

RESEARCH PAPER

Yuan-Hui Li · Takejiro Takamatsu · Yoshiki Sohrin

Geochemistry of Lake Biwa sediments revisited

Received: February 23, 2007 / Accepted: July 21, 2007 / Published online: October 29, 2007

Abstract Extensive chemical data for the Lake Biwa sediments were examined with statistical factor analysis to find any correlation patterns among elements and among samples. Based on those patterns, a series of x - y correlation plots of the concentrations of selected elements was constructed to see in detail how the concentrations of elements vary among different sample groups and explain the observed variation patterns.

Key words Lake Biwa · Sediments · Factor analysis · Correlation plot

Introduction

Lake Biwa is located in Shiga Prefecture, east of Kyoto, and is the largest freshwater lake in Japan (Fig. 1). Many scientific studies on Lake Biwa have been nicely summarized by Horie (1984), Takamatsu (1985), and Fujinaga et al. (2005; and references therein). The lake is separated into Northern (N-) and Southern (S-) basins with respective surface areas of 616 and 58 km² and mean depths of 44 and 3.5 m. The total catchment area of the lake is about 3170 km². More than 100 rivers and streams flow into the lake. The outflows from the lake are River Seta and Kyoto Canal in the southern part of the S-basin. The lake is surrounded by Quaternary alluvium and terrace deposits, Plio-Pleistocene Kobiwako Group sediments, and mostly Mesozoic basement rocks. The Mesozoic basement rocks consist of an

accretionary complex of sediments mixed with some limestone and chert layers and granitic and basaltic igneous rocks and ash (Yokoyama 1984; and see the geological map given in http://www.aist.go.jp/RIODB/db084/index_e.html by the Geological Survey of Japan). Based on the bulk density and ¹⁴C and fission track dating of samples from a 200-m-long core taken in the N-basin (Yamamoto 1984), the sediment accumulation rate in the lake is about 0.08 ± 0.02 g/cm² year for the past 0.5 million years, or equivalent to 0.5 ± 0.1 mm/year, assuming an average bulk density of 1.5 g/cm³ or porosity of 0.7. Sediment cores in the deeper part of the N-basin (water depth >80 m) are mostly silty-clay with many intercalated thin layers of earthquake-induced turbidites, and even a few layers of tephra (Inouchi et al. 1996). The color of the surface sediments (1–2 cm) is brown, owing to oxic conditions; and becomes dark bluish gray below, indicating an anoxic condition. Sulfate in anoxic pore water is reduced into sulfide and forms iron sulfide minerals or even vivianite [Fe₃(PO₄)₂·8H₂O] when ferrous iron was not totally bound by sulfide (Murphy et al. 2001). The littoral zone sediments have a higher content of gravel and sand, and the median grain size can be greater than 1/16 mm (Kumon et al. 1993). On the basis of the C/N ratio and δ¹⁵N analysis of organic matter in the lake sediments, Murase and Sakamoto (2000) concluded that large fractions of organic matter in the littoral sediments are of riverine origin (allochthonous) and are relatively refractory. In contrast, organic matter in the deeper lake sediments is mostly produced within the lake (autochthonous) by photosynthesis in the water column and is relatively labile. Organic carbon and nitrogen contents in surface sediments generally increase with the water depth and clay content of samples. Major minerals in the lake sediments detected by X-ray powder diffractograms are kaolinite, chlorite, illite, feldspar, and quartz (Shigesawa 1984).

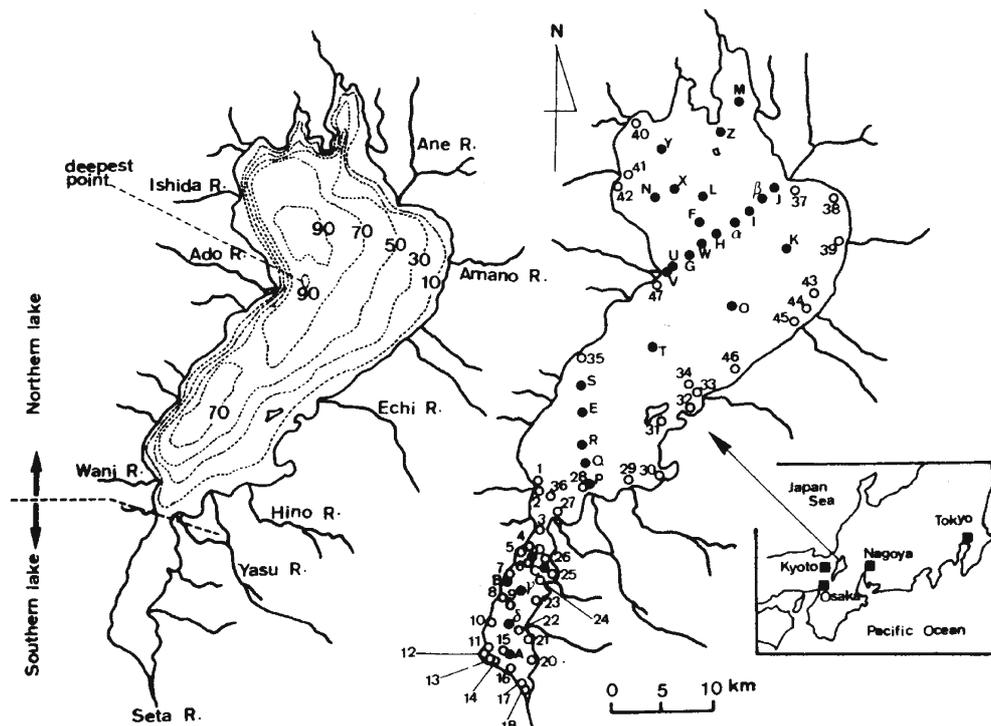
Takamatsu (1985) provided extensive chemical data on the Lake Biwa sediments, discussed spatial distribution patterns of elements in the lake, and explained differences between the average compositions of surface (0–2 cm) and subsurface (>10 cm) sediments. However, during the averaging process, important information on the relationships

Y.-H. Li (✉)
Department of Oceanography, University of Hawaii, Honolulu,
HI 96822, USA
yhli@soest.hawaii.edu

T. Takamatsu
Center for Water Environment Studies, Ibaraki University, Ibaraki,
Japan

Y. Sohrin
Institute for Chemical Research, Kyoto University, Uji, Japan

Fig. 1. Bathymetry and sampling locations for dredged (*numbers*) and core (*letters*) sediments in Lake Biwa. (Adopted from Takamatsu 1985)



among various elements and among various samples from a data matrix set is lost. Statistical factor analysis is a useful tool to remedy this problem (Davis 1973). It can help us to sort out which groups of elements co-vary and which groups of samples are similar or distinct in chemical compositions. Based on those groupings of elements and samples, a series of x - y correlation plots of the concentrations of selected elements can be constructed to study in detail the variation patterns of elements among different groups of samples. The purpose of the present work is to apply statistical techniques – analysis of variance (ANOVA), t test, and factor analysis – to those data sets to gain additional understanding of the geochemical behavior of elements in the bottom sediments of a freshwater lake. All statistical PC programs are adopted from the Statistical Package for the Social Sciences (SPSS).

