 1.10) and the following comments may be made.

Zn, Cu, Pb and Hg : The high concentrations of Zn, Cu, Pb and Hg up to 899, 154, 311 and 1.42mg·kg^{-1} respectively were recorded for S-lake. An area of very high concentration, along with the southwestern margin of the lake extended as far as the outlet to the Seta River. These high concentrations should be the result of human activity, as pointed out by

Kurata (1978) and Tatekawa (1979, 1980).

Ca and Sr : The concentrations of these elements were higher on the eastern shore of N-lake than on the western side. This is related to the rich source of Ca and Sr from the calcareous bedrock in the watershed.

Mn and As : Pollution has not influenced the amount of either one of these elements, even in the surface sediments taken from the western shore of S-lake where the sediment should be the most contaminated by human activity. Therefore, the Mn and As accumulated in the offshore sediments of N-lake can be concluded to be mostly of natural origin.

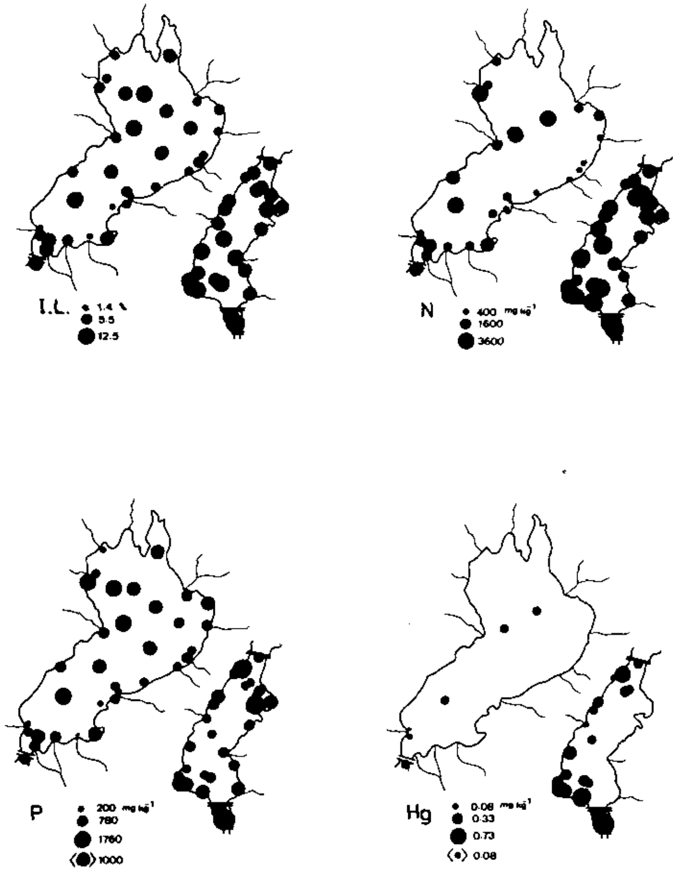

Fig. 1.7 Regional distribution of I.L., N, P and Hg in bottom surface sediments
⟨ ⟩ : content in the earth's crust.

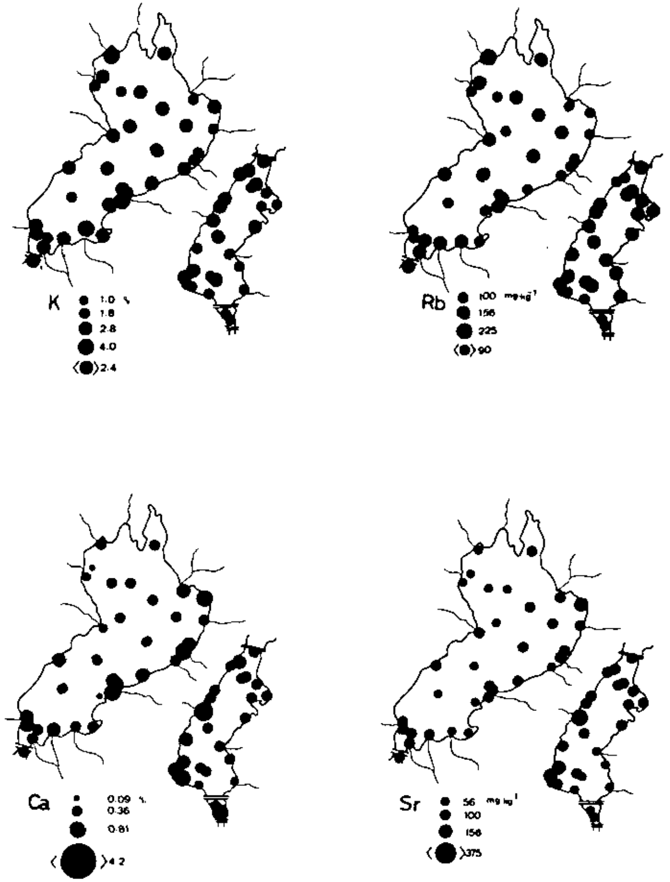

Fig. 1.8 Regional distribution of K, Rb, Ca and Sr in bottom surface sediments
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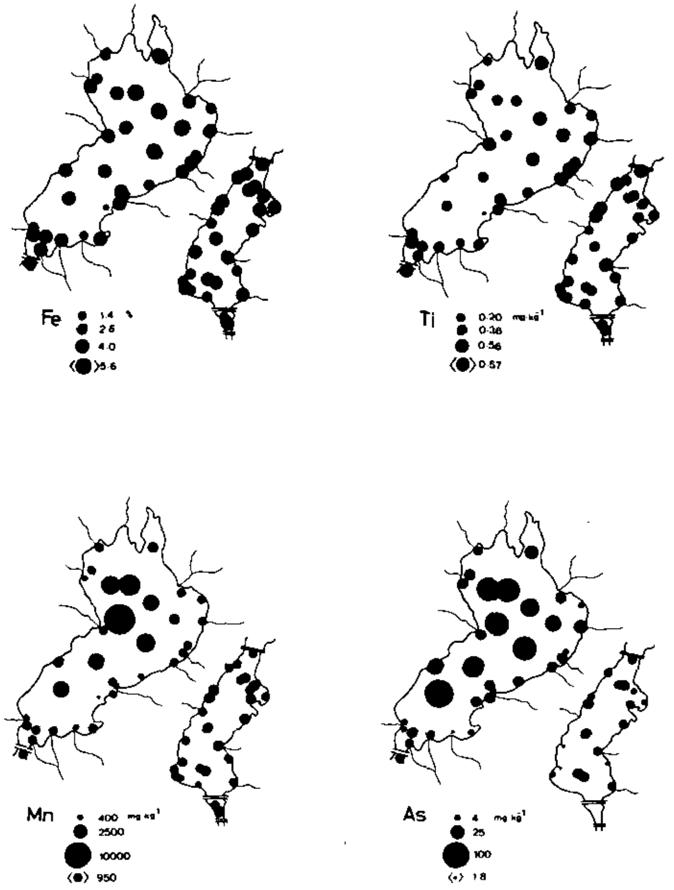

Fig. 1.9 Regional distribution of Fe, Ti, Mn and As in bottom surface sediments
〈 〉: content in the earth's crust.

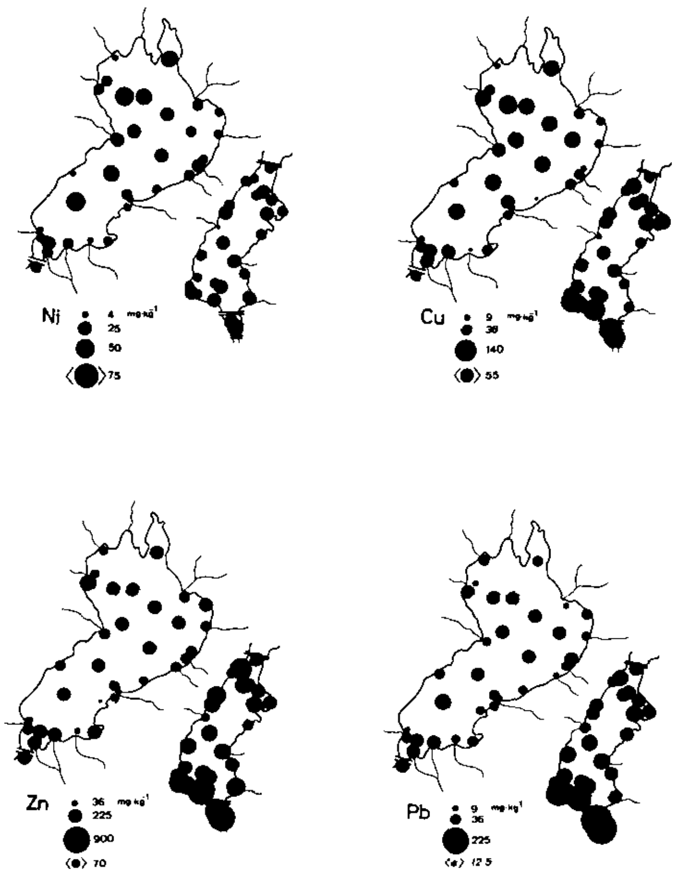

Fig. 1.10 Regional distribution of Ni, Cu, Zn and Pb in bottom surface sediments
〈 〉: content in the earth's crust.

CHAPTER II

The Role of Mn^{2+}-Rich Hydrous Manganese Oxide in the Accumulation of Arsenic in Lake Sediments

T. Takamatsu, M. Kawashima and M. Koyama

ABSTRACT

Arsenic is present at high concentrations in the upper layer of Lake Biwa sediments and shows a depth profile similar to that of Mn. Adsorption experiments of As onto synthetic hydrous Mn oxide (HMO) in the presence of Mn^{2+} and the speciation of Mn in the sediment cores, suggest that the accumulation of As at the sediment surface results from post-depositional migration of arsenite in the sediment pore water followed by oxidation to arsenate at the sediment surface and adsorption onto Mn^{2+}-rich HMO.

1. INTRODUCTION

Arsenic commonly accumulates in the uppermost layers of lake sediments. High concentrations have been found in Lake Washington (Crecelius, 1975) and in Loch Lomond (Farmer & Cross, 1979) with reported values of 210 and $474 mg \cdot kg^{-1}$ respectively in the upper 1cm of the sediments compared to concentrations of 12 and $18 mg \cdot kg^{-1}$ deeper down. In Lake Biwa, the concentration of As is also high in the uppermost layers of the sediment. For example, in the central basin, a concentration of $198 mg \cdot kg^{-1}$ As was found in the surface 2mm layer of the sediment compared to $25 mg \cdot kg^{-1}$ lower down (see Appen. 15 ; Takamatsu *et al.*, 1980b).

Up to the present time the fixation of As in lake sediments has usually been attributed to adsorption onto hydrous Fe oxide (Kanamori, 1965 ; Neal *et al.*, 1979 ; Farmer & Cross, 1979) because arsenate is chemically similar to phosphate and the role of hydrous Fe oxide in the P dynamics of aquatic environments is well recognized. This behaviour can be explained by the fact that hydrous Fe oxide has a pH_{pzc} (point of zero charge) of about 8.6 (Schott, 1977 ; Kinniburgh *et al.*, 1976) and so has a net positive surface charge in natural lake environments. In contrast, hydrous Mn oxide (HMO) has a pH_{pzc} of about 2.3 (Murray, 1974 ; McKenzie, 1981) and therefore carries a net negative surface charge at the pH of most lake sediments (pH 5 or greater). This suggests that HMO would not adsorb As. However, strong correlations between As and Mn in lake sediments have been observed suggesting that As is associated with Mn as well as Fe (Crecelius, 1975).

In this chapter, the role of Mn in the accumulation of As at the oxidised surface of L. Biwa sediments was demonstrated by studying both the adsorption of As onto synthetic HMO and the association of Mn and As in the sediment cores.

2. METHODS

Adsorption of arsenate onto synthesised HMO : HMO was prepared from the oxidation of manganous ion by permanganate (Murray, 1974). A solution (400ml) containing $KMnO_4$ (1.149g) and NaOH (0.368g) was slowly added to a solution (400ml) containing $MnCl_2 \cdot 4H_2O$ (2.159g) with constant stirring. The resulting suspension (δ-MnO_2, Murray, 1974) was filtered (Millipore CX-10) and washed successively with distilled water, Na_2SO_4 (0.2M), and distilled water, to remove excess K^+ and Mn^{2+} adsorbed on the oxide. Finally the suspension was diluted to 1 litre to give a stock suspension containing 1mg $Mn \cdot ml^{-1}$ as HMO. This stock suspension was well mixed before each experiment.

The effect of divalent cations on the adsorption of arsenate onto HMO was studied by the following procedure. A solution containing arsenate (5μg As) was added to a solution (40ml) containing the stock suspension of HMO (5ml) and one divalent cation (0 to 2mg) e.g. Mn^{2+}, Ni^{2+}, Sr^{2+} or Ba^{2+}. The mixed solution was adjusted to the desired pH with NaOH or HCl, diluted to 50ml with water and allowed to reach equilibrium by standing overnight with gentle stirring under a N_2 atmosphere. The solution was then filtered (0.45μm) to remove the HMO, the pH was measured and the concentration of As was determined by atomic absorption spectrophotometry.

Chemical forms of Mn in sediments : The sediment cores were separated into sections of desired length immediately after sampling. The wet samples were extracted sequentially to produce two fractions : (1) *exchangeable Mn* by extracting the sample with Na_2SO_4 solution (0.2M, 1 hour) and (2) *reactive Mn oxide* by extracting the residue from (1) with sodium dithionite solution (5%) adjusted to pH 6.5 with citrate buffer (0.2M). The residual Mn, which should be contained mainly within the crystal structure of unweathered primary minerals, was estimated by subtracting fractions (1) and (2) from the total concentration of Mn in the sample. The extractions (1) and (2) were performed in a polyethylene centrifuge tube with continuous mechanical shaking at room temperature. After each extraction, the leachate was separated by centrifugation followed by filtration. The residue was washed with a minimum volume of distilled water prior to the following extraction. Manganese concentrations in the leachates were determined by atomic absorption spectrophotometry. The total concentration of Mn was analysed after acid digestion with $HClO_4$-HF (Kawashima *et al.*, 1978).

3. RESULTS AND DISCUSSION

Profiles of As in the sediment cores from 3 sites (T, X and G) near the central basin (for site locations, see Fig. 1.1 in Chap. I) are presented in Fig. 2.1 (Takamatsu *et al.*, 1980b). Arsenic has accumulated to high concentrations in the thin surface layers (0–2 and 0–5mm depth). The sedimentation rate, 1.2 to 1.6mm·y^{-1} (Kamiyama *et al.*, 1982) suggests that the As-rich layers were deposited within the 4 years prior to sampling but no dramatic increase of As inflow to the lake has been observed for that period. On the other hand, the coincident depth profiles of As and Mn concentrations in the cores, (correlation coefficients, $r=0.986$, 0.930, 0.998 at sites T, X and G respectively) and As concentrations up to 721mg·kg^{-1} in Mn concretions (Chap. I; Takamatsu *et al.*, 1980b) suggest that the surface accumulation of As may result from a dissolution-deposition cycle within the sedimentary column associated with that known to occur for Mn.

The results of the adsorption experiments are shown in Fig. 2.2. In the absence of a divalent cation, no appreciable adsorption of arsenate onto HMO occurred between pH 6 and 8, a range often encountered in aquatic environments. On the other hand, there was a substantial increase in the amount of arsenate adsorbed by HMO in the presence of the

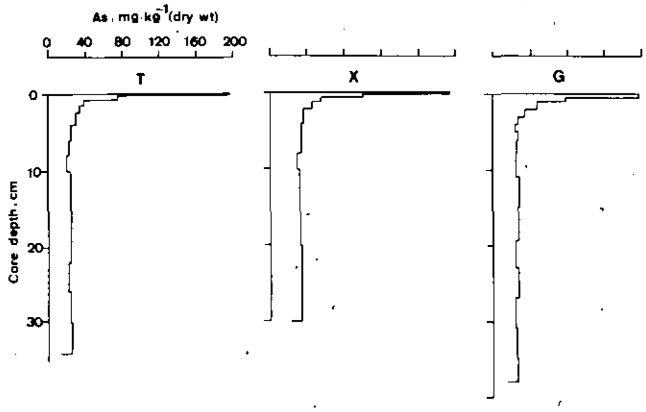

Fig. 2.1 Distribution of As in sediment cores from L. Biwa
Date of sampling : Aug. 1976–Nov. 1977. Water depth (m) : G 97, T 71, X 90.

divalent cations Mn^{2+}, Sr^{2+}, Ba^{2+} and Ni^{2+}. For example, when Mn^{2+} was added to the experimental solution of HMO prior to the addition of arsenate, quantitative adsorption of arsenate occurred up to pH 8. This result can be explained by a change in the surface charge of HMO due to the added cation. Divalent cations, such as Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, are adsorbed onto the HMO (Morgan & Stumm, 1964 ; Murray, 1975a ; Takematsu, 1979) and H^+ is released to solution by exchange of divalent cations with H^+ on the oxide surface. The amount of H^+ released was found to be about one mole for each mole of divalent cation adsorbed (Murray, 1975a ; McKenzie, 1979). Since the ratio of charge equivalents released to charge equivalents adsorbed was less than one, the adsorption of such cations should lead to a decrease in the negative surface charge, and finally to a positive surface charge on the HMO. This mechanism was confirmed by electrophoresis experiments (Murray, 1975b). Therefore, the HMO which is positively charged as a result of binding significant amounts of a divalent cation, has the ability to remove anions from solution.

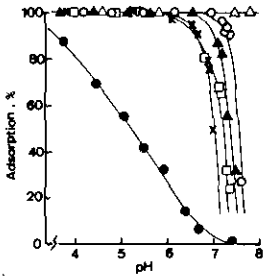

Fig. 2.2 Effect of divalent cations on the adsorption of arsenate onto HMO
HMO : 5mg Mn. Divalent cation : (●) none ; (○) Mn^{2+}, (▲) Sr^{2+}, (□) Ba^{2+}, (×) Ni^{2+}, 1mg for each ; (△) Mn^{2+}, 2mg. Arsenate : 5μg As. Total volume : 50ml. pH adjustment : HCl or NaOH.

Fig. 2.3 shows the fractionation of Mn obtained by extractions of the sediment cores. The samples analysed included three (G, X, T) from the central region and one (γ) from the shallow southern basin of the lake. The reactive Mn oxide was relatively enriched in the surface sediments. Its surface enrichment extended to a sediment depth of ca. 4cm in the southern basin and a depth of 1 or 2cm in the central region. Exchangeable Mn (Mn^{2+}) was depleted in the highly oxidised surface sediment (0–0.2cm layer) from the southern basin but the much higher concentrations of Mn^{2+} (up to 40% of total Mn) were found in the surface sediments from the central region. The bottom water and the sediment of the southern basin

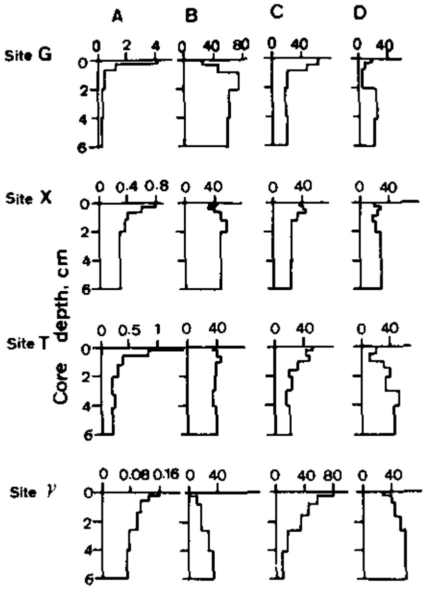

Fig. 2.3 Fractionation of Mn by sequential chemical extraction
A : total sediment concentration (%) of Mn ; B : exchangeable Mn/total Mn, % ;
C : reactive Mn oxide/total Mn, % ; D : 100−(B+C), %.

usually had higher levels of DO (and Eh) than those of the central region. The slow decrease of Eh values, observed just below the sediment surface of the southern basin, indicated that DO diffuses into the deeper layers of sediment in the southern basin compared to the central region (Kawashima *et al.*, 1978). This should bring about the differences in the distributions of Mn-species between two areas, though a small differences in the sedimentation rates (Kamiyama *et al.*, 1982) may be a minor factor. The coexistence of the abundant Mn^{2+} and Mn oxide in the surface sediments of the central region might contribute to the adsorption of arsenate onto HMO and cause the high surface concentrations of As in these sediments (see cores G, X, T on Fig. 2.1).

These results suggest the following mechanism for the surface accumulation of As (Fig. 2.4). Mn^{2+} continuously diffusing upward from the deeper reduced sediment forms a Mn^{2+}-rich layer of HMO on the oxidised sediment surface. The redox potential in the reduced sediment is near that of the As^{5+}–As^{3+} couple (Kawashima *et al.*, 1978) and part of the buried As is likely to be present as arsenite. In fact, Takamatsu *et al.* (1979a) found As present entirely as arsenate at the sediment surface but the ratio of arsenite to arsenate increased with depth. Therefore, it can be expected that arsenite dissolves easily in the pore water of reduced sediment due to the low content of sulfides in lake environments (Deuel & Swoboda, 1972). Manganese oxide is known to readily oxidise arsenite (Oscarson *et al.*, 1981) and arsenite which migrated to the sediment surface and came in contact with HMO would be rapidly oxidised to arsenate and adsorbed due to the positive surface charge induced by Mn^{2+}. The stability of the adsorbed As is likely to be increased by the formation of insoluble arsenate salts with Mn^{2+}, Ni^{2+} and the alkaline earth cations (K_{sp} Mn $10^{-28.7}$, Ba $10^{-50.1}$, Sillén & Martell, 1964 ; see Appen. 18).

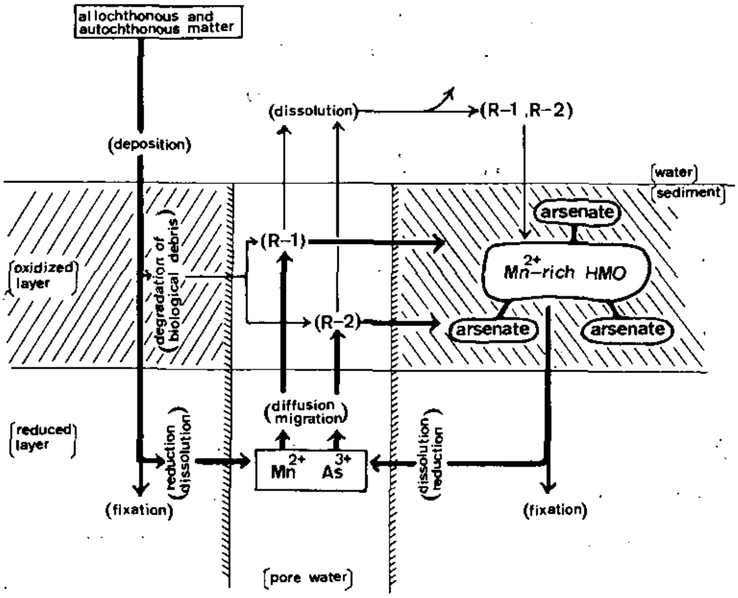

Fig. 2.4 Mechanism for the surface accumulation of As
R-1 : biological and/or catalytic oxidation of Mn^{2+} ; adsorption of Mn^{2+} onto HMO. R-2 : oxidation of arsenite to arsenate by HMO ; adsorption of arsenate onto Mn^{2+}-rich HMO.

High arsenic concentrations in Mn concretions from L. Biwa, is further evidence for the accumulation of As into the Mn^{2+}-rich HMO at the sediment surface.

We conclude that hydrous Mn oxides, positively charged from the adsorption of Mn^{2+} ions, could play a significant role in the accumulation of As on the surface of lake sediments.

CHAPTER III

Phosphate Adsorption onto Hydrous Manganese Oxide in the Presence of Divalent Cations

M. Kawashima, T. Hori, M. Koyama and T. Takamatsu

ABSTRACT

Previous studies showing the ability of hydrous Mn oxide (HMO) to adsorb arsenate at near neutral pH in the presence of divalent cations have been extended to examine the interaction of this oxide with phosphate. Alkaline earth cations, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, and transition metal ions, Mn^{2+}, Co^{2+}, Ni^{2+}, cause HMO to strongly adsorb phosphate between pH 6 and 9 depending on the cation. The effectiveness of the alkaline earth cations to cause P adsorption was $Ba>Sr>Ca>Mg$, which is the same order as their affinities for the oxide. Changes with time were found in the abilities of the transition metals to cause P adsorption onto HMO and this may be due to conversion of the adsorbed cation to its oxide.

1. INTRODUCTION

Phosphate which exists as $H_2PO_4^-$ and HPO_4^{2-} in most freshwaters can be rapidly removed from aerobic solutions by adsorption onto inorganic substances. Hydrous Fe (III) oxide, hydrous Al oxide and clay minerals are thought to be the only important adsorbents for phosphate since all these substances have positive surface charges at slightly acid to neutral pH and therefore high affinities for anions(Stumm & Morgan, 1970). On the other hand, hydrous manganese oxide (HMO) has negative surface charge at near neutral pH, i.e. its pH_{pzc} (point of zero charge) is about 2.3 (Murray, 1974 ; McKenzie, 1981), and has not been thought to adsorb anions. It does, however, have a high capacity to adsorb cations.

In the previous chapter HMO in a solution containing divalent cations, such as Mn^{2+}, Ni^{2+} and the alkaline earth cations, was shown to adsorb As at near neutral pH. It was concluded that the fixation of arsenate in the oxidised surface sediment of Lake Biwa could be partly due to the adsorption of arsenate onto HMO in the presence of Mn^{2+}.

In the present study the ability of HMO to adsorb phosphate at near neutral pH was examined. In particular, different divalent cations and the change of phosphate adsorption with time were considered in an attempt to further elucidate the adsorption mechanism.

2. MATERIALS AND METHODS

Hydrous manganess oxide was prepared by oxidising Mn (II) with permanganate in alkaline solution (Murray, 1974). The HMO was then washed with Na_2SO_4 (0.2M) and water to remove adsorbed K^+ and Mn^{2+} (Chap. II). No coagulation of the stock suspension occurred for at least three months. The HMO suspension was standardised by atomic absorption spectrophotometry after dissolving an aliquot in ascorbic acid solution.

The adsorption experiments were performed as follows : HMO suspension, phosphate and the divalent cation were added in this order to the buffer solution contained in a teflon beaker. The HMO suspension was ultrasonicated just before use. After standing for a selected time (20 hours for equilibrium experiments or 5 min, 2 and 6 hours for kinetic experiments) at a constant temperature (25°C), the solution was filtered (0.45μm Millipore). The pH of the filtrate was measured. The precipitates on the filter was dissolved with ascorbic acid (0.2M) and phosphate in this solution was measured spectrophotometrically (Murphy & Riley, 1962). When necessary, phosphate in the filtrate was also determined. In experiments involving Ba^{2+}, this cation was removed as $BaSO_4$ by centrifuging before measuring phosphate.

The divalent cation solutions were prepared from the corresponding chloride salts and standardised by atomic absorption spectrophotometry.

3. RESULTS

Fig. 3.1 shows the percent (%) adsorption of phosphate onto HMO as a function of pH. In the absence of divalent cations, HMO did not adsorb phosphate at near neutral and alkaline pH (Fig. 3.1a) but some phosphate was adsorbed as the solution became more acid. Addition of alkaline earth cations, e.g. Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} (Fig. 3.1a) increased the percent adsorption of phosphate with a maximum near pH 6.5. Preliminary experiments showed that alkaline earth metal phosphates do not precipitate below pH 10 under these conditions, i.e. phosphate (3.2×10^{-6} M) and cations (2×10^{-4} M).

Transition metal ions were also effective in causing the adsorption of phosphate onto HMO at near neutral pH (Fig. 3.1b) although the adsorption curves obtained were sharper and displaced to higher pH than those obtained for the alkaline earth metals.

The effectiveness of the alkaline earth cations to promote adsorption of phosphate onto HMO appears from the data on Fig. 3.1 to be Ba>Sr>Ca>Mg. This was confirmed by

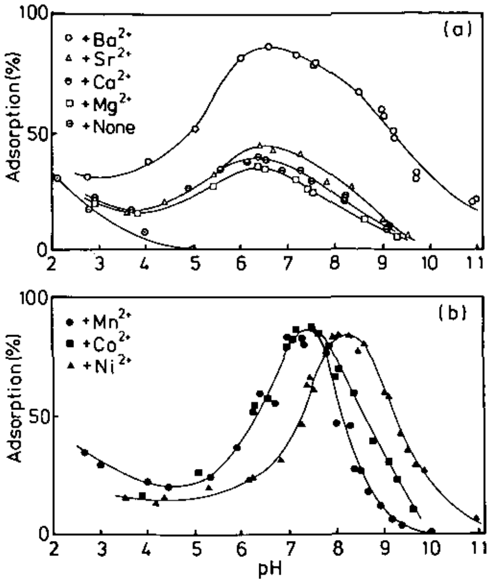

Fig. 3.1 Effects of alkaline earth (a) and transition metal ions (b) on the adsorption of phosphate onto HMO
HMO : 3.6×10^{-4}M. Phosphate : 3.2×10^{-6}M. Metal ion : 2×10^{-4}M. Buffer solution : 0.01M Na-acetate or NH_3-NH_4Cl. Aging time : 20h (25°C).

experiments carried out at constant total cation concentration. The results in Fig. 3.2 show that at all concentrations of phosphate in solution the amount of phosphate adsorbed on a given amount of HMO were greatest for the addition of Ba^{2+} and least for Mg^{2+}.

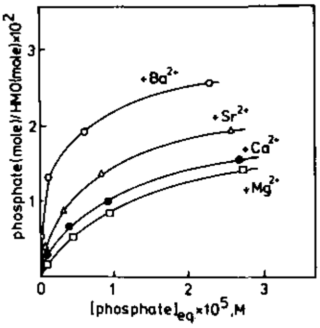

Fig. 3.2 Adsorption isotherm for phosphate in the solution of the constant alkaline earth cation concentration
Metal ion : 2×10^{-4}M. pH : 6.5 (0.005M acetate buffer). Aging time : 20h (25°C).

In the absence of HMO, the precipitation of phosphate by the transition metals was examined as a function of pH (Fig. 3.3). Loss of phosphate from solution or the formation of $Ni(OH)_2$ was not detected at any time after the addition of Ni^{2+}. Five minutes after adding Co^{2+} a high proportion of the phosphate was precipitated between pH 9 and 11 but after standing for 20 hours the percent of phosphate adsorbed had decreased at pH$>$9.1 and increased between pH 8.7 and 9.1. A light-blue precipitate of $Co(OH)_2$ formed at pH$>$8.5 after 5 minutes, but after standing for 20 hours the precipitate in solutions with pH 9 turned brown. The addition of Mn^{2+} also caused adsorption of phosphate after 5 minutes reaching almost 100% at pH 10. A brown precipitate, presumably HMO, formed in this solution. After 20 hours, however, the percent adsorption of phosphate was zero at pH 10 and the maximum was only 10% occurring at pH 9.

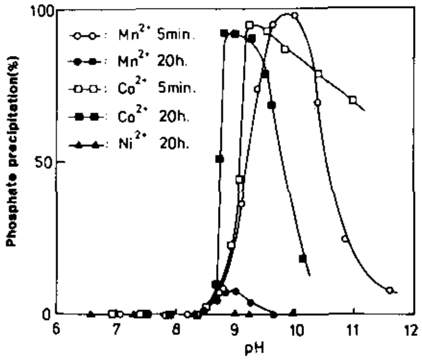

Fig. 3.3 Interaction between phosphate and transition metal ions as a function of pH Phosphate : 3.2×10^{-6}M. Metal ion : 2×10^{-4}M. Buffer solution : 0.01M Na-acetate or NH_3-NH_4Cl. Aging time : 5min or 20h (25°C).

The adsorption of phosphate onto HMO in the presence of divalent cations was examined as a function of time. With added Sr^{2+} (Fig. 3.4a) no change in the percent adsorption was found between 2 and 20 hours. In contrast to this, at pH$>$7.5 for Mn^{2+} and Co^{2+} and pH$>$8 for Ni^{2+} phosphate adsorption decreased with time (Figs. 3.4b, c, d).

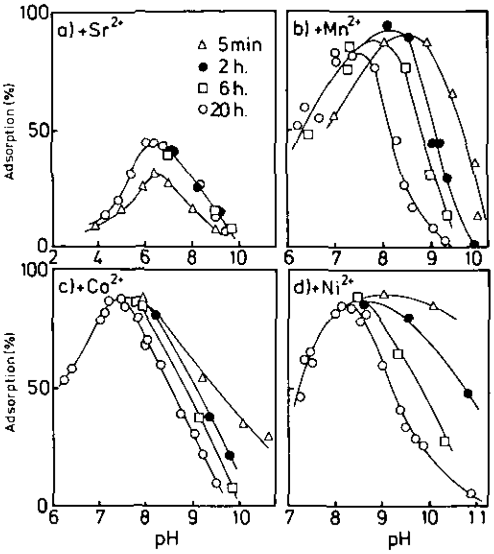

Fig. 3.4 Time dependence of the phosphate adsorption on HMO after addition of Sr^{2+} (a), Mn^{2+} (b), Co^{2+} (c) and Ni^{2+} (d)
Phosphate : 3.2×10^{-6}M. HMO : 3.6×10^{-4}M. Metal ion : 2×10^{-4}M. Temp : 25°C.

4. DISCUSSION

The results obtained in this study for phosphate are similar to those found previously for arsenate (Chap. II). It was suggested in the earlier chapter that the surface charge on HMO, normally negative at near neutral pH, was reversed by exchange of H^+ on the HMO surface for divalent cations from solution. A positively charged surface thus resulted leading to the adsorption of arsenate onto the HMO. A similar mechanism seems likely for phosphate with all the divalent cations tested showing the ability to cause substantial phosphate adsorption onto HMO. At pH<5 less than 50% of phosphate in solution was adsorbed in the presence of divalent cations, but for arsenate the corresponding figure (see Fig. 2.2 in Chap. II) was 100%. This difference appears to arise from a much higher affinity of arsenate for HMO at acid pH in the absence of divalent cations. For example, at pH 4 approximately 10% adsorption of phosphate occurred (Fig. 3.1a) while 80% of arsenate was adsorbed under these conditions.

The order of the effectiveness of alkaline earth metal ions to cause adsorption of phoshate onto HMO was $Ba^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}$. This order is the same as the order of affinity of the alkaline earths themselves for HMO (Posselt *et al.*, 1968 ; Murray, 1975a).

The adsorption behaviour of these cations was attributed to the size of the hydrated radii, $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$, and the ability of the smaller ions to approach closer to the active surface of HMO. A higher charge density would result with the smaller ions and this is likely to favour adsorption of anions.

The adsorption of cations onto HMO is favoured by increasing pH (Murray, 1975a) and the adsorption of phosphate also increased from pH 3.5 to approximately pH 7. Above this pH, however, mechanisms operate to reduce the phosphate adsorption onto HMO. Either the phosphate in solution changes form e.g. complexes with the cation to produce an ion with positive charge, or the surface charge on the HMO becomes less positive and finally reverses. The first of these possibilities is unlikely because any complexes formed will probably be anionic. The most likely reason for the decrease in phosphate adsorption with increasing pH in the presence of the alkaline earth cations is competition from hydroxide ions either by preferential adsorption in place of phosphate or by the formation of hydroxy complexes e.g. $Ca(OH)^+$, and hydroxides on the surface of the HMO. The time course experiments showed no change with time after an initial 2 hour period in the percent adsorption of phosphate onto HMO in a solution containing Sr^{2+}. This is consistent with the formation of stable hydroxy complexes and hydroxides above pH 7.

A similar pattern was found with the transition metals ; phosphate adsorption decreased with increasing pH. Unlike the results for Sr^{2+}, however, the percent adsorption at alkaline pH in the presence of the transition metals decreased with time. The decrease with increasing pH for Co and Ni is probably due to the formation of hydroxy complexes and hydroxides on the surface of HMO. The decreasing adsorption with time could be explained by the hydroxides of these two metals changing to the oxides, CoO and NiO, which may reduce even further the tendency of phosphate to adsorb to the HMO surface. The initial formation of $Co(OH)_2$ in the absence of HMO and its subsequent change to a brown precipitate (probably CoO) at alkaline pH is evidence for the proposed mechanism. In the solution containing Co without HMO, the increase with time of phosphate adsorption between pH 8.7 and 9.1 does not have an obvious explanation. Perhaps some of the initially formed $Co(OH)_2$ slowly reacts with the phosphate in solution to form an insoluble substance, whereas at higher pH CoO is formed. When Mn^{2+} was added to an alkaline solution containing phosphate, HMO formed immediately. The excess Mn^{2+} in solution generated a positively charged surface on the HMO and phosphate was adsorbed. With time, the surface adsorbed Mn^{2+} was oxidized autocatalytically by O_2(Stumm & Morgan, 1970) and phosphate then released back into solution. The same mechanism explains the decrease in phosphate adsorption with time in an alkaline solution containing added HMO and Mn^{2+}.

In most freshwaters, Ca^{2+} and Mg^{2+} are present at concentrations similar to those used in this study, suggesting that HMO could act as a scavenger of phosphate in lakes. This was confirmed by the addition of HMO to filtered (0.45μm) Lake Biwa water (Ca^{2+} : 2.5×10^{-4} M, Mg^{2+} : 8×10^{-5} M). HMO in the presence of divalent cations could, therefore, be an important adsorbent of anions in natural aquatic systems. In lakes, this will be most important in the oxidised surface sediment, because the formation of HMO usually occurs here from the oxidation of Mn (II) which has diffused upward from the reduced sediment. Total phosphorus often shows a marked increase in concentration toward the sediment-water interface (e.g. see Appen. 15) and this is considered to be due to the upward migration of dissolved phosphorus from the reduced layer, followed by precipitation in the oxidised layer (Carignan & Flett, 1981). The results of this study suggest that HMO in the presence of divalent cations could be at least partly responsible for this precipitation. The fixation of arsenate into the surface sediment was suggested to result partly from the adsorption of arsenate onto Mn^{2+}-rich HMO (Chap. II). Although hydrous Fe (III) oxide, hydrous Al oxide and clay minerals are important adsorbents of phosphate in natural waters, the present study demonstrates a new role for hydrous manganese oxide as an adsorbent of anions.

