

RESEARCH PAPER

Masahito Sugiyama · Toshitaka Hori · Sorin Kihara  
Masakazu Matsui

## Geochemical behavior of trace elements in Lake Biwa

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**Abstract** A monthly survey of dissolved concentrations of various trace elements was performed in Lake Biwa. Particulate concentrations of the elements were also measured in early autumn and winter. Based on these results, the geochemical behaviors of trace elements are discussed. The redox-sensitive elements Mn and Fe showed characteristic vertical distribution profiles. Profiles of Mn changed drastically with the progression of the stagnation period. The dynamics of Ba were affected by the redox cycle of Mn. Dissolved V concentration showed a clear seasonal variation. In contrast, dissolved concentrations of Sr, Mo, Cu, Zn, and Ni were almost uniform, i.e., not dependent on the season or the depth. The distribution ratios of these elements between lake water and Mn nodules formed in the lake were calculated to assess their geochemical behaviors.

**Key words** Trace elements · Geochemical behavior · Lake Biwa · Distribution ratio between water/manganese nodules

### Introduction

The geochemical behavior of trace elements in natural water may often reflect minute changes (which are difficult to recognize from the behavior of the major components) in the chemical, biological, and physical conditions of an aquatic environment. For example, Mn and Fe change their

chemical forms and concentrations according to the redox condition of the water (e.g., Davison 1993; Stumm and Morgan 1996). Distribution profiles of some bio-elements such as P, N, Si, and Zn are sensitively affected by biological activity (e.g., Riley and Chester 1983; Horne and Goldman 1994). Because of the geoscientific significance of such trace elements, many workers have studied their geochemical behaviors over long periods of time. In marine domains, many kinds of trace elements have been measured in various areas of the ocean, and the mean concentrations for almost all elements have now been elucidated (e.g., Nozaki 1992; Donat and Bruland 1994). In limnetic areas also, trace element concentrations have been determined in many lakes throughout the world (e.g., Borg 1994; Nojiri 1992; Falkner et al. 1997). However, compared to the works for eutrophic or anthropogenically polluted lakes, there are few reports for lakes at lower trophic levels or in a state little affected by human activities; in such lakes, trace element concentrations are extremely low and their analysis is very difficult.

The chemical dynamics of trace elements in a lake are greatly affected by the trophic state and pollution level of the lake. Therefore, to meaningfully discuss the geochemical behavior of limnetic trace elements, it is necessary to reveal the behaviors of the elements in lakes at various trophic and pollution levels and to study them comparatively.

Lake Biwa, the largest lake in Japan, consists of two basins, the southern and northern basins, which differ in their limnological characteristics (Fujinaga and Hori 1982; Horie 1984). The northern basin of the lake is the main basin and is classified as a mesotrophic lake with thermal stratification in summer. On the other hand, the southern basin is a shallow eutrophic lake and is not thermally stratified throughout the year. These characteristics are very opportune for studying the effects of the trophic state of a lake on the geochemical behavior of trace elements.

In addition to the above characteristics, Lake Biwa has other remarkable limnological features (Fujinaga and Hori 1982; Horie 1984): it is an ancient lake, being more than 5 million years old; there is a variety of biota in the lake,

M. Sugiyama (✉) · T. Hori  
Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-Nihonmatsu, Sakyo-ku, Kyoto 606-8501, Japan  
Tel. +81-75-753-6836; Fax +81-75-753-7879  
e-mail: masahito.sugiyama@sojin0206.mbox.media.kyoto-u.ac.jp

S. Kihara  
Department of Chemistry, Kyoto Institute of Technology, Kyoto, Japan

M. Matsui  
Institute for Chemical Research, Kyoto University, Uji, Japan

comprising more than 1000 species; abundant endemic species number more than 50; and it is significant as a water resource utilized by 14 million people. Thus, this lake has been investigated for several decades by numerous chemists, biologists, and physicists, and many limnological reports have been devoted to the study of this lake. Of course, the chemical aspects of the lake also have been discussed frequently. However, there are few reports on the geochemical behavior of trace elements (Haraguchi et al. 1998; Mito et al. 2002, 2004; Takaku et al. 2003) compared to the many studies of major elements and nutrients (e.g., Fujinaga and Hori 1982; Horie 1984; Somiya 2000).

Previously, we developed simultaneous determination methods for some major and trace elements in natural water and suspended particulate matter using inductively coupled plasma atomic emission spectrometry (Sugiyama et al. 1986, 1992; Sugiyama 1996). These methods are not only convenient for the chemical analysis of natural samples but are also very useful for studies in geochemistry because both absolute and relative concentrations among the major and trace elements can be easily obtained. Using these methods, we analyzed more than ten elements in dissolved and particulate states in water from Lake Biwa. In this paper, we report the geochemical behaviors of various trace elements in Lake Biwa based on vertical distribution profiles in its northern basin. Additionally, the results in the southern basin are discussed in comparison with those in the northern basin.