Materials and methods

There are two kinds of sediment samples from Lake Biwa (Takamatsu 1985): dredged surface samples near shore (sites 1 to 47 in Fig. 1), and gravity-core samples, mostly from offshore (sites A to Z, α , β , and δ in Fig. 1). Most of the dredged samples were taken from a water depth of less than 5 m and a few between 5 and 23 m. Core samples were taken from water depths between 20 and 98 m. The cores are between 18 and 44 cm long and are sectioned into 0.2- to 2-cm intervals. Most of the samples were analyzed for IL (ignition loss), N, P, Na, K, Rb, Mg, Ca, Sr, Ti, Mn, Fe, Ni, Cu, Zn, As, Pb, and Hg using colorimetry, X-ray fluorescence analysis (XRF), atomic absorption spectrophotometry

(AA), and neutron activation analysis (NAA). Analytical results from XRF and AA for Mn and from XRF and NAA for Fe, As, and Rb all agree within the analytical uncertainties. Therefore, only XRF results for those metals are adopted here. The precision (or reproducibility) of chemical analyses is better than 5% for most of elements, except for Ni (~10%). Core samples along the transect between the Ane and Ado rivers (sites J to V in Fig. 1) were analyzed for the additional elements Na, Sc, Cr, Co, Br, Sb, Cs, Ba, REE (rare earth elements), Hf, Ta, Th, and U by NAA. The precision of NAA is better than 5% for Na, Sc, Co, Br, La, Ce, Sm, and Th; 5%–10% for Cr, Sb, Eu, Yb, Lu, and Hf; and 10%–15% for Cs and U. The precision for Ba, Nd, and Ta is as high as 20%, and thus those elements are excluded from the factor analysis.

For the factor analysis, both principal component and varimax analyses were performed. Because varimax analyses provide clearer end-member components for our study, only varimax results are presented here. Useful outputs of SPSS include means and standard deviations of variables, correlation coefficient matrix, eigenvalues, communalities, factor loadings of variables on new factors, and factor scores (proxy concentrations) of new factors for each sample.

Sediment samples from the N- and S-basins are classified into three types: core-top (0–2 cm) and down-core (>2 cm) samples, mostly from deeper water, and dredged surface samples near shore. There are many missing data for Na, Mg, and Hg, so they are not included in the final factor analysis. Also, from the correlation matrix obtained for each data set, Na and Mg do not correlate significantly with any other elements. Many data for N and IL (ignition loss) are also missing, so N and/or IL data are also excluded from the

final factor analysis. The total numbers of dredged samples are relatively small; therefore, some missing As data for some dredged samples were interpolated, using the high correlation between As and Mn. There are many more down-core samples than core-top samples. Therefore for clarity, only down-core samples along the transect between sites J and V were retained in the N-basin data set (together with all dredged and core-top samples). Here are 74 samples from the S-basin with complete chemical data on P, K, Rb, Ca, Sr, Ti, Mn, Fe, Ni, Cu, Zn, As, and Pb and 168 samples from the N-basin with additional IL (ignition loss) data.

Results and discussion

Comparison of means

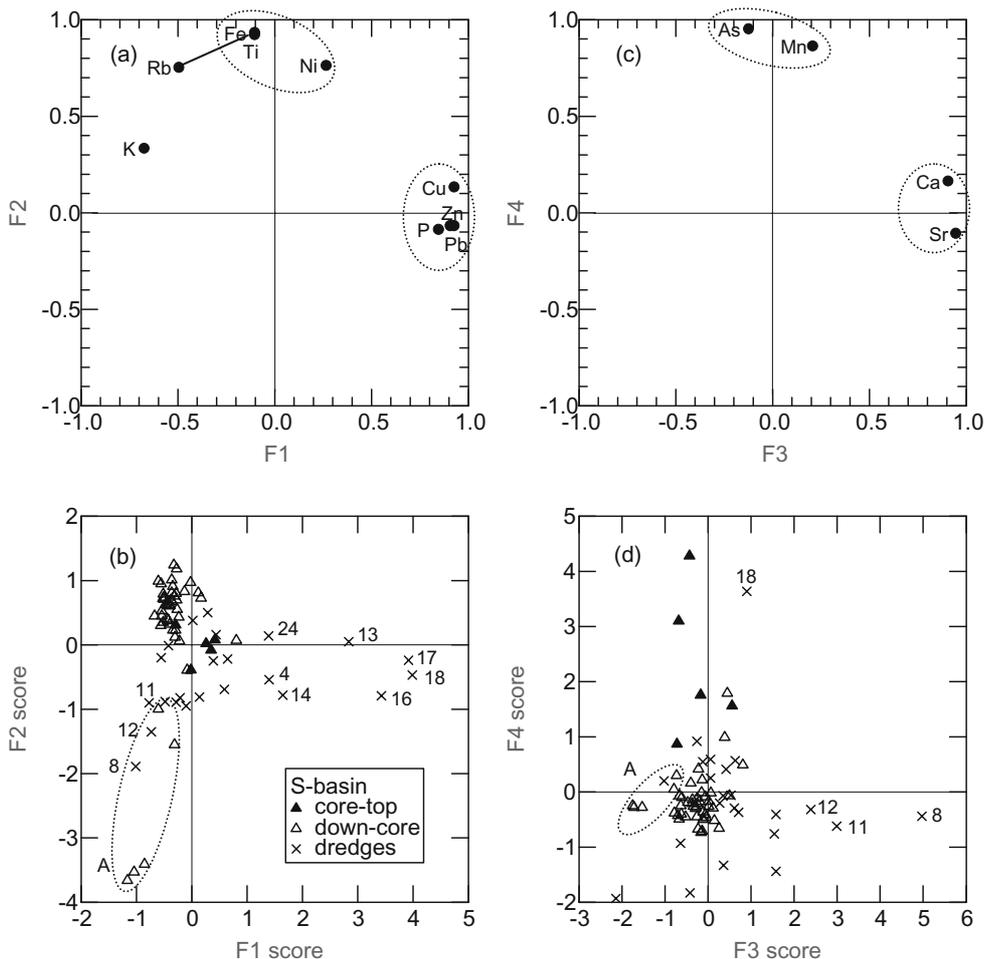
The average compositions of core-top (0–2 cm), down-core (>2 cm), and dredge type samples from the N- and S- basins are summarized in Table 1 along with percent standard deviation ($100 * \delta / \text{mean}$), and numbers of samples (n). The percent standard deviations of most elements in the different sediment types are greater than the precision of chemical analysis (<5% for all elements, except 10% for Ni). Therefore, a large fraction of chemical variation can be attributed to natural variability. Based on the General Linear Model (GLM) univariate analysis (from the SPSS