CHAPTER IV

The Role of Biological Debris in the Removal of Zn and Cu from a Water Column

T. Takamatsu, M. Kawashima and M. Koyama

ABSTRACT

The fine depth prefiles of Zn, Cu, Pb and Hg are distinct from one another in metal-rich upper sediment. Although the source of these elements should be attributed to human factors, a process has been proposed in relation to the difference between the fine profiles of Zn and Cu. These possibly result from the deposition of planktonic debris rich in these metals and their viability during the early-degradation of debris and the subsequent slower process of humification.

1. INTRODUCTION

As shown in Chap. I, Zn, Cu, Pb and Hg were enriched in the upper layers of sediment and had characteristic depth profiles. The increased levels of these elements (except Zn) reached to a 4-5cm depth in the offshore sediments of the northern lake (N-lake). According to the sedimentation rates of 1.2-1.6mm/y observed in the central region of N-lake (Kamiyama *et al.*, 1982), a sediment depth of 4-5cm corresponds to sediment deposited 30-40 years ago. In the southern lake (S-lake) sediment, the metal-rich layers were 15-25cm in depth and enrichment of the metals must have begun more than 60 years ago, judging from the sedimentation rate of 2.4mm/y in that area (Kamiyama *et al.*, 1982). As pointed out for this lake (Kurata, 1978 ; Tatekawa, 1979, 1980) and many others (Taylor, 1979 ; Nriagu *et al.*, 1979 ; Wahlen & Thompson, 1980), the increase in anthropogenic metal fluxes in the lake may be the most plausible explanation for the increased levels of the metals because the watershed of S-lake was land-developed, populated, and industrialized much earlier than that of N-lake.

However, the detailed profiles of the elements are distinct from one another even in the metal-rich upper sediments possibly due to differences in the removal process of elements from the water column and subsequent dissolution and fixation mechanisms in the sedimentary column.

2. MATERIALS AND METHODS

Phytoplankton was collected with a plankton net (NXX 25) from S-lake on 9 Oct. 1980 and a submerged plant, *Vallisneria Biwaensis*, was taken from Seta River on 12 Sept. 1980. The plankton consisted of *Staurastrum* (97.2%), *Closterium* (1.27%), *Pediastrum* (0.86%), *Melosila Italica* (0.35%), and *Gloeocystis* (0.33%). After the samples were air-dried and dried again at 80°C for 5h, they were analysed by neutron activation and X-ray fluorescence in a similar manner to that for the sediments (Appens. 3 and 4 ; Takamatsu, 1978 ; Takamatsu *et al*., 1982b).

The analytical data on the sediments used were those determined in Chap. I.

Acid-leachable sulfide-S was determined as described previously (Kawashima *et al*., 1978).

Humic acid in the sediment was determined according to the method of Ohba (1964).

3. RESULTS AND DISCUSSION

Fig. 4.1 shows the distribution of elements in the upper 10cm of the cores at sites G and T (for site locations, see Fig. 1.1 in Chap. I), along with the profiles of humic acid and sulfide. Zinc, as in the case of Mn and As, exhibited a sharp decrease in concentration from the surface to a 2cm depth but was nearly constant in concentration at a deeper zone. Copper also showed a maximum concentration at the surface. Its concentration decreased rapidly from the surface to a 1cm depth and was generally constant from a 1 to 2cm depth (this constant level corresponds to ca. 50% excess above the base level). The concentration of Cu was the same as the base level at a 4-5cm depth. Although the concentration of Pb was markedly reduced on the surface, there was a significant increase in concentration at a depth of ca. 1cm. Below 1cm depth, the concentration of Pb decreased rapidly and reached to the base level at a 4-5cm depth. Obviously the individual profiles of Zn, Cu and Pb differ from one another.

The concentrations of elements in phytoplankton and the submerged plant from Lake Biwa are given in Table 4.1. The ratios of the concentrations of elements in the aquatic organisms exceeding the average base concentrations of elements in the N-lake sediments (below 10cm depth) are indicated in the Table, and show a significant enrichment of Cu and Zn in the organisms, compared to the sediments.

In previous studies, similar increased levels of Zn, Cu and Pb were found in diatom

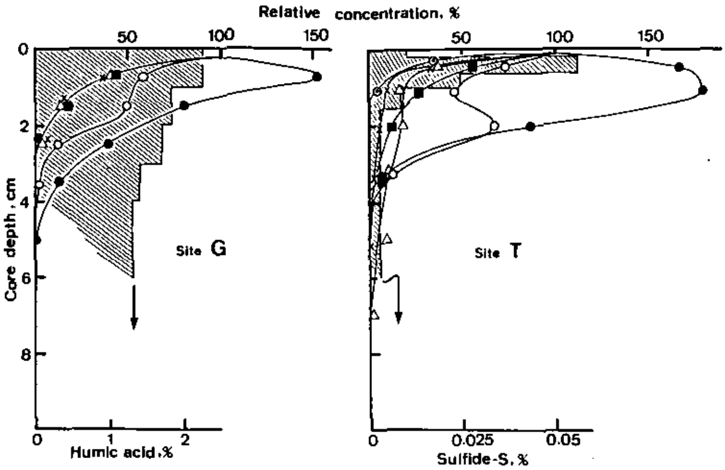

Fig. 4.1 Fine profiles of elements in the sediment cores from offshore areas of the northern lake

Excess concentrations of elements in the uppermost layer above the average concentrations of elements in the lower layers (below 10cm depth) were taken as 100%. (●) Pb ; (○) Cu ; (■) Zn ; (△) Mn ; (×) As ; (⊙) I.L.

(*Asterionella*) from Lake Windermere and it was suggested that biological uptake plays a major role in the process of the deposition of metals in the lake system (Kemp *et al.*, 1976 ; Lund, 1957 ; Taylor, 1979). The accumulation of metals (11 metals including Zn, Cu and Pb) by phytoplankton has been also reported in Lake Biwa (Kurata, 1982), though the reported concentrations are much higher than those in this study. In addition, phytoplankton is generally recognized as a major source of sedimentary organic matter (Ishiwatari, 1973 ; Jackson, 1975 ; Cranwell, 1976). Thus in Lake Biwa, we can assume that large fractions of Zn and Cu settle on the lake bottom in association with planktonic debris. After precipitation, most of the Zn and a fraction of the Cu are released within the upper thin layer of the sediment due to early microbial degradation of the debris ; this coincides to the rapid decrease in I.L. observed from the surface to a 2cm depth. However, the organic residues, which are resistant to early-degradation, cause the subsequent slower process of humification (Kemp & Johnston, 1979). During this humification, Cu, known to be strongly bound to humic materials (Takamatsu *et al.*, 1983b, 1983c), remains in the sedimentary humates and accounts for ca. 50% of the excess Cu initially observed on the sediment surface. However, Zn cannot withstand diagenesis because of the low stability of humate. These observations are supported by the following facts : (1) Humic materials

Table 4.1 Elemental concentrations of phytoplankton* and leaves of *Vallisneria Biwaensis*** and the ratio of these to the elemental concentrations of the sediment***

Element	Phytoplankton		*Vallisneria Biwaensis*	
	Concn.	Concn. ratio	Concn.	Concn. ratio
	%		%	
Na	0.25	0.29	1.88	2.19
Fe	1.00	0.22	0.15	0.03
K	1.03	0.41	8.08	3.24
Ca	0.28	0.82	0.96	2.83
	$mg \cdot kg^{-1}$		$mg \cdot kg^{-1}$	
Mn	258	0.14	3500	1.88
Ni	7.8	0.26	6.7	0.22
Cu	155	2.98	22.1	0.43
Zn	225	1.67	343	2.54
Pb	19.3	0.60	6.1	0.19
Co	4.0	0.23	5.0	0.28
Cr	16.8	0.24	N.D.	-
As	21.1	0.92	2.1	0.09
Sb	0.63	0.33	0.46	0.24
Sc	2.90	0.20	0.21	0.01
Rb	33.6	0.24	20.2	0.15
Cs	2.1	0.19	N.D.	-
Sr	24.3	0.32	43.2	0.57
Ba	451	0.66	183	0.27
Sm	1.85	0.22	0.23	0.03
Ce	19.6	0.23	3.6	0.04
Yb	1.02	0.33	N.D.	-
Lu	0.10	0.20	N.D.	-
Hf	1.05	0.20	N.D.	-
La	11.1	0.25	1.38	0.03
Br	6.5	0.93	26.0	3.71
U	1.3	0.38	N.D.	-
Th	4.31	0.26	0.54	0.03

Values are based on materials dried at 80°C for 5 h.

N.D. : not detectable.

* Phytoplankton was collected with a plankton net (NXX25) from the southern lake on 9 Oct. 1980 ; species : *Staurastrum* 97.2%, *Pediastrum Biwae* 0.86%, *Closterium* 1.27%, *Gloeocystis* 0.33%, *Melosila Italica* 0.35%.

** *Vallisneria Biwaensis* was collected from the Seta River on 12 Sept. 1980.

***Average concentrations of elements in the lower layers (below10cm depth) of the sediment cores from the northern lake.

(humic acid) have been found at a concentration exceeding 1% throughout the core although the concentration of sulfide, another significant scavenger of metals, is less than $100\text{mg}\cdot\text{kg}^{-1}$ below a 1cm depth. (2) Humic materials extracted from lake and marine sediments showed a higher concentration of Cu than that in the sediments (Nissenbaum & Swaine, 1976 ; Nriagu & Coker, 1980).

The early-degradation of biological debris may not be responsible for the characteristic profile of Pb since the concentration of Pb was found to be low in the organisms. In recent studies, Pb has been found to be adsorbed much more strongly than any other divalent cation on hydrous Fe oxide and clay minerals (Coggins *et al*., 1979 ; Naruse *et al*., 1979) and transported in rivers mostly in association with the oxide fraction of the suspended matter (Tessier *et al*., 1980 ; Florence, 1977). Therefore, some other inorganic process should be considered to account for the removal of Pb from the water column and its subsequent fixation in the sediment.

CHAPTER V

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

T. Takamatsu, R. Nakata, T. Yoshida and M. Kawashima

ABSTRACT

Three sediment cores were collected from Lake Biwa, and analysed for their dimethylarsinate (DMA), monomethylarsonate (MMA), and inorganic arsenic (I-As) content. We used an analytical technique that 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$\mu g \cdot kg^{-1}$) and MMA (20.8-44.1$\mu g \cdot kg^{-1}$) 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 & Wolfe, 1971 ; Cullen *et al.*, 1979 ; Andreae & 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 & Foreback, 1973 ; Shaikh & 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 & Alexander, 1973 ; McBride & 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.*, 1982c), the depth profiles of DMA and MMA have never been described for lake sediments.

2. MATERIALS AND METHODS

Three sediment cores (A, B and C) were collected from the central region of Lake Biwa where the accumulation of arsenic on the sediment surface had been observed previously (Chaps. I and II ; Takamatsu *et al.*, 1980b). The cores A and B were taken on 5/28, 1982 and C on 12/15, 1981. The site locations of the cores A, B and C correspond to those of sites G, T and E (see Fig. 1.1 in Chap. I) respectively. A gravity corer, consisting of a plastic core liner (3.5cm 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. 0.2cm 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 5cm 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, 1982c). The analytical procedures for DMA, MMA, and inorganic arsenic (I-As) determination are therefore only briefly outlined.

The sediment sample (1-5g) was extracted with a 5-fold volume (5-25ml) of 10M HCl by shaking mechanically at 30°C for 1h. A desired aliquot (up to 12.5ml) of extract was taken and 4.15g of KI, water and HCl were added to prepare a 25ml solution containg 1M KI and 5M HCl. Arsenic compounds including DMA, MMA, and I-As were extracted with 10ml of benzene (twice). Then, arsenic compounds were back-extracted with 5ml of water containing H_2O_2 (twice). After the aqueous phases were neutralized with $NaHCO_3$, the solution was washed with 5ml of benzene (twice). A portion of this solution was applied to an anion-exchange column (10mm i.d.×115 mm, Dowex 1×4, 200-400 mesh, acetate-form). DMA, MMA, and I-As were separated by eluting successively with 0.1% CH_3COOH, 5% CH_3COOH, and 1M HCl at a flow rate of ca. 20 drops/min and collected in 130-drop fractions. The eluates were subjected to arsenic analysis by flameless atomic absorption spectrophotometry, after adding $Mg(NO_3)_2$ 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.*, 1983a). The good accuracy of analytical results has been also supported by the recoveries (91-103%) of arsenic compounds spiked in the soil extracts (Takamatsu *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

Fig. 5.1 shows the chromatographic separation of arsenic compounds in the extracts from the the uppermost (0-0.5cm) layers of the cores. The elution patterns consisted of clear 4 peaks and were quite similar to those of arsenic compounds in the soil and pond sediment extracts (Takamatsu *et al.*, 1982a , 1982c). Three peaks were found to correspond to DMA, MMA, and I-As. The other peak (X) was assigned to the new 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.

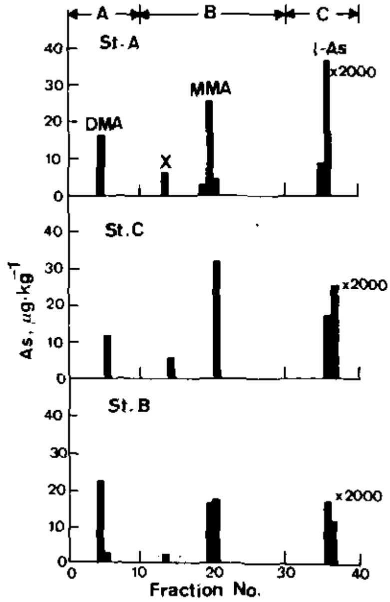

Fig. 5.1 Chromatographic separation of arsenic compounds extracted from the 0-0.5cm layers of the cores

Column : 10mm i.d.×115mm, Dowex 1×4, 200-400 mesh, acetate-form. Eluent : A 0.1% CH_3COOH, B 5% CH_3COOH, C 1M HCl. Flow rate : 20 drops/min. Fraction volume : 130 drops/fraction.

The analytical data are presented in Table 5.1. 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.*, 1982c) appeared to have higher concentrations of MMA (20.8-44.1μg·kg^{-1}) than DMA (undetectable-24.7μg·kg^{-1}).

Typical arsenic profiles were observed in the core from site A (Fig. 5.2). 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 (Chaps. I and II ; Takamatsu *et al.*, 1980b). 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 (see Chap. II). 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 (0-2cm) 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, i.e. bacterial or fungous process and algal process, 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 methylcobaramin (McBride & 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. $CH_3As^{3+}O(OH)_2 \rightarrow (CH_3)_2As^{1+}O(OH)$ in M-1 or $CH_3As^{5+}O(OH)_2 \rightarrow CH_3As^{3+}(OH)_2$ in M-2. Therefore, the pathway from MMA to DMA might be relatively accelerated in sediment layers at a depth of 0.2-2cm where the lowest redox potential was recorded although the production of MMA and DMA by microorganisms may be promoted by the large amount of carbon in the surface sediment (Takamatsu *et al.*, 1982a , 1983a). 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. $As^{3+}O(OH) \rightarrow CH_3As^{3+}O(OH)_2$, involves no redox process and that in M-2, i.e. $As^{3+}(OH)_3 \rightarrow CH_3As^{5+}O(OH)_2$, *is an oxidation process with respect to arsenic atoms. In addition, since the*

Table 5.1 Concentrations* of arsenic compounds in the sediment cores from Lake Biwa

Site	Depth (cm)	DMA	MMA	X	I-As	T-As	Carbon
		$\mu g \cdot kg^{-1}$			$mg \cdot kg^{-1}$		%
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 $\mu g \cdot kg^{-1}$)

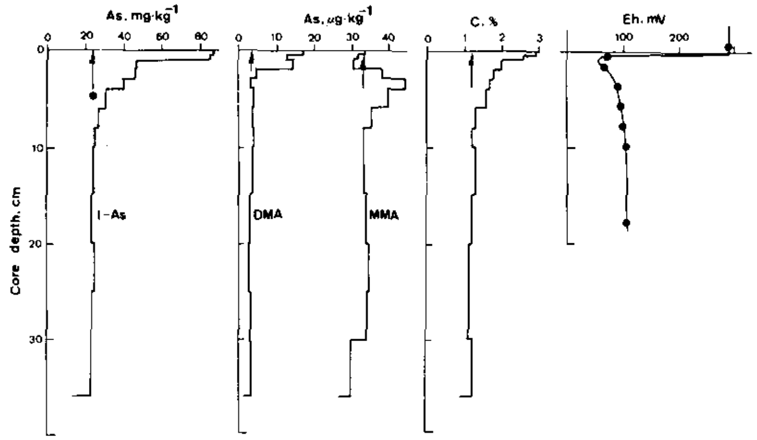

Fig. 5.2 Depth profiles of arsenic compounds in the core from site A
* : base concentrations (averages in 10-35cm layers).

concentration of arsenite (reactant of the above process) detected in the reduced sediment, e.g. 7.9mg·kg^{-1} As in the 0.5-2cm layer and 4.3mg·kg^{-1} As in the 2-4cm layer (Takamatsu *et al.*, 1979a), 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. 0.2cm) oxidized layer, should result in depletion of MMA in the upper 2cm 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. In the soils, the amount of DMA increased and that of MMA decreased with lowering the redox potential under flooded conditions although the total concentration of methylated-arsenic compounds was approximately constant. (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 those algal cells (Andreae & 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 : DMA>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 (dithiocabamate) 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 3-3.5cm because the sedimentation rates at the lake bottom near site A are 1.2-1.4mm/y (Kamiyama *et al.*, 1982). However, the increased concentrations of MMA above its base levels are extending to the deeper zone (ca. 8cm depth) of the core and the upper 2cm sediments which deposited within the recent ca. 15 years contain less amounts of MMA compared to the deeper sediments. Therefore, we 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 10cm sediment may play a significant role in determining the behavior of arsenic in bottom water and sediment.

CHAPTER VI

Redox Cycle of Manganese and Iron and the Circulation of Phosphorus in a Dredged Area of the Southern Lake

M. Kawashima, T. Hori, M. Koyama and T. Takamatsu

ABSTRACT

The vertical distribution of temperature, disolved oxygen (DO), manganese, iron, phosphorus, silicate, ammonium, nitrate, sulfate and sulfide was investigated in a dredged area of the eutrophic southern lake, Lake Biwa (period : 1981-1982). The reducing conditions in the hypolimnion proceeded with decrease in the relative electron activity ($p\varepsilon$) are as follows : (1) consumption of DO - reduction of hydrous Mn oxide (accumulation of ammonium), (2) reduction of nitrate, (3) reduction of hydrous Fe oxide (release of phosphate and silicate), and (4) production of sulfide.

Immediately above the front of DO (i.e. the lewest epilimnion), clear peaks of particulate Mn and Fe, which were separated each other, were observed. The persistence of these peaks is attributed to the rotation of the "manganous wheel" and the "ferrous wheel" between the lower epilimnion and hypolimnion. The "manganous wheel" with a small radius rotated more rapidly than the "ferrous wheel" with a big radius. The precipitation of Mn in the lower epilimnion was found to result from the microbial oxidation and adsorption of Mn^{2+} onto hydrous Mn oxide.

The circulation of phosphorus can be mainly explained by coupling to the redox cycle of Fe, but hydrous Mn oxide rich in Mn^{2+}, Ca^{2+} and Mg^{2+} appreciably influences the P cycle as the adsorbent of phosphate.

1. INTRODUCTION

Our present concern is the circulation mechanisms of elements in Lake Biwa, especially those between the sediment and bottom water.

Recently, at the southern lake of Lake Biwa, a square bottom (ca. $500m^2$) was dredged to obtain earth and sand for building a man-made island, resulting in the appearence of a square water pillar (av. depth : ca. 10m, max. depth : ca. 13m). This area, in which water stratified perfectly from Jun. to early Sept. (Terashima & Ueda, 1982); provided a suitable field for our study.

In this paper, we investigate (1) the seasonal change in concentrations of several components (reduced substances and nutrients) in the dredged area, (2) the redox mechanisms of Mn and Fe depending on DO levels and the microbial activity in the water, and (3) the circulation of P associated with planktonic activity and the redox cycle of Fe and Mn.

2. MATERIALS AND METHODS

sample collection : Fig. 6.1 shows the location of the dredged area. Water samples were collected at depths of every 2m using a van Dorn sampler (made of PVC). During the stratification period in the summer of 1982, water samples were collected within 50cm intervals near the front of dissolved oxygen (DO) (i.e. near the boundary between the epilimnion and the hypolimnion) by pumping up the water, to observe the detailed distribution of elements. An aliquot (ca. 1 l) of the sample was filtered (0.45μm. Millipore HAWP) into a polyethylene bottle containing 8ml of 12M HCl, immediately after collection.

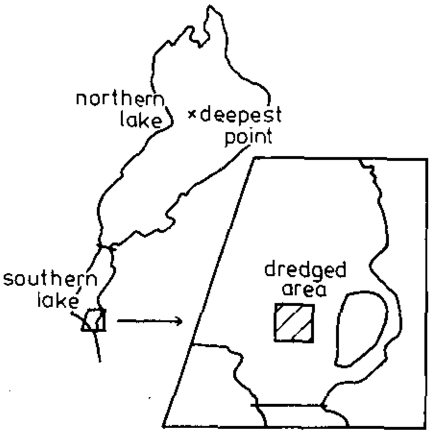

Fig. 6.1 Map of *Lake Biwa, showing the location of the dredged area*

Analytical procedure : DO was determined by the Winkler-azide method and *in situ* with a DO meter (TOA, Model 1B). The concentrations of the dissolved elements were determined from analysis of the filtered sample. The concentrations of the particulate elements were given by differences in concentrations of the dissolved elements and total concentrations obtained from analysis of the unfiltered sample. Soluble phosphate (PO_4-P) was determined by the molybdate-ascorbic acid method including solvent extraction of a blue color complex with iso-butanol (Murphy & Riley, 1962). Total phosphorus (T-P) was determined in the same way as that of PO_4-P after digestion of the sample with HNO_3-H_2SO_4-HF. Ferrous ion was determined by the ferrozine method (Gibbs, 1979) immediately after collection of the sample. Total Fe (T-Fe) was analysed in the same way as that of Fe^{2+} with the acid (HNO_3-H_2SO_4-HF) digested sample. Manganese, Na, K, Mg and Ca in the filtered sample were analysed by atomic absorption spectrophotometry. Total Mn (T-Mn) was analysed after digestion of the sample with HNO_3-HF. Sulfate and silicate were determined by the turbidimetric method (APHA, 1975) and molybdenum blue method, respectively, using the filtered sample. Ammonium in the filtered sample (glass-fiber filter, Whatmann GF/C) was determined by the thymol method (Koyama *et al.*, 1976). The concentration of nitrate was obtained from the difference in concentration of nitrite determined by the Griess-Romijn method and total concentration of nitrate and nitrite determined by the zinc powder reduction method (Nishimura & Matsunaga, 1969). For determination of sulfide, methylene blue produced by the method of Cline (1969) was measured colorimetrically.

Ionic concentrations of the sample : Concentrations of the major ions in the epilimnion were practically constant throughout the year, typical values being : (Na^+) 0.28mM, (K^+) 0.04mM, (Mg^{2+}) 0.09mM, (Ca^{2+}) 0.23mM, (Cl^-) 0.25mM, (HCO_3^-) 0.55mM, (SO_4^{2-}) 0.08mM, and the ionic strength (I) 1.4×10^{-3}. In the hypolimnion of the dredged area during the stratification period in summer, the release of cations (Fe^{2+}, Mn^{2+}, NH_4^+) from the sediment with a commensurate increase in carbonate concentration and reduction of sulfate brought about a change in ionic concentrations : (Fe^{2+}) 0.05mM, (Mn^{2+}) 0.05mM, (NH_4^+) 0.09mM, (HCO_3^-) 0.98mM, (SO_4^{2-}) 0.01mM, and (I) 1.7×10^{-3}.

3. RESULTS AND DISCUSSION

Figs. 6.2 and 6.3 show the isopleths of the water temperature and DO, respectively, in the dredged area (period : Apr. 1981-Oct. 1982). The water in this area stratified during Apr.-Sept. The DO in the bottom water began to decrease from early Apr. and anoxic water appeared in the hypolimnion (below ca. 8m depth) during Jun.-early Sept. Similar findings have been reported by Terashima and Ueda (1982). The complete disappearence of DO in the hypolimnion may be promoted not only by abundant organic matters (e.g. planktonic debris, fecal matters, etc.) in the eutrophic southern lake but also by the high water temperature (max. 22°C) in this area. The bottom water of the northern lake (temperature is approximately constant throughout the year, ca. 7°C) contains oxygen even at the end of the summer stratification (late Nov.) although the stratification period of the northern lake is longer than that of this dredged area.

Fig. 6.4 shows the isopleth of T-Mn. The Mn concentration began to increase in the hypolimnion at almost the same time as DO began to decrease and reached more than 1 mg·l^{-1} under anoxic conditions. T-Mn in the anoxic hypolimnion was identified as dissolved Mn (D-Mn, probably Mn^{2+}) filtrable by 0.45μm Millipore filter and no particultate Mn (P-Mn) was detected in this water layer (see Figs. 6.12a to f).

Figs. 6.5 and 6.6 show the isopleths of ammonium and nitrate, respectively. Ammonium, probably produced by the decomposition of organic matter, also increased with decreasing DO and the maximum concentration in the anoxic water reached more than 1mg·l^{-1}. Contrary to the case of ammonium, the nitrate concentration decreased under anoxic conditions. The decrease in nitrate concentration, observed in the upper epilimnion and the lower hypolimnion, may result from assimilation by plankton and denitrification, respectively.

Figs. 6.7, 6.8 and 6.9 show the isopleths of T-Fe, monomeric silicate (M-SiO_2) and T-P, respectively. When DO was consumed completely in the hypolimnion, T-Fe, M-SiO_2 and T-P accumulated in the bottom water. It is well known that Fe^{2+} is released from the sediment to the hypolimnion under reduced conditions as a result of the reduction of hydrous Fe oxide to Fe^{2+}. The production of Fe^{2+} and its subsequent release from the sediment take place later than those of Mn^{2+} (Mortimer, 1942), due to the lower redox potential of the Fe^{3+}-Fe^{2+} couple than that of Mn^{4+}-Mn^{2+} (Stumm & Morgan, 1970). The concentration of T-P increased in the bottom water at almost the same time as the concentration of T-Fe began to increase although phosphate should be released when ammonium is produced by the decomposition of organic matter. M-SiO_2, a part of which is probably produced by decomposition of debris such as diatom, etc., did not increase in concentration until the T-Fe concentration began to increase. Since phosphate and silicate are often occluded in natural hydrous Fe oxides, they may be released into the hypolimnion when the hydrous Fe oxides are reduced to Fe^{2+} and dissolve while decreasing the redox potential of the sediment and the bottom water (Kato, 1969 ; Stumm & Morgan, 1970).

Figs. 6.10 and 6.11 show the isopleths of sulfate and sulfide, respectively. In the middle of Jun., the sulfate concentration began to decrease and the production of sulfide was detected in the anoxic bottom water. This shows that the southern lake can bring about a highly reduced condition where sulfate reduction can occur, if the stagnation of water persists as in the case of this dredged area.

Based on Figs. 6.2 to 6.11, the reduction processes appear to proceed in the hypolimnion in the following order : (1) consumption of DO – reduction of hydrous Mn oxide to Mn^{2+} (accumulation of ammonium), (2) reduction of nitrate probably through denitrification, (3) production of Fe^{2+} by reduction of hydrous Fe oxide (release of phosphate and silicate), and (4) reduction of sulfate to sulfide. This order was the same as that of the reactions which occured in association with a decrease in relative electron activity ($p\varepsilon$), as reported by Stumm and Morgan (1970). The components produced at a higher level of $p\varepsilon$ could diffuse into a higher and more aerobic water layer than those produced at a lower level of $p\varepsilon$. Ammonium and Mn^{2+} diffused into the lower epilimnion beyond the front of DO.

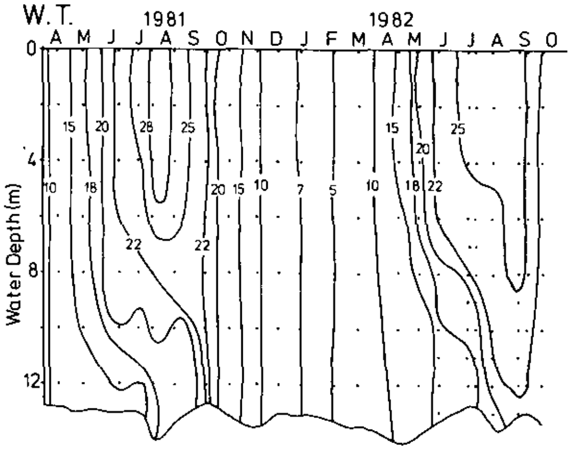

Fig. 6.2 Isopleth of water temperature, ℃

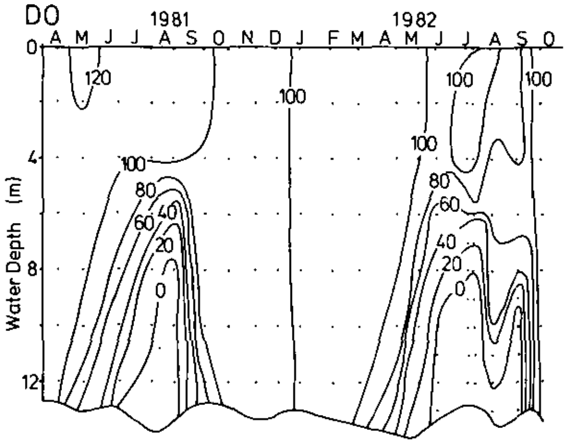

Fig. 6.3 Isopleth of dissolved oxygen, %

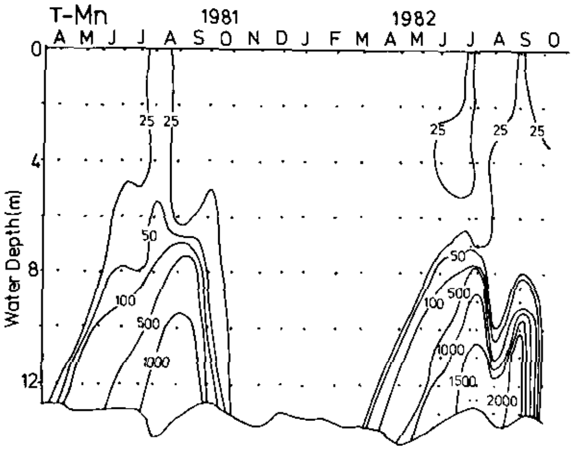

Fig. 6.4 Isopleth of total manganese, $\mu g \cdot l^{-1}$

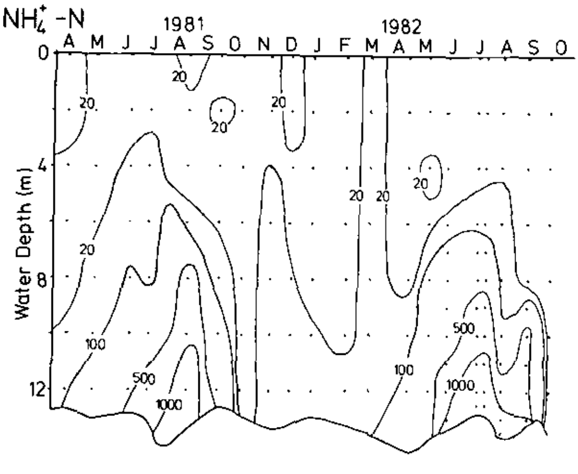

Fig. 6.5 Isopleth of ammonium nitrogen, $\mu g \cdot l^{-1}$

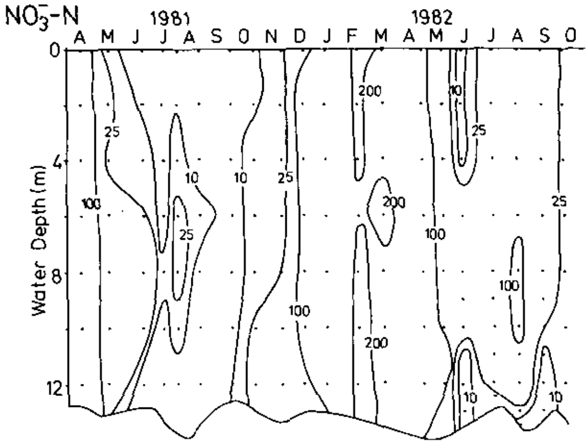

Fig. 6.6 Isopleth of nitrate nitrogen, $\mu g \cdot l^{-1}$

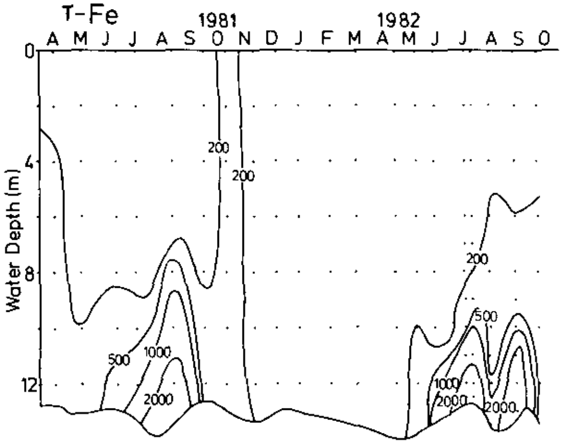

Fig. 6.7 Isopleth of total iron, $\mu g \cdot l^{-1}$

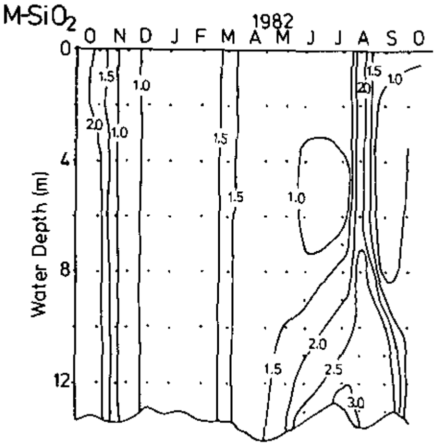

Fig. 6.8 Isopleth of monomeric silicate, mg·l^{-1}

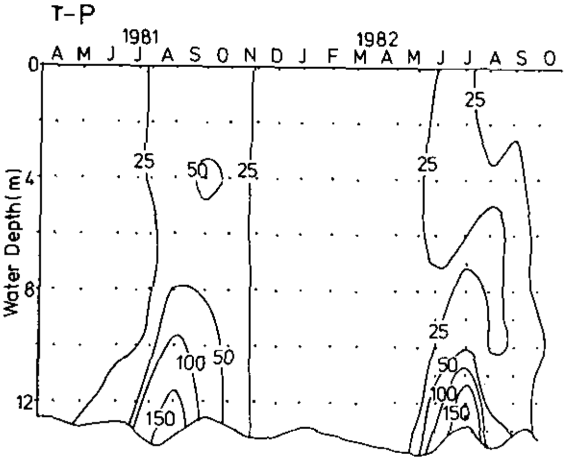

Fig. 6.9 Isopleth of total phosphorus, μg·l^{-1}

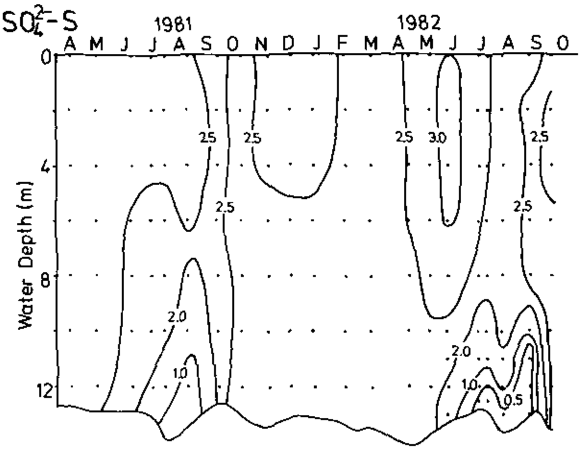

Fig. 6.10 Isopleth of sulfate sulfur, mg·l^{-1}

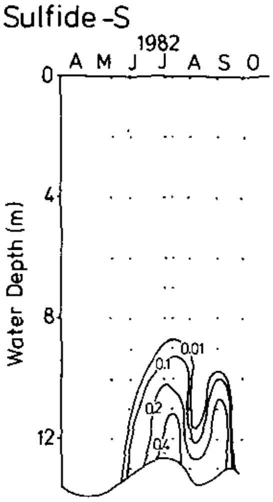

Fig. 6.11 Isopleth of sulfide sulfur, mg·l^{-1}

3.1 The"manganous wheel" and "ferrous wheel"

The typical vertical distribution of Mn (D-Mn and P-Mn) and Fe (D-Fe and P-Fe) during the period of summer stratification is shown in Fig. 6.12 along with the profiles of DO. D-Mn decreased in concentration rapidly and disappeared within a water layer of ca. 0.5m immediately above the front of DO. P-Mn was produced with a sharp concentration peak in the thin water layer (ca. 1m) where D-Mn disappeared. The persistence of this peak implies that the apparent dynamic equilibrium is maintained between the upward flux of D-

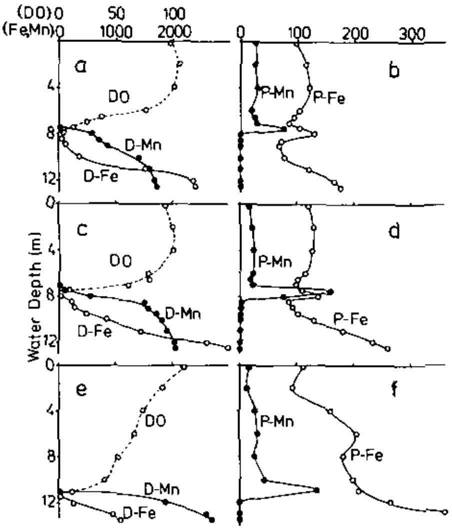

Fig. 6.12 Vertical distribution of DO, dissolved Fe and Mn (D-Fe and D-Mn), and *particulate Fe and Mn (P-Fe and P-Mn)*
Concentration unit : (DO)%, (others) $\mu g \cdot l^{-1}$. Sampling date : (a, b) July 14, 1982, (c, d) July 22, 1982, (e, f) Aug. 11, 1982.