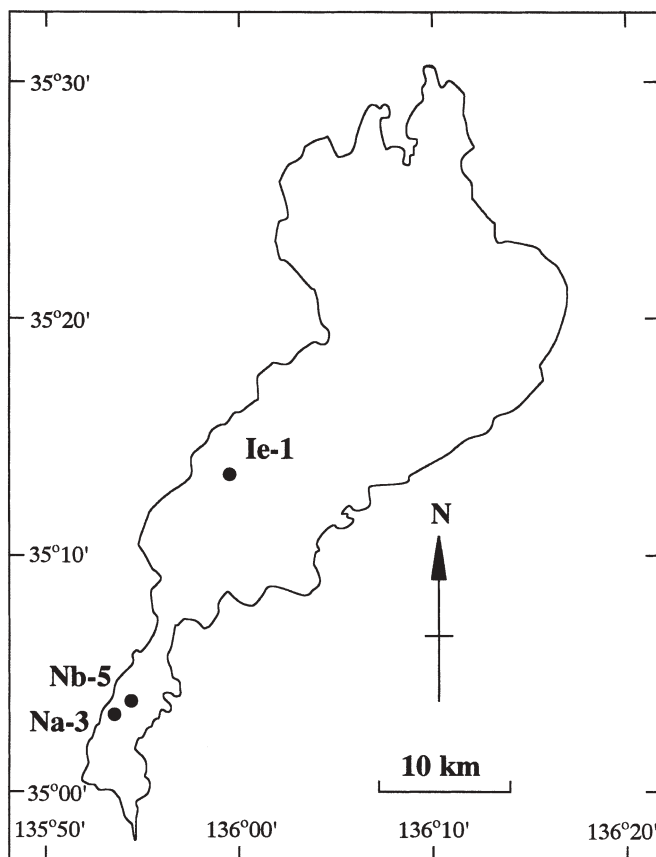


Fig. 1. Sampling locations on Lake Biwa

## Study area

The limnological features of Lake Biwa are summarized as follows (Fujinaga and Hori 1982; Lake Biwa Research Institute and National Institute for Research Advancement 1984; Horie 1984). It is located at 35°15' N and 136°05' E, and is geometrically and limnologically divided into two parts: the mesotrophic northern basin and the eutrophic southern basin. The northern basin is the main basin and has a surface area of 616 km<sup>2</sup> and a capacity of 27.3 km<sup>3</sup>. Its average and maximum depths are 44 m and 104 m, respectively. The residence time of lake water is estimated to be 5.5 years. Thermal stratification typically occurs from May to January, and convection of the lake water occurs regularly from February to April. Dissolved oxygen (DO) concentration in the bottom water reaches a minimum in early winter but is never totally depleted during the stagnation period.

The southern basin of the lake has a surface area of 58 km<sup>2</sup> and a capacity of 0.2 km<sup>3</sup>, with average and maximum depths of 3.5 m and 8 m. The residence time of water is calculated to be 0.04 years. The water in this basin is not thermally stratified and is more or less saturated with atmospheric oxygen throughout the year. Generally, for any chemical component, the concentration in the southern basin is slightly higher than that in the northern basin (Fujinaga and Hori 1982; Tanaka 1992; Somiya 2000).

## Sampling and analytical method

### Sampling

Water samples were collected at 1-month intervals from March 1986 to March 1987 using a polypropylene bellows pump equipped with Tygon tubing (inside diameter: 8 mm, Norton, Akron, OH, USA). The locations of the sampling stations, Ie-1, Nb-5, and Na-3, are shown in Fig. 1. Station Ie-1 is located in the northern basin at a depth of 73 m and stations Nb-5 (depth: 3.5 m) and Na-3 (depth: 2.0 m) are in the southern basin. Ten samples were collected at various depths at station Ie-1. Surface water alone was collected at stations Nb-5 and Na-3. Immediately after collection, lake water (3.2–3.5 l) was filtered through a 0.4- $\mu$ m Nuclepore filter (diameter: 142 mm, Corning, New York, NY, USA) on board the sampling vessel. The filtrate was acidified to pH 1 by adding hydrochloric acid that had been specially purified by isothermal distillation (Nakayama and Okazaki 1987) and was used to determine the dissolved state of major and trace elements. Suspended particulate matter, which was collected on the Nuclepore filter, was subjected to analysis for particulate elements. The water sample for pH, DO, and chlorophyll-*a* measurements was collected with a Van Dorn sampler. Sediment samples were collected with an Ekman-Berge sampler at stations Ie-1 and Nb-5 in February and March, 1995.

## Analytical method

The results for water temperature, pH, DO, and chlorophyll-*a* were cited from the report of Otsu Hydrobiological Station (1988). Water temperature and pH were measured on board the sampling vessel. DO content was determined by the standard Winkler method. Chlorophyll-*a* was measured by acetone extraction and fluorophotometric determination.

The dissolved concentrations of major and trace elements were determined as follows. Na and K were determined with a Hitachi (Tokyo, Japan) model 180-80 Zeeman atomic absorption spectrometer. Mg, Ca, Sr, Ba, and Si were simultaneously and directly determined with a Japan Jarrel Ash (Uji, Japan) model ICAP-96-953 inductively coupled plasma atomic emission spectrometer (ICPAES) (Sugiyama et al. 1992). V, Mo, Cu, Zn, Ni, and Fe were concentrated 250-fold through a solvent extraction method and determined using ICPAES. The preconcentration procedure used was essentially the same as previously reported (Sugiyama et al. 1986). A 1000-ml portion of filtered lake water was placed in a 1000-ml Teflon separatory funnel and 10 ml of 2% (w/v) ammonium tetramethylenedithiocarbamate solution was added. The pH was adjusted to  $4.3 \pm 0.1$  with aqueous ammonia, and 10 ml of 1 mol/l buffer solution (acetic acid/aqueous ammonia) was added. After the addition of 4 ml of 2-ethylhexyl acetate containing 5% (w/v) dibenzylammonium dibenzyledithiocarbamate, the mixture was shaken for 1 h. The organic phase was separated after standing for 10 min. V, Mo, Cu, Zn, Ni, and Fe in the phase were measured directly using ICPAES. Mn was also determined in a similar manner, but the pH value of the lake water sample was adjusted to  $6.9 \pm 0.1$ . Aqueous ammonia was prepared by isothermal distillation (Nakayama and Okazaki 1987). Reagent and buffer solutions were purified by solvent extraction with dithiocarbamate solution or hydrochloric acid before use.