Table 1. Mean concentrations of elements in the core-top (0–2 cm), down-core (>2 cm), and dredged sediment samples from the Northern (N-) and Southern (S-) basins of Lake Biwa

N-basin	Down-core			Core-top			Dredge		
	Mean	%std	n	Mean	%std	n	Mean	%std	n
Z									
IL %	7.78	16	108	9.96	19	43	4.66	55	25
7 N %	0.186	22	55	0.305	33	6	0.118	74	23
11 Na %	0.80	19	67	0.88	40	21			
12 Mg %	0.99	11	71	1.00	12	33	0.74		2
15 P	909	25	108	1200	32	43	654	64	25
19 K %	2.51	8	116	2.34	9.0	46	2.66	24	25
20 Ca %	0.32	34	116	0.35	22	46	0.45	46	25
22 Ti %	0.50	10	116	0.44	14	46	0.38	33	25
25 Mn	1790	39	116	4440	90	46	692	37	25
26 Fe %	4.57	12	124	4.47	9	46	3.27	28	25
28 Ni	30.4	16	116	37.7	35	46	13.0	62	25
29 Cu	55.7	20	116	80.4	21	46	33.6	65	25
30 Zn	133	11	116	210	24	46	135	53	25
33 As	24.8	23	116	68.9	70	46	12.3	66	25
37 Rb	140	5	116	129	9	46	127	23	25
38 Sr	73.2	16	116	67.4	16	46	89.9	28	25
80 Hg	0.103	30	36	0.188	11	4	0.045		2
82 Pb	30.9	21	116	51.3	23	46	32.2	58	25
S-basin	Down-core			Core-top			Dredge		
Z	Mean	%std	n	Mean	%std	n	Mean	%std	n
IL %	9.07	23	33	10.1		2	10.3	21	23
7 N %	0.262	28	34	0.407		2	0.337	33	23
11 Na %	0.933	10	18	1.07		1			
12 Mg %	0.825	6	12	0.823	0.7	3			
15 P	439	32	46	750	14	5	1130	60	23
19 K %	2.36	5	64	2.25	5	6	2.19	13	23
20 Ca %	0.332	19	64	0.393	11	6	0.471	41	23
22 Ti %	0.450	19	64	0.430	13	6	0.387	15	23
25 Mn	766	23	64	1400	21	6	898	34	23
26 Fe %	4.15	16	64	4.24	3	6	3.64	18	23
28 Ni	22.6	29	64	29.5	23	6	18.4	44	23
29 Cu	42.9	20	64	68.0	30	6	68.0	58	23
30 Zn	186	38	64	373	26	6	366	59	23
33 As	8.00	38	64	24.2	48	6	6.78	128	23
37 Rb	146	17	64	142	3	6	128	15	23
38 Sr	77.5	14	64	75.8	19	6	101	38	23
80 Hg	0.142	34	36	0.20	17	3	0.485	71	16
82 Pb	49.3	21	64	64.8	12	6	100	79	23

Major elements are in %; others are in ppm; std% indicates the percent standard deviation (std/mean %); n is the number of samples. Mean values in bold indicate the same mean for a given element between any pair among the core-top, down-core, and dredge type samples with 95% confidence interval for N- and S-basin samples separately, using the independent-samples t test (from the SPSS program)

Fig. 2. Four factor loadings [diagrams (a) and (c)] and factor scores [diagrams (b) and (d)] obtained by the factor analysis of the Southern (S-)basin sediment samples. The open triangles within the dotted ovals in b and d are core samples from site A. Numbers are sampling sites for some dredged samples



program), only Ca, Sr, and Rb have the same means between N- and S-basin samples at a 95% confidence level. Therefore, N- and S-basin samples are treated separately in the factor analysis.

Mean values in bold in Table 1 indicate the same mean for a given element between any pair among the core-top, down-core, and dredge type samples with 95% confidence interval for N- and S-basin samples separately, using the independent-samples *t* test (from the SPSS program). For N-basin samples, only 4 elements (Na, Mg, Ca, and Fe) of 18 have the same means between the core-top and down-core types. The mean concentrations of IL (ignition loss), N, P, Mn, Ni, Cu, Zn, Pb, and As in the core-top type are significantly higher than those in the down-core type. Similarly, of 17 elements, only 3 (K, Zn, and Pb) have the same means when comparing the down-core and dredge types. The mean concentrations of IL, N, P, Mg, Fe, Ti, Mn, Ni, Cu, As, Rb, and Hg are much lower in the dredge type as compared with those in the down-core type. Between the core-top and dredge types, only Rb has the same mean. The means of Ca and Sr in the dredge type are the highest among three types. Therefore, the three sediment types from the N-basin are statistically quite distinct.

Similar conclusions can be drawn for the three sediment types from the S-basin. The mean concentrations of IL, N, P, Cu, Zn, and Pb in the core-top and dredge type samples

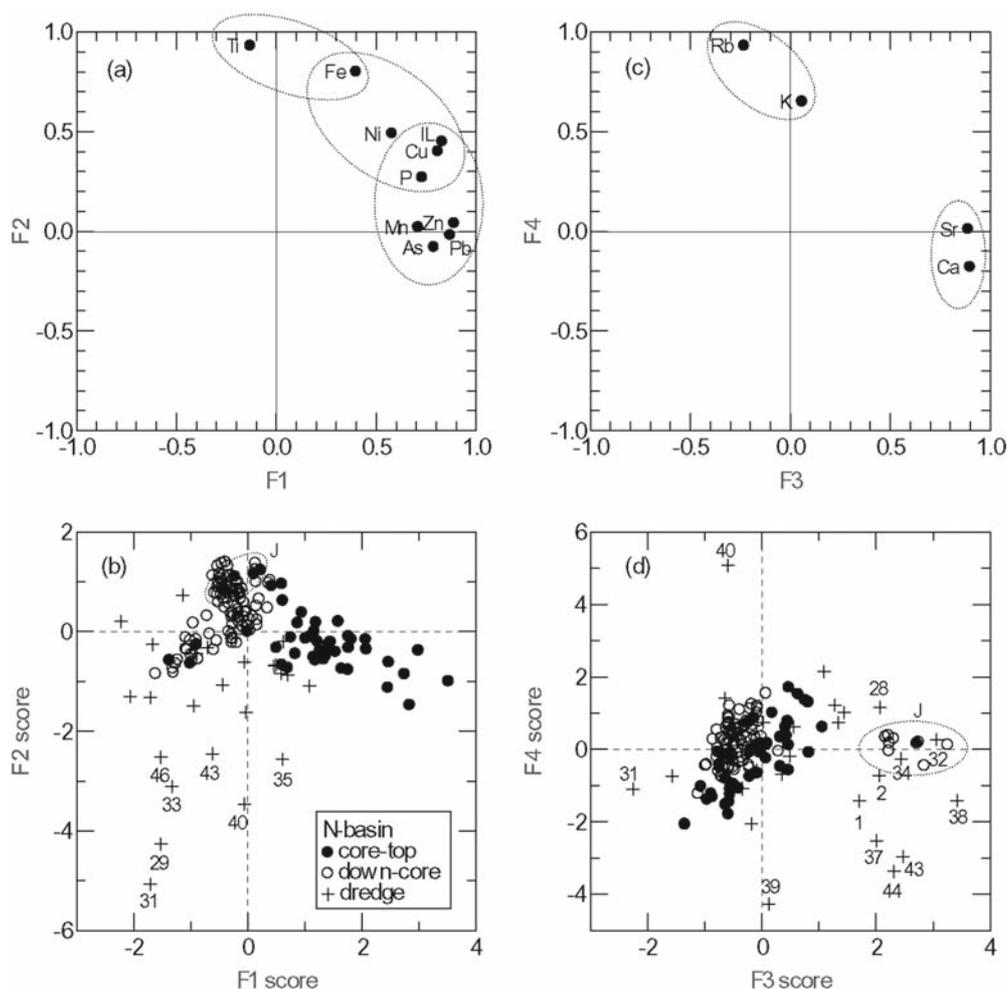
are much higher than those in the down-core type. In addition, Mn and As are the highest in the core-top among the three types; and P, Ca, and Sr in the dredge type are the highest among three types.