Mn diffusing from the upper hypolimnion and the downward flux of P-Mn sinking from the lower epilimnion (Spencer & Brewer, 1971). Both the oxidation of D-Mn (Mn^{2+}) and dissolution of P-Mn (hydrous Mn oxide) should occur rapidly within a thin water layer (ca. 1m in thickness) near the front of DO.

The distribution of D-Fe differed from that of D-Mn : the concentration gradient of D-Fe was always greater than that of D-Mn throughout the stratification period in the water layer of ca. 2 or 3m directly above the bottom (see Figs. 6.12a and c). P-Fe also formed a sharp peak near the front of DO, but the peak position of P-Fe was located in a deeper water layer than that of P-Mn. This peak separation should result from fractional precipitation in the course of the oxidation of Mn^{2+} and Fe^{2+}. The redox potential of Mn^{4+}-Mn^{2+} couple is higher than that of Fe^{3+}-Fe^{2+}. Therefore, when the particulate forms (hydrous Mn oxide and hydrous Fe oxide) were sinking into the anoxic hypolimnion through the front of DO, hydrous Mn oxide was reduced and dissolved more rapidly than hydrous Fe oxide. In *addition, Mn^{2+} can diffuse in the more upper layer of the water than* Fe^{2+} before *oxidation* (Krauskopf, 1957).

The redox cycles of Mn and Fe, observed in the water column of the dredged area, have been referred to as the "manganous wheel" (Mayer *et al.*, 1982) and the "ferrous wheel"

(Campbell & Torgersen, 1980), respectively. Since the peak of P-Fe was somewhat broader than that of P-Mn and the redox potential of Fe lower than that of Mn, the "manganous wheel" appeared to rotate more rapidly with a small radius compared to the "ferrous wheel" with a big radius. These two "wheels" may also have the effect of enhancing water respiratory metabolism in the dredged area (Mayer *et al.*, 1982).

P-Fe increased again in concentration below a 10m depth (Figs. 6.12b and d). As sulfide was produced in the anoxic bottom water below ca. 10m depth (see Fig. 6.11), the P-Fe was presumed to consist of insoluble ferrous sulfide. The existence of sulfide was supported by the fact that the black precipitate on the filter (0.45μm), collected from the bottom water just after sampling, turned brown upon exposure to air. The molar ratios of S/Fe in these precipitates ranged from 0.7 to 1.0 on July, 14 and from 1.2 to 1.6 on July, 22. That the S/Fe ratios are approximately unity supports the existence of FeS but the excess sulfur may be due to the presence of colloidal sulfur produced by oxidation of sulfide near the front of DO.

The ionic activity products (IAP) were calculated from the concentration data obtained in the hypolimnion (pH : 6.8) on July, 14 and July, 22. The concentration of the dissolved total sulfide was approximated as the difference between the concentrations of total sulfide and P-Fe, since any other sulfide, other than FeS, scarcely contributed to the concentration of the particulate sulfide (the total concentration of Cu, Pb, Hg and Zn were lower than 3×10^{-8}M, 2×10^{-8}M, 1×10^{-10}M and 8×10^{-8}M, respectively ; cf. the concentration order of P-Fe : 10^{-6}M). The equilibrium concentration of S^{2-} was calculated using the acid dissociation constants of H_2S. Before calculating, the pK values of H_2S ($pK_1=7.22$ and $pK_2=14.34$ at $I=0$; Smith & Martell, 1976) were corrected for the ionic strength of the actual water sample ($I=1.7\times10^{-3}$), using the Güntelberg equation (Stumm & Morgan, 1970) and the values of $pK_1=7.20$ and $pK_2=14.28$ were thus obtained. The activity coefficients used for IAP calculations were obtained by the extended Debye-Hückel equation at $I=1.7\times10^{-3}$.

Consequently, the IAP value for FeS, i.e. (activity of D-Fe)×(activity of S^{2-}), were calculated to be ca. $10^{-17.6}$ and found consistent with those for pyrrhotite ($10^{-18.9}$), freshly precipitated FeS ($10^{-16.86}$–$10^{-17.06}$) and mackinawite ($10^{-17.6}$) (Berner, 1967). The value also agreed with $10^{-16.7}$–$10^{-17.05}$, measured directly in the lake water (Davison & Heaney, 1978) and $10^{-17.7}$ for the pond sediment including mackinawite (Doyle, 1968).

The IAP of 6×10^{-18}, calculated for MnS, was much lower than the K_{sp} of MnS (3.16×10^{-11}, at 25°C, $I=0$) (Smith & Martell, 1976) and suggested the absence of the precipitate of MnS in the hypolimnion.

The IAP value between Fe^{2+} and CO_3^{2-} was calculated so as to determine whether siderite was produced in the hypolimnion. The calculation was done using the maximum value of the D-Fe (5.4×10^{-5}M) and alkalinity (0.9 meq·l^{-1}) during the stratification period. The value obtained, 9.9×10^{-12}, was smaller than the range of K_{sp} values, 2.2×10^{-11}–1×10^{-10} (Mayer *et al.*, 1982), and thus the formation of $FeCO_3$ did not appear to occcur in this area. The absence of $MnCO_3$ precipitation (rhodochrosite), as evident from the absence of the P-Mn in the lower hypolimnion (see Figs. 6.12b, d and f), also indicated $FeCO_3$ not to be produced since the carbonates had almost the same values of K_{sp}. Many authors have reported that the solubilities of Fe and Mn may be regulated by carbonate formation in anoxic hypolimnions (Delfino & Lee, 1968 ; Hoffmann & Eisenreich, 1981 ; Verdouw & Dekkers, 1980 ; Mayer *et al.*, 1982). Although the hypolimnion of this area is not saturated with respect to $FeCO_3$ and $MnCO_3$ at present, the increase of alkalinity and the concentration of Fe^{2+} and Mn^{2+} along with the progress of eutrophication may provide formation of these carbonates.

3.2 Circulation mechanism of phosphorus

It is well known that phosphate accumulates in the anoxic hypolimnion (see Figs. 6.9, 6.13a and c) according to the following mechanisms : (1) decomposition of biological debris, and (2) reduction of hydrous Fe oxide including phosphate (Stumm & Morgan, 1970). The vertical distribution of P (Fig. 6.13) suggested the release of phosphate from the sediment surface as well as in the dissolution process of P-Fe rich in phosphate. The profiles of D-Fe and PO_4-P in the lower hypolimnion and the peak profiles of P-Fe and particulate P (P-P) near the front of DO were quite similar to each other, respectively. The scavenging process of phosphate by hydrous Fe oxide is well recognized (Mayer *et al.*, 1982 ; Tessenow, 1974) ; that is, phosphate precipitates in the form of partially hydrolyzed ferric phosphate until the phosphate content is exhausted, and subsequently hydrous Fe oxide precipitates. Therefore, this process should be responsible for the coincident distribution of P and Fe in the dredged area. The peaks of P-P (see Figs. 6.13b and d) were somewhat broad, relative to those of the P-Fe and they spread over the formation region of P-Mn. As described in Chap. III, hydrous Mn oxide which adsorbed large amounts of divalent cations can adsorb phosphate. Ca^{2+} (0.23mM) and Mg^{2+} (0.09mM) are the major cations in the water of Lake Biwa and Mn^{2+} diffuses continuously into the lower epilimnion from the anoxic bottom water. Therefore, in the water layer near the front of DO, hydrous Mn oxide, rich in Ca^{2+}, Mg^{2+} and Mn^{2+}, is produced and should act as an effective scavenger for phosphate. This mechanism may contribute to broadening the peak of P-P.

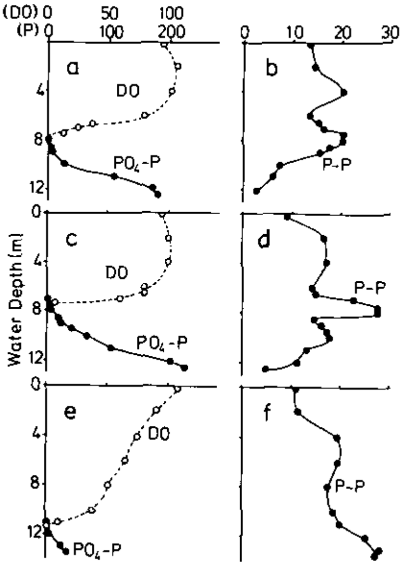

Fig. 6.13 Vertical distribution of DO, phosphate phosphorus (PO_4-P), and particulate phosphorus (P-P)
Concentration unit : (DO)%, (PO_4-P and P-P) $\mu g \cdot l^{-1}$. Sampling date : (a, b) July 14, 1982, (c, d) July 22,1982, (e, f) Aug. 11, 1982.

High concentrations of P-P around 4m depth appeared related to the activity of phytoplankton, since these distributions of P-P were in agreement with those of chlorophyll-*a*, though the data on chlorophyll-*a* are not shown here. Phosphate and organic P produced by decomposition of planktonic remains in the upper epilimnion probably diffuse downward into the water layers where P-Mn and P-Fe are produced, and this may be another reason why the peaks of P-P were broad.

The results of Aug. 11, 1982 (Figs. 6.12e, f and 6.13e, f) were obtained after the front of DO suddenly went down from ca. an 8m to 11.5m depth by a typhoon with heavy rain (see Fig. 6.3). Compared with the distribution shown in Figs. 6.12a, c and 6.13a, c, the concentrations of D-Fe and PO_4-P decreased in the hypolimnion, while a large portion of D-Mn remained. The sudden supply of DO to the anoxic hypolimnion brought about the sedimentation of ferric phosphate and hydrous Fe oxide, and thus the clear peaks of P-Fe and P-P disappeared near the front of DO. Since the reduction of hydrous Mn oxide to Mn^{2+} was easy and rapid, the "manganous wheel" was still operating as can be seen from the persistent peak of P-Mn around 10m depth.

3.3 Oxidation mechanisms of Mn^{2+} and Fe^{2+}

To maintain the peaks of P-Mn and P-Fe near the front of DO, the rapid oxidation of Mn^{2+} and Fe^{2+} is necessary. The rapid oxidation of Fe^{2+} proceeds chemically in a pH range from neutral to alkaline under aerobic conditions, and the kinetics of this reaction are first-order with respect to the concentrations of Fe^{2+} and DO and second-order for OH^- (Stumm & Lee, 1961). Therefore, in the lower epilimnion of the dredged area (pH : ca. 6.8, slightly aerobic), the chemical oxidation of Fe^{2+} to Fe^{3+} should take place rapidly. This reaction may be accelerated by the presence of phosphate diffusing from the hypolimnion, as pointed out by Stumm and Morgan (1970).

The oxidation of Mn^{2+} occurs only in a pH range of higher than 8.5 ($P_{O_2}=0.2$ atm) and is autocatalytic with respect to the hydrous Mn oxide generated (Stumm & Morgan, 1970 ; Pankow & Morgan, 1981). Since the pH of the hypolimnion water is low and constant throughout the year (ca. 6.8), the above auto-oxidation mechanism of Mn^{2+} in alkaline solution cannot be responsible for this case. The P-Mn should be produced by another rapid oxidation mechanism such as a microbial or inorganic catalytic reaction.

The oxidation mechanisms of Mn^{2+} have been studied in various natural environments, e.g. soils (van Veen, 1973 ; Uren & Leeper, 1978 ; Douka, 1980), marine waters (Arcuri & Ehrlich, 1979 ; Nealson & Ford, 1980), tile lines (Meek *et al.*, 1973), cold springs (Mustoe, 1981), and inlets (Emerson *et al.*, 1982). It was found that microorganisms can oxidize Mn^{2+} to hydrous Mn oxides aerobically even at a pH of 6-8 and this oxidation proceeds more rapidly than any non-biological reaction.

Figure 6.14 (curves A1-A3) shows the change of D-Mn (Mn^{2+}) concentrations when the unfiltered waters obtained from the anoxic hypolimnion were aerated. Mn^{2+} decreased at the most rapid rate in the sample from the water layer near the front of DO (curve A1). However, production of P-Mn could not be detected when the water sample was filtered (0.45μm, Millipore) immediately after collection (curve B) and Na_2SO_4 or NaCl was added to the unfiltered sample (curve C). The addition of chloroform or toluene (final concentration : 0.5% v/v) also prevented Mn^{2+} from being oxidized, as shown in Fig. 6.15 (curve C). These results indicate that the oxidation of Mn^{2+} was inhibited by the sterilization of water or removal of particulate matter. Therefore, the precipitation reaction of Mn in the water samples should be linked to microbial oxidation and adsorption of Mn^{2+} onto the hydrous Mn oxide generated. Since the oxidation of Mn^{2+} occurred even in water containing chloroform or toluene on raising the pH of the water higher than 9, the catalytic activity of microorganisms seemed unnecessary for the oxidation of Mn^{2+} at this pH.

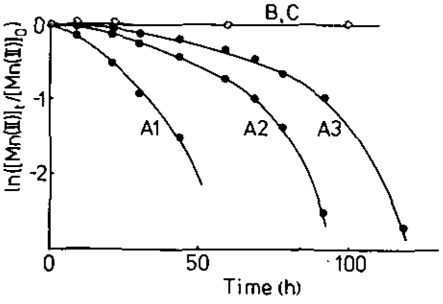

Fig. 6.14 Aeration experiment to estimate the oxidation rates of Mn^{2+}
Water samples : anoxic hypolimnetic waters, (pH) 6.8-7.2, (Temp) 25°C, (sampling date) June 12, 1981. (A) Oxidation of Mn^{2+} in the unfiltered samples ; (A1) $[Mn(II)]_0=102\mu g \cdot l^{-1}$, taken from 10m depth ; (A2) $[Mn(II)]_0=270\mu g \cdot l^{-1}$, taken from 12m depth ; (A3) $[Mn(II)]_0=750\mu g \cdot l^{-1}$, taken from 13m depth. (B) Oxidation of Mn^{2+} in the filtered sample. (C) Oxidation of Mn^{2+} in the unfiltered sample with 0.1M Na_2SO_4 or 0.1M NaCl.

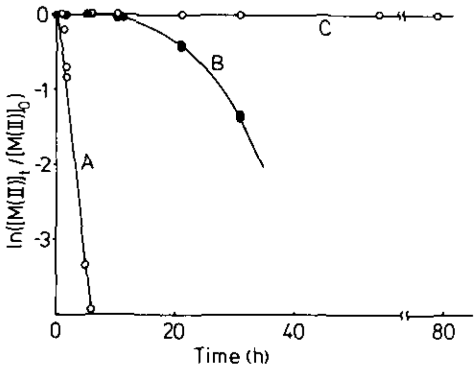

Fig. 6.15 Aeration experiment to estimate the oxidation rates of Mn^{2+} and Fe^{2+}
Water samples : anoxic hypolimnetic (12m depth) water, (pH) 6.8-7.0, (Temp) 25°C, (sampling date) Aug. 20, 1982. $[Mn(II)]_0=3.04mg \cdot l^{-1}$. $[Fe(II)]_0=2.19 mg \cdot l^{-1}$. (A) Oxidation of Fe^{2+} with or without chloroform and toluene. (B) Oxidation of Mn^{2+} without chloroform and toluene. (C) Oxidation of Mn^{2+} with chloroform or toluene.

The oxidation of Fe^{2+} did not necessitate the catalytic activity of microorganisms and other particulate matter, as shown in Fig. 6.15 (curve A). On the curves B and C in Fig. 6.14 and C in Fig. 6.15, P-Mn is not detected in the samples in spite of the formation of P-Fe (hydrous Fe oxide), which demonstrates that hydrous Fe oxide does not operate either as a catalyzer for oxidation or adsorbent of Mn^{2+} under the given conditions. The non-interaction between hydrous Fe oxide and Mn^{2+} at pH 6.8 appeared to be the major factor bringing about the clear separation of the peak of P-Mn from that of P-Fe near the front of DO during the stratification period in summer (see Figs. 6.12b and d).

CHAPTER Ⅶ, -Note-

Manganese Concentration in the Sediment as an Indicator of Water Depth,
−Paleo-Water Depth during the Last Few Million Years−

T. Takamatsu, M. Kawashima and M. Koyama

ABSTRACT

Good quadratic correlations were observed between Mn (or As) concentrations in the short cores and water depth at sites at which these cores were sampled. By applying these relations to the concentrations of elements in the three long (200, 1000, and 1400m) cores drilled by Horie *et al.*, the paleo-water depth during the last ca. 2 million years at the drilling sites could be estimated. The results indicate that the lake bottom near site E has remained under water depth conditions (ca. 60m) similar to those of the present for the last ca. 0.4 m.y. From ca. 2 to 0.4 m.y. ago the area had frequently been shallow. The 1000m core taken at the mouth of Yasu River was found to consist primarily of littoral sediments.

Three long boring cores (200, 1000, and 1400m length) were taken by Horie *et al.* (Yokoyama & Horie, 1974 ; Yokoyama *et al.*, 1976) to investigate environmental changes in Lake Biwa during the past few million years not only out of local interest but from a global viewpoint as well. The 200m and 1400m cores were drilled at the pelagic part of the lake (near site E, see Fig. 1.1 in Chap. Ⅰ) in 1971 and 1982, respectively, and the 1000m core at the mouth of Yasu River in 1976. From analysis of the cores, new information relating to many branches of science including geology, biology, limnology, geochemistry, geophysics, and meteorology was obtained. The information on water depth has been of particular interest to geologists. Although particle size distribution in the cores should be very useful for estimating historical change in water depth, another promising method based on the Mn (or As)-water depth correlation is proposed here.

Fig. 7.1 shows the concentrations of Mn and As in the lower layers (below 10cm depth) of the short cores from the northern lake as a function of water depth at the sampling sites.

The concentration of these elements increased remarkably with increasing depth. Below 10cm from the bottom surface, the sediment appeared to be uncontaminated and any extensive change in elemental composition by early-diagenesis to have already been completed. Therefore, the concentrations of Mn and As in these layers should be fixed to preserve in much deeper zones of the sediment.

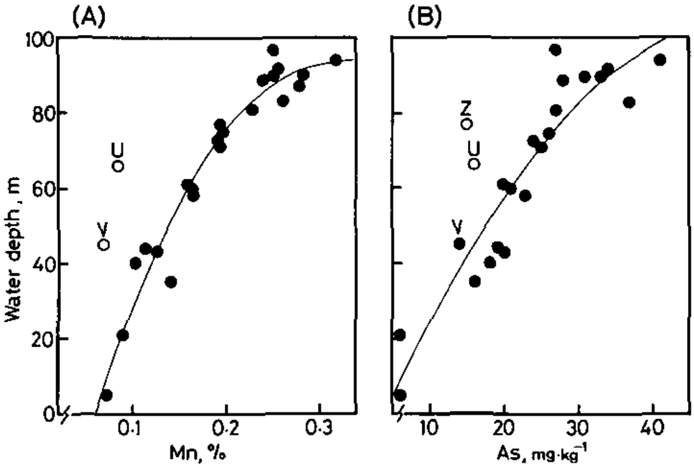

Fig. 7.1 Relationship between manganese (A) or arsenic (B) concentration in the lower layers (below 10cm depth) of the short cores and water depth at sites where the cores were sampled

The data indicated by open circles were excluded for computation of the regression equations.

Data points were fitted to quadratic polynominal functions with good correlation coefficients of 0.975 for Mn and 0.937 for As as follows :

$$WD = -1476.6X_{Mn}^{2} + 915.2X_{Mn} - 48.7 \qquad (1)$$

$$WD = -0.045X_{As}^{2} + 4.710X_{As} - 18.501 \qquad (2)$$

WD is related to water depth (meter), X_{Mn} to the concentration of Mn (%), and X_{As} to the concentration of As ($mg{\cdot}kg^{-1}$).

In the case of Mn, deviations in data points from the calculated curve are within several percent in most cases and the water depth of sampling site can be estimated from the above correlation within a standard deviation of 6.03m. The As-water depth correlation is also seen but deviations in data points from the calculated curve become much larger than in the case of Mn (standard deviation : 9.64m).

It should be pointed out that these relations of Mn and As with water depth are only empirical or phenomenological ones derived from chemical compositions of a recent era (back to ca. 300 B.P.) when the lake environment should have been the same as that of the present in a geological sense. There must be several important factors which influence directly or indirectly the concentrations of Mn and As in the sediment and, in most case, are not understood.

The possible factors are as follows : (1) size of watershed, (2) lake size in area, volume and water depth, (3) soil and rock composition of the watershed, (4) mean residence time of lake water, (5) biological activity around and within the lake, (6) sudden heavy deposition of volcanic ash or clay minerals by violent flood, both of which shut down the interaction between the lake water and sediment at the bottom surface, (7) mass water flow in sediment layers, i.e. spring welling up from the lake bottom, and (8) change in flow of lake bottom water.

Some of these factors may have changed considerably during the past ca. 2m.y., and the consequent change of Mn (or As)-water depth correlation is also likely. Therefore, it is an anxious point in our approach that the recent relations of Mn (or As)-water depth, i.e. equations (1) and (2), can apply to what depth of the cores.

After the long cores had been divided into sublayers of roughly equal length, the sediments collected from every layer were subjected to elemental analysis by X-ray fluorescence and neutron activation (Koyama *et al.*, 1977a , 1977b ; Takamatsu *et al.*, 1979b).

Table 7.1 shows the concentrations of Mn and As recorded in the long cores along with

Table 7.1 Concentrations of Mn and As in the long cores and water depth calculated according to equations (1) and (2)

	200 m	1000 m	1400 m			
Concentration(mg·kg^{-1})	Mn				As	
number of subsamples	158	275	141	38	137	37
range	720-4360	249-4343	211-3590	(1136-2685)	2.2-27.9	(13.7-27.9)
average	1653	651	1143	(1765)	12.4	(22.3)
CV(%)	32.2	71.8	60.5	(23.5)	57.4	(15.2)
Water depth(m)						
range	9.5-92.7	0-93.1	0-90.6	(36.2-90.6)	0-77.9	(37.6-77.9)
average	58.1	1.4	29.6	(64.3)	30.8	(63.5)
CV(%)	28.5	1761	122.8	(23.8)	79.0	(14.8)

Parentheses show the values for the upper 200m of 1400m core.

the water depth calculated from equations (1) and (2). The relative frequencies (RF) of the calculated water depth in the cores are also given in Fig. 7.2.

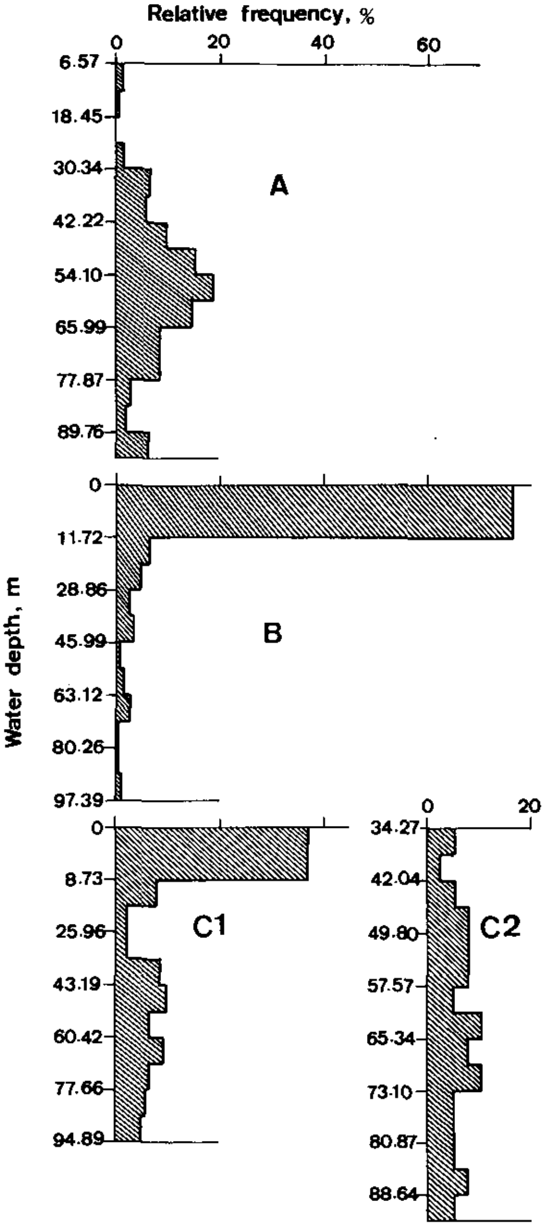

Fig. 7.2 Histogram of the calculated water depth in the long cores
(A) 200m core, (B) 1000m core, (C1) the whole of 1400m core, (C2) the upper 200m part of 1400m core.

Although the Mn concentrations analysed in the 200m core ranged from 720 to 4360mg·kg^{-1} with an average concentration of 1653mg·kg^{-1}, most (ca. 75%) of the Mn concentrations were within 1200-2000mg·kg^{-1}, corresponding to a water depth of 40-75m. The paleo-water depth at the core site had usually been about 60m, except on several occasions (RF<2%) of a water depth of less than 15m.

The drilling site of the 1400m core was near that of the 200m core. However, the Mn concentration in the 1400m core were lower than those in the 200m core. This is a result of the high RF (ca. 40%) of low Mn concentrations corresponding to a water depth of less than 15m. This is particularly the case at a core depth below 200m. Although the samples analysed were limited to a small number, in the upper 200m of the 1400m core, water depths calculated from the Mn and As concentrations were essentially the same as those in the 200m core.

Based on age determination (Yokoyama *et al.*, 1982), the lake bottom near site E has apparently remained under water depth conditions similar to those of the present for the last ca. 0.4m.y. although the area had frequently been shallow from ca. 2 to 0.4m.y. ago.

The Mn concentrations in the 1000m core were generally less than 500mg·kg^{-1} and a water depth shallower than 15m found in Rf of ca. 80%, implying the core to consist primarily of littoral sediments. In this core, there were several samples containing very high concentrations of Mn. One sample consisted mainly of organic substances and several others of fine clay. Evidence from other fields in regard to particle size analysis, organic compound etc. will be needed to determine whether these high concentrations of Mn are really due to the water depth when the sediments are deposited. However, these different cores certainly provide a basis for applying the Mn (or As)-water depth relation to the analysis of the past history of lake sediments in general.

CHAPTER VIII, -Note-

The Total Amounts of Mn and As Accumulated in the Sediment Surface

T. Takamatsu, M. Kawashima and M. Koyama

ABSTRACT

The total amounts of Mn and As accumulated in the surface of the lake floor were calculated from the differences of the elemental concentrations in the upper (0-2cm)and lower layers of the cores (below 10cm depth). The amounts were found to be 4350 and 73 metric tons for Mn and As , respectively.

The surface oxidized sediment of Lake Biwa accumulates large amounts of Mn and As in the form of Mn oxide and by the adsorption of Mn and As to Mn oxide as described in Chaps. I and II. Since the bottom water contains ca. $4mg\cdot l^{-1}$ of dissolved oxygen even at the end of the summer stratification (Naka, 1973 ; Kawashima *et al*., 1978) , a thin oxidized layer covers nearly the entire bottom surface and contributes to efficiently accumulating Mn and As. If the concentration of dissolved oxygen in the bottom water undergoes a continued reduction due to pollution and eutrophication, as pointed out by Naka (1973) , the oxidized layer at a water depth below the thermocline (ca. 20m depth) may possibly disappear, causing the release of Mn and As into the lake.

Assuming average concentrations of Mn and As in the northern lake cores (see Table 1. 1 in Chap. I) to be approximately those in the sediment from a water depth below 20m, the excess concentrations of Mn and As accumulated in the upper 2cm layer of the sediment can be estimated by the differences in the concentrations in the upper 2cm layer (Mn : 3760, As : $55mg\cdot kg^{-1}$) and in the lower layer (Mn : 1860, As : $23mg\cdot kg^{-1}$) to be 1900 and $32mg\cdot kg^{-1}$, respectively. If we assume the water content of the sediment to be 78% and the density of dry sediment $2.62g\cdot cm^{-3}$ (Yamamoto, private communication) in the upper 2cm layer, the net excess of Mn and As should amount to 4350 and 73 metric tons respectively in the lake floor under the thermocline (ca. $458km^2$) . The volume of water in Lake Biwa is $27.6km^3$. Therefore, if all the excess Mn and As were to be dissolved and mixed perfectly in the lake water, additional concentrations would be approximately $160 \mu g \cdot l^{-1}$ for Mn and $2.7 \mu g \cdot l^{-1}$ for As.

Although such a situation is unlikely, these concentrations, especially that of Mn, should be given due consideration in view of the recommended values for Mn and As ($50 \mu g \cdot l^{-1}$) in drinking water (FWPCA, 1968).

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琵琶湖底泥中の元素に関する陸水学及び環境化学的研究

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この一連の研究は当研究所，水質土壌環境部，土壌環境研究室の経常研究の一課題として昭和52年に開始され，現在までの約8年間滋賀大学教育学部化学教室及び京都大学原子炉実験所の協力を得て進められてきた。ここに得られた成果の一部をまとめた。

湖は地球規模での元素循環を反映する一つの反応槽と考えられる。溶存状態や粒子状で河川から流入した元素は一部はそのままの状態で堆積したり，河川から流出したりするが，多くは生物，化学，物理作用などを受けて湖水中で存在形態を変える。しかしいずれは湖底への堆積，大気への揮散，河川への流出などにより系外に除かれる。また湖底に堆積した元素も続成作用で存在形態を変えたり，底泥中を移動，局在したり，湖水に再溶出したりすることが知られている。したがって，湖内での元素挙動を湖環境や対象元素自身が持つ化学特性との関連で明らかにすることは，その湖に固有の環境や元素挙動の解明に役立つばかりか，地球規模での元素循環の仕組を知る手懸かりにもなる。

上の観点で研究を進めるに当たって様々なアプローチが考えられたが，ここでは環境試料とりわけ底泥試料を元素分析し，その分析結果の解析から元素挙動を推測する方法に重点をおいた。多様な環境試料の中で特に底泥に注目した理由は，この試料が比較的元素濃度の高い試料で，一度乾燥処理すれば保存中や分析操作中に目的元素が揮散，吸着などで失われたり，逆に汚染されたりする危険性が少ないこと，またけい光X線分析法や中性子放射化分析法を用いれば，煩雑な元素の前濃縮や分離を行うことなく試料を非破壊で分析できることなど，いくつかの分析上の利点が考えられたからである。また底泥は湖環境の履歴を湖水中での生物，化学，物理反応や堆積後の続成作用の結果として保存していることも他の試料に比べ興味深い点であった。

また底泥の元素分析から元素の挙動に関する知見を得るためには，不確定な原因でかく乱されていない試料を得る必要があった。この点，琵琶湖とりわけ北湖中心部の底泥は(1) 70 m 以上に及ぶ水深のために風波によるかく乱が少ない，(2) 河川流入物の直接影響が少ない，すなわち陸源堆積物の割合やその変動が少ない，(3) 底棲生物によるかく乱が少ない，(4) 厚さ1,000 m 以上に及ぶ湖底堆積物のため，湧水によるかく乱が少ないなどの条件を備え，良い試料を提供してくれた。またこの湖には温泉水の流入や湖底での火山ガスの噴出など火山活動の影響がないことや北湖の流域が近年まで比較的人間活動の希薄な地域であったことも分析結果の解析を容易にする好都合な条件であった。

第1章　琵琶湖底泥及びマンガン塊中の36元素の分布

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湖全域から，底泥コア（長さ30～40 cm）を30試料とエツクマン採泥器による表面泥を47試料採取した。また湖心部付近の底泥表面からはMn塊も採取した。試料は分割，乾燥などを行った後，中性子放射化，けい光X線，原子吸光，比色などの分析法で元素分析した。定量した元素は次の36種である：Mn, P, As, Sb, Fe, Ni, Co, Zn, Cu, Pb, Hg, Cr, Ti, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Hf, La, Ce, Sm, Eu, Yb, Lu, U, Th, Au, Ta, Nd, Br, N。

元素分布を元素間で統計的に比較したり，元素の底泥表面（鉛直方向）と岸から湖心部（水平方向）への濃縮係数を算出したりすることにより，底泥中の元素分布の現況を明らかにした。また各元素の分布を支配している元素の移動，固定機構を底泥環境や元素自身が持つ化学特性との関連で考察した。

第2章　2価マンガンを多量に含む水和酸化マンガンが底泥表面へのヒ素の蓄積に果たす役割

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琵琶湖では底泥の薄い表層に高濃度のAsが蓄積されており，底泥中のAsの深度分布はMnのそれと酷似する。また湖心部の底泥表面にしばしば小さなMn塊が発見されるが，ここにも高濃度のAs（721 $\mu g \cdot g^{-1}$）が含まれる。これらの事実はAsの蓄積がMnとの関連で起こっていることを予想させたので，ここでは水和酸化Mn(HMO)へのAsの吸着実験と底泥コア試料中のMnの化学形態分析を行って，As蓄積に関するHMOの役割を示唆した。

琵琶湖の底泥表面酸化層には下層の還元層から常に豊富なMn^{2+}が供給され，Mn^{2+}を多量に含む水和酸化Mn(Mn^{2+}-HMO)が形成される。この相は正の表面電荷を持ち，ヒ酸の吸着に大変有効である。一方Asも下層で還元されて亜ヒ酸として表層に運ばれるが，表層でHMOと接触すると直ちにヒ酸に酸化され，最終的にMn^{2+}-HMOに吸着，吸蔵されて保持される。

第3章　2価カチオン共存下での水和酸化マンガンによるリン酸の吸着

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第2章で，2価カチオンが共存すれば，水和酸化Mn(HMO)は中性付近でヒ酸を有効に吸着し，この機構が琵琶湖底泥表面へのAsの蓄積に寄与していることを示した。ここではこの知見を拡大し，2価カチオンを吸着したHMOのリン酸吸着特性について検討した。その結果，HMOはアルカリ土類金属イオンやMn^{2+}, Co^{2+}, Ni^{2+}などの遷移金属イオンが共存すればpH 6～9の範囲でリン酸を強く吸着することが分かった。アルカリ土類金属間の比較では，リン酸吸着に関する有効性はBa＞Sr＞Ca＞Mgの順で，金属イオン自身の吸着能の順と一致した。遷移金属イオンを含む系では時間とともにリン酸吸着曲線が変化したが，これは吸着した金属イオンが酸化物（例えばMnO_2，CoO，NiO)に変化したためと考えられた。実験結果は，琵琶湖底泥表面へのリンの蓄積に2価カチオンを多量に吸着したHMOが少なからず寄与していることを示唆した。

第4章　亜鉛と銅の湖水から底泥への移行過程における生物遺骸の役割

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Zn，Cu，Pb及びHgは北湖の底泥では表面から4～5 cmの深さにおいて，南湖では15～25 cmの深さにおいて高濃度を示し，人為的負荷によるものと判断できる。これらの金属分布を詳細に観察すると，濃度の高い表層で元素ごとに分布の様子が異なる。例えばZnとCuの分布を比較すると，北湖では両元素とも表面で濃度が高いが，Zn濃度は表面直下で急速に減少し，一方Cu濃度の高い層はより深部にまで至っている。湖内から採取した植物プランクトンに多量のZnとCuが含まれたので，琵琶湖ではこれらの元素の多くはプランクトンの遺骸とともに沈殿すると推測した。沈殿後，遺骸の初期分解に伴ってZnの大部分は底泥表面近くで急速に放出され湖水に回帰するが，腐植質と強固に結合するCuの一部は遺骸の分解，腐植化過程において残存する。

第5章　ジメチルアルシン酸，モノメチルアルソン酸及び無機ヒ素の鉛直分布

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湖心部から3本の底泥コア試料（長さ30～40 cm）を採取した。試料は0.5，1，2及び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)及び無機ヒ素(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10 MHCl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及びI-Asを分離し，最後にフレームレス原子吸光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と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 $\mu g \cdot kg^{-1}$の範囲を，MMAで20.8から44.1 $\mu g \cdot kg^{-1}$の範囲を示した。底泥はI-Asのほぼ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。

第6章　南湖しゅんせつ穴でのマンガン，鉄の酸化還元サイクルとリンの循環

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富栄養化した南湖のしゅんせつ穴で，1981～1982年に水温，溶存酸素(DO)，マンガン，鉄，リン，ケイ酸，アンモニア，硝酸，硫酸，硫化物の分布を調査した。その結果，成層期間中の底層水の還元過程は相対電子活動度（$p\epsilon$）の減少とともに次の順で進行した：(1) DOの消費－水和酸化Mn(HMO)の還元（アンモニアの蓄積），(2) 硝酸の還元，(3) 水和酸化鉄の還元（リン酸とケイ酸の放出），及び(4) 硫化物の生成。

成層期には，DOが0になる境界の直上（表層水の最下部）で，粒状MnとFeのピークがはっ

きりと分離して現れた。この現象は表層水下部と底層水の間で通常“Manganous wheel”あるいは“Ferrous wheel”と呼ばれる両元素の酸化還元サイクルが機能していることを示した。表層水下部でのMnの沈でんは微生物酸化によるHMOの生成と生成したHMOへのMn^{2+}の吸着によるものと考えられた。

リンの循環はFeの酸化還元サイクルに随伴したが，Mn^{2+}，Ca^{2+}，Mg^{2+}を吸蔵したHMOもリンの循環に少なからず寄与した。

第7章　水深指標としての底泥中マンガン濃度

—過去200万年の古水深の予測—

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表面底泥コア（長さ30〜40 cm）中のMnとAs濃度は試料を採取した地点の水深と非常に良い相関を示した。ここではこの相関関係を堀江らによって掘削された深層ボーリングコア（200 m，1,000 m及び1,400 mコア）中のMn濃度に適用して，掘削地点の古水深を予測した。その結果，地点E付近の湖底は約200万年前から40万年前にかけて頻繁に浅くなったが，40万年前から近年に至る間は現在とほぼ同様の水深（約60 m）にあったと推測される。1,000 mコアは全般にMn濃度が低く，そのコアの採取地点である野州川河口はずっと岸近くに位置してきたと考えられる。

第8章　底泥表層に蓄積されたマンガンとヒ素の量

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底泥表層に蓄積されたMnとAsの量を底泥コアの表層（0〜2 cm層）と下層（10 cm以深）に含有される両元素の平均濃度の差から推算した。その結果，Mnは4,350トン，Asは73トン表層に過剰に蓄積されていることが分かった。仮にこれらが湖水に溶出し，混合されたとすれば，湖水濃度はMnで160 $\mu g \cdot l^{-1}$，Asで2.7 $\mu g \cdot l^{-1}$増加することになる。

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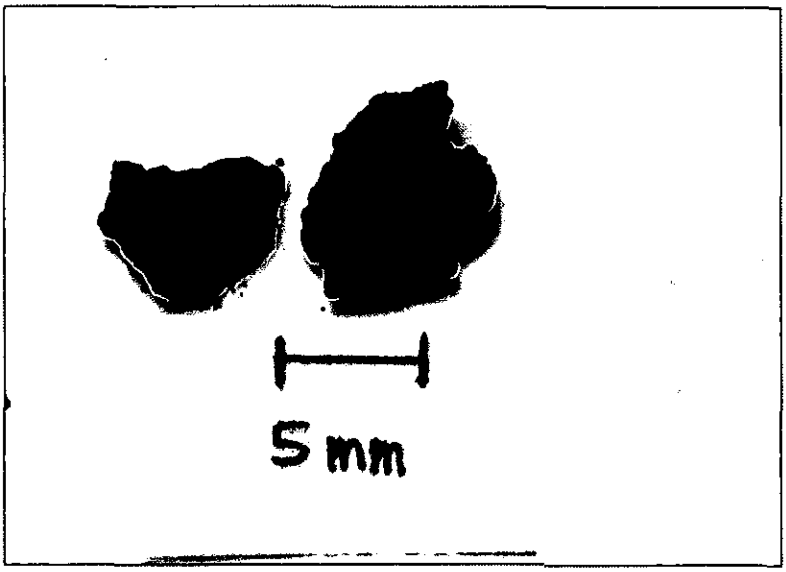
Appendix 1 *Morphometric features of Lake Biwa*

Item	Total	Northern lake	Southern lake
Location	35 N, 136 E		
Lake surface area (km^2)	681	623	58
Lake volume (km^3)	27.6	27.3	0.29
Mean depth (m)		41	4
Maximum depth (m)		104	7
Drainage area (km^2)	3848		
Affluent river	113		
Effluent river	2		

Appendix 2 Photograph of Mn concretions sampled from the sediment surface at site G



Appendix 3 The method of neutron activation analysis

Determination of Rb, Cs, Ba, Fe, Co, Cr, As, Sb, Br, Sc, La, Ce, Nd, Sm, Eu, Yb, Lu, U, Th, Hf, Ta and Au : Each dried sample of 200-300mg was heat-sealed in a polyethylene tube wrapped in a clean polyethylene bag to prevent contamination during handling and irradiation. For determination of long-lived unclides, eight samples were packed in an irradiation capsule along with neutron spectrum monitors consisting of Co (50μg) , Cr (50μg) , Sb (25μg) and U (10μg) impregnated in a sheet of Millipore filter (HAWP, 47mm i.d.). Irradiation was carried out for 1h in a pneumatic tube (thermal neutron flux : 2.75×10^{13} ; epithermal neutron flux : 1.09×10^{12} n $cm^{-2}s^{-1}$) of Kyoto University Reactor (KUR). After the irradiated samples were allowed to stand for 7-10 days, γ-ray spectra were determined for 1h using a Ge (Li) diode detector with an active volume of 53ml (ORTEC) coupled to a 4K-channel pulse height analyzer (NAIG) and tape-recorded. The programs, designated as COVIDN and GAMMA, both developed by the authors, were used to identify the peaks, calculate peak areas, identify nuclides and finally allot concentrations by normalizing cooloing periods, detector efficiency, nuclear constants and neutron spectrum with which the samples and spectrum monitors were irradiated. The neutron spectrum, that is, the ratio of the thermal to epithermal neutron fluxes was determined using a set of Co, Cr, Sb and U monitors. COVIDN made it possible to calculate peak areas in a manner similar to manual calculation and GAMMA operates by fitting peaks to a Gaussian function plus an exponential with a base line of quadratic form.