Particulate concentrations of Mg, Ca, Sr, Ba, V, Mo, Cu, Zn, Ni, Fe, Mn, and Al were measured for the samples collected in October 1986 and February 1987 by a similar method to that previously reported (Sugiyama 1996). The Nuclepore filter, on which suspended particulate matter was collected by filtering 3.2–3.5 l of lake water, was placed in a 30-ml Teflon screw vial and was mixed with 0.5 ml of 25% aqueous ammonia to hydrolyze the filter. After standing for 12 h, the mixture was dried at 120°C. The residue was mixed with 1.0 ml of 70% perchloric acid. After lidding loosely, the mixture was heated to 150°C for 2 h. After addition of 1.0 ml of 65% nitric acid, the mixture was heated to 170°C for 6 h. The lid was taken off and then the mixture was dried completely. Hydrofluoric acid (40%, 0.5 ml) was added to the vial. The mixture was stirred for 10 min and heated to dryness. The residue was dissolved in 5 ml of 0.1 mol/l hydrochloric acid, and then the concentrations of the above elements were determined simultaneously using ICPAES. All the samples were manipulated in a clean box with a 0.1- $\mu$ m air filter. All reagents used were of ultrapure grade (Cica-Merck, Tokyo, Japan). Sediment samples were dried at 80°C

and analyzed similarly to the measurement of the particulate concentration.

## Digestion of dissolved organic matter under UV irradiation

To examine the effect of dissolved organic complexes of trace elements on the present preconcentration method, the lake water sample collected in October 1986 was irradiated by UV light to decompose the complexes, using a similar procedure to that reported by Batley and Farrar (1978), and was then analyzed. A 250-ml portion of filtered lake water was transferred to a 300-ml quartz erlenmeyer flask and was mixed with 10 ml of 5 mol/l nitric acid and 0.3 ml of 30% hydrogen peroxide. The mixture was irradiated for 6 h under a 400-WHg lamp to decompose the dissolved organic matter. Thereafter, trace elements in this sample were determined by the above procedure.

## Results and discussion

### Distribution profiles of water temperature, DO, pH, and chlorophyll-*a*

Figure 2 shows the time–depth profiles of water temperature, DO, pH, and chlorophyll-*a* at station Ie-1. Lake water in the northern basin was thermally stratified between May 1986 and January 1987. During most of this period, the thermocline was formed at a depth of 15–25 m. The thermocline moved deeper with time after November and disappeared in late January.

The vertical profile of DO in the stagnation period showed a depression near the thermocline and at the bottom. The minimum concentration of 141  $\mu$ mol/l (37% of saturation) was observed at a depth of 70 m in October. Bottom water at the end of the stagnation period (January) had DO levels of 194  $\mu$ mol/l (51% of saturation).

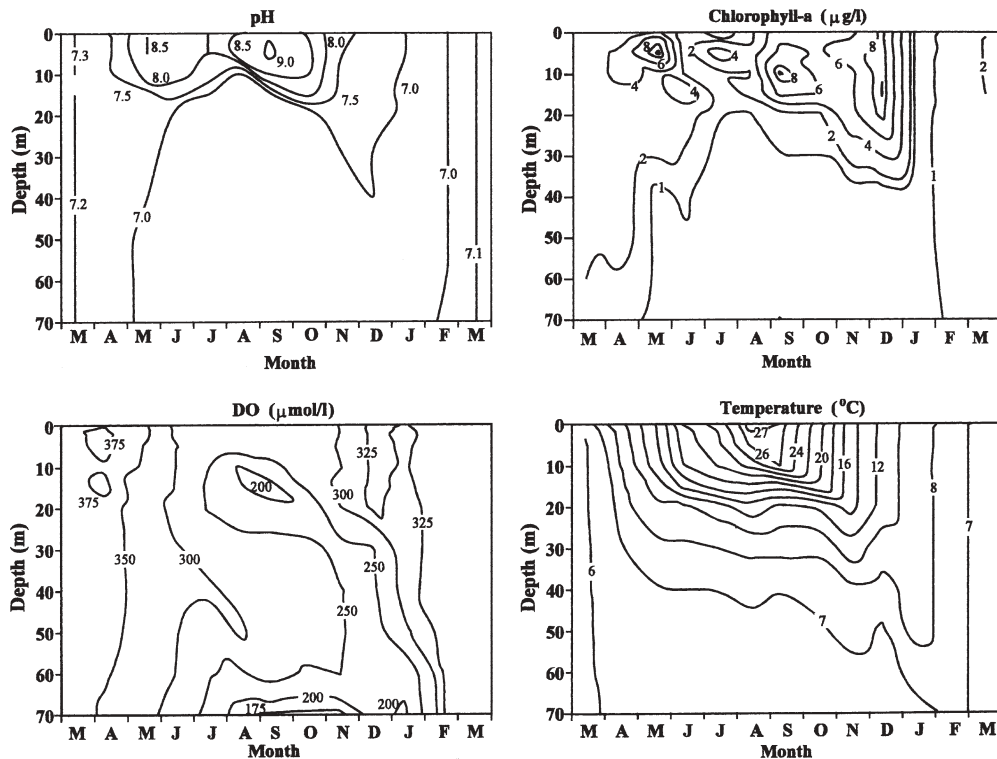
The pH value in the epilimnion started to increase in March, reached a maximum of 8.8 at the surface of the lake in September, and had decreased by the following January. In the bottom water, pH in the stagnation period (6.7–7.0) was a little lower than that in the circulation period (7.0–7.2), and showed a minimum of 6.7 in October and January.