As is shown by the following factor analysis, the distinctive chemical characteristics of three sediment types from N- and S-basins result mainly from the contributions of end-components, such as clay minerals, quartz, organic matter, manganese oxides, carbonates, and heavy minerals, in different proportions. Results from the varimax factor analysis are summarized in Figs. 2 and 3 for the S- and N-basins, respectively. In those figures, any pair of elements within a dotted oval or connected by solid line has correlation coefficient of equal to or greater than 0.5.

Factor analysis of S-basin sediments

Four factors with eigenvalue greater than 1 were extracted from the S-basin data set, and these four factors can explain 85% of the total variance. Factor one (F1; 32% of variance) consists of P, Cu, Zn, and Pb (Fig. 2a). Based on the correlation matrix, IL and N are also highly correlated with those elements. Therefore, F1 mainly represents sedimentary organic matter that is enriched in IL, N, P, Cu, Zn, and Pb. Dredged samples (sites 4, 13, 14, 16, 17, 18, and 24 in Fig. 1)

Fig. 3. Four factor loadings [diagrams (a) and (c)] and factor scores [diagrams (b) and (d)] obtained by the factor analysis of the Northern (N-)basin sediment samples. The circles within the dotted ovals in diagrams b and d are core samples from site J. Numbers are sampling sites for some dredged samples



are high in F1 scores (Fig. 2b), thus high in IL, N, P, Cu, Zn, and Pb content. Factor 2 (F2; 22% of variance) consists of Fe, Ti, Ni, and partly Rb, mainly representing clay phases. Most of the down-core samples (cores >2cm in Fig. 2b) are high in F2 score. However, a few core samples from site A and dredged samples from sites 8 and 12 have large negative F2 scores, probably indicating the dilution effect by quartz particles in the sediments. The importance of quartz particles in sediments is discussed again later. F3 (16% of variance) represents carbonate phases (Ca and Sr in Fig. 2c), and the nearshore dredged samples tend to have high F3 scores, especially for sites 8, 11, and 12 (Fig. 2d). Those littoral sites may contain small carbonate shell fragments formed within the lake. F4 (15% of variance) represents manganese oxide phases (Mn and As), and the F4 scores are high in the dredged sample at site 18 and all core-top samples (cores <2cm in Fig. 2d).

Factor analysis of N-basin sediments

Four factors with eigenvalue greater than 1 were also extracted from the N-basin data set, and these four factors can explain 80% of the total variance. The major difference

from the S-basin result is that manganese oxide and organic matter phases merge together to form F1 (Mn, As, IL, P, Zn, Pb, and Cu in Fig. 3a). F1 (37% of variance) is mainly represented by the core-top samples (Fig. 3b), and most of the dredged samples are low in F1 scores (i.e., low in manganese oxides and organic matter). F2 (17% of variance) again consists of Ti, Fe, and partly Ni (clay phases), and is represented mainly by the down-core samples. The nearshore dredged samples tend to have negative F2 scores (Fig. 3b; sites 29, 31, 33, 40, 43, 46), again indicating the dilution effect of quartz particles. Fe and Ni are also partly correlated to the F1 group elements of IL, P, and Cu (Fig. 3a). F3 (14% variance) is a carbonate factor (Ca and Sr) and is represented by the nearshore dredged samples (Fig. 3d; sites 1, 2, 28, 32, 34, 37, 38, 43, 44) and the core samples from site J, which is close to the Ane river mouth (see Fig. 1). Although quartz (-F2) and carbonates (F3) tend to concentrate in the littoral zone, samples with high negative F2 scores rarely correspond to those with high F3 scores (Fig. 3b,d). The implication is that quartz particles may be introduced to nearshore sediments by rivers and carbonates by shell fragments produced within the lake. F4 (12% variance) may represent feldspar, or independent K fertilizer input from the surrounding area, or just indicate the

general geochemical similarity between K and Rb (Fig. 3c).

Correlation plots

Factor analysis provides only general correlation patterns among elements and among samples. For more detailed pictures, one needs to look back to the original raw data. Figures 4 and 5 provide the x - y correlation plots of the concentrations of selected elements (based on the factor analysis results) in sediments to illustrate in detail the variation patterns of elements among different sample groups.

The raw data are all from Takamatsu (1985). The solid line in each subfigure represents the line connecting X_{10} values (average concentrations of elements in core samples 10 cm below the core top from the N-basin; Takamatsu et al. 1985a) to the origin, and the dotted line is simply the extension of the solid line with the same slope. One exception is Mn, whose X_{10} is replaced by the average concentration of Mn in the average shale (Li 2000) to highlight the overall high Mn content in the N-basin core samples. The solid and dotted lines are hereafter collectively called the sloped line.