Mn concretions, obtainable only in small amounts, were analysed for long-lived nuclides as follows : about 30mg of each dried sample were sealed in a quartz tube in vacuum and irradiated for 10h with Co, Cr, Sb and U monitors spotted on a piece of aluminum foil of 99.9 % purity in the hydraulic tube (thermal neutron flux : 8.15×10^{13} ; epithermal neutron flux : 5.95×10^{12} n $cm^{-2}s^{-1}$). The irradiated sample was analysed as described above.

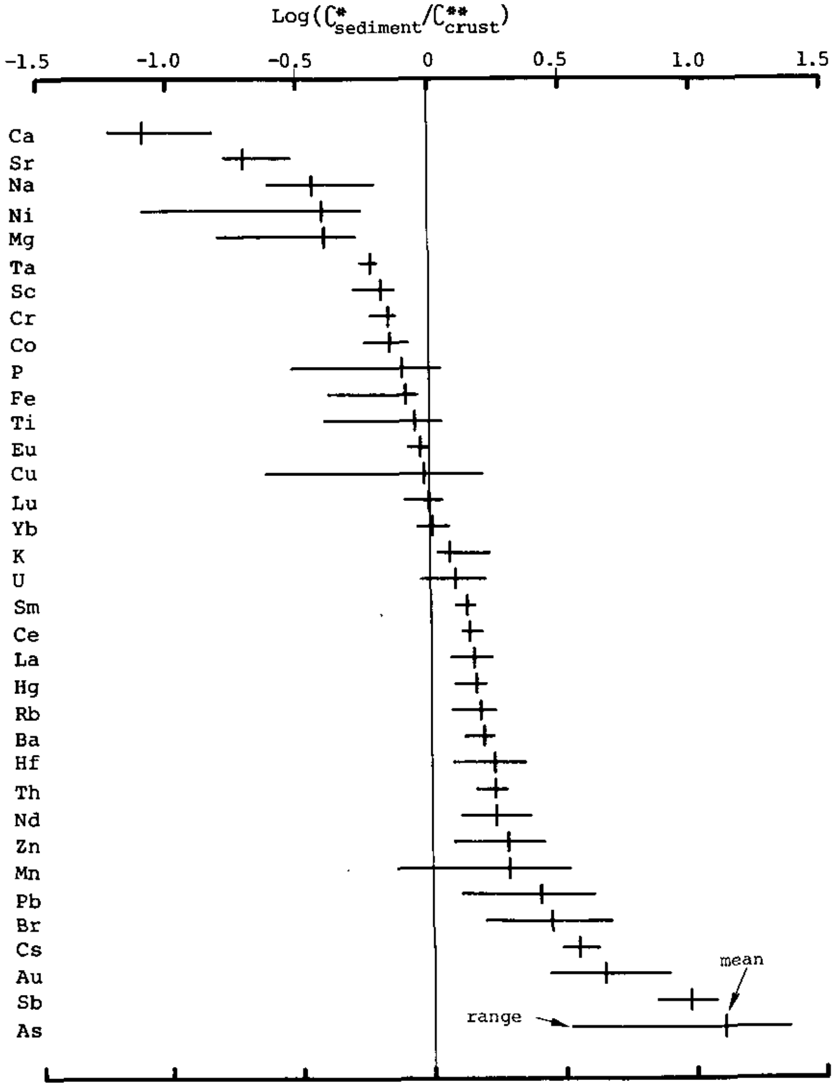
Determination of Na, K and Mn : Ten dried samples of 20-30mg sealed in polyethylene tubes and the thermal neutron flux monitor of Mn (25μg) impregnated in a sheet of Millipore filter were packed together in a capsule and irradiated at KUR for 5min. These samples were cooled for 2-3h prior to determination of the γ-ray spectra. The concentrations of the elements were calculated in a way similar to that for long-lived nuclides, using the ratio of thermal to epithermal neutron fluxes already determined for long-lived nuclides.

Appendix 4 The method of X-ray fluorescence analysis

Twenty-50μl of the internal standard solution (Cs : 100mg/ml, Se : 1mg/ml) were added to 200-500mg of the dried samples. After drying again at 110°C for 1h and mixing in an agate ball-mill for 30 min, the analysis based on direct measurement of powdered samples was performed with an energy-dispersion X-ray fluorescence spectrometer (ORTEC, Model TEFA-6111) equipped with a PDP-11/05 computor. The measurement conditions of the instrument are as follows : target : Mo, voltage : 50kV, current : 50μA, filter : Mo, X-ray path : air, and counting time : 4K-8K sec. Spectrum analysis was performed with a SEEK program (developed by ORTEC) which includèd background subtraction, peak searching, and Gaussian peak fitting. The analytical lines used were the $L_{\alpha 1}$ for Pb and the $K_{\alpha 1}$ for the other elements. The $L_{\alpha 1}$ line of Cs was used as an internal standard for K, Ca, Ti, Mn and Fe, and the $K_{\alpha 1}$ line of Se was selected as the internal standard for Ni, Cu, Zn, As, Pb, Rb and Sr. Internal standardization is preferable in order to compensate for instrumental and sample loading variations. The calibration curves were established by plotting the peak ratio, $I_x/I_{i.s.}$, where I_x and $I_{i.s.}$ are the peak intensities of the desired element and internal standard, respectively. A series of artificial reference standards, prepared by adding known amounts of the desired elements to dried anhydrous sedimentary silicates, were made available as primary standards. In analysing the sediment, Fe and sometimes Mn, usually the major metallic elements in such samples, absorb X-rays of elements such as Ni, Cu and Zn. This matrix effect often results in an underestimation of the analytical values of Ni, Cu and Zn. Therefore, in the present work, the matrix effect correction was performed by referring to the content of Fe (and Mn).

To analyse samples such as the upper 0.2cm layer of the sediment core and the Mn concretions obtainable only in small amounts, a simple dilution procedure was also used instead of the internal standard method. The sample preparation was as follows : the samples or the calibration standards were thoroughly mixed with a tenfold weight of microcrystalline cellulose (Merk, for column chromatography) in an agate ball-mill. Two hundred mg of the resultant mixture were then made into pellets (13mm i.d., ca. 1mm thick) using a die for the infrared spectrophotometry. Cellulose acted not only as a binder, but also made it possible to minimize matrix interference.

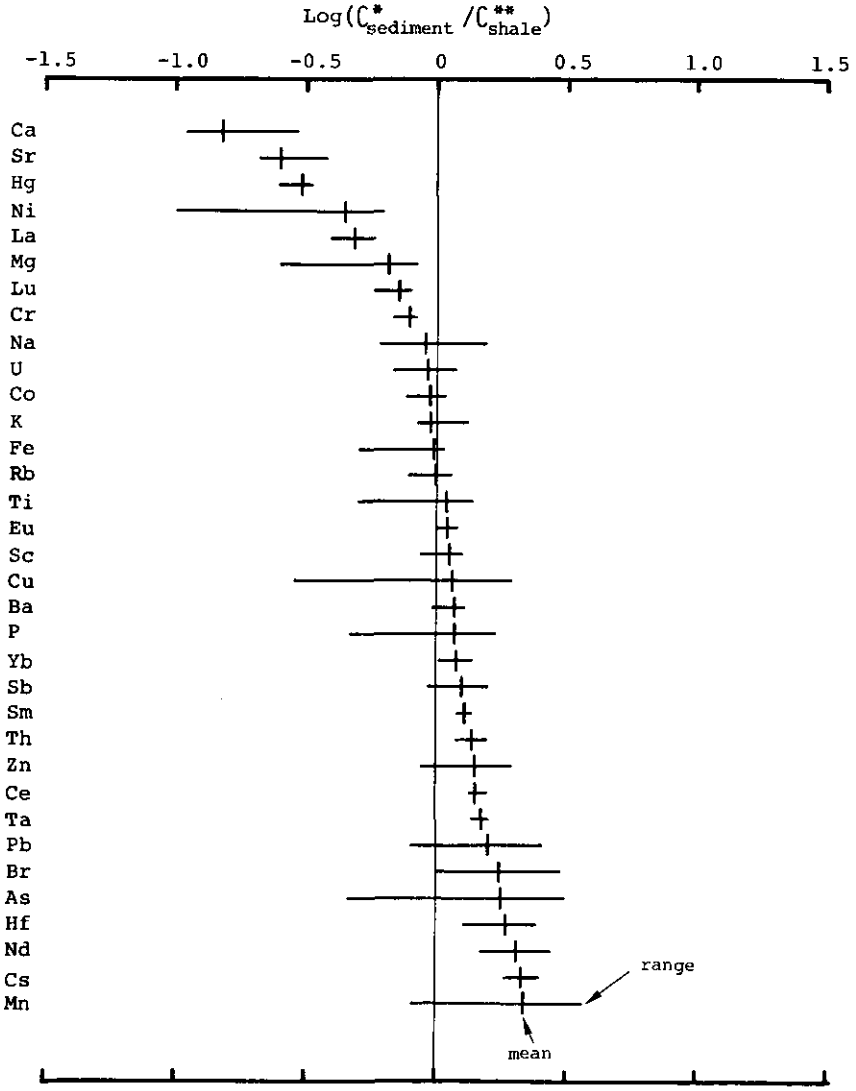
Appendix 5 Relative concentrations of elements in sediments from Lake Biwa to those on average earth's crust



*) Elemental concentrations in the lower layers (below 10 cm depth) of the sediment cores from the northern lake.

**) Taylor, 1964.

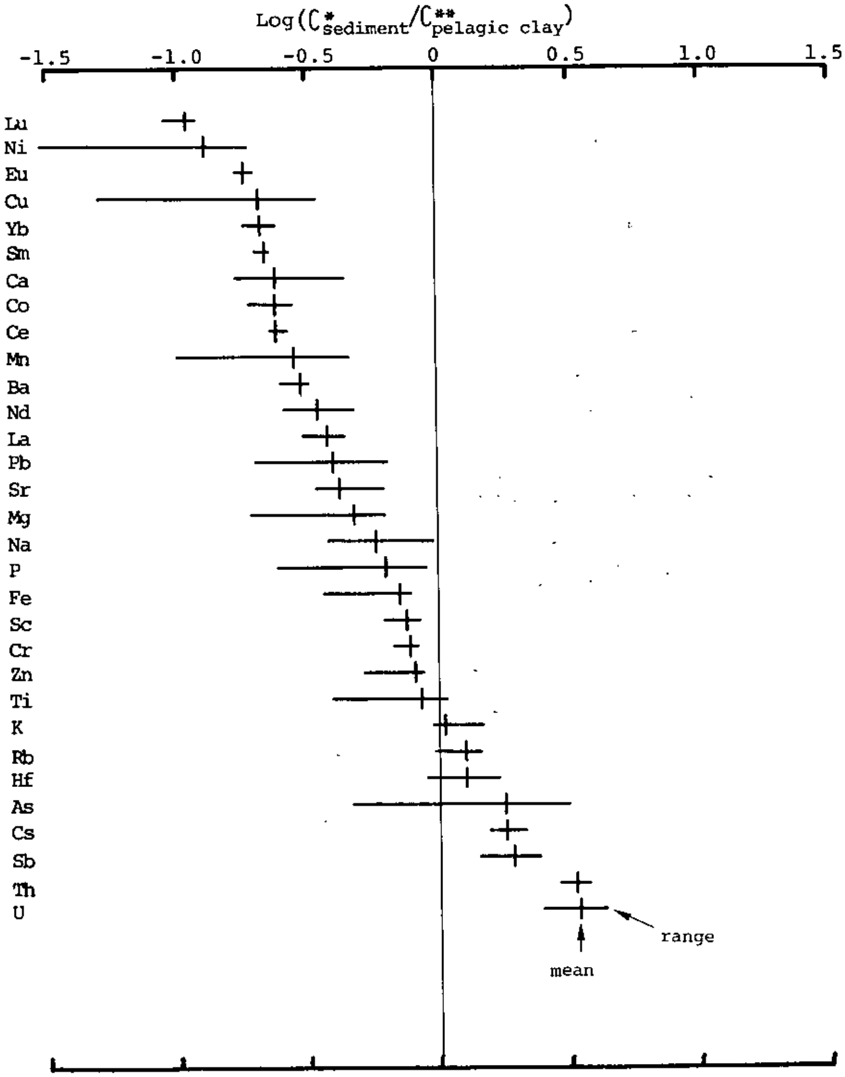
Appendix 6 Relative concentrations of elements in sediments from Lake Biwa to those of shale



*) Elemental concentrations in the lower layers (below 10cm depth) of the sediment cores from the northern lake.

**) Turekian and Wedepohl, 1961.

Appendix 7 Relative concentrations of elements in sediments from Lake Biwa to those of pelagic clay



*) Elemental concentrations in the lower layers (below 10 cm depth) of the sediment cores from the northern lake.

**) Sugimura, 1972.

Appendix 8　Vertical distribution correlation between elements in the sediment core from site G

	C.D.	Na	K	Rb	Cs	Ca	Sr	Ba	Sc	Ti	Cr	Mn	Fe	Co
C.D.	1.000													
Na	−0.399	1.000												
K	0.238	0.322	1.000											
Rb	0.416	0.079	0.779	1.000										
Cs	0.534	0.261	0.577	0.555	1.000									
Ca	−0.690	0.612	−0.099	−0.461	−0.014	1.000								
Sr	0.151	0.498	0.325	0.619	0.455	−0.120	1.000							
Ba	−0.090	0.051	−0.369	−0.386	−0.001	0.189	−0.216	1.000						
Sc	0.608	0.185	0.702	0.669	0.774	−0.273	0.405	−0.042	1.000					
Ti	0.850	−0.346	0.404	0.498	0.444	−0.616	0.215	−0.131	0.710	1.000				
Cr	0.489	0.261	0.317	0.438	0.503	−0.205	0.582	−0.083	0.513	0.470	1.000			
Mn	−0.408	−0.225	−0.764	−0.940	−0.551	0.343	−0.676	0.397	−0.689	0.512	−0.491	1.000		
Fe	0.571	−0.295	0.124	0.313	0.338	−0.330	0.173	−0.223	0.530	0.653	0.293	−0.277	1.000	
Co	0.180	0.421	0.366	0.138	0.727	0.262	0.256	−0.005	0.587	0.124	0.234	−0.146	0.318	1.000
Ni	−0.105	−0.268	−0.271	−0.437	−0.169	−0.020	−0.530	0.452	−0.281	−0.185	−0.149	0.641	−0.156	0.004
Cu	−0.455	−0.058	−0.789	−0.922	−0.492	0.379	−0.510	0.382	−0.657	−0.614	−0.439	0.927	−0.319	0.014
Zn	−0.363	−0.358	−0.806	−0.906	−0.573	0.242	−0.705	0.409	−0.692	−0.468	−0.547	0.978	−0.217	−0.195
Pb	−0.650	0.038	−0.715	−0.624	−0.537	0.372	−0.232	0.206	−0.730	−0.808	−0.368	0.702	−0.253	−0.116
As	−0.425	−0.197	−0.756	−0.944	−0.536	0.363	−0.663	0.398	−0.677	−0.525	−0.498	0.998	−0.284	−0.106
Sb	−0.421	−0.092	−0.777	−0.891	−0.448	0.351	−0.502	0.409	−0.599	−0.560	−0.385	0.942	−0.208	0.050
Br	−0.243	0.149	−0.765	−0.778	−0.279	0.369	−0.234	0.436	−0.450	−0.498	−0.161	0.705	−0.174	0.094
La	−0.163	0.519	0.778	0.581	0.346	0.185	0.259	−0.052	0.586	0.072	0.156	−0.600	0.035	0.284
Ce	−0.230	0.469	0.651	0.551	0.171	0.052	0.284	−0.006	0.499	0.018	0.165	−0.514	0.014	0.153
Sm	−0.083	0.429	0.788	0.650	0.407	0.102	0.274	−0.074	0.635	0.143	0.163	−0.659	0.084	0.267
Yb	−0.148	0.360	0.586	0.539	0.108	−0.032	0.328	0.005	0.413	0.050	0.199	−0.567	−0.187	0.068
Lu	−0.148	0.354	0.539	0.317	−0.004	0.042	−0.017	−0.167	0.446	0.056	0.042	−0.352	0.079	0.093
Hf	0.460	−0.209	0.169	0.197	0.009	−0.461	−0.142	0.207	0.283	0.399	0.169	−0.300	0.059	−0.183
Th	−0.082	0.396	0.796	0.597	0.346	0.114	0.151	−0.128	0.593	0.128	0.158	−0.586	0.139	0.270
U	0.234	0.231	0.242	0.372	0.544	0.015	0.363	0.064	0.664	0.257	0.353	−0.432	0.587	0.588

	Ni	Cu	Zn	Pb	As	Sb	Br	La	Ce	Sm	Yb	Lu	Hf	Th	U
Ni	1.000														
Cu	0.519	1.000													
Zn	0.635	0.918	1.000												
Pb	0.371	0.798	0.710	1.000											
As	0.637	0.941	0.977	0.709	1.000										
Sb	0.615	0.980	0.932	0.810	0.953	1.000									
Br	0.222	0.844	0.691	0.702	0.715	0.815	1.000								
La	−0.234	−0.578	−0.642	−0.392	−0.587	−0.554	−0.551	1.000							
Ce	−0.119	−0.485	−0.537	−0.224	−0.504	−0.434	−0.455	0.926	1.000						
Sm	−0.265	−0.638	−0.676	−0.447	−0.648	−0.611	−0.597	0.983	0.916	1.000					
Yb	−0.384	−0.485	−0.583	−0.310	0.556	−0.523	−0.438	0.718	0.720	0.683	1.000				
Lu	−0.155	−0.350	−0.389	−0.260	−0.346	−0.324	−0.338	0.811	0.846	0.793	0.519	1.000			
Hf	−0.055	−0.272	−0.251	−0.440	−0.314	−0.336	−0.204	0.188	0.103	0.198	0.278	0.230	1.000		
Th	−0.186	−0.581	−0.599	−0.383	−0.578	−0.544	−0.534	0.951	0.910	0.959	0.636	0.826	0.176	1.000	
U	−0.290	−0.240	−0.377	−0.118	−0.410	−0.193	0.009	0.460	0.430	0.516	0.244	0.366	0.162	0.499	1.000

C.D. : depth of core.

Appendix 9 Vertical distribution correlation between elements in the sediment core from site D

	C.D.	I.L.	N	P	Na	K	Rb	Cs	Ca	Sr	Sc	Ti	Cr	Mn
C.D.	1.000													
I.L.	−0.720	1.000												
N	−0.768	0.941	1.000											
P	*−0.962*	*0.569*	*0.630*	*1.000*										
Na	−0.757	0.350	0.437	0.762	1.000									
K	0.685	−0.258	−0.315	−0.688	−0.528	1.000								
Rb	0.688	−0.209	−0.345	−0.768	−0.777	0.591	1.000							
Cs	0.477	−0.473	−0.611	−0.377	−0.552	0.286	0.375	1.000						
Ca	−0.822	0.740	0.698	0.810	0.440	−0.560	−0.431	−0.170	1.000					
Sr	−0.800	0.284	0.388	0.867	0.726	−0.643	−0.686	−0.404	0.611	1.000				
Sc	0.846	−0.515	−0.620	−0.829	−0.823	0.423	0.635	0.464	−0.511	−0.794	1.000			
Ti	0.791	−0.746	−0.850	−0.673	−0.569	0.561	0.599	0.692	−0.580	−0.576	0.679	1.000		
Cr	0.810	−0.449	−0.468	−0.755	−0.669	0.599	0.448	0.403	−0.523	−0.799	0.813	0.600	1.000	
Mn	−0.741	0.230	0.267	0.788	0.685	−0.567	−0.610	−0.052	0.628	0.690	−0.618	−0.276	−0.607	1.000
Fe	0.479	−0.502	−0.606	−0.375	−0.378	0.211	0.468	0.620	−0.220	−0.417	0.537	0.831	0.491	0.070
Co	0.225	0.326	0.116	−0.374	−0.472	0.397	0.454	0.039	−0.093	−0.454	0.357	−0.008	0.179	−0.500
Ni	−0.291	0.319	0.282	0.293	−0.002	−0.154	−0.270	0.186	0.544	−0.013	0.100	−0.108	0.038	0.386
Cu	−0.920	0.778	0.842	0.889	0.592	−0.640	−0.603	−0.455	0.866	0.683	−0.727	−0.818	−0.600	0.577
Zn	−0.894	0.441	0.537	0.941	0.691	−0.771	−0.814	−0.371	0.714	0.880	−0.769	−0.726	−0.744	0.693
Hg	−0.865	0.384	0.503	0.891	0.849	−0.758	−0.857	−0.570	0.559	0.893	−0.820	−0.748	−0.797	0.640
Pb	−0.934	0.504	0.561	0.948	0.767	−0.685	−0.692	−0.455	0.720	0.930	−0.848	−0.679	−0.871	0.774
As	−0.744	0.707	0.668	0.733	0.331	−0.457	−0.348	0.050	0.922	0.453	−0.503	−0.481	−0.397	0.601
La	0.802	−0.403	−0.526	−0.851	−0.656	0.419	0.709	0.220	−0.642	−0.846	0.843	0.588	0.645	−0.708

	Fe	Co	Ni	Cu	Zn	Hg	Pb	As	La
Fe	1.000								
Co	−0.202	1.000							
Ni	0.043	0.105	1.000						
Cu	−0.448	−0.249	0.289	1.000					
Zn	−0.480	−0.435	0.206	0.858	1.000				
Hg	−0.573	−0.437	0.053	0.750	0.933	1.000			
Pb	−0.424	−0.354	0.111	0.822	0.932	0.914	1.000		
As	−0.095	−0.104	0.521	0.822	0.613	0.406	0.585	1.000	
La	0.445	0.342	−0.202	−0.708	−0.796	−0.749	−0.808	−0.641	1.000

C. D. : depth of core

Appendix 10 Vertical distribution correlation between elements in the sediment cores from the northern lake (average values of the correlation coefficients in 24 cores)

	C.D.	I.L.	N	P	Na	K	Rb	Cs	Mg	Ca	Sr	Ba	Sc	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb	As	Sb	Br	La	Ce	Sm	Yb	Lu	Hf	Th	U
C.D.	1.00																																	
I.L.	-0.29	1.00																																
N	-0.18	0.85	1.00																															
P	-0.25	0.79	0.67	1.00																														
Na	-0.19	0.05	-0.08	-0.01	1.00																													
K	-0.01	-0.43	-0.20	-0.41	[illegible]	1.00																												
Rb	0.16	-0.39	-0.51	-0.48	0.02	0.51	1.00																											
Cs	-0.03	0.03	0.23	0.07	0.22	0.24	0.47	1.00																										
Mg	0.18	0.18	0.07	0.20	0.09	-0.05	0.08	0.63	1.00																									
Ca	-0.24	0.15	0.38	0.25	0.24	0.12	-0.34	-0.01	0.10	1.00																								
Sr	0.12	-0.32	-0.07	-0.21	0.31	0.31	0.31	0.29	0.23	0.33	1.00																							
Ba	0.03	0.09	0.14	0.08	0.36	-0.04	0.04	0.21	0.51	0.13	0.12	1.00																						
Sc	0.39	-0.08	-0.05	-0.15	0.25	0.24	0.41	0.51	0.32	-0.12	0.04	0.31	1.00																					
Ti	0.49	-0.07	-0.07	-0.12	-0.21	0.16	0.26	0.17	0.50	-0.21	0.04	-0.11	0.51	1.00																				
Cr	0.14	0.07	0.06	0.09	0.28	0.22	0.25	0.34	0.35	0.07	0.20	0.16	0.51	0.32	1.00																			
Mn	-0.45	0.70	0.75	0.71	0.07	-0.20	-0.38	-0.08	-0.01	0.33	-0.17	0.03	-0.31	-0.29	-0.04	1.00																		
Fe	0.20	0.10	0.30	0.15	-0.11	0.29	0.09	0.29	0.20	0.10	0.09	-0.08	0.34	0.53	0.23	0.14	1.00																	
Co	0.08	0.43	0.39	0.35	0.19	0.01	-0.04	0.39	0.39	0.25	0.02	0.26	0.53	0.18	0.37	0.24	0.29	1.00																
Ni	0.05	0.39	0.18	0.36	-0.13	-0.26	-0.24	-0.03	0.28	0.01	-0.28	0.10	0.15	0.21	0.20	0.22	0.03	0.39	1.00															
Cu	-0.47	0.69	0.75	0.61	0.08	-0.18	-0.39	-0.03	0.16	0.32	-0.21	0.17	-0.13	-0.16	0.05	0.66	0.02	0.38	0.38	1.00														
Zn	-0.48	0.80	0.78	0.68	-0.04	-0.29	-0.37	-0.01	0.09	0.23	-0.37	0.10	-0.07	-0.17	0.08	0.73	0.02	0.36	0.42	0.86	1.00													
Hg	-0.17	0.49	0.71	0.38	-0.27	-0.19	-0.41	0.11	-0.30	0.34	0.22	0.27	-0.14	-0.07	-0.08	0.64	0.35	0.22	-0.01	0.68	0.74	1.00												
Pb	-0.63	0.68	0.60	0.54	0.02	-0.18	-0.16	0.09	0.06	0.18	-0.23	0.03	-0.13	-0.28	0.06	0.65	-0.03	0.23	0.23	0.74	0.81	0.55	1.00											
As	-0.47	0.74	0.80	0.71	0.03	-0.22	-0.47	-0.08	0.01	0.33	-0.30	0.05	-0.25	-0.29	-0.07	0.80	0.03	0.24	0.32	0.73	0.63	0.58	0.62	1.00										
Sb	-0.48	0.60	0.57	0.52	-0.04	-0.19	-0.40	-0.01	0.08	0.34	-0.38	0.22	-0.03	-0.16	0.09	0.62	0.02	0.28	0.37	0.69	0.83	0.55	0.76	0.77	1.00									
Br	-0.39	0.67	0.75	0.58	0.15	-0.38	-0.65	-0.17	0.11	0.46	-0.23	0.14	-0.18	-0.28	0.09	0.55	-0.04	0.25	0.25	0.72	0.73	0.48	0.56	0.78	0.73	1.00								
La	0.07	-0.25	-0.34	-0.21	0.43	0.39	0.52	0.41	0.23	-0.15	0.05	0.21	0.65	0.11	0.33	-0.30	0.01	0.17	-0.05	-0.33	-0.25	-0.61	-0.10	-0.28	-0.00	-0.29	1.00							
Ce	-0.08	0.01	-0.14	0.01	0.41	0.33	0.53	0.45	0.21	-0.06	0.05	0.25	0.63	0.05	0.28	-0.04	0.08	0.28	0.02	-0.14	-0.03	-0.26	0.13	-0.07	0.17	-0.20	0.94	1.00						
Sm	-0.01	-0.01	-0.16	-0.00	0.38	0.30	0.55	0.52	0.30	-0.08	0.04	0.22	0.70	0.08	0.28	-0.17	0.07	0.31	0.07	-0.15	-0.06	-0.41	0.09	-0.16	0.09	-0.30	0.97	0.93	1.00					
Yb	-0.07	0.12	0.09	0.23	0.23	0.39	0.26	0.29	0.20	0.06	-0.07	0.12	0.39	0.14	0.24	-0.11	0.13	0.12	0.03	0.03	0.01	-0.04	0.07	0.01	0.15	-0.24	0.62	0.59	0.63	1.00				
Lu	0.07	0.16	0.06	0.16	0.16	0.30	0.37	0.37	0.13	-0.08	-0.08	0.11	0.53	0.08	0.23	-0.05	0.09	0.31	0.09	-0.02	0.04	-0.31	0.13	-0.00	0.09	-0.24	0.70	0.69	0.72	0.51	1.00			
Hf	0.37	-0.27	-0.39	-0.16	0.06	-0.03	0.16	-0.01	0.09	-0.14	-0.02	0.15	0.24	0.05	0.02	-0.20	-0.08	-0.00	-0.07	-0.34	-0.22	-0.30	-0.25	-0.26	-0.12	-0.20	0.22	0.20	0.20	0.07	0.08	1.00		
Th	0.04	-0.25	-0.38	-0.20	0.39	0.32	0.56	0.53	0.19	-0.18	0.13	0.21	0.63	0.00	0.27	-0.25	0.01	0.15	-0.07	-0.34	-0.25	-0.53	-0.10	-0.25	-0.03	-0.31	0.91	0.89	0.92	0.57	0.66	0.29	1.00	
U	0.06	0.05	-0.15	0.04	0.24	0.04	0.09	0.12	0.33	0.08	0.06	0.32	0.28	-0.00	0.07	-0.06	-0.04	0.18	0.03	0.00	0.03	-0.04	-0.04	0.02	0.10	0.00	0.32	0.39	0.41	0.25	0.28	0.19	0.33	1.00

C.D. : depth of core

Appendix 11 Horizontal distribution correlation between elements in the upper 2cm layers of the sediment cores along the transect from Ado River to Ane River

	W.D.	I.L.	N	P	Na	K	Rb	Cs	Ca	Sr	Ba	Sc	Ti	Cr	Mn	Fe
W.D.	1.000															
I.L.	0.621	1.000														
N	0.697	0.969	1.000													
P	0.873	0.902	0.939	1.000												
Na	−0.924	−0.507	−0.611	−0.725	1.000											
K	−0.604	−0.890	−0.874	−0.852	0.445	1.000										
Rb	−0.530	−0.454	−0.431	−0.636	0.168	0.574	1.000									
Cs	0.556	0.882	0.848	0.728	−0.616	−0.706	−0.036	1.000								
Ca	−0.364	0.435	0.247	0.056	0.483	−0.284	−0.086	0.347	1.000							
Sr	−0.629	0.147	−0.034	−0.251	0.686	0.016	0.143	0.118	0.947	1.000						
Ba	0.721	0.270	0.399	0.461	−0.908	−0.306	0.140	0.497	−0.624	−0.749	1.000					
Sc	0.324	0.907	0.817	0.660	−0.279	−0.678	−0.175	0.894	0.690	0.480	0.067	1.000				
Ti	−0.683	0.081	−0.087	−0.329	0.684	0.107	0.284	0.110	0.903	0.989	−0.708	0.444	1.000			
Cr	−0.439	0.079	−0.042	−0.114	0.648	0.118	−0.271	−0.171	0.733	0.771	−0.891	0.280	0.722	1.000		
Mn	0.885	0.702	0.727	0.898	−0.677	−0.823	−0.789	0.480	−0.129	−0.435	0.460	0.366	−0.542	−0.260	1.000	
Fe	0.568	0.947	0.942	0.811	−0.576	−0.815	−0.164	0.966	0.356	0.107	0.440	0.901	0.084	−0.109	0.557	1.000
Co	0.146	0.843	0.717	0.548	−0.045	−0.654	−0.234	0.766	0.841	0.651	−0.168	0.966	0.599	0.455	0.289	0.793
Ni	−0.623	0.122	−0.074	−0.253	0.729	−0.009	0.029	0.044	0.945	0.987	−0.805	0.423	0.956	0.794	−0.374	0.040
Cu	0.427	0.948	0.857	0.737	−0.352	−0.840	−0.287	0.910	0.614	0.357	0.176	0.956	0.301	0.110	0.541	0.929
Zn	0.675	0.910	0.868	0.826	−0.646	−0.877	−0.289	0.933	0.275	−0.011	0.521	0.807	−0.061	−0.260	0.716	0.928
Pb	0.781	0.862	0.867	0.854	−0.784	−0.842	−0.263	0.908	0.070	−0.212	0.681	0.706	−0.250	−0.418	0.757	0.905
As	0.913	0.828	0.904	0.981	−0.796	−0.829	−0.595	0.673	−0.119	−0.416	0.583	0.536	−0.483	−0.274	0.913	0.764
Sb	0.645	0.988	0.953	0.907	−0.521	−0.825	−0.478	0.865	0.434	0.151	0.240	0.911	0.084	0.148	0.689	0.918
Br	0.831	0.893	0.960	0.974	−0.732	−0.885	−0.522	0.751	0.006	−0.288	0.542	0.640	−0.350	−0.230	0.857	0.854
La	−0.838	−0.872	−0.878	−0.888	0.837	0.745	0.284	−0.919	−0.068	0.208	−0.655	−0.744	0.241	0.307	−0.736	−0.896
Ce	−0.754	−0.525	−0.467	−0.617	0.724	0.312	0.298	−0.611	0.013	0.213	−0.468	−0.478	0.249	0.152	−0.565	−0.479
Sm	−0.286	0.402	0.311	0.146	0.464	−0.574	−0.295	0.164	0.692	0.597	−0.465	0.412	0.524	0.397	0.134	0.311
Yb	0.669	0.703	0.802	0.724	−0.769	−0.729	−0.031	0.789	−0.157	−0.369	0.794	0.518	−0.362	−0.592	0.588	0.836
Lu	0.247	0.819	0.747	0.670	0.010	−0.815	−0.643	0.505	0.669	0.435	−0.256	0.745	0.330	0.473	0.551	0.653
Hf	−0.862	−0.670	−0.804	−0.845	0.865	0.724	0.324	−0.629	0.355	0.597	−0.795	−0.365	0.622	0.565	−0.784	−0.711
Th	0.918	0.700	0.779	0.862	−0.903	−0.766	−0.375	0.693	−0.293	−0.566	0.816	0.411	−0.607	−0.598	0.861	0.722
U	0.755	0.961	0.956	0.975	−0.579	−0.888	−0.648	0.762	0.275	−0.033	0.292	0.778	−0.121	0.061	0.842	0.850

	Co	Ni	Cu	Zn	Pb	As	Sb	Br	La	Ce	Sm	Yb	Lu	Hf	Th	U
Co	1.000															
Ni	0.619	1.000														
Cu	0.926	0.330	1.000													
Zn	0.706	−0.033	0.920	1.000												
Pb	0.562	−0.243	0.826	0.977	1.000											
As	0.401	−0.419	0.638	0.788	0.852	1.000										
Sb	0.840	0.123	0.920	0.870	0.824	0.821	1.000									
Br	0.518	−0.306	0.735	0.841	0.884	0.982	0.871	1.000								
La	−0.579	0.251	−0.803	−0.933	−0.963	−0.866	−0.875	−0.876	1.000							
Ce	−0.331	0.221	−0.478	−0.611	−0.635	−0.562	−0.603	−0.483	0.776	1.000						
Sm	0.588	0.643	0.504	0.283	0.132	0.074	0.310	0.207	0.031	0.427	1.000					
Yb	0.346	−0.435	0.627	0.812	0.890	0.788	0.636	0.843	−0.817	−0.324	0.095	1.000				
Lu	0.829	0.466	0.789	0.601	0.481	0.563	0.795	0.647	−0.449	−0.118	0.771	0.314	1.000			
Hf	−0.186	0.629	−0.487	−0.719	−0.835	−0.926	−0.632	−0.918	0.804	0.410	0.039	−0.917	−0.318	1.000		
Th	0.238	−0.575	0.567	0.823	0.917	0.923	0.666	0.898	−0.882	−0.586	−0.057	0.884	0.316	−0.956	1.000	
U	0.709	−0.032	0.839	0.847	0.828	0.918	0.965	0.939	−0.858	−0.576	0.307	0.654	0.803	−0.733	0.761	1.000

W.D. : water depth at the sampling site.