Chlorophyll-*a* concentration in the epilimnion was high in May, September and December. Its maximum concentration of 9.3  $\mu$ g/l was observed at a depth of 5 m in May.

### Dissolved organic species of trace elements

Some trace metals have been reported to form dissolved organic species such as complexes with water-soluble organic ligands or methylated metals in natural waters (e.g., Matsunaga and Igarashi 1982; Irgolic 1991; Borg 1994; Sohrin et al. 1997). If these species are very stable in lake water, they may be difficult to extract into an organic phase for determination by the present method. To examine this

**Fig. 2.** Time–depth profiles of water temperature, dissolved oxygen (DO), pH, and chlorophyll-*a* at station Ie-1 from March 1986 to March 1987



**Table 1.** Comparison between analytical results (nmol/l) by the present method with and without UV irradiation

Sample	Depth	Mn		Fe		Cu		Zn		Ni		Mo		V	
		With	Without	With	Without	With	Without	With	Without	With	Without	With	Without	With	Without
Ie-1	1m	5.6	5.4	38.4	35.1	8.5	8.1	2.3	2.3	2.7	2.5	2.6	3.2	4.8	5.0
	10m	5.4	5.2	35.4	34.4	8.3	8.2	2.2	1.0	3.0	2.8	3.4	3.0	4.6	4.9
	40m	1.3	1.2	4.5	4.3	7.0	6.8	2.5	2.6	2.0	2.5	1.8	2.5	1.7	1.5
Na-3	0m	4.3	4.5	44.7	40.0	9.0	8.1	1.2	1.3	2.8	2.5	2.9	4.8	6.5	6.6

Samples were collected in October 1986

effect, we tried to decompose dissolved organic matter by UV irradiation. Batley and Farrar (1978) reported that dissolved organic carbon in river water decreased from 8.2mg/l to 0.2mg/l by irradiation for 4h using a 550-WHg lamp after addition of nitric acid and hydrogen peroxide. We also decomposed dissolved organic matter in lake water samples by UV irradiation as described above and then analyzed trace elements in the samples. Table 1 compares the analytical results with and without UV irradiation. The pairs of values agree well for all elements except Mo. The result for Mo in the irradiated sample was lower than that in the unirradiated sample. This was caused by an unextractable species, for example peroxomolybdate, being formed by this oxidizing procedure (Campbell et al. 1989).

To evaluate the accuracy of the present analytical method, Mn and Fe concentrations in lake water were also directly determined by graphite furnace atomic absorption spectrometry (GFAAS). These values were also in good correspondence with those obtained by the present method

**Table 2.** Comparison between analytical results (nmol/l) by the present method (ICPAES) and direct determination with graphite furnace atomic absorption spectrometry (GFAAS)

Sample	Depth	Mn		Fe	
		ICPAES	GFAAS	ICPAES	GFAAS
Ie-1	1m	11.8	11.8	67.0	68.1
	10m	8.4	8.6	68.3	64.5
	50m	1.3	1.5	9.1	7.2
Na-3	0m	6.9	7.1	51.3	66.3

Samples were collected in June 1986

ICPAES, inductively coupled plasma atomic emission spectrometry

(Table 2). The above two results from UV irradiation and GFAAS determination suggest that organic species unextractable by the present method were scarce in water from Lake Biwa.

**Table 3.** Dissolved concentrations of major and trace elements in water from Lake Biwa

Element	This study				Haraguchi et al. <sup>a</sup>		Mito et al. <sup>b</sup>	
	Northern basin		Southern basin		Northern basin		Northern basin	Southern basin
	Range	Mean	Range	Mean	Range	Range	Range	
Na (mmol/l)	270–303	286	269–338	305				
Ca ( $\mu$ mol/l)	259–279	273	239–287	274	269–272		205–311	232–321
Mg ( $\mu$ mol/l)	80.2–90.1	85.3	76.1–89.3	84.8	84–86		61.3–103	70.7–101
K ( $\mu$ mol/l)	34.8–47.8	44.4	43.0–50.6	47.5				
Si ( $\mu$ mol/l)	2.5–36.7	18.7	2.8–58.4	27.3			0.6–201	2.6–41.4
Sr (nmol/l)	453–493	478	461–542	502	470–480		354–636	409–644
Ba (nmol/l)	48.2–64.2	57.7	57.7–87.6	71.2				
Mn (nmol/l)	0.7–710	25.1	4.4–1171	129	7.5–13		0.4–1240	3.0–154
Fe (nmol/l)	4.1–68.2	24.5	18.6–218	80.5	72		<0.1–3220	5.1–284
Cu (nmol/l)	6.3–14.6	7.9	4.9–14.5	9.6				
Zn (nmol/l)	0.9–35.9	4.2	0.9–40.1	6.1	11–31		<0.1–68	<0.1–40
Ni (nmol/l)	1.4–38.3	3.6	2.2–8.7	3.6	4.8–16		1.6–28.9	1.5–15.8
Mo (nmol/l)	1.7–4.6	2.9	2.6–5.5	3.7				
V (nmol/l)	1.2–5.1	2.3	1.3–11.6	4.0	3.9		0.8–16.0	0.9–8.6