The correlation matrixes obtained from the S- and N-basin data sets show high correlation among IL, P, and N,

Fig. 4. The x - y plots among IL (ignition loss), N, P, As, and Mn data from the Lake Biwa sediments. The *solid line* in each diagram represents the line connecting X_{10} value (average concentration of an element in the N-basin core samples 10 cm below the core top) to the origin (except Mn, whose X_{10} is replaced by the average shale value), and the *dotted line* is simply the extension of the solid line with the same slope

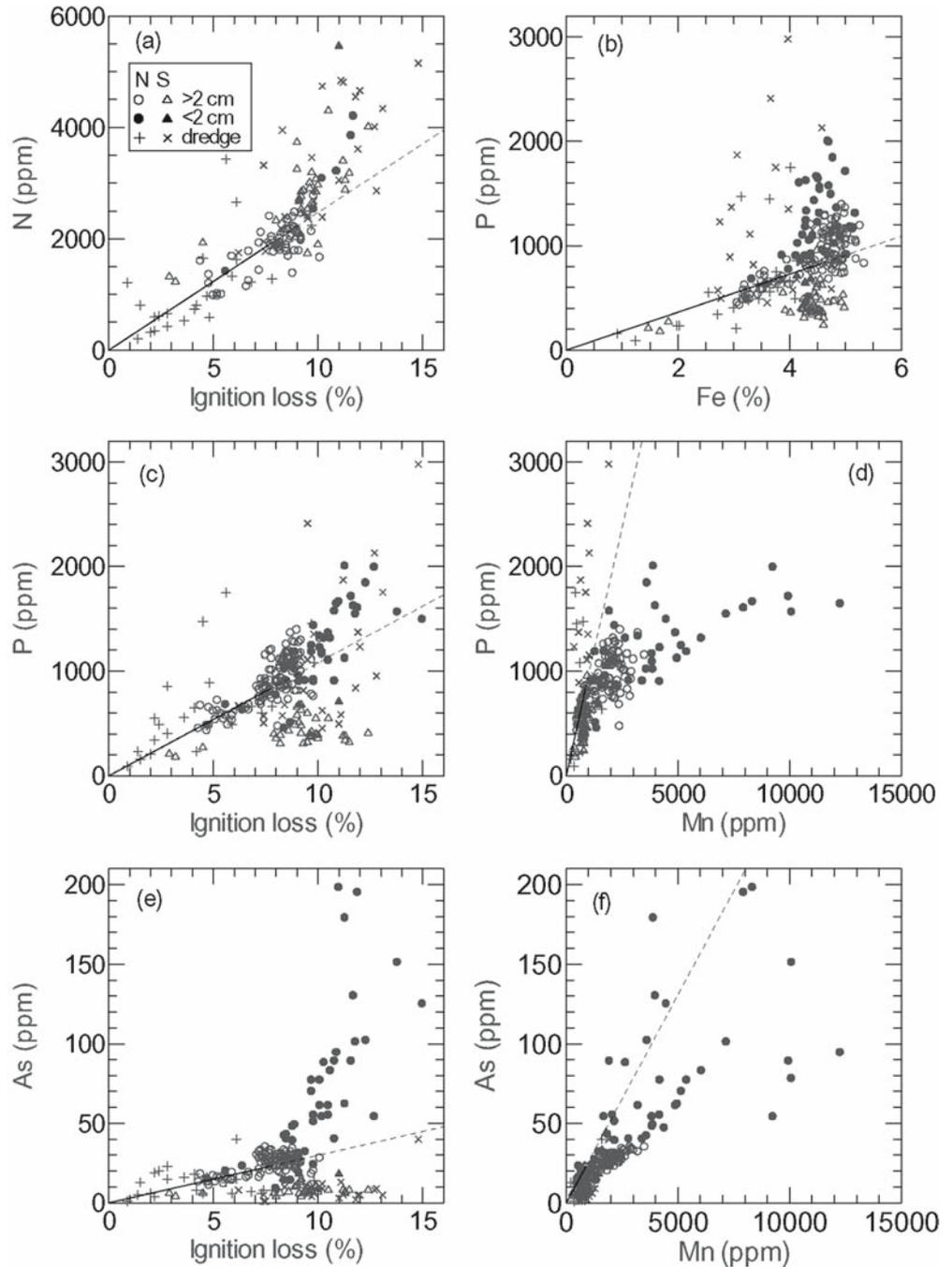
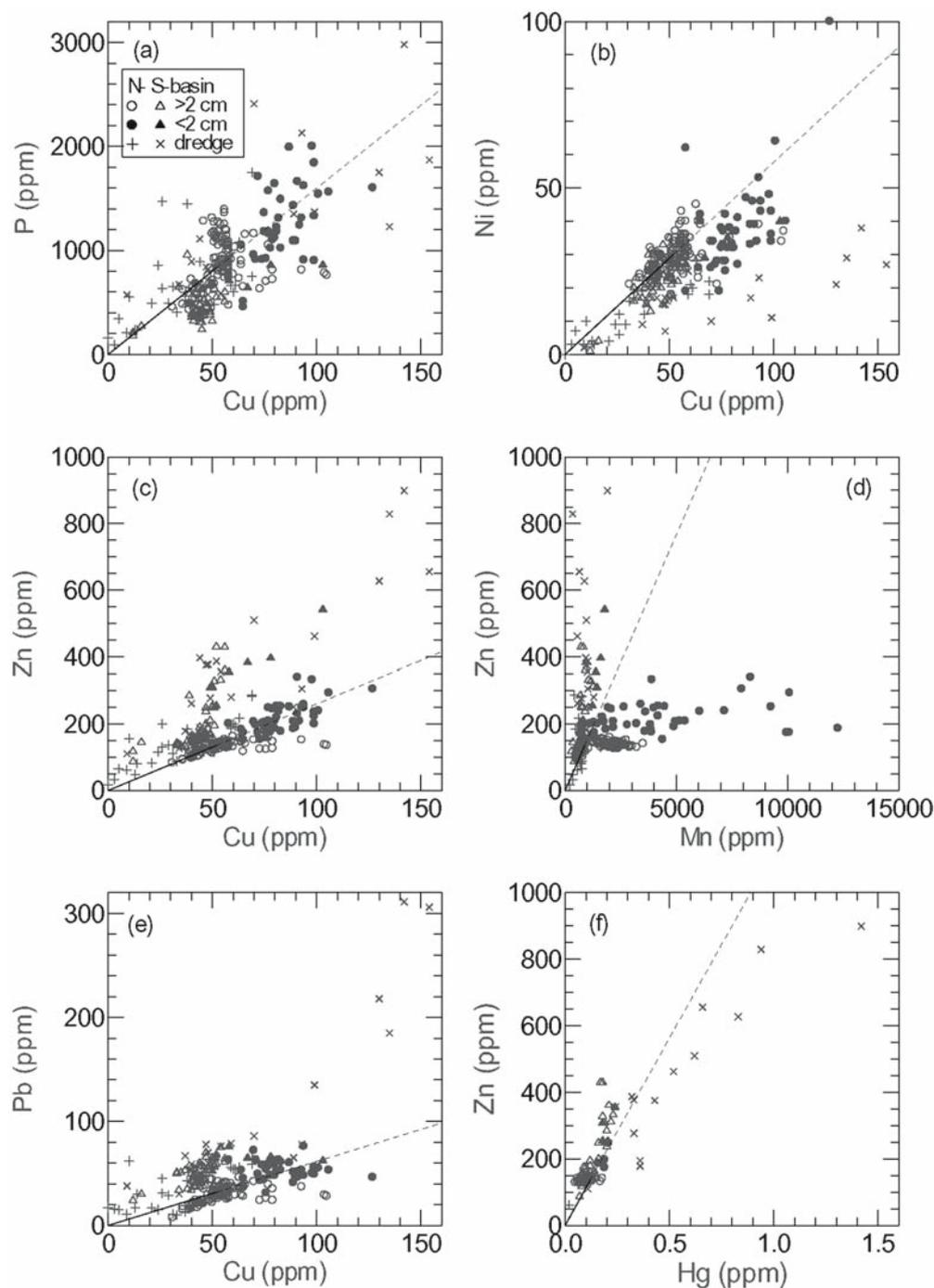