Appendix 12 Horizontal distribution correlation between elements in the lower layers (below 10cm depth) of the sediment cores along the transect from Ado River to Ane River

	W.D.	I.L.	N	P	Na	K	Rb	Cs	Ca	Sr	Ba	Sc	Ti	Cr	Mn	Fe
W.D.	1.000															
I.L.	0.474	1.000														
N	0.508	0.992	1.000													
P	0.827	0.838	0.852	1.000												
Na	−0.889	−0.561	−0.557	−0.891	1.000											
K	−0.556	−0.912	−0.918	−0.876	0.701	1.000										
Rb	0.125	−0.653	−0.692	−0.332	−0.081	0.609	1.000									
Cs	0.849	0.791	0.787	0.891	−0.855	−0.819	−0.149	1.000								
Ca	−0.465	0.430	0.418	−0.064	0.474	−0.129	−0.712	−0.142	1.000							
Sr	−0.753	−0.034	−0.037	−0.499	0.821	0.311	−0.483	−0.561	0.886	1.000						
Ba	0.283	−0.651	−0.604	−0.248	−0.091	0.409	0.682	−0.102	−0.862	−0.602	1.000					
Sc	0.701	0.937	0.931	0.967	−0.811	−0.925	−0.431	0.898	0.118	−0.353	−0.438	1.000				
Ti	0.135	0.797	0.760	0.501	−0.179	−0.488	−0.508	0.446	0.739	0.388	−0.860	0.651	1.000			
Cr	−0.367	−0.325	−0.356	−0.488	0.544	0.682	0.318	−0.432	0.398	0.576	−0.174	−0.436	0.289	1.000		
Mn	0.899	0.792	0.818	0.957	−0.875	−0.855	−0.265	0.958	−0.153	−0.564	−0.072	0.915	0.394	−0.519	1.000	
Fe	0.744	0.922	0.913	0.962	−0.823	−0.887	−0.354	0.929	0.094	−0.375	−0.398	0.993	0.664	−0.366	0.928	1.000
Co	0.234	0.917	0.910	0.627	−0.250	−0.689	−0.719	0.555	0.724	0.330	−0.816	0.758	0.940	0.023	0.557	0.751
Ni	0.314	0.934	0.894	0.695	−0.426	−0.729	−0.528	0.673	0.567	0.133	−0.793	0.840	0.942	−0.016	0.612	0.843
Cu	−0.245	0.628	0.617	0.163	0.261	−0.329	−0.749	0.108	0.968	0.750	−0.885	0.342	0.856	0.302	0.090	0.327
Zn	0.635	0.964	0.950	0.896	−0.692	−0.861	−0.441	0.889	0.278	−0.193	−0.528	0.967	0.785	−0.245	0.866	0.978
Pb	0.707	0.936	0.922	0.937	−0.775	−0.862	−0.368	0.913	0.168	−0.301	−0.455	0.983	0.728	−0.287	0.901	0.995
As	0.861	0.842	0.867	0.983	−0.858	−0.878	−0.347	0.931	−0.058	−0.487	−0.183	0.950	0.479	−0.489	0.990	0.954
Sb	0.151	0.839	0.825	0.532	−0.154	−0.554	−0.652	0.450	0.782	0.427	−0.852	0.669	0.978	0.197	0.441	0.670
Br	−0.115	0.501	0.553	0.157	0.302	−0.272	−0.812	0.045	0.842	0.701	−0.603	0.238	0.618	0.198	0.142	0.218
La	−0.218	−0.928	−0.939	−0.624	0.242	0.807	0.854	−0.573	−0.663	−0.274	0.728	−0.752	−0.781	0.248	−0.598	−0.722
Ce	−0.479	−0.918	−0.917	−0.759	0.443	0.698	0.548	−0.703	−0.536	−0.118	0.657	−0.841	−0.911	−0.030	−0.710	−0.856
Sm	0.345	0.376	0.413	0.340	−0.317	−0.613	−0.338	0.535	−0.187	−0.356	0.204	0.355	−0.165	−0.766	0.527	0.334
Yb	0.867	0.809	0.822	0.925	−0.855	−0.860	−0.242	0.988	−0.131	−0.551	−0.093	0.913	0.419	−0.503	0.988	0.932
Lu	0.562	0.791	0.830	0.748	−0.566	−0.919	−0.614	0.779	0.070	−0.294	−0.178	0.772	0.294	−0.724	0.830	0.742
Hf	−0.804	−0.720	−0.735	−0.911	0.906	0.901	0.257	−0.896	0.294	0.682	0.017	−0.873	−0.206	0.760	−0.936	−0.857
Th	0.904	0.460	0.475	0.776	−0.917	−0.664	0.117	0.871	−0.585	−0.874	0.331	0.687	−0.031	−0.649	0.874	0.709
U	0.784	0.682	0.705	0.711	−0.571	−0.553	−0.139	0.852	0.076	−0.259	−0.087	0.709	0.547	−0.022	0.825	0.774

	Co	Ni	Cu	Zn	Pb	As	Sb	Br	La	Ce	Sm	Yb	Lu	Hf	Th	U
Co	1.000															
Ni	0.944	1.000														
Cu	0.868	0.736	1.000													
Zn	0.859	0.925	0.502	1.000												
Pb	0.797	0.884	0.399	0.992	1.000											
As	0.635	0.676	0.179	0.900	0.931	1.000										
Sb	0.983	0.926	0.902	0.794	0.729	0.529	1.000									
Br	0.740	0.481	0.866	0.362	0.269	0.218	0.749	1.000								
La	−0.941	−0.853	−0.808	−0.816	−0.749	−0.658	−0.871	−0.750	1.000							
Ce	−0.958	−0.933	−0.720	−0.930	−0.895	−0.772	−0.939	−0.630	0.862	1.000						
Sm	0.118	0.097	−0.064	0.306	0.289	0.452	−0.055	0.061	−0.407	−0.102	1.000					
Yb	0.570	0.648	0.117	0.885	0.910	0.968	0.453	0.118	−0.615	−0.712	0.576	1.000				
Lu	0.571	0.535	0.261	0.725	0.712	0.818	0.411	0.351	−0.768	−0.581	0.834	0.841	1.000			
Hf	−0.396	−0.496	0.074	−0.758	−0.806	−0.919	−0.249	0.060	0.509	0.510	−0.637	−0.929	−0.853	1.000		
Th	0.111	0.252	−0.370	0.582	0.653	0.810	−0.021	−0.315	−0.198	−0.304	0.607	0.877	0.682	−0.914	1.000	
U	0.622	0.625	0.300	0.799	0.792	0.802	0.574	0.348	−0.568	−0.787	0.350	0.845	0.611	−0.595	0.626	1.000

W.D. : water depth at the sampling site.

Appendix 13 Horizontal distribution correlation between elements in the upper 2 cm layers of the sediment cores and the Ekman dredge sediments

	W.D.	I.L.	N	P	K	Rb	Ca	Sr	Ti	Mn	Fe	Ni	Cu	Zn	Hg	Pb	As
W.D.	1.000																
I.L.	0.197	1.000															
N	0.100	0.863	1.000														
P	0.222	0.630	0.540	1.000													
K	−0.007	−0.580	−0.509	−0.583	1.000												
Rb	0.051	0.067	0.037	−0.356	0.523	1.000											
Ca	−0.178	−0.045	−0.070	0.019	0.038	−0.205	1.000										
Sr	−0.289	−0.051	−0.081	−0.170	0.029	0.010	0.712	1.000									
Ti	0.168	0.237	0.002	0.214	−0.392	−0.318	0.142	0.022	1.000								
Mn	0.803	0.268	0.176	0.294	−0.082	0.008	−0.135	−0.218	0.100	1.000							
Fe	0.440	0.571	0.411	0.409	−0.476	−0.023	0.008	−0.071	0.749	0.393	1.000						
Ni	0.553	0.622	0.544	0.541	−0.545	−0.155	−0.213	−0.400	0.435	0.401	0.617	1.000					
Cu	0.274	0.760	0.699	0.772	−0.580	−0.250	−0.093	−0.287	0.260	0.246	0.443	0.705	1.000				
Zn	−0.138	0.696	0.744	0.701	−0.603	−0.298	−0.016	−0.174	0.080	−0.009	0.207	0.442	0.805	1.000			
Hg	−0.221	0.673	0.534	0.767	−0.718	−0.543	0.119	−0.321	−0.278	−0.139	−0.197	0.382	0.819	0.935	1.000		
Pb	−0.093	0.635	0.678	0.662	−0.478	−0.260	0.046	−0.143	−0.052	0.017	0.088	0.380	0.818	0.901	0.884	1.000	
As	0.902	0.151	0.099	0.175	−0.041	0.029	−0.198	−0.342	0.121	0.719	0.439	0.529	0.196	−0.173	−0.284	−0.147	1.000

W.D. : water depth at the sampling site.

Appendix 14 Analytical data on the Ekman dredge sediments

Sampling site	Sampling Date	Water Depth (m)	pH	I.L. (%)	N	P	Si	K	Ca	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr	Hg
					$(\mu g \cdot g^{-1})$		(%)	(%)		$(\mu g \cdot g^{-1})$		(%)		(%)	$(\mu g \cdot g^{-1})$							$(\mu g \cdot g^{-1})$
					C		C	XRF		AA	XRF	C	XRF	XRF	XRF							AA
1	'76,11,20	1.2	—	2.0	322	207	36	2.92	0.51	486	561	2.02	3.04	0.45	3	9	62	11	6	107	119	0.02
2		11.0	6.9	5.9	1330	494	31	2.61	0.53	664	626	3.50	4.10	0.47	9	29	136	29	6	116	118	0.07
3		8.0	7.2	8.4	2400	678	—	2.42	0.36	987	843	4.12	4.13	0.48	17	44	188	46	10	130	103	0.19
4		1.5	6.7	9.5	2420	2410	—	2.30	0.50	1170	956	2.91	3.66	0.41	10	70	510	86	N.D.	106	114	0.62
5		1.7	7.4	6.2	1750	671	—	2.41	0.41	863	710	3.30	3.54	0.50	19	34	126	30	8	121	111	0.10
6		4.0	7.7	10.2	4740	455	—	2.24	0.40	779	725	3.43	3.60	0.35	16	49	277	61	12	142	88	0.33
7		2.5	7.6	9.7	3460	1150	—	2.25	0.39	1490	1030	3.81	4.41	0.47	17	52	387	66	4	129	99	0.32
8		3.0	7.2	7.4	3320	574	28	2.40	1.04	848	737	2.40	2.72	0.26	2	9	110	38	N.D.	135	233	0.11
9	〃	4.5	7.3	11.1	4840	586	24	2.36	0.39	1250	1010	4.70	4.75	0.42	26	54	356	76	13	149	77	0.24
10		3.0	7.4	11.8	4550	841	—	2.15	0.62	1070	947	3.94	4.20	0.40	15	47	375	78	2	135	124	0.43
11		3.5	6.2	7.4	1950	507	—	2.79	0.68	675	691	2.68	3.14	0.29	7	48	195	70	1	161	157	0.36
12		2.5	7.4	11.0	3050	497	29	2.66	0.66	934	735	3.39	2.77	0.30	9	37	178	67	3	133	141	0.36
13		3.0	7.3	13.1	4340	1750	—	2.02	0.41	1200	862	3.81	3.75	0.39	21	130	627	218	N.D.	115	93	0.83
14		2.2	7.0	11.9	3610	1370	29	2.20	0.72	624	547	2.93	2.96	0.39	11	99	462	135	N.D.	104	105	0.52
15		4.0	7.4	8.3	3950	576	—	2.18	0.35	1090	949	3.72	4.06	0.34	15	48	377	70	16	135	78	0.33
16		3.5	5.8	—	4660	1230	21	1.47	0.21	483	344	2.79	2.75	0.37	29	135	829	185	N.D.	85	50	0.94
17		2.5	7.1	11.2	4810	1870	—	1.82	0.42	666	640	2.86	3.06	0.36	27	154	656	306	N.D.	96	68	0.66
18		1.5	7.0	14.8	5150	2980	—	1.80	0.80	1830	1900	3.45	3.97	0.35	38	142	899	311	N.D.	100	73	1.42
19		—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20	'77,1,22	1.2	7.2	9.5	2370	1110	—	1.88	0.27	1050	925	3.33	3.29	0.40	28	44	397	59	8	128	70	—
21		2.5	6.8	7.5	1780	892	—	2.12	0.28	668	564	3.10	2.93	0.39	20	40	261	59	1	134	73	—
22		3.5	6.6	12.8	2860	957	25	2.16	0.34	1470	1280	4.59	4.66	0.46	25	59	280	79	9	156	75	—
23		2.3	7.3	10.2	2390	626	29	2.27	0.42	1420	1120	3.63	3.48	0.39	15	39	170	54	9	132	105	—
24		1.2	7.7	12.7	4010	2130	—	1.97	0.42	1310	1020	4.68	4.58	0.40	23	93	305	78	8	132	94	—
25		1.5	7.3	9.8	2630	1350	—	2.18	0.37	1130	972	3.97	3.98	0.40	17	89	251	65	6	135	90	—
26		1.8	7.2	9.3	2450	818	—	2.22	0.38	1340	1160	3.34	3.35	0.37	17	48	196	60	6	142	99	—
27		5.0	7.1	7.8	1280	662	—	2.30	0.36	956	764	3.95	4.00	0.40	18	59	187	56	8	142	102	—
28		6.0	7.4	6.8	1220	663	—	2.60	0.48	1050	856	3.79	3.82	0.41	20	61	192	54	7	144	110	—
29		3.0	7.1	0.9	1210	92	37	4.38	0.29	276	339	0.85	1.24	0.20	3	3	33	16	1	134	61	—
30		3.0	7.4	9.7	2240	1450	—	2.30	0.29	893	472	3.59	3.64	0.43	12	38	184	43	6	126	72	—
31	'77,3,19	3.0	7.1	1.5	808	158	—	2.85	0.14	184	203	0.84	0.91	0.01	N.D.	N.D.	17	17	13	125	42	—
32		7.0	6.5	2.4	614	493	—	3.49	0.93	570	689	2.87	3.45	0.43	4	21	83	17	20	128	107	—
33		3.5	7.2	1.4	200	235	—	3.35	0.46	342	339	1.93	1.98	0.25	4	13	48	17	5	142	86	—
34		16.0	6.0	4.7	972	476	—	2.73	0.64	816	719	3.49	3.27	0.42	17	51	115	32	16	123	115	—
35		23.0	7.6	6.1	2660	636	—	2.79	0.53	1500	1600	3.34	3.42	0.22	6	26	130	45	40	176	91	—
36		16.5	7.2	9.8	2860	1080	—	2.11	0.31	755	613	5.19	4.22	0.41	28	63	218	56	14	127	82	—
37	'77,4,4-5	3.0	—	4.1	740	649	—	2.24	0.66	701	731	3.64	3.90	0.42	16	31	111	11	18	99	116	—
38		4.0	7.1	4.5	1650	1470	—	2.28	0.70	770	757	3.03	3.13	0.35	12	26	200	31	6	115	149	—
39		4.0	—	2.8	428	857	—	1.89	0.43	843	785	4.00	4.13	0.56	9	24	116	15	23	77	79	—
40		12.0	—	4.2	808	234	—	4.00	0.30	745	725	2.03	2.02	0.20	3	14	81	30	8	215	59	—
41		17.0	—	2.8	660	404	—	2.54	0.13	741	753	3.11	3.00	0.36	17	33	88	10	15	136	61	—
42		7.0	6.1	5.6	3430	1750	—	2.03	0.23	308	415	4.40	4.02	0.41	18	69	287	64	13	118	57	—
43		7.0	—	2.2	595	552	—	1.93	0.55	769	744	2.56	2.55	0.34	10	10	156	62	4	81	123	—
44		6.0	—	4.8	590	890	—	1.98	0.94	867	936	4.01	4.24	0.60	23	44	153	23	15	85	80	—
45		7.5	—	3.6	529	558	—	2.35	0.39	714	823	3.56	3.65	0.49	19	37	122	13	16	109	70	—
46		6.5	—	2.2	351	342	—	3.19	0.50	623	748	2.15	2.71	0.30	7	5	65	15	19	120	78	—
47		16.0	—	6.1	1630	645	—	2.79	0.25	764	677	3.60	3.58	0.46	25	46	116	26	15	147	88	—
A	'76,11,20	4.0	7.4	11.0	5460	710	—	2.29	0.36	1580	1380	4.49	4.13	0.36	27	58	355	76	18	140	74	0.24
B		3.0	7.1	9.1	2670	680	—	2.38	0.42	1500	1440	4.48	4.38	0.51	24	50	308	52	18	143	93	0.18
C		2.0	—	—	1380	255	—	—	—	652	—	1.80	—	—	—	—	—	—	—	—	—	—
D		4.0	7.7	10.3	3220	585	—	2.33	0.45	1460	1230	3.99	4.04	0.40	22	52	254	68	15	149	94	0.18
E	'76,8,5	75.0	—	11.7	4200	1620	26	2.03	0.31	3840	4000	4.19	4.30	0.35	46	94	247	76	130	116	56	0.21
O	'77,4,4	61.0	—	9.7	—	1180	—	2.55	0.38	4650	5400	4.87	5.09	0.46	25	77	208	58	77	136	77	—
G		97.0	—	10.9	3210	1640	—	2.35	0.32	13900	15300	4.87	4.63	0.40	27	75	199	59	85	123	65	0.16
X	'77,11,4	90.0	—	9.8	—	1590	—	2.12	0.33	5030	5270	5.08	4.36	0.41	49	99	215	49	77	117	57	—

(—)not analysed. N.D. : undetectable. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.1 Analytical data on the sediment core

Sampling site : A. Sampling date : 11/20, 1976. Water depth : 4.0m.

Depth(cm)	I.L. (%)	N	P	K	Ca	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr	Hg
		($\mu g \cdot g^{-1}$)		(%)		($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)				($\mu g \cdot g^{-1}$)
		C		XRF		AA	XRF	C	XRF	XRF				XRF				AA
0-2	11.0	5460	710	2.29	0.36	1580	1380	4.49	4.13	0.36	27	58	355	76	18	140	74	0.24
2-4	10.5	4300	550	2.39	0.31	1290	1050	4.21	3.88	0.36	22	54	332	75	8	139	72	0.23
4-6	9.0	3730	580	2.23	0.29	1000	683	3.79	3.25	0.29	15	39	285	57	11	122	65	0.20
6-8	4.5	1930	270	2.00	0.14	490	359	2.05	1.83	0.18	4	16	145	30	6	94	57	0.13
8-10	2.9	1320	210	2.21	0.15	330	291	1.53	1.47	0.17	1	12	118	24	6	88	56	0.08
10-12	3.2	1230	180	2.07	0.15	360	410	1.73	1.68	0.18	3	12	87	24	4	85	52	0.07
12-14	9.7	3190	380	2.26	0.26	840	761	4.11	3.92	0.33	13	41	143	48	8	131	59	0.15
14-16	12.4	4010	410	2.66	0.31	990	834	4.91	4.98	0.44	28	49	165	59	8	165	66	—
16-18	11.2	3400	380	2.27	0.30	940	781	4.77	4.53	0.43	22	49	153	59	8	165	68	0.14
18-20	11.3	3050	380	2.39	0.31	410	759	4.71	4.51	0.44	20	46	157	56	7	162	67	—
20-22	11.5	3180	320	2.40	0.34	900	776	4.12	4.52	0.46	27	50	160	56	8	153	64	0.12
22-24	11.3	2880	340	2.23	0.27	890	740	4.53	4.40	0.44	31	44	159	60	6	159	66	—
24-26	10.0	1900	360	2.28	0.25	890	711	4.72	4.37	0.46	21	44	160	57	7	160	65	0.10
26-28	9.5	1740	320	2.29	0.29	900	755	4.79	4.52	0.48	23	41	157	46	10	159	64	—
28-30	—	1420	240	2.27	0.27	910	784	4.76	4.61	0.50	28	45	163	48	6	157	65	0.14

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.2 Analytical data on the sediment core

Sampling site : B. Sampling date : 11/20, 1976. Water depth : 3.0m.

Depth(cm)	I.L. (%)	N	P	K	Ca	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr	Hg
		$(\mu g \cdot g^{-1})$		(%)		$(\mu g \cdot g^{-1})$		(%)		(%)				$(\mu g \cdot g^{-1})$				$(\mu g \cdot g^{-1})$
		C		XRF		AA	XRF	C	XRF	XRF				XRF				AA
0–2	9.1	2670	680	2.38	0.42	1500	1440	4.48	4.38	0.51	24	50	308	52	18	143	93	0.18
2–4	9.0	3250	660	2.32	0.42	1680	1420	4.55	4.47	0.50	25	49	308	53	21	141	94	0.19
4–6	9.2	2760	680	2.35	0.42	1450	1270	4.55	4.55	0.54	35	50	312	56	15	144	94	0.22
6–8	9.2	2840	630	2.50	0.45	1350	1160	4.64	4.50	0.53	27	51	328	56	11	143	97	0.18
8–10	9.5	2530	600	2.40	0.42	1130	912	4.68	4.48	0.51	28	56	361	61	9	144	95	0.21
10–12	9.1	2720	510	2.40	0.41	920	813	4.20	4.47	0.54	29	56	429	64	6	151	101	0.18
12–14	9.9	2840	550	2.35	0.37	920	712	4.52	4.45	0.51	27	52	430	59	10	147	89	0.17
14–16	8.9	2030	490	2.41	0.36	920	699	4.72	4.38	0.50	29	47	200	50	10	153	84	0.16
16–18	9.2	2460	480	2.37	0.37	850	737	4.56	4.56	0.52	23	44	190	46	13	151	84	0.18
18–20	9.7	2640	420	2.28	0.33	920	719	4.58	4.31	0.50	30	44	176	44	7	150	82	0.09
20–22	9.6	3010	400	2.36	0.35	910	741	4.42	4.24	0.50	28	46	175	45	7	153	83	0.10
22–24	9.9	3070	400	2.50	0.33	900	705	4.42	4.45	0.50	20	44	154	37	11	147	79	0.11
24–26	10.0	2970	390	2.29	0.33	870	719	4.54	4.24	0.49	25	43	146	43	9	145	79	0.10
26–28	9.6	2910	370	2.42	0.32	950	751	4.50	4.42	0.53	30	42	152	37	11	142	78	0.08
28–30	9.3	2870	310	2.54	0.34	780	780	3.99	4.61	0.53	25	45	157	43	6	148	81	0.08
30–32	9.2	2530	410	2.34	0.33	980	735	4.90	4.39	0.51	28	46	152	45	4	147	82	—
32–34	8.0	2330	360	2.36	0.30	890	672	3.55	4.01	0.48	25	43	147	44	4	149	85	—
34–36	8.2	2110	310	2.38	0.32	720	661	3.85	4.26	0.52	26	44	151	42	6	145	78	—
36–38	8.6	1990	430	2.40	0.31	900	809	4.63	4.44	0.52	25	42	147	41	7	152	80	—
38–40	8.2	1940	390	2.45	0.30	870	750	4.48	4.31	0.50	27	44	149	42	6	151	82	—
40–42	7.9	1870	400	2.34	0.29	900	778	4.61	4.21	0.51	17	41	146	42	6	151	82	—

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.3 *Analytical data on the sediment core*

Sampling site : D. Sampling date : 11/20, 1976. Water depth : 4.0 m.

Depth (cm)	I.L. (%)	N	P	Na	Ca	K	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb	As		Hg	Co	Cr	Cs	Sc	La
		($\mu g \cdot g^{-1}$)		(%)	(%)		($\mu g \cdot g^{-1}$)		(%)			(%)			($\mu g \cdot g^{-1}$)				($\mu g \cdot g^{-1}$)		($\mu g \cdot g^{-1}$)			($\mu g \cdot g^{-1}$)		
		C		NAA	XRF		AA	XRF	C	XRF	NAA	XRF			XRF				XRF	NAA	AA			NAA		
0-1	10.1	3310	599	1.07	0.45	2.33	1570	1230	3.99	4.04	3.90	0.40	22	52	254	68	94	149	15	29	0.17	12.8	52	6.3	12.3	46.5
1-2	10.5	3120	570				1340		3.99												0.19					
2-3	10.8	3270	577	1.05	0.39	2.38	1210	1030	3.84	3.84	3.64	0.39	24	47	248	66	90	144	8	21	0.20	16.1	54	5.4	12.7	49.0
3-4	9.8	3320	560				1310		4.32												0.20					
4-5	10.2	3120	533	1.09	0.40	2.45	1070	895	3.89	3.83	3.39	0.40	15	47	237	70	98	151	8	20	0.22	15.7	42	5.3	11.6	47.1
5-6	10.8	3160	605				1050		4.09												0.17					
6-7	10.5	3550	538	1.11	0.39	2.35	950	770	3.83	3.74	3.71	0.37	18	50	250	62	90	143	10	21	0.21	14.5	61	5.6	12.1	48.6
7-8	10.4	3340	550				1000		3.94												0.20					
8-9	10.1	3620	506	1.01	0.39	2.33	900	731	3.94	3.69	3.96	0.36	18	50	253	65	94	149	6	17	0.21	13.7	53	4.7	12.8	50.7
9-10	10.1	3800	493				850		3.83												0.20					
10-12	10.8	3270	493	0.90	0.40	2.40	930	756	4.12	3.83	3.74	0.38	18	51	249	64	88	151	10	26	0.16	16.8	62	5.9	13.1	51.7
12-14	11.2	3900	499	0.88	0.42	2.44	870	735	4.03	4.03	3.61	0.41	21	51	195	58	85	155	13	23	0.12	15.3	75	5.8	13.4	51.4
14-16	11.7	3510	434	0.89	0.43	2.45	820	669	3.84	3.83	3.48	0.40	24	45	179	57	83	156	11	18	0.12	19.2	61	6.1	13.9	54.1
16-18	11.0	3500	409	0.87	0.40	2.42	780	674	3.94	3.86	3.49	0.42	23	49	171	57	81	152	8	18	—	17.5	75	5.8	14.0	53.6
18-20	10.8	3350	366	0.88	0.36	2.43	790	623	3.98	3.84	3.43	0.39	17	41	143	55	83	158	7	19	0.11	19.8	64	5.6	13.6	53.2
20-22	11.0	3650	386	0.96	0.37	2.40	790	624	4.02	3.79	3.70	0.39	21	42	137	49	83	158	10	17	—	13.8	60	6.2	13.9	56.7
22-24	10.7	3650	359	0.97	0.35	2.60	790	657	3.77	3.83	3.44	0.40	19	42	134	53	80	154	6	15	0.10	16.6	78	5.4	13.1	52.6
24-26	10.3	3090	381	0.98	0.34	2.33	830	666	4.05	3.91	3.86	0.41	22	44	140	47	75	150	11	17	—	16.6	68	6.7	13.9	55.3
26-28	8.9	2340	372	0.90	0.35	2.47	820	691	4.03	4.02	3.48	0.42	17	40	136	50	78	159	5	10	—	11.9	68	5.6	13.3	53.2
28-30	8.8	1820	339	0.96	0.34	2.42	800	694	3.73	4.13	3.97	0.44	17	37	133	53	80	156	3	13	0.11	15.4	77	5.6	14.6	59.9
30-32	8.4	990	342	0.84	0.34	2.44	800	644	3.87	4.00	3.61	0.43	17	35	134	51	80	162	3	11	—	12.9	74	5.9	14.3	57.2
32-34	7.7	1510	309	0.84	0.30	2.50	740	624	3.64	4.01	3.72	0.45	16	33	135	51	80	159	3	11	0.09	14.8	66	6.6	13.7	55.7
34-36	8.1	1510	353	0.84	0.35	2.49	720	659	3.58	4.13	4.02	0.44	20	33	137	51	78	153	6	18	—	12.8	64	7.5	14.9	54.8
36-38	7.2	1130	324	0.82	0.34	2.51	780	633	3.70	4.01	3.67	0.45	20	33	143	50	84	153	4	15	0.09	16.0	88	6.6	14.9	53.0

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron *activation analysis.*

Appendix 15.4 Analytical data on the sediment core

Sampling site : E. Sampling date : 8/5, 1976. Water depth : 75.0m.

Depth(cm)	I.L. (%)	N	P	Na	Ca	K	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb	As	Hg	Co	Cr	Cs	Sc	La
		($\mu g \cdot g^{-1}$)		(%)	(%)		($\mu g \cdot g^{-1}$)		(%)			(%)	($\mu g \cdot g^{-1}$)							($\mu g \cdot g^{-1}$)	($\mu g \cdot g^{-1}$)				
		C		NAA	XRF		AA	XRF	C	XRF	NAA	XRF	XRF							AA	NAA				
0-2	11.7	4200	1620	0.59	0.31	2.03	3840	4000	4.19	4.30	4.80	0.35	46	94	247	76	56	116	130	0.21	17.2	46	13.4	14.0	37
2-4	10.2	3350	1220	0.70	0.34	2.36	3010	2690	4.76	4.07	4.98	0.40	45	91	250	82	64	128	58	0.30	18.7	66	12.5	16.5	44
4-6	8.7	2500	1040	0.75	0.37	2.41	2550	2530	4.85	4.69	4.82	0.43	44	90	232	72	67	130	37	0.24	18.6	60	12.9	16.4	47
6-8	9.0	2970	1060	0.71	0.36	2.27	2630	2630	4.72	4.37	5.01	0.43	38	100	251	73	66	130	41	0.26	19.2	61	15.5	17.0	46
8-10	8.8	2720	1040	0.77	0.32	2.33	2680	2430	5.31	4.29	4.92	0.40	50	99	232	67	68	125	37	0.22	19.3	56	12.8	16.2	47
10-12	8.7	2540	1170	0.74	0.36	2.35	3070	2780	4.86	4.61	—	0.41	46	95	214	66	67	128	38	0.18	—	—	—	—	—
12-14	8.6	2280	1190	0.80	0.35	2.36	2860	2670	5.03	4.38	4.69	0.39	36	96	199	57	68	128	39	0.14	16.9	60	11.9	14.6	44
14-16	7.7	2020	1040	0.81	0.34	2.58	2420	2320	4.79	4.57	4.83	0.43	41	85	187	48	66	133	32	0.10	17.1	61	12.5	16.3	47
16-18	7.8	2080	840	0.79	0.36	2.54	2180	1800	4.72	4.14	—	0.43	44	76	181	51	67	133	25	0.08	—	—	—	—	—
18-20	8.0	2100	970	0.79	0.33	2.40	2400	2140	5.04	4.36	5.20	0.42	41	73	179	44	62	126	30	0.09	19.3	59	11.9	17.5	56
20-22	8.0	2950	1130	0.81	0.34	2.42	2150	1990	4.91	4.11	4.60	0.42	46	78	184	50	61	134	27	0.08	17.0	64	10.3	15.9	55
22-24	8.2	2030	910	0.76	0.32	2.42	2250	1690	4.99	3.90	4.54	0.44	44	75	186	49	57	129	25	0.08	17.0	55	11.0	16.0	53
24-26	8.2	1820	690	0.75	0.30	2.48	1780	1500	4.75	4.03	4.24	0.43	50	70	176	47	61	135	25	0.08	16.0	58	10.5	16.3	54
26-28	8.2	1760	970	0.69	0.28	2.50	2030	1830	4.80	4.39	4.48	0.44	35	67	183	54	62	144	25	0.08	16.3	57	12.1	17.1	56
28-30	8.1	1750	840	0.77	0.31	2.59	1930	1700	4.73	4.35	4.20	0.44	37	58	172	53	61	142	20	0.08	15.2	65	13.9	15.9	53
30-32	7.1	1720	870	0.70	0.30	2.62	1950	1730	4.74	4.29	4.27	0.45	42	78	201	54	61	140	27	0.09	14.8	57	12.4	16.4	50

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.5 Analytical data on the sediment core

Sampling site : F. Sampling date : 8/5, 1976.
Water depth : 87.0m.

Depth (cm)	P	Mn	Fe	N
	($\mu g \cdot g^{-1}$)		(%)	
	C	AA	C	
0−2	1220	4720	4.98	2880
2−4	1030	4460	4.64	2930
4−6	1300	5390	5.10	3430
6−8	1720	5460	5.33	2490
8−10	1340	3770	5.11	2370
10−12	1030	3180	4.83	1990
12−14	1110	3060	4.95	2130
14−16	1060	3000	4.94	1650
16−18	1160	2180	4.99	2030
18−20	977	2780	4.18	1830
20−22	1120	2920	5.01	1750
22−24	985	2660	5.12	1880
24−26	−	−	−	−
26−28	980	2840	5.12	2060
28−30	−	−	−	−
30−32	1170	3040	5.62	2090
32−34	−	−	−	−
34−36	1200	3030	5.26	1820
36−38	−	−	−	−
38−40	884	2290	5.12	2090
40−42	−	−	−	−
42−44	1080	2770	5.36	1750
44−46	−	−	−	−
46−48	835	2330	5.26	1740

(−)not analysed. Analytical method :
(C)colorimetry,
(AA)atomic absorption spectrophotometry.

Appendix 15.6 Analytical data on the sediment core

Sampling site : G-1. Sampling date : 4/4, 1977. Water depth : 97.0m.

Depth(cm)	Na	Ca	K	Mn	Fe		Ti	Ni	Cu	Zn	Pb	Sr	Rb		As		Co	Cr	Sb	Ba
	(%)	(%)		($\mu g\cdot g^{-1}$)	(%)		(%)			($\mu g\cdot g^{-1}$)			($\mu g\cdot g^{-1}$)		($\mu g\cdot g^{-1}$)			($\mu g\cdot g^{-1}$)		
	NAA	XRF		XRF	XRF	NAA	XRF	XRF					XRF	NAA	XRF	NAA	NAA			
0-0.5	0.62	0.33	2.29	22340	4.44	4.76	0.43	39	91	230	46	55	114	150	158	139	17.4	58	4.9	846
0.5-1	0.69	0.28	2.31	10100	4.57	4.92	0.41	33	76	174	54	69	137	177	78	83	16.7	69	3.7	760
1-2	0.77	0.33	2.52	4400	4.55	5.13	0.43	28	73	153	43	68	136	157	47	52	18.8	68	3.0	701
2-3	0.80	0.34	2.75	2500	4.63	5.23	0.46	30	60	132	37	73	148	205	34	40	20.6	75	2.5	718
3-4	0.77	0.32	2.76	2080	4.60	4.74	0.48	33	53	132	33	70	147	178	27	29	17.3	71	1.8	763
4-5	0.70	0.30	2.60	1700	4.28	4.30	0.46	26	55	135	31	67	144	168	24	25	15.2	67	1.5	745
5-6	0.74	0.33	2.70	1950	4.49	4.93	0.44	29	58	131	33	66	144	173	27	28	18.4	67	1.9	749
6-8	0.75	0.30	2.89	1940	4.59	5.08	0.48	31	55	133	31	64	148	183	26	30	18.0	68	1.9	725
8-10	0.65	0.27	2.76	1600	4.37	4.27	0.44	34	56	140	36	66	154	145	25	26	17.1	63	1.9	661
10-12	0.68	—	—	—	—	4.82	—	—	—	—	—	—	—	185	—	27	16.9	68	2.0	737
12-14	0.68	0.29	2.70	1970	4.70	5.16	0.48	34	58	143	36	64	149	169	29	31	18.2	70	2.3	811
14-16	0.62	—	—	—	—	4.65	—	—	—	—	—	—	—	141	—	27	17.7	69	2.5	600
16-18	0.60	0.27	2.65	1720	4.83	4.87	0.52	29	57	147	32	67	150	155	27	26	18.4	59	2.0	745
18-20	0.61	—	—	—	—	4.70	—	—	—	—	—	—	—	155	—	24	18.4	65	1.7	660
20-22	0.58	0.28	2.60	1940	4.92	4.57	0.52	29	51	141	33	65	148	154	23	23	16.2	73	1.7	500
22-24	0.65	—	—	—	—	4.58	—	—	—	—	—	—	—	201	—	28	19.6	69	1.9	821
24-26	0.69	0.26	2.77	1620	4.64	4.73	0.53	31	58	130	26	68	146	161	27	25	18.7	73	2.0	613
26-28	0.69	—	—	—	—	4.64	—	—	—	—	—	—	—	181	—	25	19.7	78	2.0	782
28-30	0.66	0.26	2.56	1490	4.61	4.77	0.54	33	57	139	28	70	147	185	23	26	17.2	79	2.1	858
30-32	0.72	—	—	—	—	5.15	—	—	—	—	—	—	—	230	—	29	20.1	83	2.3	891
32-34	0.66	0.28	2.78	1780	4.66	4.70	0.51	33	57	136	31	66	150	178	25	27	19.3	78	2.0	752
34-36	0.70	—	—	—	—	4.73	—	—	—	—	—	—	—	182	—	26	21.8	70	1.9	655
36-38	0.70	0.28	2.60	1940	4.82	5.07	0.52	29	56	136	29	68	146	167	26	30	18.7	70	2.0	755
38-40	0.67	—	—	—	—	5.20	—	—	—	—	—	—	—	141	—	26	18.0	78	1.9	631
40-42	—	0.28	2.63	1850	4.75	—	0.52	29	53	134	28	64	143	—	25	—	—	—	—	—

Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br
						($\mu g\cdot g^{-1}$)							
						NAA							
10.0	12.8	7.3	70	3.0	0.50	3.3	15.4	3.1	—	1.1	0.78	36.2	12.5
9.6	13.1	7.8	79	3.6	0.53	4.0	16.2	3.3	—	0.6	0.80	38.6	11.9
11.7	14.0	8.5	78	3.5	0.55	4.7	18.2	3.5	—	1.0	0.98	40.9	12.1
14.5	15.7	9.3	85	3.8	0.56	4.6	19.3	2.1	59	1.0	1.03	44.5	8.2
11.9	14.3	9.1	84	3.6	0.55	3.7	19.3	3.4	—	1.1	0.91	44.5	5.9
10.3	13.8	8.5	79	4.1	0.54	3.3	17.4	3.6	—	1.2	0.98	41.2	7.4
13.0	14.8	9.6	82	3.8	0.59	4.4	19.5	4.1	65	—	0.99	46.0	6.9
11.6	15.7	10.2	94	4.1	0.71	4.4	22.6	3.8	70	1.3	1.18	48.5	7.2
12.4	14.0	9.0	82	3.5	0.55	3.6	18.9	3.2	43	1.0	1.02	42.2	5.2
11.9	14.6	9.6	88	3.7	0.62	4.4	21.4	3.6	42	1.5	0.97	46.0	6.7
12.1	15.6	9.8	90	4.0	0.64	4.8	20.9	4.0	52	0.9	0.97	46.8	6.8
12.0	14.9	8.8	81	3.2	0.53	4.3	18.7	3.5	53	—	1.03	42.6	5.2
12.2	15.3	8.9	80	3.8	0.53	4.5	18.4	3.6	44	—	—	42.1	6.1
11.1	15.4	8.9	79	3.4	0.55	4.5	20.1	3.9	48	—	0.93	42.6	6.1
11.3	14.4	8.5	77	3.3	0.56	4.2	18.3	3.3	—	—	—	40.2	5.6
14.2	15.1	9.3	70	3.6	0.60	4.6	19.6	3.6	—	1.0	1.02	42.6	7.5
11.8	15.4	8.5	79	3.7	0.59	3.8	17.6	3.9	40	—	—	41.6	5.8
13.6	16.2	8.5	79	3.4	0.56	4.3	17.5	3.9	—	1.1	1.07	41.2	5.8
13.1	15.6	8.8	81	3.6	0.54	4.5	17.8	4.2	—	—	—	41.2	8.0
12.9	17.0	9.2	87	3.8	0.56	4.6	19.8	4.0	—	1.2	1.04	43.7	8.6
14.2	15.4	8.4	76	3.8	0.49	4.2	18.3	4.0	—	—	—	40.7	8.0
13.7	15.6	8.6	73	3.5	0.51	4.0	18.7	5.2	—	1.3	0.98	41.6	8.3
13.9	15.8	8.4	76	3.2	0.55	4.4	17.5	3.6	—	—	—	40.2	10.0
13.2	15.0	8.4	74	3.8	0.53	4.8	17.6	5.3	—	—	1.09	39.2	6.9
—	—	—	—	—	—	—	—	—	—	—	—	—	—

(—) undetectable or not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA)neutron activation analysis.