<sup>a</sup>Haraguchi et al. (1998)<sup>b</sup>Mito et al. (2004)**Table 4.** Particulate concentrations of major and trace elements in water from Lake Biwa

Element	This study				Mito et al. <sup>a</sup>	
	Northern basin		Southern basin		Northern basin	Southern basin
	Range	Mean	Range	Mean	Range	Range
Al ( $\mu$ mol/l)	0.322–1.22	0.797	5.33–12.1	8.57	0.13–7.9	0.38–63
Fe ( $\mu$ mol/l)	0.097–0.406	0.260	1.31–2.97	2.04	0.029–2.4	0.33–19
Ca ( $\mu$ mol/l)	0.113–0.233	0.150	0.360–1.10	0.707	0.037–2.2	0.45–7.9
Mg ( $\mu$ mol/l)	0.058–0.168	0.124	0.541–1.36	0.964		
Mn (nmol/l)	30.8–560	110	54.6–411	230	27–1000	34–2000
Ba (nmol/l)	0.64–3.52	2.03	5.61–16.1	11.4		
Zn (nmol/l)	0.32–2.04	1.11	7.80–13.1	10.4		
V (nmol/l)	0.23–1.10	0.68	2.83–6.82	5.05		
Cu (nmol/l)	0.40–1.28	0.58	1.74–3.48	2.59		
Sr (nmol/l)	0.25–0.63	0.43	1.40–4.15	2.72		
Ni (nmol/l)	0.07–0.29	0.18	0.18–1.74	0.96		

<sup>a</sup>Mito et al. (2002)

### Mean concentrations of major and trace elements

Table 3 lists the minimum, maximum, and mean concentrations of dissolved elements obtained in the present study together with corresponding values found in Lake Biwa by other researchers. The results for particulate elements are listed in Table 4. As shown in the tables, the present results were in the same range as the concentrations previously reported for the lake. The concentration in the southern basin for most of the elements analyzed was slightly higher than that in the northern basin because of differences in the trophic state and pollution level between the two basins.

### Distribution profiles of dissolved and particulate elements in the northern basin

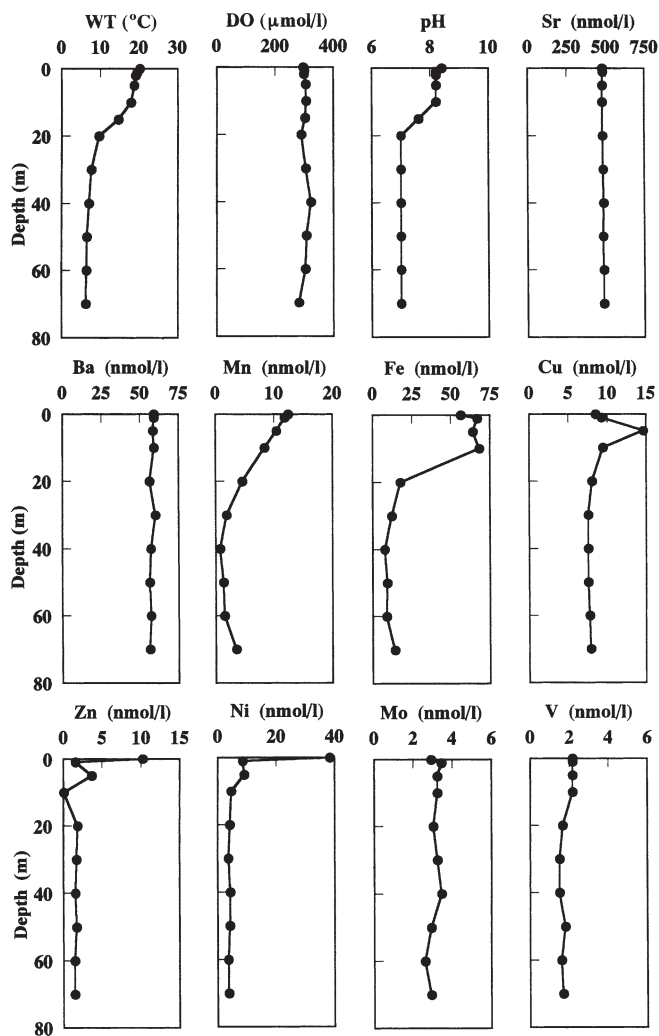
The vertical distribution profiles of dissolved elements at station Ie-1 are shown in Figs. 3–6. Although the dissolved

concentrations were analyzed monthly, only representative results are shown in the figures. Particulate concentrations were measured only in October 1986 and February 1987. Their profiles are shown in Figs. 7 and 8.