Fig. 5. The x - y plots among P, Mn, Zn, Cu, Pb, and Hg data from the Lake Biwa sediments



representing organic matter in the lake sediments; this is confirmed by the x - y plots in Fig. 4a,c. Most of the dredged samples from the S-basin and some from the N-basin have high concentrations of these elements, indicating abundant organic matter in the littoral sediments. Eutrophication of Lake Biwa, especially in the S-basin, has been a chronic problem since the 1950s (Murase and Sakamoto 2000). Core samples from both N- and S- basins show a similar concentration range for IL and N (Fig. 4a). However, N-basin core samples, especially the core-top samples, tend to have much higher P than do S-basin core samples (Fig. 4c). The high P content in N-basin core samples, especially the core-top

samples, is directly related to the additional P contribution from manganese oxide phases in these samples (Fig. 4d). As shown by Kawashima et al. (1985), hydrous manganese oxide ($\text{MnO}_2 \cdot \text{H}_2\text{O}$) in the presence of divalent cations is an efficient scavenger of phosphate ion in Lake Biwa. Some vivianite in the down-core samples (Murphy et al. 2001) may explain the positive correlation between P and Fe shown in the factor analysis of the N-basin samples (Fig. 3a). However, as shown in Table 1, the mean concentration of Fe for the N- and S- basins core samples is all the same, while the P mean concentration increases from the S-basin cores to the N-basin down-core and core-top samples. Figure

4b shows a similar trend. Therefore, the N-basin core samples above the sloped line in Fig. 4b do not contain much of P contributed from iron minerals such as hydrous iron oxides and vivianite.

Even though As and IL are highly correlated among the N-basin samples, the content of As in the core-top samples is much higher than others (above the sloped line in Fig. 4e) as a result of additional As contribution from manganese oxide phases. As shown in Fig. 4f, As and Mn are highly correlated among all samples (both N- and S-basins). This close coupling of As and Mn is explained by the postdepositional migration of arsenite (H_2AsO_3^-) and Mn^{2+} in sediment pore water and by subsequent oxidation to arsenate (HAsO_4^{2-}) and hydrous manganese oxide at the water-sediment interface, followed by adsorption of arsenate onto Mn^{2+} -enriched hydrous manganese oxide (Takamatsu et al. 1985b). Kawashima et al. (1988) also emphasized the importance of bacteria in the oxidation of Mn^{2+} into hydrous manganese oxides. As shown by Takamatsu et al. (1985c), the concentrations of Mn and As in the core-top samples from the N-basin both increase according to quadratic functions of water depth, again suggesting similar enrichment processes. In contrast, most of the dredged samples (from both N- and S-basins) are relatively low in As and Mn content, even when P and IL content is high (Fig. 4d,e). In

the nearshore shallow environment of Lake Biwa, the redox potential (Eh) must be relatively high (Koyama et al. 1984), thus precluding the reductive dissolution/oxidative deposition cycle of Mn and As near the water-sediments interface.

Because P in the core-top samples from the N-basin is mainly contributed by both organic matter and manganese oxide phases, other F1 group elements (Cu, Zn, Pb, and Ni) are also contributed by these two major phases. However, the x - y plots among those elements for all samples display some subtle differences. For example, in the plots of Cu versus P (Fig. 5a) or Ni (Fig. 5b), all show general positive correlation. However, Cu content in the dredged sample from the S-basin all falls significantly below the sloped line in Fig. 5b, indicating a large Cu pollution input. Similarly, at a given Cu value, Zn and Pb in the S-basin samples, especially in the dredged samples, are always much higher than those from the N-basin core samples (Fig. 5c,e), probably suggesting large additional pollution inputs of Zn and Pb as well as Hg (Fig. 5f) over Cu from the area surrounding the S-basin. As cited by Takamatsu et al. (1985a), the area around the S-basin is more urbanized and industrialized than that around the N-basin. Furthermore, the S-basin samples are relatively low in Mn and As (Figs. 4d,e, 5d). Thus, P, Cu, Zn, Pb, and Hg are mainly associated with

Fig. 6. Four factor loadings [diagrams (a) and (c)] and factor scores [diagrams (b) and (d)] obtained by the factor analysis of the N-basin sediment core data between sites J and V