Sampling site : G-2. Sampling date : 4/4, 1977.

Depth(cm)	I.L. (%)	N	P	Mg	Hg
		($\mu g\cdot g^{-1}$)		($\mu g\cdot g^{-1}$)	
		C		AA	
0-2	10.9	3210	1640	0.97	0.16
2-4	8.3	2250	1100	0.96	0.12
4-6	7.8	2030	1200	1.04	0.07
6-8	7.8	1970	1120	1.06	0.06
8-10	8.3	—	900	1.01	0.06
10-12	8.1	1830	910	0.99	0.07
12-14	8.3	—	930	1.00	—
14-16	8.2	1840	940	1.09	0.10
16-18	8.6	—	1190	1.06	—
18-20	8.3	1860	1080	1.01	0.10
20-22	8.7	—	1080	1.01	—
22-24	9.2	1970	1000	0.99	0.10
24-26	8.3	—	840	1.06	—
26-28	9.2	1980	1290	1.06	0.11
28-30	8.7	—	1070	1.06	—
30-32	8.6	2160	1170	1.00	0.12
32-34	9.1	—	1140	1.04	—
34-36	8.4	2110	1140	0.83	0.12
36-38	8.8	—	870	1.04	—
38-40	8.6	2340	870	0.98	0.12

Appendix 15.7 Analytical data on the sediment core

Sampling site : H. Sampling date : 4/4, 1977. Water depth : 89.0 m.

Depth(cm)	I.L. (%)	N	P	Na	Ca	K	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb		As	
		($\mu g \cdot g^{-1}$)		(%)	(%)		($\mu g \cdot g^{-1}$)		(%)			(%)			($\mu g \cdot g^{-1}$)			($\mu g \cdot g^{-1}$)		($\mu g \cdot g^{-1}$)	
		C		NAA	XRF		AA	XRF	C	XRF	NAA	XRF			XRF			XRF	NAA	XRF	NAA
0-2	11.6	3850	1710	0.70	0.34	2.46	8560	9960	5.80	5.01	5.13	0.44	27	72	173	49	71	127	170	89	91
2-4	8.7	2040	1360	0.74	0.34	2.75	2860	3230	5.00	5.00	5.09	0.46	25	56	129	36	77	144	181	32	35
4-6	9.2	2000	1170	0.68	0.30	2.50	2380	2380	4.93	4.62	4.68	0.43	31	51	125	36	73	140	150	26	26
6-8	8.5	1830	1250	0.69	0.30	2.35	2310	2390	5.04	4.76	5.10	0.43	28	54	126	32	69	140	173	28	29
8-10	8.8	1380	1280	0.62	0.28	2.47	2300	2190	5.03	4.63	4.64	0.44	25	46	126	35	72	146	146	28	26
10-12	9.1	1780	1270	0.63	0.28	2.59	2320	2230	5.17	4.86	4.86	0.45	28	51	131	34	66	143	182	28	29
12-14	9.1	—	1050	0.66	0.27	2.49	2150	1930	5.02	4.71	4.94	0.46	30	53	137	42	71	148	192	27	30
14-16	10.1	1660	1310	0.66	0.28	2.42	2430	2130	5.47	4.99	5.46	0.49	29	50	141	44	72	148	147	28	31
16-18	8.9	—	1140	0.61	0.29	2.42	2380	2100	5.22	4.91	5.01	0.49	34	52	137	33	67	139	156	28	30
18-20	8.5	1880	1180	0.57	0.27	2.33	2490	2120	5.24	4.75	4.69	0.47	23	51	136	32	68	141	—	28	26
20-22	—	—	—	0.61	0.27	2.22	—	2180	—	4.76	4.96	0.48	28	50	132	31	64	128	159	26	27
22-24	8.2	2000	1110	0.62	0.29	2.33	2320	2150	5.14	4.92	4.93	0.50	28	52	135	31	72	133	155	28	28
24-26	—	—	—	0.62	0.31	2.24	—	2150	—	4.74	4.77	0.50	32	51	128	29	72	138	—	28	25
26-28	7.7	2400	1190	0.59	0.33	2.49	2260	2120	5.57	5.27	4.59	0.58	34	57	141	29	71	136	125	31	26
28-30	—	—	—	—	0.30	2.19	—	2150	—	4.90	—	0.50	30	51	131	28	66	128	—	29	—
30-32	8.9	2470	1180	0.68	0.28	2.15	2500	2350	5.16	4.87	5.35	0.50	37	53	133	30	70	133	141	30	31
32-34	—	—	—	0.74	0.28	2.18	—	2250	—	4.86	5.48	0.50	35	53	140	31	69	129	144	28	29
34-36	8.7	2180	1110	0.69	0.29	2.16	2500	2460	5.28	5.04	5.13	0.51	28	52	136	29	70	134	138	30	30
36-38	—	—	—	0.66	0.27	2.25	—	2390	—	5.03	5.32	0.51	26	52	129	32	70	133	144	28	29
38-40	8.8	2390	1070	0.69	0.29	2.23	2500	2370	5.05	4.79	5.18	0.49	39	55	139	28	69	130	—	30	29
40-42	—	—	—	0.64	0.30	2.44	—	2400	—	5.13	4.95	0.55	29	58	135	33	73	141	162	28	28
42-44	9.0	2110	1390	0.65	0.33	2.31	2600	2430	5.24	4.94	4.86	0.51	30	56	135	32	72	137	174	28	31

Hg	Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
($\mu g \cdot g^{-1}$)										($\mu g \cdot g^{-1}$)									
AA										NAA									
0.19	19.1	74	4.1	717	11.1	14.5	7.8	80	3.5	0.54	4.3	16.4	3.0	—	—	1.0	39.5	13	0.014
0.08	18.4	74	2.2	728	12.6	15.2	9.0	88	3.6	0.59	3.6	19.5	2.7	41	—	1.4	43.3	10	—
0.07	18.3	65	1.8	629	12.0	14.4	8.5	82	2.8	0.56	3.2	17.5	3.1	49	—	1.0	42.1	9	—
0.07	18.5	71	2.0	739	13.0	15.7	9.4	87	3.7	0.64	3.4	19.9	3.3	43	—	—	46.2	8	—
0.10	16.5	70	1.9	588	11.3	14.2	8.7	83	3.7	0.59	3.5	19.5	3.0	—	1.3	—	42.6	7	0.019
0.06	17.2	71	2.1	680	10.4	14.7	8.9	86	4.2	0.62	3.6	18.9	3.7	50	—	—	44.4	6	—
—	18.0	73	2.7	690	12.1	16.2	9.7	92	3.5	0.62	3.6	20.5	2.9	64	1.3	1.2	46.9	8	—
0.09	19.4	75	2.7	632	12.7	16.8	9.6	92	4.1	0.64	3.8	20.2	5.3	58	—	1.1	45.7	8	—
—	18.3	66	2.2	785	11.3	16.2	9.1	85	3.7	0.59	3.4	20.2	3.6	47	—	0.8	44.2	8	0.010
0.10	15.7	66	1.7	513	10.9	15.0	8.2	77	2.8	0.49	3.4	17.8	3.3	55	—	1.2	40.1	5	—
0.11	17.0	66	1.8	646	10.8	15.5	9.1	87	3.8	0.59	3.1	18.5	3.5	—	1.6	1.1	42.9	10	0.014
0.13	18.8	64	1.8	603	11.1	15.7	8.8	79	3.2	0.56	4.1	17.7	3.1	64	—	1.0	40.2	9	—
—	19.0	69	1.8	715	11.3	15.6	8.3	79	2.7	0.56	3.9	17.4	3.2	43	—	1.1	40.3	8	—
0.18	17.9	71	2.0	593	11.0	15.3	7.7	74	2.9	0.51	3.0	15.2	3.3	—	1.0	0.9	37.1	8	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.13	19.0	71	2.1	633	12.0	16.6	8.4	80	3.6	0.51	3.3	17.8	3.9	—	—	0.9	42.6	10	—
—	20.8	75	1.9	779	12.8	17.0	8.8	80	3.5	0.62	4.2	18.5	3.6	—	—	—	43.7	8	—
0.13	20.3	67	2.1	692	12.3	16.3	8.3	79	3.3	0.56	4.5	17.9	3.8	—	—	—	41.4	7	—
—	18.3	74	1.8	771	10.8	15.7	7.7	74	3.0	0.49	3.2	16.3	3.8	—	—	0.8	38.7	7	—
0.11	20.5	75	2.1	687	10.8	16.8	8.2	81	3.3	0.49	4.0	17.6	3.6	—	—	0.7	41.1	10	—
—	18.8	69	2.0	749	12.1	15.9	7.8	78	3.0	0.59	4.2	17.1	3.4	—	—	—	39.3	7	—
0.12	19.5	70	1.9	642	11.3	16.0	7.8	75	3.3	0.51	3.5	16.6	4.1	—	—	—	37.6	10	—

(—) undetectable or not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15. 8 Analytical data on the sediment core

Sampling site : I. Sampling date : 4/4, 1977. Water depth : 73.0m.

Depth(cm)	I.L. (%)	N	P	Na		Ca	K	Mg	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb	
		($\mu g \cdot g^{-1}$)		(%)		(%)		(%)	($\mu g \cdot g^{-1}$)		(%)			(%)			($\mu g \cdot g^{-1}$)			($\mu g \cdot g^{-1}$)	
		C		AA	NAA	XRF		AA	AA	XRF	C	XRF	NAA	XRF			XRF			XRF	NAA
0-2	10.2	3080	1160	0.80	0.69	0.37	2.52	0.92	3360	3850	5.22	5.14	5.10	0.48	28	77	197	59	77	138	152
2-4	8.5	2170	1160	1.02	0.69	0.35	2.53	0.94	2630	2750	5.17	5.03	4.88	0.47	34	70	151	42	75	140	155
4-6	8.5	1830	820	0.90	0.73	0.31	2.47	0.90	1940	2100	5.01	4.80	5.00	0.46	31	57	138	36	77	149	185
6-8	8.2	1790	870	0.95	0.66	0.32	2.55	0.85	1960	1980	5.17	4.89	5.02	0.47	31	52	129	37	71	147	172
8-10	7.9	1760	830	0.96	0.68	0.31	2.73	0.84	1920	2160	5.12	5.34	5.07	0.54	27	49	140	44	71	153	158
10-12	8.6	1680	730	0.67	0.72	0.29	2.56	0.90	1720	1670	5.07	4.94	5.11	0.53	45	63	155	46	70	150	187
12-14	—	—	—	—	0.72	0.33	2.55	—	—	1640	—	5.20	5.19	0.56	32	59	146	40	68	144	175
14-16	8.5	1770	860	0.70	0.59	0.28	2.27	0.90	1790	1590	5.06	4.76	4.80	0.50	33	55	139	39	68	144	141
16-18	—	—	—	—	0.58	0.34	2.34	—	—	1770	—	5.11	4.80	0.56	43	56	146	33	68	135	148
18-20	8.9	1780	1270	0.72	0.61	0.31	2.32	0.89	2030	1900	5.26	4.85	5.15	0.50	35	53	142	29	69	141	156
20-22	—	—	—	—	0.64	0.41	2.56	—	—	1950	—	5.38	5.41	0.60	39	65	150	36	72	142	155
22-24	9.2	2030	1080	0.73	0.72	0.35	2.35	0.93	1920	1790	5.18	4.93	5.01	0.55	29	58	138	31	74	142	160
24-26	—	—	—	—	0.70	0.31	2.44	—	—	1800	—	5.05	4.85	0.55	33	56	141	32	72	147	157
26-28	8.8	2220	1050	0.79	0.65	0.35	2.54	0.97	1870	2050	5.20	5.19	4.99	0.57	31	57	138	29	74	144	183
28-30	—	—	—	—	0.63	0.30	2.28	—	—	1850	—	4.93	4.80	0.53	34	56	136	35	72	138	151
30-32	9.1	2080	1160	0.84	0.55	0.31	2.20	0.89	1970	2010	5.09	4.95	4.64	0.51	35	50	132	28	74	135	129
32-34	8.9	2200	1140	1.00	0.64	0.28	2.33	0.89	1980	1920	5.21	4.93	5.16	0.50	30	51	132	29	71	139	155

As		Hg	Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
($\mu g \cdot g^{-1}$)		($\mu g \cdot g^{-1}$)										($\mu g \cdot g^{-1}$)									
XRF	NAA	AA										NAA									
54	54	0.19	18.9	62	3.4	824	12.4	14.6	7.7	79	3.7	0.47	3.6	16.4	3.8	—	0.8	1.2	39.1	10	—
32	32	0.09	16.7	70	2.1	715	11.0	14.3	7.6	73	3.4	0.42	3.7	15.6	4.3	—	1.2	1.0	40.1	7	—
26	29	0.07	17.0	69	2.0	729	10.9	15.4	9.1	91	3.8	0.53	4.3	19.2	4.2	—	1.0	1.2	45.3	5	0.017
23	26	0.05	18.9	66	2.0	647	11.5	15.8	9.2	88	3.7	0.61	4.1	20.7	4.9	48	1.1	1.0	47.1	4	—
23	27	0.11	17.3	65	2.2	584	11.8	16.5	9.4	97	3.3	0.53	3.6	20.9	4.2	—	1.4	1.5	48.5	—	—
24	30	—	20.5	75	2.9	516	13.0	16.7	9.4	88	3.7	0.55	3.1	21.6	3.9	—	1.3	1.1	49.4	3	—
23	25	0.08	19.7	73	2.5	630	12.9	17.0	8.9	89	3.4	0.55	3.3	18.4	4.3	—	1.6	1.3	47.9	4	—
20	17	—	17.1	67	1.9	513	11.6	15.9	8.7	83	3.7	0.55	2.9	18.6	4.2	36	1.4	1.3	45.5	—	—
24	19	0.11	17.3	66	1.8	543	10.9	15.5	8.4	81	3.5	0.50	5.2	17.5	3.8	—	0.8	1.2	42.2	6	—
28	31	—	20.4	66	2.2	682	11.2	16.2	8.5	85	3.1	0.55	2.8	18.6	5.4	—	0.9	0.8	44.5	—	—
23	30	0.11	18.2	79	2.3	749	11.0	17.2	8.2	79	3.8	0.52	3.6	17.4	4.0	—	0.9	1.2	42.9	—	—
25	22	—	20.2	70	1.9	577	11.4	15.7	8.0	79	3.1	0.46	3.7	17.0	4.5	—	1.0	1.4	41.4	—	—
23	23	0.15	18.6	74	2.2	725	11.4	15.8	7.7	80	2.8	0.49	4.0	16.2	4.7	—	—	0.9	40.2	—	—
27	24	—	18.4	77	1.6	636	14.2	16.2	7.9	78	3.1	0.45	4.1	16.3	4.4	—	0.8	1.3	39.9	—	—
20	28	0.13	18.1	70	2.0	621	10.9	15.3	7.5	74	3.4	0.43	3.6	15.3	3.7	—	0.8	—	40.4	—	—
25	32	—	18.5	72	1.6	513	10.2	14.7	7.2	74	2.6	0.39	2.5	15.4	4.5	—	—	—	39.5	—	—
24	22	0.17	20.0	72	2.1	645	12.3	16.1	8.1	84	3.2	0.50	3.8	17.9	4.3	—	1.2	1.2	42.6	—	—

(—) undetectable or not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.9 Analytical data on the sediment core

Sampling site : J. Sampling date : 4/4, 1977. Water depth : 44.0 m.

Depth (cm)	I.L. (%)	N	P	Na	Ca	K	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb		As	
		($\mu g \cdot g^{-1}$)		(%)	(%)		($\mu g \cdot g^{-1}$)			(%)		(%)			($\mu g \cdot g^{-1}$)			($\mu g \cdot g^{-1}$)		($\mu g \cdot g^{-1}$)	
		C		NAA	XRF		AA	XRF	C	XRF	NAA	XRF			XRF			XRF	NAA	XRF	NAA
0-2	9.8	2530	920	0.97	0.74	2.56	1380	1200	4.49	4.39	4.43	0.60	37	76	157	31	110	130	125	24	—
2-4	9.0	2160	810	1.10	0.90	2.53	1350	1210	4.36	4.37	4.43	0.57	37	79	146	35	107	129	122	23	28
4-6	8.9	2470	810	1.27	0.76	2.54	1120	910	4.40	4.30	4.71	0.57	39	93	151	37	103	128	144	22	25
6-8	7.2	1430	700	1.21	0.80	2.42	930	730	3.98	3.88	4.13	0.50	28	76	123	26	110	125	148	16	13
8-10	6.7	1240	630	1.25	0.61	2.62	960	770	4.00	4.00	3.98	0.57	21	73	124	24	110	130	160	19	—
10-12	6.6	1140	650	1.02	0.58	2.49	1170	940	3.97	3.73	3.91	0.49	29	65	116	28	117	141	145	16	21
12-14	8.1	1900	720	1.36	0.60	2.53	1210	1060	4.21	4.19	4.49	0.56	35	79	126	24	115	139	154	20	—
14-16	9.8	2770	760	1.02	0.61	2.65	1060	880	4.41	4.46	4.34	0.59	37	105	135	28	108	127	123	20	19
16-18	9.7	2130	780	1.03	0.61	2.54	1060	930	4.27	4.33	4.28	0.58	34	104	137	29	105	128	137	18	17

Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
									($\mu g \cdot g^{-1}$)									
									NAA									
21.8	84	3.4	504	10.3	14.9	8.5	83	2.8	0.55	3.6	14.4	6.9	—	1.0	1.0	42.4	7	—
21.6	84	3.8	542	11.0	14.7	8.8	94	3.1	0.51	3.0	16.4	6.6	—	1.8	1.1	44.6	14	—
21.5	82	4.7	630	11.1	15.6	9.5	92	3.6	0.50	3.8	15.9	6.6	—	1.3	1.1	45.6	9	—
18.4	71	2.7	680	8.8	14.1	7.8	74	2.7	0.46	4.1	14.2	7.6	85	1.1	1.0	37.7	—	0.026
17.5	77	2.5	566	8.0	13.5	7.7	77	2.7	0.48	5.6	13.5	7.4	—	1.1	1.0	39.2	7	—
17.4	71	2.0	570	10.5	12.9	7.8	76	2.5	0.50	3.7	14.3	7.7	—	1.3	1.0	38.5	—	—
20.2	74	2.6	596	10.9	14.4	9.0	89	2.9	0.46	4.4	18.4	7.1	—	1.1	1.2	43.9	—	—
23.2	73	2.4	645	8.3	14.5	7.8	74	2.7	0.53	3.1	11.9	5.3	30	—	1.3	36.9	12	0.010
21.9	78	2.4	450	10.1	13.8	8.1	76	3.5	0.51	3.1	12.9	5.6	45	0.9	1.3	39.1	12	0.012

(—) undetectable. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray flutrencence analysis, (NAA) neutron activation analysis.

Appendix 15.10 Analytical data on the sediment core

Sampling site : K. Sampling date : 4/4, 1977. Water depth : 35.0 m.

Depth(cm)	I.L. (%)	P	K	Ca	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr
		$(\mu g \cdot g^{-1})$	(%)		(%)	$(\mu g \cdot g^{-1})$		(%)		(%)	$(\mu g \cdot g^{-1})$						
		C	XRF		AA	AA	XRF	C	XRF	XRF	XRF						
0-2	9.4	910	2.54	0.42	1.00	1790	1460	5.26	5.03	0.56	19	74	200	58	32	133	81
2-4	7.9	820	2.65	0.41	0.96	1710	1430	4.98	5.09	0.57	30	68	159	42	26	137	80
4-6	7.4	670	2.62	0.38	0.95	1530	1160	4.68	4.69	0.53	21	48	129	34	18	144	81
6-8	7.4	700	2.60	0.36	0.92	1510	1160	4.51	4.73	0.53	24	48	136	36	18	144	75
8-10	7.7	640	2.60	0.34	0.94	1420	1110	4.75	4.88	0.58	29	54	142	41	19	141	74
10-12	8.1	740	2.55	0.35	0.97	1400	1110	4.85	5.06	0.62	33	55	143	35	19	141	77
12-14	—	—	2.42	0.39	—	—	1120	—	4.89	0.61	32	52	138	33	16	132	78
14-16	8.6	900	2.30	0.41	0.99	1470	1230	4.92	4.87	0.61	30	53	142	29	19	134	81
16-18	—	—	2.50	0.41	—	—	1150	—	4.92	0.64	30	59	144	31	18	127	80
18-20	8.5	930	2.47	0.40	1.01	1480	1240	4.86	5.05	0.66	35	51	135	33	17	141	88
20-22	—	—	2.26	0.36	—	—	1000	—	4.36	0.57	32	49	138	30	16	138	88
22-24	8.2	850	2.43	0.39	0.99	1420	1090	4.69	4.67	0.61	34	52	136	28	16	131	82
24-26	—	—	2.40	0.40	—	—	1140	—	4.74	0.61	29	47	129	28	16	136	92
26-28	7.8	840	2.26	0.39	1.02	1410	1030	4.67	4.50	0.59	30	49	127	29	14	132	92
28-30	—	—	2.40	0.40	—	—	944	—	4.64	0.61	33	51	130	28	16	133	89
30-32	8.0	690	2.45	0.43	1.00	1270	978	4.37	4.52	0.60	33	49	134	28	14	135	89

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.11 Analytical data on the sediment core

Sampling site : L. Sampling date : 4/4, 1977. Water depth : 92.0 m.

Depth(cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	K (%)	Ca (%)	Mg (%)	Mn ($\mu g \cdot g^{-1}$)		Fe (%)		Ti (%)	Ni	Cu	Zn	Pb ($\mu g \cdot g^{-1}$)	As	Rb	Sr
		C	XRF		AA	AA	XRF	C	XRF	XRF	XRF						
0-2	10.6	1310	2.26	0.36	0.94	6530	6010	5.20	5.18	0.45	37	82	237	63	83	129	73
2-4	8.4	960	2.72	0.37	0.94	3150	3550	5.00	5.22	0.49	26	66	153	38	45	144	80
4-6	8.0	1060	2.37	0.31	0.94	3090	3020	5.09	4.74	0.40	28	55	134	33	37	136	72
6-8	8.3	890	2.42	0.32	0.89	2670	2630	5.06	4.79	0.43	29	54	128	30	35	139	72
8-10	8.0	840	2.45	0.28	0.89	2490	2420	4.97	4.74	0.45	29	54	131	32	35	143	70
10-12	8.0	750	2.70	0.31	0.90	2430	2500	5.08	4.99	0.48	29	54	135	35	33	146	70
12-14	—	—	2.43	0.28	—	—	2330	—	4.71	0.47	30	58	144	40	30	144	70
14-16	8.7	990	2.52	0.31	0.95	2400	2460	5.26	5.25	0.55	29	61	146	37	32	148	73
16-18	—	—	2.30	0.27	—	—	2450	—	5.05	0.52	30	51	135	33	29	140	70
18-20	9.0	1120	2.27	0.30	0.89	2700	2580	5.30	4.94	0.51	31	52	142	32	33	134	72
20-22	—	—	2.31	0.32	—	—	2360	—	5.05	0.54	34	58	147	28	38	136	70
22-24	8.5	1000	2.18	0.26	0.98	2550	2440	5.33	4.86	0.51	39	55	133	27	34	136	73
24-26	—	—	2.40	0.31	—	—	2750	—	5.13	0.56	38	55	137	31	32	141	72
26-28	8.7	1050	2.42	0.28	0.99	2580	2600	5.32	5.03	0.51	28	61	145	33	35	146	71
28-30	—	—	2.41	0.27	—	—	2870	—	5.19	0.57	41	59	145	30	36	144	71
30-32	8.9	940	2.24	0.28	0.94	2500	2630	5.10	4.94	0.50	35	56	143	27	34	132	67
32-34	—	—	2.23	0.29	—	—	2860	—	5.05	0.50	35	54	137	32	35	136	70
34-36	8.9	1130	2.43	0.29	0.94	2590	2820	5.21	5.15	0.51	36	56	146	31	35	140	72
36-38	—	—	2.30	0.29	—	—	3100	—	5.29	0.51	41	59	141	28	37	134	66
38-40	8.7	1100	2.25	0.31	0.96	2670	2970	5.22	5.21	0.51	36	59	143	27	39	133	67

(—)not analysed. Analytical method: (C) colorimetry, (AA)atomic abstrption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.12 Analytical data on the sediment core

Sampling site : M. Sampling date : 4/4, 1977. Water depth : 40.0 m.

Depth(cm)	I.L. (%)	P	Na	K	Ca	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr
		($\mu g \cdot g^{-1}$)	(%)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)			
		C	AA	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-2	8.8	1180	1.83	2.40	0.43	1.07	1710	1300	3.15	4.87	0.54	38	75	204	44	27	128	83
2-4	7.6	630	1.06	2.37	0.44	1.09	1000	880	3.29	4.39	0.62	31	59	145	31	12	135	91
4-6	7.9	1130	1.42	2.08	0.55	1.11	1100	1010	4.58	4.56	0.57	38	40	117	21	16	112	108
6-8	8.0	1490	1.30	2.23	0.61	1.18	1210	940	4.47	4.54	0.60	37	42	119	21	16	110	108
8-10	8.3	1230	1.26	2.29	0.65	1.24	1120	997	4.15	4.83	0.63	34	48	112	18	18	107	109
10-12	8.3	900	1.72	2.27	0.63	1.22	1060	929	4.63	4.65	0.63	35	51	119	17	20	111	112
12-14	—	—	—	2.27	0.66	—	—	870	—	4.69	0.64	35	50	109	15	18	107	114
14-16	7.7	720	1.49	2.49	0.67	1.22	960	842	3.69	4.54	0.64	40	54	114	16	19	109	115
16-18	—	—	—	2.38	0.66	—	—	833	—	4.57	0.68	39	51	108	20	16	108	117
18-20	7.7	750	1.49	2.30	0.61	1.21	1000	870	3.90	4.46	0.65	40	52	113	20	17	109	114
20-22	—	—	—	2.36	0.61	—	—	862	—	4.48	0.65	32	57	110	17	19	106	114
22-24	7.8	900	1.31	2.29	0.65	1.12	1040	867	4.22	4.39	0.64	39	47	113	19	17	109	118
24-26	—	—	—	2.29	0.59	—	—	907	—	4.79	0.65	40	47	118	18	18	112	120
26-28	7.5	900	1.39	2.20	0.59	1.16	1030	858	3.69	4.53	0.60	40	47	110	18	18	102	110
28-30	—	—	—	2.39	0.65	—	—	899	—	4.72	0.63	31	42	110	14	19	103	110

(—) not analysed. Analytical methed : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.13 Analytical data on the sediment core

Sampling site : N. Sampling date : 4/4, 1977. Water depth : 94.0 m.

Depth(cm)	I.L. (%)	P	Na	K	Ca	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr
		($\mu g \cdot g^{-1}$)	(%)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)			
		C	AA	XRF		AA	AA	XRF	C	XRF	XRF	XRF						
0-2	10.5	1360	1.94	2.13	0.37	0.98	4660	4900	5.06	4.85	0.42	32	75	191	57	61	126	70
2-4	8.3	1090	1.28	2.29	0.35	0.98	3850	3860	4.66	4.67	0.41	29	66	139	39	44	130	73
4-6	7.7	910	1.12	2.55	0.33	0.98	3580	4040	4.09	5.13	0.45	23	54	127	32	44	136	71
6-8	7.8	1060	1.22	2.26	0.31	0.97	3760	4240	5.09	5.17	0.45	26	52	123	30	43	132	70
8-10	7.9	1030	1.17	2.24	0.31	0.96	3230	3470	4.86	4.82	0.42	25	52	127	34	38	133	67
10-12	7.5	820	1.12	2.54	0.30	0.95	3120	3290	4.60	4.96	0.44	31	48	138	33	42	141	69
12-14	–	–	–	2.52	0.28	–	–	3170	–	4.94	0.46	26	53	132	32	42	145	71
14-16	7.5	920	1.04	2.50	0.30	1.03	2960	3190	4.95	5.24	0.48	26	55	136	38	39	136	66
16-18	–	–	–	2.47	0.28	–	–	2850	–	5.02	0.50	31	61	144	36	40	143	71
18-20	8.3	1000	1.27	2.33	0.29	1.01	3110	3330	4.79	5.24	0.52	27	55	137	33	39	139	68
20-22	–	–	–	2.27	0.26	–	–	3220	–	5.00	0.48	29	50	132	30	36	134	66
22-24	8.6	870	1.13	2.08	0.26	0.98	3220	3010	4.86	4.71	0.45	27	53	132	32	40	136	69
24-26	–	–	–	2.36	0.33	–	–	3340	–	5.22	0.52	23	54	132	30	41	134	72
26-28	7.9	1160	1.15	2.34	0.32	1.08	3390	3620	5.07	5.38	0.56	31	60	137	27	44	134	73
28-30	–	–	–	2.20	0.29	–	–	3380	–	5.12	0.52	27	55	127	31	40	132	69
30-32	8.6	1170	1.21	2.14	0.30	1.03	3370	3510	4.84	5.08	0.51	25	53	131	29	42	131	72
32-34	–	–	–	2.37	0.31	–	–	3380	–	5.19	0.53	30	51	131	30	39	134	70
34-36	8.1	980	1.20	2.50	0.32	1.18	3120	3270	4.87	5.20	0.54	35	60	151	30	43	139	68
36-38	–	–	–	2.28	0.33	–	–	3130	–	5.17	0.56	38	55	143	32	44	137	71

(–) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.14 Analytical data on the sediment core

Sampling site : O. Sampling date : 4/4, 1977. Water depth : 61.0 m.

Depth(cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	Na (%)	K (%)	Ca	Mg (%)	Mn ($\mu g \cdot g^{-1}$)		Fe (%)		Ti (%)	Ni	Cu	Zn	Pb ($\mu g \cdot g^{-1}$)	As	Rb	Sr
		C	AA	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-2	9.7	1180	0.92	2.55	0.38	1.03	4650	5400	4.87	5.09	0.46	25	77	208	58	77	136	77
2-4	8.2	890	0.97	2.41	0.35	1.03	2150	2220	4.38	4.80	0.47	26	65	149	47	26	143	79
4-6	8.3	840	0.90	2.58	0.35	0.99	1750	1770	4.61	4.89	0.49	26	58	140	36	23	139	73
6-8	8.3	790	0.84	2.50	0.32	0.91	1700	1680	4.64	4.99	0.48	31	56	138	39	22	147	70
8-10	8.3	690	0.88	2.63	0.32	0.94	1560	1490	4.76	4.90	0.51	21	54	147	42	23	148	69
10-12	8.5	700	0.88	2.35	0.30	1.00	1430	1270	4.85	4.73	0.54	31	60	149	36	23	148	73
12-14	—	—	—	2.26	0.31	—	—	1600	—	4.94	0.54	26	54	148	39	18	139	68
14-16	8.8	870	1.00	2.31	0.37	1.16	1560	1550	4.70	4.98	0.57	28	52	137	34	20	141	75
16-18	—	—	—	2.30	0.34	—	—	1390	—	4.70	0.56	34	58	146	32	21	141	75
18-20	9.0	940	1.06	2.42	0.29	1.05	1670	1590	4.84	5.06	0.57	32	55	143	35	18	143	75
20-22	—	—	—	2.41	0.35	—	—	1600	—	4.92	0.50	28	52	131	29	22	137	74
22-24	8.3	1050	0.92	2.36	0.32	0.98	1750	1550	4.73	5.01	0.52	33	56	148	27	24	132	67
24-26	—	—	—	2.19	0.30	—	—	1590	—	4.91	0.50	24	49	134	31	18	136	72
26-28	8.9	1130	0.94	2.40	0.32	1.01	1660	1580	4.88	5.03	0.52	30	53	134	31	18	136	73
28-30	—	—	—	2.30	0.29	—	—	1280	—	4.51	0.48	30	57	140	29	20	134	73
30-32	8.2	880	0.89	2.39	0.36	1.03	1410	1460	4.59	4.95	0.52	33	53	134	28	20	131	73

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.15 Analytical data on the sediment core

Sampling site : P. Sampling date : 11/4, 1977. Water depth : 5.0 m.

Depth(cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	Ca (%)	K (%)	Mg (%)	Mn ($\mu g \cdot g^{-1}$)	Mn ($\mu g \cdot g^{-1}$)	Fe (%)	Fe (%)	Ti (%)	Ni	Cu	Zn	Pb ($\mu g \cdot g^{-1}$)	Sr	Rb	As
		C	XRF	XRF	AA	AA	XRF	C	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF
0-1	7.4	750	0.41	2.37	0.75	1000	761	4.05	3.76	0.38	22	69	283	59	90	144	8
1-2	7.3	600	0.40	2.44	0.72	870	669	3.92	3.78	0.42	21	60	200	54	93	150	6
2-4	7.0	580	0.45	2.61	0.75	960	811	3.33	3.67	0.41	18	60	187	54	106	152	10
4-6	4.5	420	0.41	3.23	0.57	660	539	2.69	2.74	0.30	8	30	131	41	110	164	6
6-8	3.4	420	0.43	3.48	0.48	570	481	2.16	2.26	0.26	6	23	94	33	110	161	5
8-10	4.6	370	0.45	3.40	0.58	740	665	2.62	2.72	0.30	7	29	119	44	112	163	4
10-12	3.8	350	0.48	3.63	0.52	770	704	2.40	2.60	0.29	8	23	102	36	107	158	6
12-14	3.8	290	0.45	3.54	0.49	700	627	2.27	2.33	0.26	10	18	94	33	114	161	6
14-16	3.2	340	0.44	3.44	0.49	740	583	2.31	2.22	0.26	6	19	92	33	113	163	7
16-18	3.0	310	0.45	3.25	0.49	680	545	2.35	2.13	0.24	5	20	93	32	113	160	6
18-20	3.3	310	0.50	3.79	0.47	760	681	2.32	2.50	0.27	9	21	97	36	115	163	4

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.16 Analytical data on the sediment core

Sampling site : Q. Sampling date : 11/4, 1977. Water depth : 21.0 m.

Depth(cm)	I.L. (%)	P	Ca	K	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	Sr	Rb	As
		($\mu g \cdot g^{-1}$)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)			
		C	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0–1	9.1	900	0.40	2.50	0.91	1300	1130	4.44	4.28	0.44	19	58	201	63	77	149	19
1–2	8.0	770	0.35	2.48	0.94	1020	840	4.22	3.99	0.45	62	56	182	55	78	156	9
2–4	7.5	510	0.33	2.59	0.91	990	790	4.31	4.05	0.44	18	48	163	55	73	155	8
4–6	7.4	440	0.29	2.61	0.83	940	748	4.18	3.95	0.42	27	41	152	53	73	159	4
6–8	7.7	460	0.29	2.39	0.81	950	704	4.11	3.78	0.43	25	40	145	52	71	158	4
8–10	7.3	410	0.31	2.35	0.77	980	765	4.39	4.04	0.46	21	38	148	45	68	148	6
10–12	6.1	430	0.40	2.74	0.63	1000	768	4.61	4.46	0.38	10	29	121	31	73	130	8
12–13	4.9	360	0.43	2.74	0.46	880	715	4.65	4.64	0.29	10	18	98	22	78	122	9
13–14	3.6	370	0.44	2.73	0.36	890	757	5.19	5.14	0.21	7	10	81	23	77	110	5
14–16	3.3	320	0.42	2.62	0.25	930	630	5.75	4.57	0.14	2	5	63	23	80	108	3
16–18	2.5	280	0.44	2.51	0.21	810	679	4.83	4.65	0.13	—	2	58	16	78	99	6

(–)undetectable. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.17 Analytical data on the sediment core

Sampling site : R. Sampling date : 11/4, 1977. Water depth : 60.0 m.