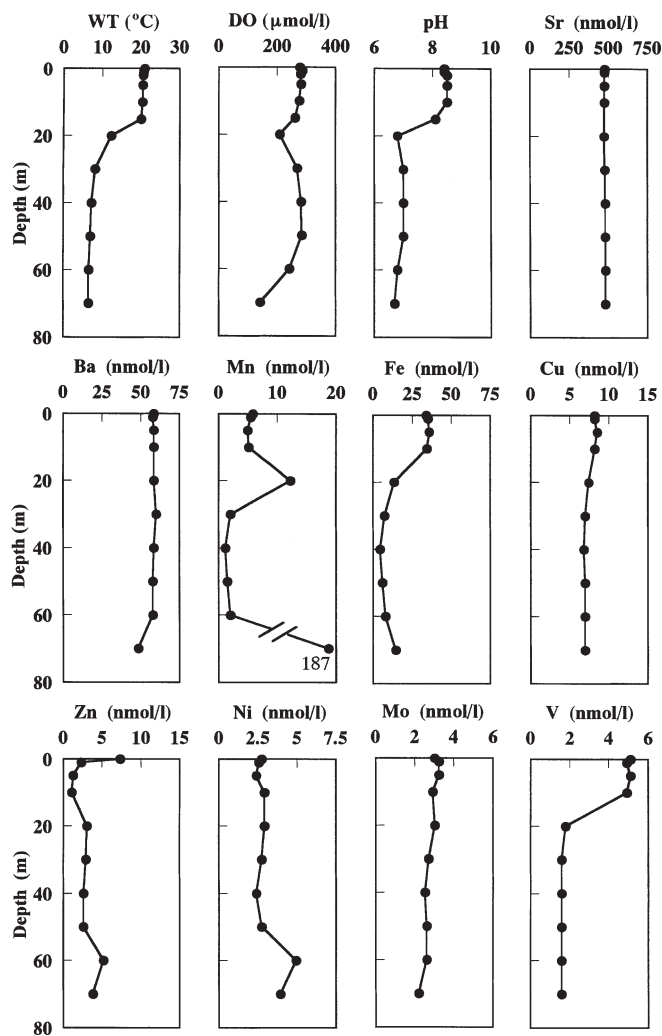
### Estimation of terrigenous and authigenic fractions in particulate matter

Aquatic suspended particulate matter contains an unreactive terrigenous fraction. This fraction mostly consists of aluminosilicates and is supplied through river inflow and resuspension of bottom sediment. In oceanic areas, this fraction is usually estimated by referring to particulate Al (P-Al) concentration and by using the mean crustal abundance ratio (MCAR) of an element in relation to Al (Brewer et al. 1980). However, we cannot immediately use the MCAR, because the MCAR may be different from the element/Al ratio in limnetic terrigenous matter that reflects the specific geology of the drainage area. Therefore,





**Fig. 3.** Vertical distribution of dissolved trace elements, water temperature (*WT*), dissolved oxygen (*DO*), and pH at the early stage of the stagnation period (June 11, 1986)



**Fig. 4.** Vertical distribution of dissolved trace elements, water temperature (*WT*), dissolved oxygen (*DO*), and pH at the middle stage of the stagnation period (October 15, 1986)

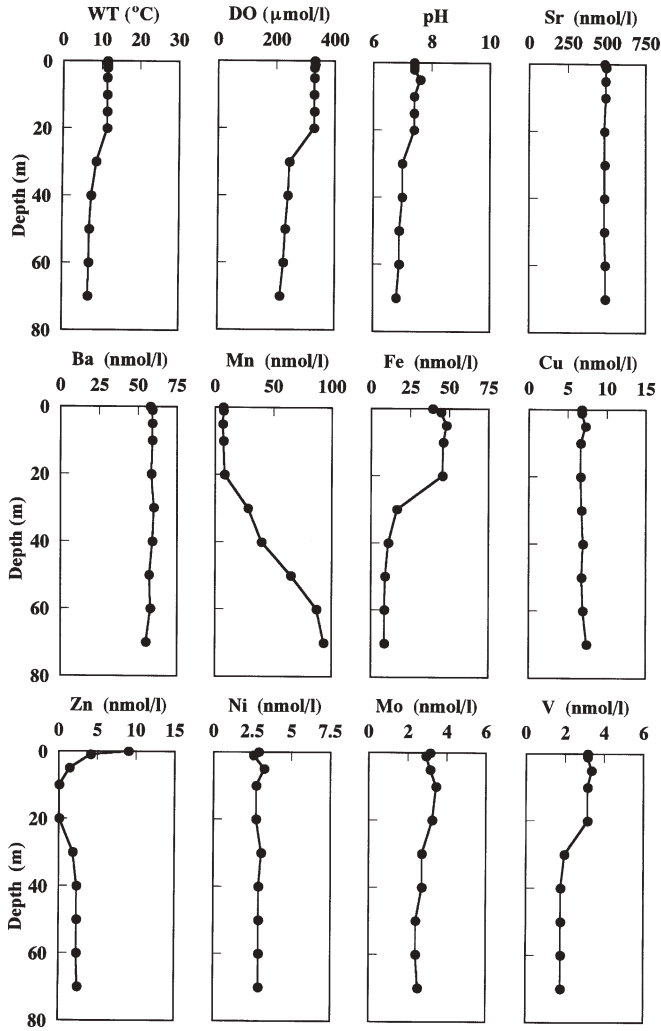
Sholkovitz and Copland (1982) and Mito et al. (2002) assumed that biological and geochemical activity was very low in winter months when the lake was completely overturned, and estimated the element/Al ratio for limnetic terrigenous matter from the ratio in the suspended particulate matter from that period. We also obtained the element/Al ratios in the terrigenous matter of Lake Biwa in the same manner as the above reports.