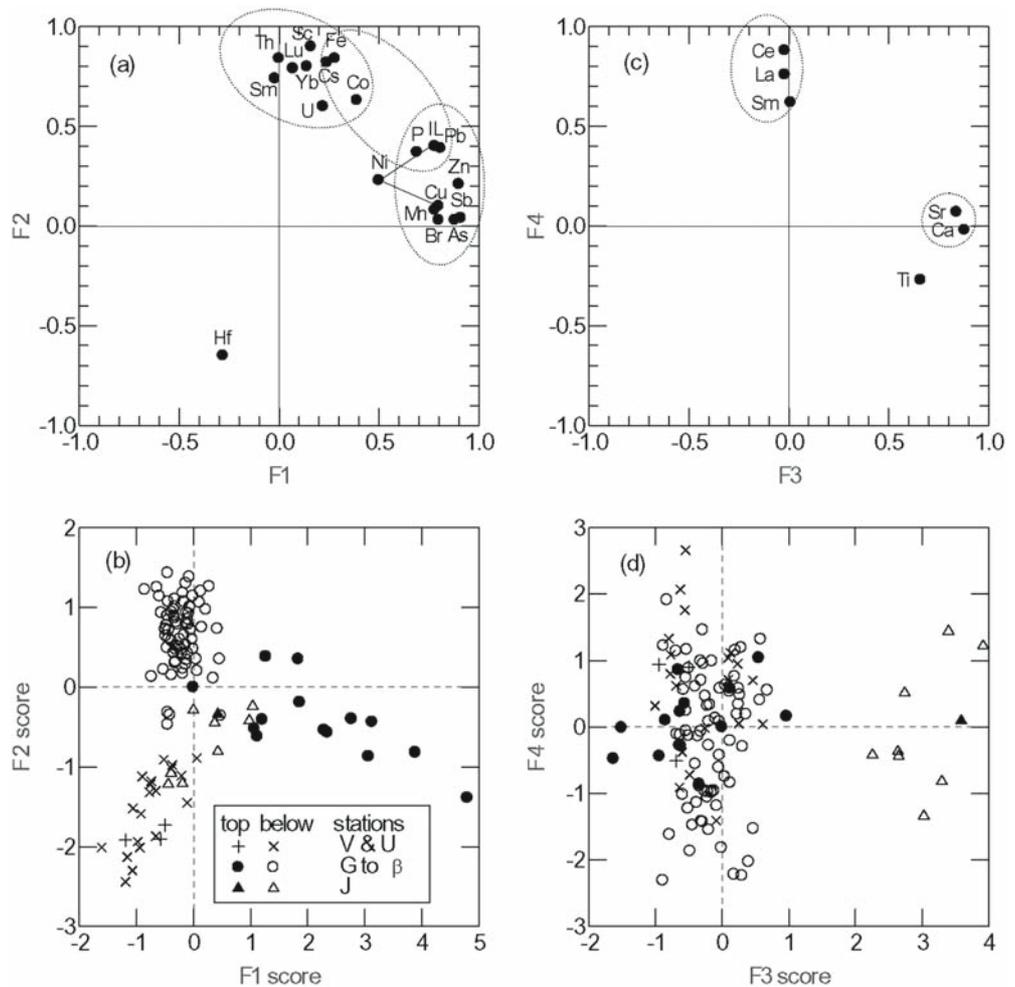
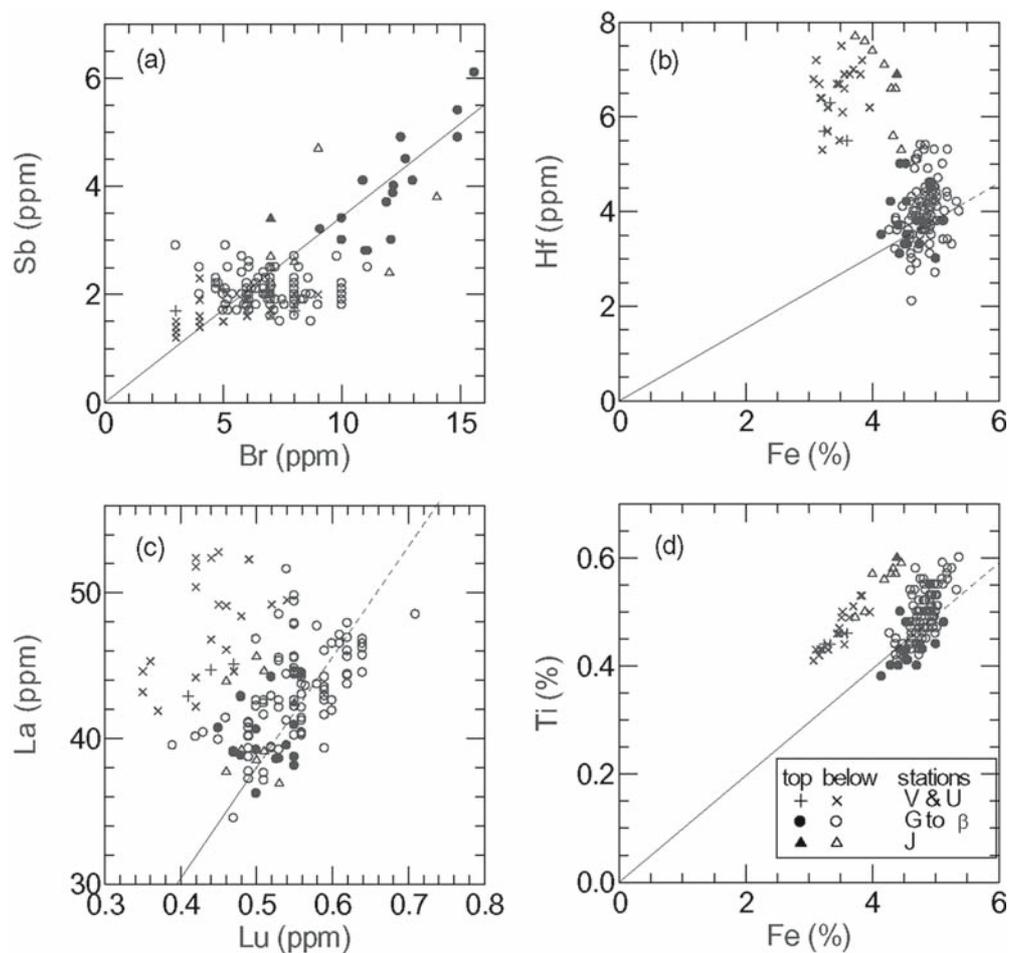


Fig. 7. The x - y plots among Fe, Ti, Hf, Sb, Br, Lu, and La data from the N-basin core samples between sites J and V



organic matter in the S-basin samples, as also confirmed by the factor analysis (see Fig. 2).

Factor analysis of N-basin core samples between sites J and V

As mentioned earlier, core samples along the transect between sites J and V in Fig. 1 were analyzed for additional elements Sc, Cr, Co, Br, Sb, Cs, Ba, REE, Hf, Ta, Th, and U by NAA. The results of factor analysis and some x - y correlation plots for those samples are shown in Figs. 6 and 7 to show how those additional elements relate to various phases discussed earlier. Four factors can explain 70% of the total variance (F1 = 25%, F2 = 24%, F3 = 11%, and F4 = 10%). The F1 to F3 in Fig. 6a and 6c are almost identical to those in Fig. 3a,c. The additional elements Sb and Br belong to F1 (manganese oxides and organic matter; Fig. 6a). The additional elements Cs, Co, Sc, Sm, Yb, Lu, Th, and U all belong to F2 (clay minerals; Fig. 6a). Interestingly, Hf belongs to negative F2 (inversely correlated to F2; Fig. 6a), and is represented by core samples from nearshore sites J, V, and U (Figs. 6b, 7b). Those samples may contain quartz and heavy minerals such as zircon (ZrSiO_4), ilmenite (FeTiO_3), and rutile (TiO_2), which are enriched in Hf-Zr. Decoupling of Ti

from Fe (Fig. 6a,c) is caused by the enrichment of Ti in the same core samples from sites J, V, and U (Fig. 7d). Similarly, those samples are also enriched in La, Ce, and Sm (Figs. 6c,d, 7c). Therefore, those core samples from sites J, V, and U are also high in heavy minerals such as monazite [(Ce, La, Th) PO_4]. The implication is that Adu and Ane Rivers have been carrying into Lake Biwa quartz particles and weathering-resistant heavy minerals, such as ilmenite, rutile, zircon, and monazite, and depositing them on the littoral zone of Lake Biwa.