Depth(cm)	I.L. (%)	P	Ca	K	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	Sr	Rb	As
		($\mu g \cdot g^{-1}$)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)			
		C	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-0.2	15.0	1490	0.37	2.30	0.86	4070	4490	5.12	4.75	0.40	41	83	252	61	64	132	125
0.2-0.7	10.5	1100	0.33	2.22	0.92	2330	2080	5.06	4.24	0.40	38	79	244	59	63	134	55
0.7-1.5	9.1	956	0.34	2.47	0.94	1930	1760	4.62	4.59	0.40	26	70	206	72	78	151	31
1.5-3	7.6	884	0.37	2.54	0.96	2050	1840	4.85	4.63	0.41	26	66	178	54	80	148	29
3-4	7.4	723	0.36	2.81	0.94	1810	1850	4.47	4.95	0.46	27	51	152	50	80	151	23
4-6	7.0	673	0.33	2.57	0.92	1800	1610	4.58	5.58	0.43	22	50	150	44	79	158	24
6-8	7.2	584	0.28	2.62	0.89	1620	1550	3.78	4.52	0.41	22	47	139	44	73	149	20
8-10	7.5	618	0.29	2.52	0.85	1600	1410	4.25	4.42	0.44	27	45	149	44	72	151	21
10-14	7.4	657	0.26	2.41	0.78	1560	1360	4.52	4.48	0.43	24	45	147	47	71	156	22
14-18	7.5	558	0.26	2.31	0.84	1540	1300	4.62	4.38	0.44	28	46	157	49	64	146	20
18-22	8.5	657	0.27	2.26	0.78	1600	1360	3.99	4.46	0.45	25	51	158	35	63	140	23
22-26	8.7	648	0.29	2.17	0.81	1520	1390	4.10	4.35	0.45	29	50	158	42	63	136	20
26-30	8.5	869	0.30	2.42	0.88	1780	1640	4.32	4.80	0.50	28	50	147	37	65	135	19
30-34	8.4	607	0.31	2.35	0.93	1770	1630	4.60	5.00	0.51	32	54	152	40	66	137	23

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.18 Analytical data on the sediment core

Sampling site : S. Sampling date : 11/4, 1977. Water depth : 43.0 m.

Depth(cm)	I.L. (%)	P	Ca	K	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	Sr	Rb	As
		$(\mu g \cdot g^{-1})$	(%)		(%)	$(\mu g \cdot g^{-1})$		(%)		(%)				$(\mu g \cdot g^{-1})$			
		C	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-0.2	10.8	1570	0.35	2.52	0.85	2140	1950	5.22	4.71	0.41	42	77	248	57	60	144	89
0.2-0.7	10.2	1180	0.33	2.45	0.87	2050	1700	4.80	4.29	0.40	37	81	219	53	62	146	54
0.7-1.5	8.5	1050	0.36	2.41	0.86	2380	1850	4.74	4.36	0.38	26	64	183	53	64	134	43
1.5-2.5	8.0	1080	0.34	2.62	0.95	2800	2870	4.62	5.00	0.43	26	71	167	54	73	146	46
2.5-4	7.8	1040	0.37	2.47	0.96	3220	3210	4.38	4.97	0.41	31	60	149	43	71	140	55
4-6	7.5	1120	0.34	2.69	0.92	2870	2940	4.37	5.18	0.42	21	63	156	45	71	143	46
6-8	7.2	801	0.32	2.59	0.90	1700	1670	3.90	4.37	0.40	27	50	139	46	72	155	25
8-10	7.1	500	0.35	2.72	0.80	1390	1180	3.53	3.92	0.38	22	45	134	43	74	167	18
10-14	7.0	840	0.37	2.65	0.78	1200	1120	3.99	4.44	0.43	21	48	145	47	77	152	15
14-18	5.9	430	0.47	2.62	0.76	1570	1450	4.82	6.00	0.37	27	37	145	31	87	137	23
18-22	6.0	374	0.36	2.78	0.94	945	829	3.86	4.08	0.51	38	55	143	34	78	150	19
22-26	6.2	401	0.34	2.89	1.03	978	819	4.12	4.32	0.50	36	56	143	35	80	165	18
26-30	6.0	360	0.33	2.88	1.05	960	868	3.78	4.27	0.50	42	54	140	35	81	161	19
30-34	6.0	618	0.35	2.87	0.95	1470	1260	4.77	4.95	0.48	41	66	153	29	75	147	24
34-38	6.0	688	0.37	2.76	0.90	1650	1460	4.65	4.86	0.44	33	50	135	32	75	160	23

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.19 Analytical data on the sediment core

Sampling site : T. Sampling date : 11/4, 1977. Water depth : 71.0 m.

Depth(cm)	I.L. (%)	P	Na	K	Ca	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr
		($\mu g \cdot g^{-1}$)	(%)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)			
		C	AA	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-0.2	13.4	1660	0.53	2.10	0.32	0.91	8740	8350	5.43	4.49	0.38	39	91	339	51	198	125	56
0.2-0.7	10.1	1220	0.60	2.31	0.33	0.99	4100	4200	5.20	4.51	0.40	32	81	253	61	77	131	61
0.7-1.5	8.5	910	0.63	2.51	0.33	1.01	2980	2810	4.86	4.69	0.45	34	71	196	63	40	145	71
1.5-2.5	8.6	1300	0.69	2.46	0.32	0.99	3020	2980	5.15	4.85	0.44	27	79	166	49	36	140	68
2.5-4	7.9	880	0.65	2.62	0.34	1.01	2420	2310	5.02	4.88	0.45	33	59	148	37	31	149	69
4-6	7.5	1010	0.80	2.56	0.33	1.03	2430	2370	5.07	4.89	0.46	23	54	136	37	26	148	68
6-8	8.3	740	0.57	2.59	0.29	0.92	2010	1820	4.69	4.58	0.42	26	50	143	39	24	151	62
8-10	7.9	860	0.61	2.37	0.25	1.19	2090	1820	4.88	4.46	0.42	30	47	140	44	21	154	63
10-14	7.7	830	0.61	2.45	0.22	0.95	1780	1600	4.86	4.53	0.46	28	53	148	42	25	154	62
14-18	7.9	800	0.62	2.47	0.27	0.98	1920	1670	5.05	4.72	0.48	34	55	146	40	25	151	63
18-22	8.5	980	0.53	2.17	0.22	0.96	1900	1600	4.88	4.43	0.46	28	54	137	32	25	147	64
22-26	8.7	830	0.53	2.30	0.26	0.99	1900	1550	4.89	4.45	0.47	33	52	140	34	23	149	64
26-30	8.5	890	0.73	2.36	0.28	1.07	2040	1760	5.07	4.63	0.49	37	55	144	38	25	150	65
30-34	8.6	1100	0.43	2.25	0.29	1.05	2110	1990	5.12	4.75	0.50	27	53	136	31	26	141	64

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.20 Analytical data on the sediment core

Sampling site : U. Sampling date : 11/4, 1977. Water depth : 66.0 m.

Depth (cm)	I.L. (%)	N	P	Na		Ca	K	Mg	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb		As	
		($\mu g \cdot g^{-1}$)		(%)		(%)		(%)	($\mu g \cdot g^{-1}$)		(%)			(%)	($\mu g \cdot g^{-1}$)					($\mu g \cdot g^{-1}$)		($\mu g \cdot g^{-1}$)	
		C		AA	NAA	XRF		AA	AA	XRF	C	XRF	NAA	XRF	XRF					XRF	NAA	XRF	NAA
0−2	5.6	1410	680	1.09	0.79	0.21	2.85	0.80	820	695	3.41	3.33	3.35	0.44	27	42	114	21	69	133	134	20	20
2−4	5.9	1680	580	1.11	0.88	0.25	2.84	0.81	790	684	3.50	3.53	3.15	0.50	24	45	113	24	76	146	152	19	16
4−6	7.2	1920	750	0.93	0.81	0.24	2.58	0.85	940	745	3.91	3.56	3.68	0.46	29	48	121	29	76	148	157	21	26
6−8	8.2	1930	860	1.01	0.93	0.26	2.77	0.84	1010	888	4.01	3.96	3.98	0.50	35	56	128	33	81	151	175	19	21
8−10	7.3	2110	710	1.06	1.07	0.24	2.70	0.86	930	744	3.90	3.56	4.10	0.44	23	50	114	25	81	149	168	18	25
10−12	4.8	1350	480	0.98	0.95	0.23	2.78	0.77	650	555	3.17	3.16	3.32	0.42	23	36	91	18	76	135	147	11	12
12−14	5.2	970	620	1.04	0.99	0.25	2.70	0.84	700	570	3.35	3.20	3.26	0.43	24	36	93	15	78	138	126	16	13
14−16	5.2	1010	720	1.49	0.86	0.24	2.71	0.85	810	667	3.52	3.48	3.34	0.46	23	40	101	19	82	145	147	16	15
16−18	5.4	1000	590	0.98	1.08	0.26	2.96	0.84	780	662	3.50	3.51	3.47	0.49	30	43	102	17	84	143	168	16	20
18−20	4.8	1190	650	1.00	1.03	0.25	2.92	0.85	910	800	3.68	3.64	3.76	0.49	22	41	102	21	87	154	162	13	26
20−22	5.0	980	620	0.96	0.89	0.28	3.10	0.91	1010	731	3.78	3.70	3.74	0.51	28	51	119	26	83	157	156	17	19
22−24	4.4	1600	670	0.96	0.89	0.25	3.03	0.88	940	755	3.77	3.84	3.88	0.53	28	50	112	22	74	153	182	18	18
24−26	6.7	1770	680	1.00	0.90	0.28	2.91	0.93	990	753	3.88	3.81	3.93	0.53	29	49	117	24	80	154	159	17	20

Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
									($\mu g \cdot g^{-1}$)									
									NAA									
13.5	71	2.1	680	8.5	11.3	6.9	78	2.7	0.41	2.9	14.8	6.3	46	1.1	0.9	42.9	5	−
12.2	65	1.6	532	8.7	10.5	6.3	76	2.6	0.37	2.9	13.1	6.1	−	0.9	0.8	41.9	6	−
16.1	72	2.0	729	9.3	11.9	7.5	85	2.7	0.44	3.0	15.3	6.6	53	1.0	1.3	46.8	9	−
16.6	87	2.0	622	10.8	12.6	7.9	86	2.6	0.48	3.3	15.6	6.2	−	1.4	1.1	48.4	8	0.016
17.7	80	1.7	677	10.5	12.8	8.3	90	2.8	0.45	3.3	16.8	6.9	79	−	0.9	49.2	7	−
12.7	68	1.4	637	8.1	11.2	7.1	80	2.2	0.36	3.5	13.8	6.7	59	0.6	1.1	45.3	−	−
13.7	65	1.4	687	7.7	10.6	6.8	77	2.3	0.35	2.3	13.2	6.4	−	0.8	1.1	43.2	4	0.032
13.2	68	1.4	714	8.4	11.1	7.0	80	2.6	0.35	2.4	14.4	6.7	−	1.0	1.2	44.6	3	−
16.0	80	1.7	807	8.8	11.9	8.3	93	3.2	0.44	4.6	16.5	7.5	67	1.2	1.2	52.4	6	−
15.8	81	1.9	753	9.6	12.4	8.2	98	2.7	0.42	3.5	16.8	6.9	75	1.7	1.2	52.4	−	−
18.9	79	1.8	739	9.4	12.7	8.2	94	2.8	0.42	4.1	16.7	7.0	58	1.5	1.0	51.8	8	−
16.0	80	2.3	726	11.6	12.8	8.3	96	3.0	0.45	3.1	16.7	7.2	54	0.9	1.2	52.8	4	−
17.7	77	1.9	791	11.4	12.8	8.0	89	2.9	0.42	3.3	15.8	6.9	86	1.2	1.3	50.4	6	−

(−) undetectable. Analytical method : (C)colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.21 Analytical data on the sediment core

Sampling site : V. Sampling date : 11/4, 1977. Water depth : 45.0 m.

Depth (cm)	I.L. (%)	P	Na	Ca	K	Mg	Mn		Fe			Ti	Ni	Cu	Zn	Pb	Sr	Rb		As	
		$(\mu g \cdot g^{-1})$	(%)	(%)		(%)	$(\mu g \cdot g^{-1})$		(%)			(%)			$(\mu g \cdot g^{-1})$			$(\mu g \cdot g^{-1})$		$(\mu g \cdot g^{-1})$	
		C	NAA	XRF		AA	AA	XRF	C	XRF	NAA	XRF			XRF			XRF	NAA	XRF	NAA
0-1	6.4	628	0.89	0.26	2.70	0.90	710	564	3.50	3.60	3.46	0.46	30	46	126	21	70	132	175	23	21
1-2	4.7	484	0.94	0.21	2.64	0.88	661	562	3.09	3.24	3.23	0.44	25	40	97	16	73	133	127	15	15
2-4	4.7	430	0.95	0.23	2.49	0.88	600	496	3.05	3.11	3.24	0.43	22	39	108	19	74	133	123	13	14
4-6	5.1	534	0.89	0.21	2.78	0.91	728	601	3.46	3.44	3.24	0.46	31	42	110	24	73	137	141	13	14
6-8	5.6	578	0.99	0.21	2.68	0.97	736	659	3.35	3.48	3.69	0.47	27	46	121	24	77	146	192	16	17
8-10	5.9	572	1.07	0.26	2.56	0.96	750	554	3.35	3.18	3.81	0.43	28	43	117	21	84	145	159	14	16
10-12	5.7	488	1.06	0.23	2.73	0.95	657	514	3.29	3.29	3.56	0.44	21	39	102	15	78	141	181	15	15
12-14	5.9	529	1.01	0.28	2.74	0.96	681	517	3.29	3.30	3.65	0.43	23	44	104	19	78	143	177	15	15
14-16	5.5	540	0.97	0.21	2.62	0.96	634	490	3.06	3.21	3.38	0.43	32	41	98	22	80	148	150	12	14
16-20	4.3	453	1.07	0.25	2.67	0.86	792	655	2.95	3.07	3.16	0.41	21	31	82	7	80	135	149	13	13

Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
									$(\mu g \cdot g^{-1})$									
									NAA									
13.6	70	1.7	617	7.4	10.7	8.2	92	3.0	0.47	3.0	14.4	5.5	45	–	1.2	45.1	8	–
12.9	66	1.7	669	7.9	10.4	7.9	92	2.9	0.44	2.5	15.1	5.7	76	1.4	1.0	44.7	3	–
12.9	66	1.5	745	7.3	10.7	7.7	82	2.1	0.42	2.6	14.1	7.2	–	1.4	1.2	42.2	5	0.007
13.9	75	1.5	719	7.8	10.7	8.1	89	2.8	0.42	2.6	14.1	6.7	43	1.4	0.7	44.2	3	–
17.3	70	1.5	743	9.1	12.0	9.2	102	2.5	0.52	3.0	15.9	5.5	60	–	1.2	49.2	5	–
15.3	76	1.6	814	8.6	12.0	9.8	104	2.8	0.49	3.7	17.1	6.4	–	–	–	52.3	4	–
14.0	72	1.6	752	9.4	11.9	8.0	96	2.7	0.46	3.3	16.6	5.7	58	1.0	1.3	49.1	7	–
15.4	68	1.5	798	9.7	11.9	9.2	98	3.1	0.54	3.0	17.1	6.2	45	1.8	1.0	49.5	4	–
15.4	74	1.3	738	10.1	11.3	8.5	91	2.5	0.46	2.7	14.9	5.3	66	1.2	0.8	46.1	3	–
12.8	70	1.2	671	7.8	10.7	7.9	91	2.6	0.47	2.7	15.5	6.8	–	–	0.8	44.6	3	–

(–) undetectable. Analytical methed : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.22 Analytical data on the sediment core

Sampling site : W. Sampling date : 11/4, 1977. Water depth : 90. 0m.

Depth (cm)	I.L. (%)	P (μg·g^{-1})	Ca (%)	K	Mn (μg·g^{-1})		Fe (%)		Ti (%)	Ni	Cu	Zn (μg·g^{-1})	Pb	Sr	Rb (μg·g^{-1})		As (μg·g^{-1})	
		C	XRF		AA	XRF	C	XRF	XRF			XRF			XRF	NAA	XRF	NAA
0-0.5	12.7	1990	0.31	2.16	7950	9270	5.38	4.71	0.40	47	87	251	54	56	110	—	151	145
0.5-1	9.7	1240	0.31	2.11	4920	5170	4.80	4.30	0.40	34	92	208	50	60	120	—	70	74
1-1.5	8.9	1020	0.29	2.08	4110	3890	4.94	4.15	0.38	32	78	175	48	63	117	—	49	52
1.5-2	8.8	1090	0.31	2.11	3770	3860	5.02	4.42	0.40	33	89	185	41	58	112	—	48	48
2-3	7.5	1150	0.35	2.44	3450	3520	5.11	4.80	0.45	30	66	140	39	71	137	—	35	40
3-4	7.5	761	0.32	2.42	3000	2880	4.67	4.60	0.44	28	53	131	30	67	136	—	35	37
4-6	7.3	921	0.32	2.44	2870	2910	4.70	4.75	0.42	25	51	129	33	65	133	—	33	32
6-8	7.2	826	0.29	2.52	2390	2760	4.73	4.82	0.47	31	58	135	34	66	137	—	32	31
8-10	7.1	854	0.28	2.38	2660	2260	4.79	4.46	0.42	34	53	134	33	64	138	—	30	32
10-12	7.2	753	0.24	2.36	2350	2070	4.59	4.40	0.41	26	58	143	35	62	147	—	28	31
12-14	7.5	787	0.28	2.61	2410	2460	4.66	4.97	0.47	29	55	136	33	61	147	—	31	32
14-16	7.3	872	0.28	2.57	2380	2220	4.62	4.94	0.50	36	57	148	41	64	147	—	30	32
16-20	7.7	829	0.28	2.32	2310	2210	4.84	4.72	0.49	27	54	145	30	62	145	—	31	29
20-24	7.7	1010	0.28	2.38	2600	2570	4.66	5.00	0.50	40	58	142	26	61	136	—	33	34
24-28	8.1	471	0.32	2.35	2540	2400	4.81	4.82	0.52	32	58	141	27	62	135	147	30	28
28-32	7.8	1010	0.30	2.51	2510	2620	4.82	4.91	0.53	40	64	147	29	65	145	—	33	29
32-36	8.4	1110	0.29	2.16	2760	3020	4.75	4.96	0.49	35	53	133	26	58	126	—	33	30
36-40	8.8	995	0.30	2.36	2620	2930	5.18	4.94	0.48	35	57	134	25	59	136	—	34	29

Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
									(μg·g^{-1})									
									NAA									
22.3	72	6.1	683	10.7	14.8	8.4	83	2.8	0.50	4.2	17.4	3.8	50	—	0.8	39.2	15.6	0.018
18.5	71	4.5	663	11.3	15.1	8.7	86	3.5	0.50	4.1	17.6	4.2	76	—	0.7	40.6	12.7	0.012
17.8	72	3.2	670	10.9	13.8	8.2	78	3.0	0.55	3.9	16.4	3.5	37	1.1	0.8	38.1	9.1	—
17.4	74	2.8	656	10.2	14.4	8.5	80	3.2	0.55	3.6	17.0	3.7	35	0.9	1.1	38.7	11.0	0.013
17.6	66	2.5	613	11.4	14.5	8.7	83	3.2	0.52	3.7	18.1	4.1	44	—	1.1	39.4	7.2	—
17.5	79	2.3	604	13.0	14.8	9.1	85	3.6	0.60	3.9	18.0	3.5	—	—	1.1	41.9	8.0	—
16.6	62	1.8	574	10.5	13.8	8.9	82	3.7	0.56	3.8	18.0	3.3	48	1.6	0.9	40.4	6.4	—
17.0	66	2.1	653	11.8	15.1	9.8	87	3.7	0.59	3.9	20.6	4.0	60	1.2	0.7	43.5	5.1	—
17.5	69	2.2	658	12.6	15.4	10.1	89	3.5	0.61	4.8	20.9	3.7	59	1.1	1.2	46.5	4.8	—
18.1	77	2.1	739	11.8	15.8	10.4	100	3.3	0.64	4.4	20.8	3.6	59	—	1.0	46.5	4.7	0.016
17.6	72	2.5	714	12.0	15.8	10.2	98	3.8	0.55	4.3	21.2	3.8	69	—	1.1	45.5	7.0	—
19.8	76	2.9	615	12.8	16.6	10.0	90	3.5	0.58	4.7	21.2	4.6	—	1.3	1.4	43.7	5.1	—
19.0	68	1.8	569	12.7	15.7	9.6	91	3.7	0.56	4.1	19.8	5.1	—	1.2	1.2	43.0	7.6	—
20.1	76	2.2	743	12.1	16.6	10.0	93	3.8	0.62	4.3	21.0	4.5	57	1.5	1.2	44.3	6.4	—
19.3	73	1.8	672	10.3	16.0	8.4	82	3.3	0.49	3.2	16.4	3.7	—	1.0	0.9	39.3	5.1	—
18.4	68	1.9	770	12.1	15.6	8.0	77	2.9	0.49	4.5	16.5	4.0	—	—	1.2	37.7	6.1	—
16.5	66	1.5	666	9.6	14.4	7.9	78	2.8	0.49	3.8	15.5	4.4	44	—	0.9	37.2	8.7	—
16.9	65	1.7	682	10.3	13.8	7.3	74	2.8	0.47	3.8	14.6	3.5	37	—	0.9	34.5	5.2	—

(—)undetectable. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF)X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15. 23 Analytical data on the sediment core

Sampling site : X. Sampling date : 11/4 1977. Water depth : 90.0 m.

Depth(cm)	I.L. (%)	P	Na	Ca	K	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	Sr	Rb	As	
		($\mu g \cdot g^{-1}$)	(%)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)			($\mu g \cdot g^{-1}$)				($\mu g \cdot g^{-1}$)	
		C	AA	XRF		AA	AA	XRF	C	XRF	XRF			XRF				XRF	NAA
0-0.2	11.9	5350	0.52	0.34	2.06	—	7960	7950	5.22	4.18	0.39	100	127	304	46	47	106	195	155
0.2-0.7	11.8	1540	0.62	0.34	2.10	—	6470	7180	5.05	4.55	0.41	64	101	239	55	53	117	101	100
0.7-1.2	9.8	900	0.71	0.31	2.09	—	4090	4190	4.94	4.12	0.41	34	99	223	53	62	121	55	61
1.2-2	7.9	1110	0.80	0.32	2.16	—	3970	4090	5.16	4.44	0.41	36	91	172	43	58	118	46	50
2-4	7.1	1030	0.78	0.31	2.51	—	3130	3100	4.93	4.58	0.43	29	53	124	34	72	147	37	37
4-6	7.0	990	0.70	0.32	2.41	—	3080	3270	5.02	4.83	0.45	32	56	130	35	66	140	35	39
6-8	7.0	980	0.70	0.31	2.40	0.98	2890	2890	4.91	4.66	0.43	30	53	123	32	64	142	35	31
8-10	7.3	940	0.67	0.29	2.36	—	2600	2560	4.73	4.48	0.43	27	53	126	35	65	146	30	33
10-20	7.9	870	0.72	0.27	2.39	1.08	2510	2520	4.98	4.75	0.50	32	58	144	36	65	148	32	32
20-30	8.2	1000	0.64	0.30	2.36	1.06	2810	3050	4.93	5.03	0.54	33	59	135	32	65	141	34	37
30-40	7.9	1180	0.58	—	—	0.98	3180	—	4.75	—	—	—	—	—	—	—	—	—	35

Co	Cr	Sb	Cs	Sc	U	Th	La
			($\mu g \cdot g^{-1}$)				
			NAA				
20.4	63	4.9	9.2	12.9	3.9	14.0	32.0
19.6	62	4.9	8.8	12.8	3.1	12.8	33.6
17.2	67	3.4	9.3	14.0	2.6	15.7	35.5
19.3	62	2.7	9.1	13.8	3.1	15.3	37.1
20.1	65	2.0	11.8	14.0	2.3	16.2	37.1
18.1	67	1.8	11.9	13.2	1.8	16.5	34.9
18.2	70	1.8	10.7	13.7	2.3	17.9	40.6
15.5	66	1.8	11.1	14.3	2.3	17.8	39.9
19.5	72	1.8	11.3	15.8	2.2	19.4	40.2
18.5	63	1.6	10.0	15.0	2.7	14.9	35.5
18.5	65	1.8	8.7	13.3	2.5	13.4	32.6

(—) not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.24 Analytical data on the sediment core

Sampling site : Y. Sampling date : 11/4, 1977. Water depth : 83.0 m.

Depth(cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	Na (%)	K (%)	Ca (%)	Mg (%)	Mn ($\mu g \cdot g^{-1}$)	Mn ($\mu g \cdot g^{-1}$)	Fe (%)	Fe (%)	Ti (%)	Ni	Cu	Zn	Pb ($\mu g \cdot g^{-1}$)	As	Rb	Sr
		C	AA	XRF	XRF	AA	AA	XRF	C	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF
0-0.2	11.3	2000	0.86	2.04	0.38	1.31	4380	3910	5.83	4.69	0.42	48	98	332	50	179	112	53
0.2-0.7	12.3	1840	0.68	2.15	0.35	1.15	3590	3630	5.31	4.78	0.43	36	99	235	56	102	117	55
0.7-1.5	10.1	1330	0.71	2.11	0.34	1.23	3310	3230	4.96	4.31	0.42	43	99	532	49	61	117	58
1.5-2.5	8.4	1120	0.73	2.33	0.34	1.16	3350	3430	5.06	4.58	0.43	28	79	163	39	49	128	66
2.5-4	7.9	970	0.77	2.52	0.29	1.23	2910	3190	5.04	4.81	0.46	30	58	134	32	39	138	67
4-6	8.1	830	0.76	2.64	0.33	1.20	2930	3270	5.07	4.96	0.47	30	55	129	22	43	135	65
6-8	7.9	1080	0.68	2.23	0.30	1.18	3280	3500	5.30	4.84	0.44	32	54	127	28	39	129	60
8-10	8.0	1070	0.78	2.30	0.28	1.19	2800	2830	5.07	4.71	0.46	28	56	136	30	36	141	62
10-14	7.4	950	0.70	2.56	0.31	1.24	2540	2480	5.13	4.84	0.47	38	53	142	30	37	144	61
14-18	7.9	990	0.74	2.59	0.25	1.25	2640	2610	5.41	5.03	0.51	27	57	151	36	37	142	63
18-22	8.0	1050	0.66	2.20	0.28	1.23	2600	2580	5.28	4.72	0.47	30	56	144	29	36	139	62
22-26	8.0	860	0.56	2.25	0.31	1.26	2450	2480	5.14	4.90	0.52	31	57	146	30	32	134	63
26-30	7.8	1020	0.71	2.30	0.31	1.21	2630	2770	5.39	5.18	0.55	29	55	141	29	37	141	68
30-34	8.3	980	0.70	2.24	0.32	1.30	2620	2830	5.28	5.02	0.55	38	57	144	24	40	135	65
34-38	8.1	1080	0.69	2.28	0.29	1.33	2820	2900	5.51	5.04	0.53	38	57	142	30	37	136	66

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF)X-ray fluorescence analysis.

Appendix 15.25 Analytical data on the sediment core

Sampling site : Z. Sampling date : 11/4, 1977. Water depth : 77.0 m.

Depth(cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	K (%)	Ca	Mg (%)	Mn ($\mu g \cdot g^{-1}$)		Fe (%)		Ti (%)	Ni	Cu	Zn	Pb ($\mu g \cdot g^{-1}$)	As	Rb	Sr
		C	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-0.5	10.8	906	2.08	0.43	1.09	3390	3420	4.54	3.87	0.47	43	94	258	48	40	123	67
0.5-1	8.7	508	2.65	0.42	1.14	1410	1320	4.37	4.35	0.61	42	65	174	45	14	150	77
1-2	8.4	454	2.51	0.42	1.05	1370	1070	4.61	4.30	0.59	40	65	153	38	14	145	72
2-4	8.4	511	2.30	0.43	1.15	1130	933	4.59	4.36	0.59	36	58	142	30	14	144	75
4-6	8.2	533	2.36	0.44	1.10	1080	829	4.47	4.35	0.62	40	61	143	22	19	141	83
6-8	8.5	594	2.55	0.45	1.21	1090	942	4.40	4.37	0.60	43	56	146	29	18	144	82
8-10	7.8	466	2.42	0.52	1.09	991	895	4.08	4.32	0.59	37	53	129	23	16	133	105
10-12	8.9	518	2.38	0.47	1.17	1061	1000	4.22	4.46	0.63	33	56	143	30	14	143	83
12-14	11.3	637	2.23	0.42	1.09	1360	1270	4.32	4.55	0.64	47	42	158	43	15	146	77
14-16	11.6	692	2.25	0.37	1.18	1540	1480	4.69	4.55	0.63	36	42	167	41	15	151	74
16-18	11.7	645	2.26	0.42	1.14	1770	1940	4.50	4.84	0.66	31	43	168	45	14	148	74
18-20	11.8	656	2.15	0.38	1.08	2000	1890	4.60	4.56	0.64	42	39	159	44	13	156	79
20-22	11.6	662	2.32	0.38	1.18	2110	2130	4.69	4.81	0.66	42	45	167	37	19	149	77
22-24	11.5	666	2.34	0.40	1.11	2190	2220	4.68	4.81	0.66	37	44	162	45	15	147	75
24-26	11.6	656	2.21	0.38	1.15	2270	2110	4.65	4.64	0.63	42	45	161	44	15	150	77
26-28	11.5	640	2.10	0.39	1.12	2200	2100	4.95	4.56	0.60	42	43	159	40	18	151	76
28-30	11.3	665	2.31	0.38	1.17	2200	2220	4.86	4.72	0.64	34	43	167	41	15	145	73
30-32	12.0	675	2.21	0.38	1.18	2330	2280	4.94	4.74	0.64	47	42	166	43	15	148	76
32-34	11.7	676	2.26	0.42	1.16	2120	2300	5.11	4.72	0.64	39	41	169	45	16	152	78

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 15.26 Analytical data on the sedimentt core.

Sampling site : α. Sampling date : 11/4, 1977. Water depth : 81.0m.

Depth(cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	Na (%)		Ca (%)	K	Mg (%)	Mn ($\mu g \cdot g^{-1}$)		Fe (%)			Ti (%)	Ni	Cu	Zn ($\mu g \cdot g^{-1}$)	Pb	Sr	Rb ($\mu g \cdot g^{-1}$)	
		C	AA	NAA	XRF		AA	AA	XRF	C	XRF	NAA	XRF	XRF					XRF	NAA
0-0.5	13.8	1560	0.94	0.62	0.31	2.08	1.01	8520	10110	5.11	4.55	5.34	0.41	40	106	292	53	58	120	118
0.5-1	11.3	1120	0.88	0.69	0.34	2.30	1.18	4610	4980	5.43	4.76	5.32	0.44	32	80	207	62	65	132	150
1-2	8.4	1020	0.85	0.74	0.33	2.25	1.18	3250	3600	5.11	4.80	5.30	0.43	27	83	177	53	70	134	158
2-4	8.2	940	0.77	0.70	0.33	2.45	1.19	3040	2650	5.14	4.63	5.17	0.45	30	55	134	40	68	142	150
4-6	7.4	840	0.95	0.72	0.33	2.38	1.13	2400	2210	4.80	4.38	4.96	0.42	24	57	127	34	63	137	173
6-8	7.3	680	0.75	0.71	0.31	2.61	1.13	2360	2390	4.83	4.71	5.10	0.44	18	51	135	36	65	146	149
8-10	7.4	740	0.90	0.69	0.31	2.45	1.12	2280	2160	4.88	4.83	5.20	0.47	30	58	143	36	64	149	167
10-14	7.9	800	0.74	0.62	0.30	2.42	1.19	2140	1940	4.86	4.85	5.40	0.52	33	56	143	41	66	148	192
14-18	8.0	910	0.67	0.65	0.29	2.28	1.12	2240	2300	5.18	5.00	5.11	0.53	29	55	137	32	62	134	146
18-22	7.5	850	0.76	0.70	0.31	2.31	1.22	2250	2050	5.23	4.86	5.40	0.52	36	58	140	33	66	138	161
22-26	8.2	1030	0.80	0.69	0.31	2.36	1.19	2470	2480	5.29	5.20	5.48	0.58	29	61	144	29	64	133	173
26-30	7.8	740	0.69	0.68	0.29	2.45	1.23	2150	2210	5.09	4.99	5.17	0.55	40	56	143	34	68	145	144
30-34	8.4	1060	0.68	0.68	0.30	2.24	1.19	2490	2500	5.25	5.02	5.15	0.53	40	56	140	30	64	133	134
34-38	8.4	860	0.79	0.69	0.31	2.32	1.18	2250	2330	4.87	4.96	5.08	0.53	25	64	147	37	67	142	128

As ($\mu g \cdot g^{-1}$)		Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb	Lu ($\mu g \cdot g^{-1}$)	U	Th	Hf	Nd	Ta	Eu	La	Br	Au
XRF	NAA	NAA																		
151	144	19.5	70	5.4	783	11.0	14.1	7.9	75	3.6	0.48	4.1	15.2	4.2	53	—	1.2	38.8	14.9	0.015
62	68	17.0	75	4.0	760	11.3	15.0	8.3	78	3.0	0.47	3.7	16.9	3.3	29	—	1.1	39.0	12.2	0.018
42	49	17.5	68	3.0	770	11.4	14.7	8.4	80	2.9	0.45	4.3	17.0	3.8	—	—	1.2	40.7	10.0	0.007
29	35	20.2	74	2.3	748	12.8	15.6	9.1	83	3.4	0.51	3.4	18.5	4.3	59	1.1	—	42.4	6.5	0.011
28	31	17.4	81	2.1	728	12.9	15.0	9.5	83	4.1	0.55	3.1	19.4	3.8	—	—	1.3	45.6	6.2	—
25	29	17.6	67	2.0	538	11.9	15.4	9.9	86	4.3	0.62	3.7	20.2	4.4	—	—	—	45.6	5.4	—
28	33	18.0	71	2.2	928	14.5	15.9	10.2	96	4.3	0.55	4.6	21.9	4.0	—	—	0.9	47.8	4.7	—
26	34	17.7	87	2.6	922	12.7	17.0	10.0	92	4.1	0.60	4.7	20.5	4.5	—	—	0.9	46.5	6.1	—
28	30	19.5	75	1.9	647	13.1	16.5	9.8	88	3.9	0.56	4.0	19.9	4.2	—	—	1.3	44.2	7.0	—
26	32	21.2	75	2.0	750	11.0	17.2	9.6	87	4.1	0.55	4.2	18.8	4.4	—	—	1.1	44.4	6.9	—
29	31	18.3	84	2.1	745	11.4	17.0	8.9	85	4.0	0.53	4.5	19.0	3.4	35	—	1.3	42.6	6.4	—
28	35	21.1	84	2.4	765	13.1	17.1	9.0	82	4.6	0.48	5.4	18.6	4.5	—	—	1.3	42.8	6.7	—
27	29	18.3	71	1.9	753	12.7	16.0	8.3	80	3.7	0.52	5.8	16.0	4.4	—	—	1.3	39.3	8.4	—
25	29	20.6	73	2.0	796	11.6	16.1	8.6	82	3.3	0.49	4.1	17.7	3.8	48	—	—	41.0	8.7	—

(—) undetectable. Analytical methed : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.27 Analytical data on the sediment core

Sampling site : β. Sampling date : 11/4, 1977. Water depth : 58.0 m.

Depth (cm)	I.L. (%)	P ($\mu g \cdot g^{-1}$)	Na (%)	Ca (%)	K	Mg (%)	Mn ($\mu g \cdot g^{-1}$)		Fe (%)			Ti (%)	Ni	Cu	Zn ($\mu g \cdot g^{-1}$)	Pb	Sr	Rb ($\mu g \cdot g^{-1}$)		As ($\mu g \cdot g^{-1}$)	
		C	NAA	XRF		AA	AA	XRF	C	XRF	NAA	XRF			XRF			XRF	NAA	XRF	NAA
0-0.5	10.3	1310	0.77	0.37	2.45	1.06	2310	2660	4.53	4.54	5.27	0.48	53	93	250	53	66	131	134	88	85
0.5-1	9.8	1430	0.80	0.38	2.29	1.04	2870	2170	5.01	4.45	5.26	0.50	39	89	207	51	72	123	161	51	55
1-2	8.8	1090	0.87	0.37	2.63	1.06	2260	2180	4.39	4.91	4.98	0.55	46	90	189	47	77	125	131	39	43
2-3	8.2	1050	0.82	0.36	2.39	1.06	2100	2010	4.31	4.71	5.22	0.50	28	77	159	39	79	134	161	31	36
3-4	7.5	898	0.81	0.39	2.69	1.08	1760	1730	4.24	4.85	4.92	0.54	23	64	144	35	81	146	155	30	30
4-6	7.5	928	0.77	0.34	2.45	1.00	1910	1940	4.28	4.96	5.24	0.48	33	52	137	32	73	138	144	25	29
6-8	7.6	838	—	0.37	2.65	1.04	1690	1840	4.29	5.03	—	0.55	21	49	130	33	73	140	—	24	—
8-10	7.7	913	0.75	0.34	2.69	1.00	1720	1800	4.19	5.03	5.17	0.53	31	59	146	37	72	146	181	25	26
10-14	7.7	800	0.80	0.34	2.40	1.09	1600	1300	4.70	4.69	5.27	0.58	26	53	142	35	76	141	186	23	29
14-18	7.7	769	0.70	0.30	2.29	1.00	1560	1340	4.17	4.77	5.21	0.56	35	60	161	35	67	132	182	20	27
18-22	8.0	903	0.73	0.32	2.15	1.09	1540	1320	4.42	4.82	5.46	0.56	29	54	145	31	73	135	148	23	25
22-26	8.0	978	0.74	0.30	2.21	0.99	1750	1460	4.72	4.68	5.32	0.54	30	58	147	31	75	135	158	23	26
26-30	8.4	1050	0.77	0.33	2.50	1.08	1650	1750	4.67	5.12	5.40	0.59	33	58	144	33	74	138	125	23	27
30-34	8.5	1250	0.76	0.29	2.20	1.06	1790	1690	4.33	4.83	5.52	0.55	36	56	153	29	69	127	176	25	33

Co	Cr	Sb	Ba	Cs	Sc	Sm	Ce	Yb ($\mu g \cdot g^{-1}$)	Lu	U	Th	Hf	Nd	Ta	Eu	La	Br
								NAA									
19.7	79	4.9	779	14.1	15.6	8.9	86	3.4	0.48	4.2	17.9	5.0	—	—	1.0	42.9	14.9
21.8	75	4.1	721	13.9	15.8	9.6	90	3.8	0.56	4.4	18.3	5.0	—	1.1	—	44.4	10.9
20.5	71	2.8	661	13.9	15.3	9.2	88	3.7	0.52	4.1	17.7	4.6	51	1.3	1.3	44.2	11.1
19.5	73	2.5	763	12.1	16.2	9.4	84	3.4	0.54	4.6	17.6	4.4	56	1.3	0.9	44.4	11.1
16.6	72	2.4	701	11.9	15.7	9.4	87	4.8	0.55	3.8	18.6	4.3	—	—	1.3	44.6	5.8
19.1	81	2.1	708	12.3	16.0	10.0	83	4.0	0.58	4.3	19.3	4.2	—	—	1.3	47.7	6.7
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
18.5	76	2.3	714	12.6	16.4	10.4	94	4.0	0.54	5.5	21.4	4.1	—	—	—	51.6	4.7
23.8	78	2.7	929	12.2	18.3	10.4	97	4.9	0.55	5.5	20.5	5.1	—	—	1.2	49.8	5.8
18.4	79	2.0	627	13.0	18.0	10.4	97	3.4	0.62	4.1	21.1	5.4	70	—	1.4	47.9	5.4
19.9	89	2.0	826	12.3	18.2	9.9	90	3.7	0.64	4.3	19.3	4.1	—	1.6	—	44.5	6.8
21.2	78	2.0	775	13.0	17.3	9.6	91	3.4	0.55	4.3	18.5	4.9	—	—	1.0	44.8	8.5
21.7	85	2.5	928	13.3	18.1	9.7	85	3.4	0.50	4.1	19.0	5.0	—	—	—	46.8	6.1
22.0	88	2.7	793	14.1	17.5	9.7	94	3.7	0.53	4.5	18.5	5.3	—	—	—	45.5	9.8

(—)undetectable or not analysed. Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis, (NAA) neutron activation analysis.