In Fig. 9, particulate element concentration is plotted as a function of P-Al concentration at station Ie-1 in February 1987 when Lake Biwa was in the winter circulation period. These plots exhibited a good linear relationship through the origin of the coordinates for all elements analyzed. The slopes of the linear regression lines in the figure are listed in Table 5, together with the mean element/Al ratios for suspended particulate matter in 64 Japanese rivers (Sugiyama 2004) and the MCAR (Taylor and McLennan 1985). Although some of the present results for the element/Al ratios were different from the MCAR, the

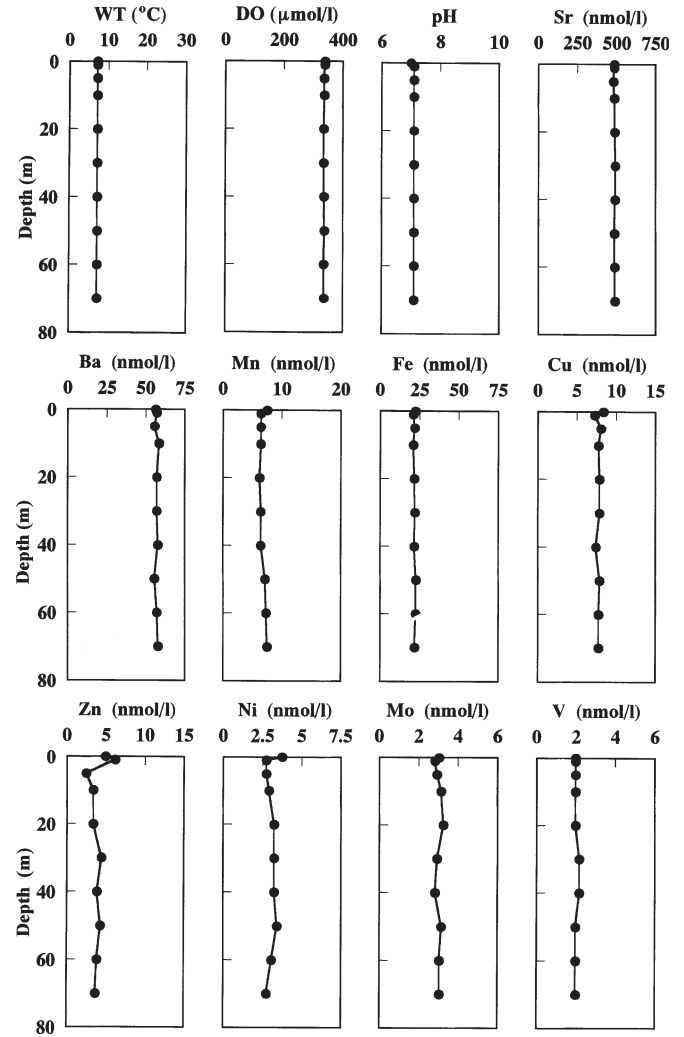
results of all elements except for Mn agreed well with the values for suspended particulate matter from Japanese rivers.

The value for Mn in the limnetic suspended particulate matter was much higher than that in the river suspended particulate matter because P-Mn concentration is affected by geochemically formed oxide particles even in the winter circulation period. Sugiyama and Hori (1996) analyzed suspended particulate matter pretreated by reductive extraction of the Mn oxide fraction and obtained a terrigenous Mn/Al ratio of  $3.3 \times 10^{-3}$  mol/mol in Lake Biwa. Therefore, in the present work, this value was used as the terrigenous Mn/Al ratio.

Mito et al. (2002) measured particulate element/Al ratios in the northern and southern basins of Lake Biwa during the circulation period and reported  $3.0 \times 10^{-1}$  mol/mol for Fe/Al,  $8.3 \times 10^{-2}$  mol/mol for Ca/Al, and  $5.6 \times 10^{-3}$  mol/mol for Mn/Al. The element/Al ratios obtained in this study also agree well with those of Mito et al.



**Fig. 5.** Vertical distribution of dissolved trace elements, water temperature (*WT*), dissolved oxygen (*DO*), and pH at the late stage of the stagnation period (December 12, 1986)



**Fig. 6.** Vertical distribution of dissolved trace elements, water temperature (*WT*), dissolved oxygen (*DO*), and pH during the circulation period (February 20, 1987)