Extensive sediment samples were collected from Lake Biwa by different research groups for measuring different parameters (Takamatsu 1985; Kumon et al. 1993; Murase and Sakamoto 2000). It is desirable to measure all the parameters using the same sample set. Additional chemical analysis of major elements Al, Si, and organic C and S will be most useful. The Si data can be used to check on the dilution effect of quartz particles as discussed earlier. As shown by Mito et al. (2002), S and P content in the suspended particles from Lake Biwa is closely related to organic matter content. What is the diagenetic change of S and its association with other trace metals in sediments? Heavy mineral analysis of sediment samples will also greatly help the interpretation of the factor analysis results.

Summary and conclusions

1. The factor analysis of the S-basin samples shows that there are five major independent factors or components: F1 (organic matter: IL, N, P, Zn, Cu, and Pb), F2 (clay: Fe, Ti, and Ni), -F2 (postulated quartz particles: Si); F3 (carbonate: Ca and Sr), and F4 (manganese oxides: Mn and As) (see Fig. 2). In contrast, organic matter and manganese oxide phases no longer vary independently in the N-basin samples and merge to form F1 (organic matter + manganese oxides: Mn, As, P, Cu, Ni, IL, N, Zn, Pb, and Hg). F2 remains clay (Ti, Fe, partly Ni), but Ni is now also closely related to F1. The signal of the postulated quartz particle factor (-F2) becomes stronger in the dredged samples, suggesting river inputs. F3 is again carbonate factor (Ca and Sr) (see Fig. 3). The nearshore dredged samples from both N-basin and S-basin tend to have high Ca and Sr content, probably indicating shell fragments in the littoral zone.
2. The factor analysis of the N-basin samples with additional elemental analysis shows that Sb and Br belong to the organic matter + manganese oxides group (F1); Cs, Co, Sc, Sm, Yb, Lu, Th, and U to the clay group (F2); and Hf to the postulated quartz particle phase (-F2; see Fig. 6). The quartz particle phase should also include some weathering-resistant heavy minerals (ilmenite, rutile, zircon, monazite, etc.) to explain the observed high content of Hf, Ti, La, Ce, and Sm in the core samples from the river mouth sites J, U, and V.
3. The S-basin dredged samples have the highest content of P, IL, N, Cu, Zn, Pb, and Hg among all S- and N-basin samples (see Figs. 4, 5), indicating large pollution inputs. However, those samples together with the S-basin cores and N-basin dredged samples tend to have the lowest Mn and As content among all samples (see Fig. 4d,e). In the nearshore environment of those samples, the redox potentials (Eh) are relatively high, and thus preclude the reductive dissolution/oxidative deposition of Mn and As near the water–sediment interface.
4. Additional analysis of major elements Al, Si, organic C and S, grain size, and heavy minerals on sediment samples will be helpful to check on the interpretation of factor analysis results.

Acknowledgments Partial financial and logistical support from the Hanse Institute for Advanced Study, Delmenhorst, Germany, and the National Science Council and National Taiwan University, Taipei, Taiwan, during Y.H.L.'s sabbatical year (2005–2006) was most generous and timely. Thoughtful comments from one anonymous reviewer were most useful in improving the manuscript. Diane Henderson provided helpful editorial assistance. This work was supported by the NOAA/OAR/OGP Grant GC02-386. SOEST contribution #7154.

References

- Davis JC (1973) *Statistics and data analysis in geology*. Wiley, New York
- Fujinaga T, Sohrin Y, Isshiki K (eds) (2005) *Chemistry of the oceans and lakes: studies using trace elements (in Japanese)*. Kyoto University Press, Kyoto
- Horie S (ed) (1984) *Lake Biwa*. Junk, Boston
- Inouchi Y, Kinugasa Y, Kumon F, Nakano S, Yasumatsu S, Shiki T (1996) Turbidites as records of intense palaeoearthquakes in Lake Biwa, Japan. *Sediment Geol* 104:117–125
- Kawashima M, Hori T, Koyama M, Takamatsu T (1985) Phosphate adsorption onto hydrous manganese oxide in the presence of divalent cations. In: Takamatsu T (ed) *Limnological and environmental studies of elements in the sediment of Lake Biwa*. Research report no. 75. National Institute for Environmental Studies, Japan, pp 25–31
- Kawashima M, Takamatsu T, Koyama M (1988) Mechanisms of precipitation of manganese (II) in Lake Biwa, a fresh water lake. *Water Res* 22:613–618
- Koyama M, Kawashima M, Takamatsu T (1984) Inorganic chemical aspects. In: Horie S (ed) *Lake Biwa*. Junk, Boston, pp 257–271
- Kumon F, Kamitani T, Sutoh K, Inouchi Y (1993) Grain size distribution of the surface sediments in Lake Biwa, Japan (in Japanese with English abstract). *Mem Geol Soc Jpn* 39:53–60
- Li YH (2000) *A compendium of geochemistry: from solar nebula to the human brain*. Princeton University Press, Princeton
- Mito S, Kawashima M, Sohrin Y (2002) Characterization of suspended solids in Lake Biwa by measuring their elemental composition of Al, Si, P, S, K, Ca, Ti, Mn, and Fe. *Limnology* 3:11–19
- Murase J, Sakamoto M (2000) Horizontal distribution of carbon and nitrogen and their isotopic compositions in the surface sediment of Lake Biwa. *Limnology* 1:177–184
- Murphy T, Lawson A, Kumagai M, Nalewajko C (2001) Release of phosphorus from sediments in Lake Biwa. *Limnology* 2:119–128
- Shigesawa K (1984) Chemical composition and clay minerals of sediments. In: Horie S (ed) *Lake Biwa*. Junk, Boston, pp 417–422
- Takamatsu T (ed) (1985) *Limnological and environmental studies of elements in the sediment of Lake Biwa*. Research report no. 75. National Institute for Environmental Studies, Japan
- Takamatsu T, Kawashima M, Koyama M (1985a) General distribution profiles of thirty-six elements in sediments and manganese concretions of Lake Biwa. In: Takamatsu T (ed) *Limnological and environmental studies of elements in the sediment of Lake Biwa*. Research report no. 75. National Institute for Environmental Studies, Japan, pp 1–18
- Takamatsu T, Kawashima M, Koyama M (1985b) The role of Mn²⁺-rich hydrous manganese oxide in the accumulation of arsenic in Lake sediments. *Water Res* 20:471–475
- Takamatsu T, Kawashima M, Koyama M (1985c) Manganese concentration in the sediment as an indicator of water depth: paleo-water depth during the last few million years. In: Takamatsu T (ed) *Limnological and environmental studies of elements in the sediment of Lake Biwa*. Research report no. 75. National Institute for Environmental Studies, Japan, pp 63–67
- Yamamoto A (1984) Grain size variation. In: Horie S (ed) *Lake Biwa*. Junk, Boston, pp 439–460
- Yokoyama T (1984) Stratigraphy of the Quaternary system around Lake Biwa and geohistory of the ancient Lake Biwa. In: Horie S (ed) *Lake Biwa*. Junk, Boston, pp 43–128