Appendix 15.28 Analytical data on the sediment core

Sampling site : δ. Sampling date : 11/4, 1977. Water depth : 2.5 m.

Depth(cm)	P	K	Ca	Mg	Mn		Fe		Ti	Ni	Cu	Zn	Pb	As	Rb	Sr
	($\mu g \cdot g^{-1}$)	(%)		(%)	($\mu g \cdot g^{-1}$)		(%)		(%)				($\mu g \cdot g^{-1}$)			
	C	XRF		AA	AA	XRF	C	XRF	XRF				XRF			
0-0.5	860	2.28	0.42	0.82	2080	1780	4.87	4.21	0.46	86	103	542	62	44	140	65
0.5-1	860	2.13	0.35	0.82	1850	1600	4.92	4.41	0.45	35	78	396	66	33	139	65
1-2	640	2.09	0.36	0.83	1300	942	4.95	4.29	0.40	29	67	383	65	17	140	64
2-4	490	2.28	0.33	0.82	990	804	4.59	4.25	0.43	25	49	211	53	11	165	70
4-6	370	2.50	0.36	0.77	920	756	4.52	4.58	0.45	28	46	169	49	8	161	64
6-8	360	2.33	0.28	0.80	940	771	4.62	4.59	0.49	26	41	162	42	8	151	63
8-10	360	2.29	0.27	0.80	880	723	4.51	4.29	0.50	30	40	159	43	6	153	68
10-12	460	2.30	0.30	0.78	950	788	4.49	4.69	0.55	25	41	161	43	7	150	63
12-14	390	2.21	0.30	0.80	960	778	4.48	4.53	0.53	27	40	153	34	11	146	68
14-16	470	2.38	0.36	0.89	1020	843	4.74	4.79	0.55	24	44	165	42	6	150	72
16-18	460	2.41	0.36	0.92	960	934	5.00	4.93	0.54	33	47	171	38	9	145	72
18-20	530	2.34	0.29	0.90	1150	982	5.11	4.96	0.53	30	46	173	43	6	153	76
20-24	620	2.15	0.32	0.84	1060	875	4.76	4.58	0.51	22	41	155	38	7	140	77
24-28	650	2.10	0.33	0.76	980	843	4.66	4.28	0.49	23	34	138	34	8	135	81
28-32	960	2.10	0.35	0.82	1100	935	4.66	4.49	0.48	20	38	148	35	11	138	84

Analytical method : (C) colorimetry, (AA) atomic absorption spectrophotometry, (XRF) X-ray fluorescence analysis.

Appendix 16 Probable species of elements in the oxidized and reduced layers of sediment in Lake Biwa

Element	Reduced layer		Accumulation	Oxidized layer		Remark
	Solid phase	Aqueous phase		Aqueous phase	Solid phase	
Fe	Fe(+2)X, FeS, FeS_2, [$Fe_2O_3 \cdot nH_2O$]	Fe^{+2}, Fe(+2)L	- - - - →	Fe(+2, +3)L	$Fe_2O_3 \cdot nH_2O$, *Fe(+2, +3)X*	2), 3), 4)
Mn	Mn(+2)X	Mn^{+2}, Mn(+2)L	→	Mn^{+2}, Mn(+2)L	Mn(+2)X, $MnO_X \cdot nH_2O$ (Eh > *ca.* 600 mV)	*ibid.*
As	As(+3)X, $XAsO_4^{-3}$, [As_2S_3]	As(+3)L, $HAsO_2$, [AsS_2^-, $H_2AsO_4^-$]	→	$H_2AsO_4^-$, [As(+3)L]	$XAsO_4^{-3}$, [As(+3)X]	Total dissolved sulfide : *10^{-6}–10^{-4}M*
Sb	Sb(+3)X, Sb_2S_3, $Sb(OH)_3$, $XSb(OH)_6$, [Sb?]	$Sb(OH)_3 \cdot aq.$, Sb(+3)L, SbS_2^-	→ ← s	$Sb(OH)_6^-$, [Sb(+3)L]	$XSb(OH)_6^-$, [Sb(+3)X]	*ibid.*
Pb	Pb(+2)X, PbS	Pb^{+2}, Pb(+2)L, [PbS_2^{-2}]	- - - - → ← s	Pb^{+2}, Pb(+2)L	Pb(+2)X, PbO_2 (Eh > *ca.* 600 mV)	*ibid.*
Hg	HgS, Hg, [Hg(+2)X]	HgS_2^{-2}, Hg, [Hg(+2)L]	← s	Hg, $HgOH^+$, Hg(+2)L	Hg, Hg(+2)X	*idid.*
Cr	Cr(+3)X, [$Cr(OH)_3$]	$Cr(OH)_2^+$, Cr(+3)L	← - - - ?	CrO_4^{-2}, *$Cr(OH)_2^+$*, Cr(+3) L	*$XCrO_4^{-2}$, Cr(+3)X*, [$Cr(OH)_3$]	
U	UO_2, U(+4)X, UO_2(+2)X	$U(OH)_2^{+2}$, $UO_2(OH)^+$, U(+4)L, UO_2(+2)L	← - - - -	$UO_2(OH)^+$, UO_2(+2)L	UO_2(+2)X	Total dissolved carbonate : 10^{-5}–10^{-3}M
V	VO(+2)X, V(+3)X, XVO_4^{-3}, [$VO(OH)_2$, $V(OH)_3$]	$H_2VO_4^-$, $VOOH^+$, VO(+2)L, $V(OH)_2^+$, V(+3)L	← - - - ?	$H_2VO_4^-$	XVO_4^{-3}	
Ce	Ce(+3)X	Ce^{+3}, Ce(+3)L	- - - - →	Ce^{+3}, Ce(+3, +4)L, $Ce(OH)_2^{+2}$, $Ce(OH)_3^+$,	Ce(+3, +4)X, $Ce(OH)_4$ (Eh > *ca.* 400 mV)	

1) Eh-pH diagram for each element was illustrated a 25°C, 1 atm. by refrence to the following literatures : G. Charlot, "L'analyse qualitative et les réactions en solution", 4ᵉ édition, 1957, Masson et Cie ; L. G. Sillén, A. E. Martell, "Stability constants of metal-ion complexes", Spec. pub. No. 17, 1964, Chem. Soc. (London).

2) J. D. Hem, Chemical factors that influence the availability of iron and manganese in aqueous systems, Geol. Soc. Amer. Bull., Spec. pap. **140**, 17-24 (1972)

3) R. R. Weiler, The interstitial water composition in the sediments of the Great Lakes. 1. Western Lake Ontario, Limnol. Oceanogr. 18, 918-931 (1973)

4) G. Brümmer, Redoxpotentiale und redoxprozesse von mangan-, eisen- und schwefelverbindungen in hydromorphen böden und sedimenten, Geoderma **12**, 207-222 (1974)

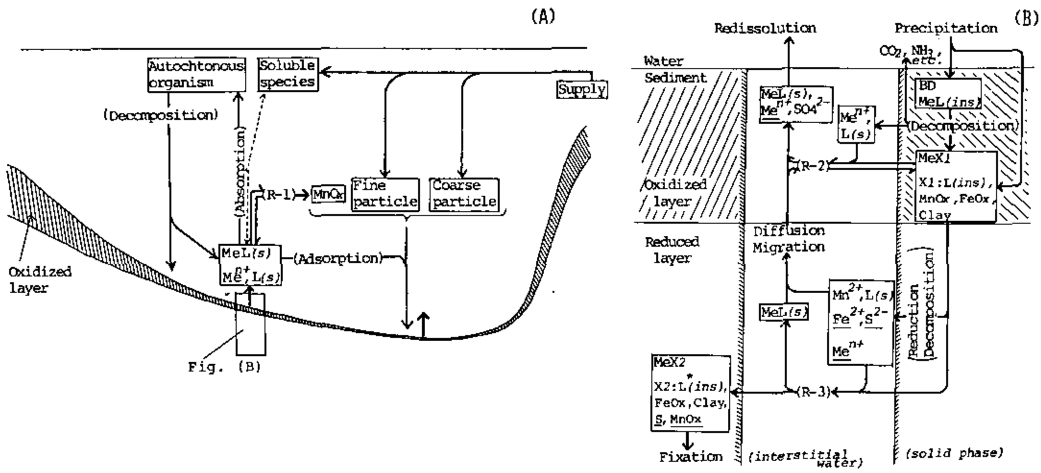
X : Insoluble organic substance, hydrous oxides of manganese and iron, or clay, etc.

L : Soluble organic substance

[ ] : Minor constituent in each phase

←— s : Rtention by sulfide formation can be expected.

Appendix 17 Model for cycles of metals in Lake Biwa



Supply : Biological detritus (BD), Organic substances (L(s) and L(ins) are soluble and insoluble organic substances respectively), Hydrous oxides of manganese (MnOx) and iron (FeOx), Clay ; Metal ions are supplyed as occluded, complexed, and adsorbed forms in addition to some simple inorganic complexes and free aquo-ions (Me^{n+}).

(R-1) : Release of metal ions by microbial decomposition of metal complexes (i.e. MeL(s) $\rightarrow$ Me^{n+}+R, R : organic residue) ; Catalytic oxidation of Mn^{2+}, catalyzer : MnOx, FeOx, quartz, feldspar, microorganism, etc.

(R-2) : Complex formation ; Oxidation ; Adsorption ; Dissolution by complex formation (MeX1+L(s) $\rightarrow$ MeL(s)+X1) ; Metal ion release with lowering of pH and by hydrous oxide (MnOx or FeOx)$-$L(s) interaction.

(R-3) : Complex formation ; Sulfide formation ; Substitution reaction {(Mn^{2+}, Me$_1^{n+}$)+Me$_2$X1 $\rightarrow$ (Mn, Me$_1$) X1+Me$_2^{n+}$} ; Dissolution by complex formation ; Metal ion release with lowering of pH and by hydrous oxide-L(s) interaction.

L*(ins) : insoluble organic substance resisted to decomposition.

_____ : underlined species shows the minor constituent in each production.

(A)

Element	-log Kso	Element	-log Kso
Mg	10.7	Ti	(3+) 35.0, (4+) 53.1, (TiO) 29.0
Ca	5.2		
Sr	3.5	Zr	50.4
Ba	2.3	Hf	53.4
Sc	29.5	Th	(4+) 43.3, (ThO) 23.3
Y	22.7	Cr	(3+) 30.2
La	20.0	U	(4+) 48.5, (UO_2) 19.3
Ce	(3+) 21.1, (4+) 50.6	Mn	(2+) 12.7, (4+) 56.0
Pr	22.7	Fe	(2+) 14.4, (3+) 37.4
Nd	22.5	Co	(2+) 14.7 (3+) 41.8
Sm	23.7	Ni	15.2
Eu	23.7	Cu	19.4
Gd	24.6	Zn	16.6
Tb	25.8	Cd	14.1
Dy	25.9	Hg	(2+) 25.6
Ho	25.7	Al	32.5
Er	24.3	Pb	(2+) 16.3, (4+) 64.8
Tm	23.5	Sb	(3+) 41.5
Yb	24.6		
Lu	24.7		

(B)

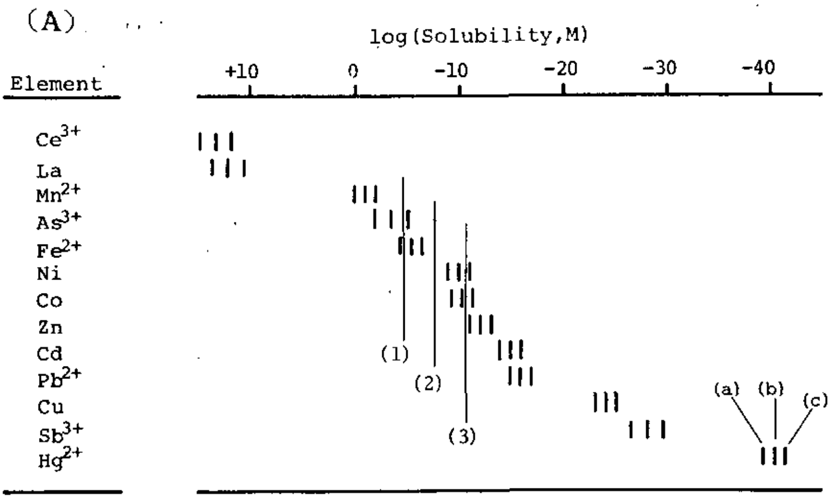
Element (2+)	-log Kso	Element (3+)	-log Kso
Hg	52.5	Sb	92.8
Cu	36.3	As	22.2*
Pb	28.1	La	12.7
Cd	27.1	Ce	10.2
Zn	24.3		
Co	22.4		
Ni	22.2		
Fe	17.7		
Mn	13.2		

(C)

Element (2+)	-log Kso	Element (3+)	-log Kso
Ba**	50.1	Fe	20.2
Pb	35.4	Cr	20.1 (at 22℃)
Cu	35.1	Al	15.8 (at 22℃)
Cd	32.7	Bi	9.4
Mn**	28.7		
Co	28.1		
Zn*	27.9		
Ni**	25.5		
Mg	19.7		
Ca*	18.2		
Sr*	18.1		

Appendix 18 Solubility products of metal-hydroxide, sulfide and arsenate

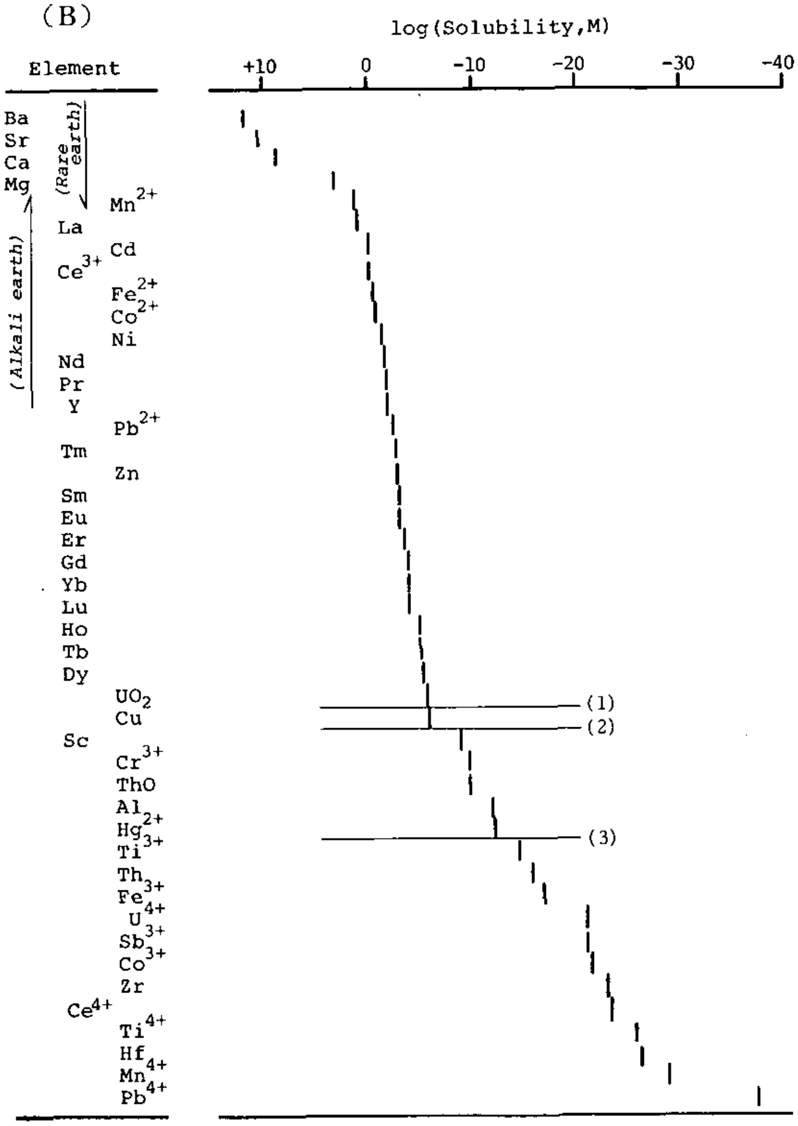
Values are based on the data compiled by Sillén and Martell (1964). (A) Hydroxide, Temp : 25℃, $K_{so} = (Me^{n+})(OH^-)^n$; (B) Sulfide, Temp : 25℃, K_{so} (2+) = $(Me^{2+})(S^{2-})$, K_{so}(3+) = $(Me^{3+})^2(S^{2-})^3$,* : Value for $(HAsO_2)^2(H_2S)^3$; (C) Arsenate, Temp : 20℃, K_{so}(2+) = $(Me^{2+})^3(AsO_4^{3-})^2$, K_{so}(3+) = $(Me^{3+})(AsO_4^{3-})$, ** : Elements which are largely accumulated in Mn concretions (concentration factor > 0.8), * : Elements which are slightly accumulated in Mn concretions (concentration factor = 0.3-0.8)



Appendix 19 Maximum solubility of metal ion as (A) sulfide and (B) hydroxide

Concentration level : (1)$mg \cdot kg^{-1}$, (2)$\mu g \cdot kg^{-1}$, (3)$pg \cdot kg^{-1}$.

(A)Temp : 25°C, pH : 6.5, Total sulfide concentration in solution : (a)10^{-6}M, (b)10^{-5}M, (c)10^{-4}M ;(B)Temp : 25°C, pH : 7.0.


(B)
log(Solubility,M)
Element
+10
0
-10
-20
-30
-40
Ba
Sr
Ca
Mg
(Rare earth)
(Alkali earth)
Mn2+
La
Cd
Ce3+
Fe2+
Co2+
Ni
Nd
Pr
Y
Pb2+
Tm
Zn
Sm
Eu
Er
Gd
Yb
Lu
Ho
Tb
Dy
UO2
Cu
Sc
Cr3+
ThO
Al
Hg2+
Ti3+
Th
Fe3+
U4+
Sb3+
Co3+
Zr
Ce4+
Ti4+
Hf
Mn4+
Pb4+
(1)
(2)
(3)

国立公害研究所特別研究成果報告

第 1 号　陸水域の富栄養化に関する総合研究 —— 霞ヶ浦を対象域として —— 昭和51年度．（1977）

第 2 号　陸上植物による大気汚染環境の評価と改善に関する基礎的研究 —— 昭和51，52年度　研究報告．（1978）

（改　称）

国立公害研究所研究報告

※第 3 号　A comparative study of adults and immature stages of nine Japanese species of the genus *Chironomus* (Diptera, Chironomidae). (1978)
（日本産ユスリカ科 ***Chironomus*** 属9種の成虫，サナギ，幼虫の形態の比較）

第 4 号　スモッグチャンバーによる炭化水素ー窒素酸化物系光化学反応の研究 —— 昭和52年度　中間報告．（1978）

第 5 号　芳香族炭化水素ー窒素酸化物系の光酸化反応機構と光酸化二次生成物の培養細胞に及ぼす影響に関する研究 —— 昭和51，52年度　研究報告．（1978）

第 6 号　陸水域の富栄養化に関する総合研究（Ⅱ）—— 霞ヶ浦を中心として． —— 昭和53年度．（1979）

※第 7 号　A morphological study of adults and immature stages of 20 Japanese species of the family Chironomidae (Diptera). (1979)
（日本産ユスリカ科20種の成虫，サナギ，幼虫の形態学的研究）

※第 8 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 —— 昭和52，53年度　研究報告．（1979）

第 9 号　スモッグチャンバーによる炭化水素－窒素酸化物系光化学反応の研究 —— 昭和53年度　中間報告．（1979）

第 10 号　陸上植物による大気汚染環境の評価と改善に関する基礎的研究 —— 昭和51～53年度　特別研究報告．（1979）

第 11 号　Studies on the effects of air pollutants on plants and mechanisms of phytotoxicity. (1980)
（大気汚染物質の植物影響およびその植物毒性の機構に関する研究）

第 12 号　Multielement analysis studies by flame and inductively coupled plasma spectroscopy utilizing computer-controlled instrumentation. (1980)
（コンピュータ制御装置を利用したフレームおよび誘導結合プラズマ分光法による多元素同時分析）

第 13 号　Studies on chironomid midges of the Tama River. (1980)
Part 1. The distribution of chironomid species in a tributary in relation to the degree of pollution with sewage water.
Part 2. Description of 20 species of Chironominae recovered from a tributary.
（多摩川に発生するユスリカの研究
—— 第1報　その一支流に見出されたユスリカ各種の分布と下水による汚染度との関係 ——
—— 第2報　その一支流に見出された Chironominae 亜科の20種について ——）

第 14 号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究 —— 昭和53，54年度　特別研究報告．（1980）

※第 15 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 —— 昭和54年度　特別研究報告．（1980）

第 16 号　計測車レーザーレーダーによる大気汚染遠隔計測．（1980）

※第 17 号　流体の運動および輸送過程に及ぼす浮力効果 —— 臨海地域の気象特性と大気拡散現象の研究 —— 昭和53，54年度　特別研究報告．（1980）

第 18 号 Preparation, analysis and certification of PEPPERBUSH standard reference material. (1980)
（環境標準試料「リョウブ」の調製，分析および保証値）

※第 19 号 陸水域の富栄養化に関する総合研究（Ⅲ）── 霞ヶ浦（西浦）の湖流 ── 昭和53，54年度．（1981）

第 20 号 陸水域の富栄養化に関する総合研究（Ⅳ）── 霞ヶ浦流域の地形，気象水文特性およびその湖水環境に及ぼす影響 ── 昭和53，54年度．（1981）

第 21 号 陸水域の富栄養化に関する総合研究（Ⅴ）── 霞ヶ浦流入河川の流出負荷量変化とその評価 ── 昭和53，54年度．（1981）

第 22 号 陸水域の富栄養化に関する総合研究（Ⅵ）── 霞ヶ浦の生態系の構造と生物現存量 ── 昭和53，54年度．（1981）

第 23 号 陸水域の富栄養化に関する総合研究（Ⅶ）── 湖沼の富栄養化状態指標に関する基礎的研究 ── 昭和53，54年度．（1981）

第 24 号 陸水域の富栄養化に関する総合研究（Ⅷ）── 富栄養化が湖利用に及ぼす影響の定量化に関する研究 ── 昭和53，54年度（1981）

第 25 号 陸水域の富栄養化に関する総合研究（Ⅸ）── *Microcystis*（藍藻類）の増殖特性 ── 昭和53，54年度．（1981）

第 26 号 陸水域の富栄養化に関する総合研究（Ⅹ）── 藻類培養試験法によるＡＧＰの測定 ── 昭和53，54年度．（1981）

第 27 号 陸水域の富栄養化に関する総合研究（Ⅺ）── 研究総括 ── 昭和53，54年度．（1981）

第 28 号 複合大気汚染の植物影響に関する研究 ── 昭和54，55年度 特別研究報告．（1981）

第 29 号 Studies on chironomid midges of the Tama River. (1981)
Part 3. Species of the subfamily Orthocladiinae recorded at the summer survey and their distribution in relation to the pollution with sewage waters.
Part 4. Chironomidae recorded at a winter survey.
（多摩川に発生するユスリカ類の研究
── 第３報 夏期の調査で見出されたエリユスリカ亜科 Orthocladiinae 各種の記載と，その分布の下水汚染度との関係について ──
── 第４報 南浅川の冬期の調査で見出された各種の分布と記載 ──）

※第 30 号 海域における富栄養化と赤潮の発生機構に関する基礎的研究 ── 昭和54，55年度 特別研究報告．（1982）

第 31 号 大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和55年度 特別研究報告．（1981）

第 32 号 スモッグチャンバーによる炭化水素－窒素酸化物系光化学反応の研究 ── 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究１）── 昭和54年度 特別研究報告．（1982）

第 33 号 臨海地域の気象特性と大気拡散現象の研究 ── 大気運動と大気拡散過程のシミュレーション ── 昭和55年度 特別研究報告．（1982）

第 34 号 環境汚染の遠隔計測・評価手法の開発に関する研究 ── 昭和55年度 特別研究報告．（1982）

第 35 号 環境面よりみた地域交通体系の評価に関する総合解析研究．（1982）

第 36 号 環境試料による汚染の長期モニタリング手法に関する研究 ── 昭和55，56年度 特別研究報告．（1982）

第 37 号 環境施策のシステム分析支援技術の開発に関する研究．（1982）

第 38 号 Preparation, analysis and certification of POND SEDIMENT certified reference material. (1982)
（環境標準試料「池底質」の調製，分析及び保証値）

第 39 号 環境汚染の遠隔計測・評価手法の開発に関する研究 ── 昭和56年度 特別研究報告．（1982）

第 40 号　大気汚染物質の単一及び複合汚染の生体に対する影響に関する実験的研究 —— 昭和56年度　特別研究報告.（1983）

第 41 号　土壌環境の計測と評価に関する統計学的研究.（1983）

第 42 号　底泥の物性及び流送特性に関する実験的研究.（1983）

※第 43 号　Studies on chironomid midges of the Tama River. (1983)

Part 5. An observation on the distribution of Chironominae along the main stream in June with description of 15 new species.

Part 6. Description of species of the subfamily Orthocladiinae recovered from the main stream in the June survey.

Part 7. Additional species collected in winter from the main stream.

(多摩川に発生するユスリカ類の研究

—— 第５報　本流に発生するユスリカ類の分布に関する６月の調査成績とユスリカ亜科に属する15新種等の記録 ——

—— 第６報　多摩本流より６月に採集されたエリユスリカ亜科の各種について ——

—— 第７報　多摩本流より３月に採集されたユスリカ科の各種について ——）

第 44 号　スモッグチャンバーによる炭化水素－窒素酸化物系光化学反応の研究 —— 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究２）—— 昭和54年度　特別研究中間報告.（1983）

第 45 号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究 —— 昭和53年～55年度　特別研究報告.（1983）

第 46 号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究 —— 昭和54，55年度　特別研究報告　第１分冊.（1983）

第 47 号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究 —— 昭和54，55年度　特別研究報告　第２分冊.（1983）

第 48 号　水質観測点の適正配置に関するシステム解析.（1983）

第 49 号　環境汚染の遠隔計測・評価手法の開発に関する研究 —— 昭和57年度　特別研究報告.（1984）

第 50 号　陸水域の富栄養化防止に関する総合研究（Ⅰ）—— 霞ヶ浦の流入負荷量の算定と評価 —— 昭和55～57年度　特別研究報告.（1984）

第 51 号　陸水域の富栄養化防止に関する総合研究（Ⅱ）—— 霞ヶ浦の湖内物質循環とそれを支配する因子 —— 昭和55～57年度　特別研究報告.（1984）

第 52 号　陸水域の富栄養化防止に関する総合研究（Ⅲ）—— 霞ヶ浦高浜入における隔離水界を利用した富栄養化防止手法の研究 —— 昭和55～57年度　特別研究報告.（1984）

第 53 号　陸水域の富栄養化防止に関する総合研究（Ⅳ）—— 霞ヶ浦の魚類及び甲殻類現存量の季節変化と富栄養化 —— 昭和55～57年度　特別研究報告.（1984）

第 54 号　陸水域の富栄養化防止に関する総合研究（Ⅴ）—— 霞ヶ浦の富栄養化現象のモデル化 —— 昭和55～57年度　特別研究報告.（1984）

第 55 号　陸水域の富栄養化防止に関する総合研究（Ⅵ）—— 富栄養化防止対策 —— 昭和55～57年度　特別研究報告.（1984）

第 56 号　陸水域の富栄養化防止に関する総合研究（Ⅶ）—— 湯ノ湖における富栄養化とその防止対策 —— 昭和55～57年度　特別研究報告.（1984）

第 57 号　陸水域の富栄養化防止に関する総合研究（Ⅷ）—— 総括報告 —— 昭和55～57年度　特別研究報告.（1984）

第 58 号　環境試料による汚染の長期的モニタリング手法に関する研究 —— 昭和55～57年度　特別研究総合報告.（1984）

第 59 号　炭化水素－窒素酸化物－硫黄酸化物系光化学反応の研究 — 光化学スモッグチャンバーによるオゾン生成機構の研究 — 大気中における有機化合物の光酸化反応機構の研究 — 昭和55～57年度　特別研究報告（第1分冊）.（1984）

第 60 号　炭化水素－窒素酸化物－硫黄酸化物系光化学反応の研究 — 光化学エアロゾル生成機構の研究 — 昭和55～57年度　特別研究報告（第2分冊）.（1984）

第 61 号　炭化水素－窒素酸化物－硫黄酸化物系光化学反応の研究 — 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究1）— 昭和55～57年度　特別研究報告（第3分冊）.（1984）

第 62 号　有害汚染物質による水界生態系のかく乱と回復過程に関する研究 — 昭和56～58年度　特別研究中間報告.（1984）

第 63 号　海域における富栄養化と赤潮の発生機構に関する基礎的研究 — 昭和56年度　特別研究報告.（1984）

第 64 号　複合大気汚染の植物影響に関する研究 — 昭和54～56年度　特別研究総合報告.（1984）

第 65 号　Studies on effects of air pollutant mixtures on plants—Part 1. (1984)
（複合大気汚染の植物に及ぼす影響 — 第1分冊）

第 66 号　Studies on effects of air pollutant mixtures on plants—Part 2. (1984)
（複合大気汚染の植物に及ぼす影響 — 第2分冊）

第 67 号　環境中の有害物質による人の慢性影響に関する基礎的研究 — 昭和54～56年度　特別研究総合報告.（1984）

第 68 号　汚泥の土壌還元とその環境に関する研究 — 昭和56～57年度　特別研究総合報告.（1984）

第 69 号　中禅寺湖の富栄養化現象に関する基礎的研究.（1984）

第 70 号　Studies on chironomid midges in lakes of the Nikko National Park (1984)
Part I.　Ecological studies on chironomids in lakes of the Nikko National Park.
Part II.　Taxonomical and morphological studies on the chironomid species collected from lakes in the Nikko National Park.
（日光国立公園の湖沼のユスリカに関する研究
— 第1部　日光国立公園の湖のユスリカの生態学的研究 —
— 第2部　日光国立公園の湖沼に生息するユスリカ類の分類学的，形態学的研究 —

第 71 号　リモートセンシングによる残雪及び雪田植生の分布解析.（1984）

第 72 号　炭化水素－窒素酸化物－硫黄酸化物系化学反応の研究. 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究2）—昭和55～57年度　特別研究報告(第4分冊). (1985)

第 73 号　炭化水素－窒素酸化物－硫黄酸化物系化学反応の研究. —昭和55～57年度　特別研究総合報告. (1985)

第 74 号　都市域及びその周辺の自然環境に係る環境指標の開発に関する研究. 環境指標 — その考え方と作成方法—昭和59年度特別研究報告. (1984)

第 75 号　Limnological and environmental studies of elements in the sediment of Lake Biwa. (1985)
琵琶湖底泥中の元素に関する陸水学および環境化学的研究

※残部なし

Report of Special Research Project the National Institute for Environmental Studies

No. 1* Man activity and aquatic environment – with special references to Lake Kasumigaura – Progress report in 1976. (1977)

No. 2* Studies on evaluation and amelioration of air pollution by plants – Progress report in 1976-1977. (1978)

[Starting with Report No. 3, the new title for NIES Reports was changed to:]

Research Report from the National Institute for Environmental Studies

※No. 3 A comparative study of adults and immature stages of nine Japanese species of the genus *Chironomus* (Diptera, Chironomidae). (1978)

No. 4* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1977. (1978)

No. 5* Studies on the photooxidation products of the alkylbenzene-nitrogen oxides system, and on their effects on Cultured Cells – Research report in 1976-1977. (1978)

No. 6* Man activity and aquatic environment – with special references to Lake Kasumigaura – Progress report in 1977-1978. (1979)

※No. 7 A morphological study of adults and immature stages of 20 Japanese species of the family Chironomidae (Diptera). (1979)

※No. 8* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1977-1978. (1979)

No. 9* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1978. (1979)

No.10* Studies on evaluation and amelioration of air pollution by plants – Progress report in 1976-1978. (1979)

No.11 Studies on the effects of air pollutants on plants and mechanisms of phytotoxicity. (1980)

No.12 Multielement analysis studies by flame and inductively coupled plasma spectroscopy utilizing computer-controlled instrumentation. (1980)

No.13 Studies on chironomid midges of the Tama River. (1980)

Part 1. The distribution of chironomid species in a tributary in relation to the degree of pollution with sewage water.

Part 2. Description of 20 species of Chironominae recovered from a tributary.

No.14* Studies on the effects of organic wastes on the soil ecosystem – Progress report in 1978-1979. (1980)

※No.15* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1977-1978. (1980)

No.16* Remote measurement of air pollution by a mobile laser radar. (1980)

※No.17* Influence of buoyancy on fluid motions and transport processes – Meteorological characteristics and atmospheric diffusion phenomena in the coastal region – Progress report in 1978-1979. (1980)

No.18 Preparation, analysis and certification of PEPPERBUSH standard reference material. (1980)

※No.19* Comprehensive studies on the eutrophication of fresh-water areas – Lake current of Kasumigaura (Nishiura) – 1978-1979. (1981)

No.20* Comprehensive studies on the eutrophication of fresh-water areas – Geomorphological and hydrometeorological characteristics of Kasumigaura watershed as related to the lake environment – 1978-1979. (1981)

No.21* Comprehensive studies on the eutrophication of fresh-water areas – Variation of pollutant load by influent rivers to Lake Kasumigaura – 1978-1979. (1981)

No.22* Comprehensive studies on the eutrophication of fresh-water areas – Structure of ecosystem and standing crops in Lake Kasumigaura – 1978-1979. (1981)

No.23* Comprehensive studies on the eutrophication of fresh-water areas – Applicability of trophic state indices for lakes – 1978-1979. (1981)

No.24* Comprehensive studies on the eutrophication of fresh-water areas – Quantitative analysis of eutrophication effects on main utilization of lake water resources – 1978-1979. (1981)

No.25* Comprehensive studies on the eutrophication of fresh-water areas – Growth characteristics of Blue-Green Algae, *Mycrocystis* – 1978-1979. (1981)

No.26* Comprehensive studies on the eutrophication of fresh-water areas – Determination of argal growth potential by algal assay procedure – 1978-1979. (1981)

No.27* Comprehensive studies on the eutrophication of fresh-water areas – Summary of researches – 1978-1979. (1981)

No.28* Studies on effects of air pollutant mixtures on plants – Progress repot in 1979-1980. (1981)

No.29 Studies on chironomid midges of the Tama River. (1981)

Part 3. Species of the subfamily Orthocladiinae recorded at the summer survey and their distribution in relation to the pollution with sewage waters.

Part 4. Chironomidae recorded at a winter survey.

※No.30* Eutrophication and red tides in the coastal marine environment – Progress report in 1979-1980. (1982)

No.31* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1980. (1981)

No.32* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system – Progress report in 1979 – Research on the photochemical secondary pollutants formation mechanism in the environmental atmosphere (Part 1). (1982)

No.33* Meteorological characteristics and atmospheric diffusion phenomena in the coastal region – Simulation of atmospheric motions and diffusion processes – Progress report in 1980. (1982)

No.34* The development and evaluation of remote measurement methods for environmental pollution – Research report in 1980. (1982)

No.35* Comprehensive evaluation of environmental impacts of road and traffic. (1982)

No.36* Studies on the method for long term environmental monitoring – Progress report in 1980-1981. (1982)

No.37* Study on supporting technology for systems analysis of environmental policy – The evaluation laboratory of Man-environment Systems. (1982)

No.38 Preparation, analysis and certification of POND SEDIMENT certified reference material. (1982)

No.39* The development and evaluation of remote measurement methods for environmental pollution – Research report in 1981. (1983)

No.40* Studies on the biological effects of single and combined exposure of air pollutants – Research report in 1981. (1983)

No.41* Statistical studies on methods of measurement and evaluation of chemical condition of soil. (1983)

※No.42* Experimental studies on the physical properties of mud and the characteristics of mud transportation. (1983)

※No.43 Studies on chironomid midges of the Tama River. (1983)

Part 5. An observation on the distribution of Chironominae along the main stream in June, with description of 15 new species.

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* in Japanese
※ out of stock