**Table 5.** Element/Al ratio in the terrigenous fraction of suspended particulate matter

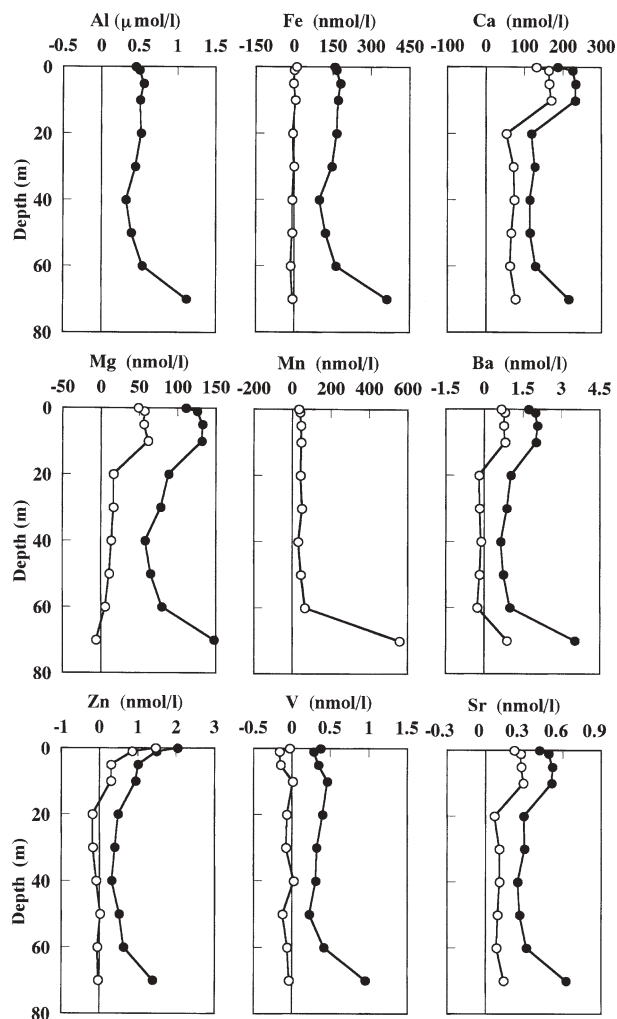
Element	Element/Al ratio (mol/mol)		
	This study <sup>a</sup>	Japanese rivers <sup>b</sup>	MCAR <sup>c</sup>
Fe	$3.29 \times 10^{-1}$ (0.981)	$3.51 \times 10^{-1}$	$4.1 \times 10^{-1}$
Ca	$1.24 \times 10^{-1}$ (0.952)	$1.14 \times 10^{-1}$	$4.2 \times 10^{-1}$
Mg	$1.38 \times 10^{-1}$ (0.972)	$1.32 \times 10^{-1}$	$4.2 \times 10^{-1}$
Mn	$1.16 \times 10^{-1}$ (0.917)	$8.35 \times 10^{-3}$	$8.2 \times 10^{-3}$
Ba	$2.37 \times 10^{-3}$ (0.972)	$1.55 \times 10^{-3}$	$5.8 \times 10^{-4}$
Zn	$1.27 \times 10^{-3}$ (0.790)	$1.46 \times 10^{-3}$	$3.9 \times 10^{-4}$
V	$8.89 \times 10^{-4}$ (0.856)	$6.8 \times 10^{-4}$	$1.4 \times 10^{-3}$
Sr	$4.36 \times 10^{-4}$ (0.981)	$6.4 \times 10^{-4}$	$9.5 \times 10^{-4}$

MCAR, mean crustal abundance ratio

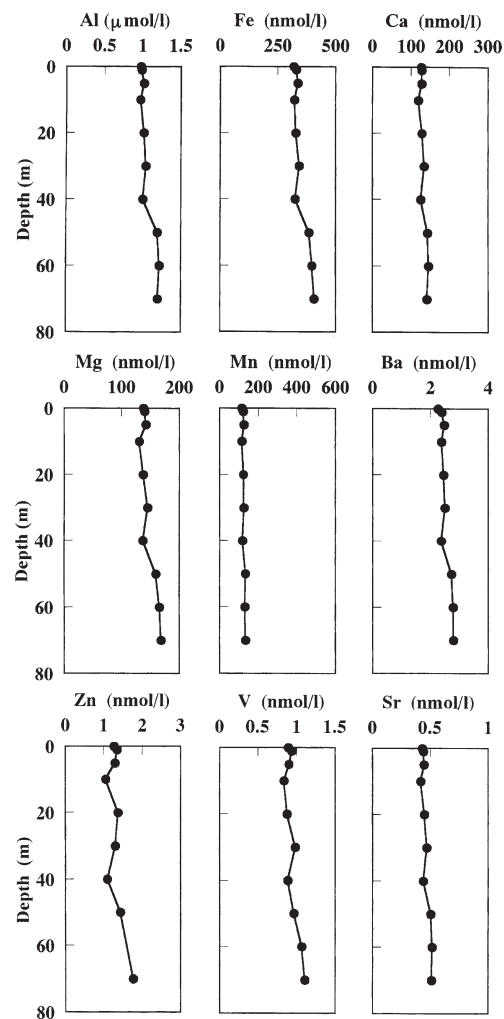
<sup>a</sup>Element/Al ratio is the slope of the linear regression line in Fig. 9 and the value in parenthesis is the correlation coefficient of the line

<sup>b</sup>Sugiyama (2004)

<sup>c</sup>Taylor and McLennan (1985)



**Fig. 7.** Vertical distribution of particulate elements at the middle stage of the stagnation period (October 15, 1986). Authentic particulate concentration (○), total particulate concentration (●)



**Fig. 8.** Vertical distribution of particulate elements in the circulation period (February 20, 1987)

The authigenic fraction of a particulate element ( $P-EI_{AF}$ ), which was formed biologically or geochemically in the lake, was estimated from the following equation using the terrigenous element/Al ratio ( $EI/Al$ ):

$$P-EI_{AF} = P-EI_T - (EI/Al) \times P-Al_T$$

where  $P-EI_T$  and  $P-Al_T$  are the total particulate concentrations of the element and Al, respectively. Vertical profiles of authigenic particulate concentrations in October 1986 are shown in Fig. 7, together with those of total particulate concentrations.

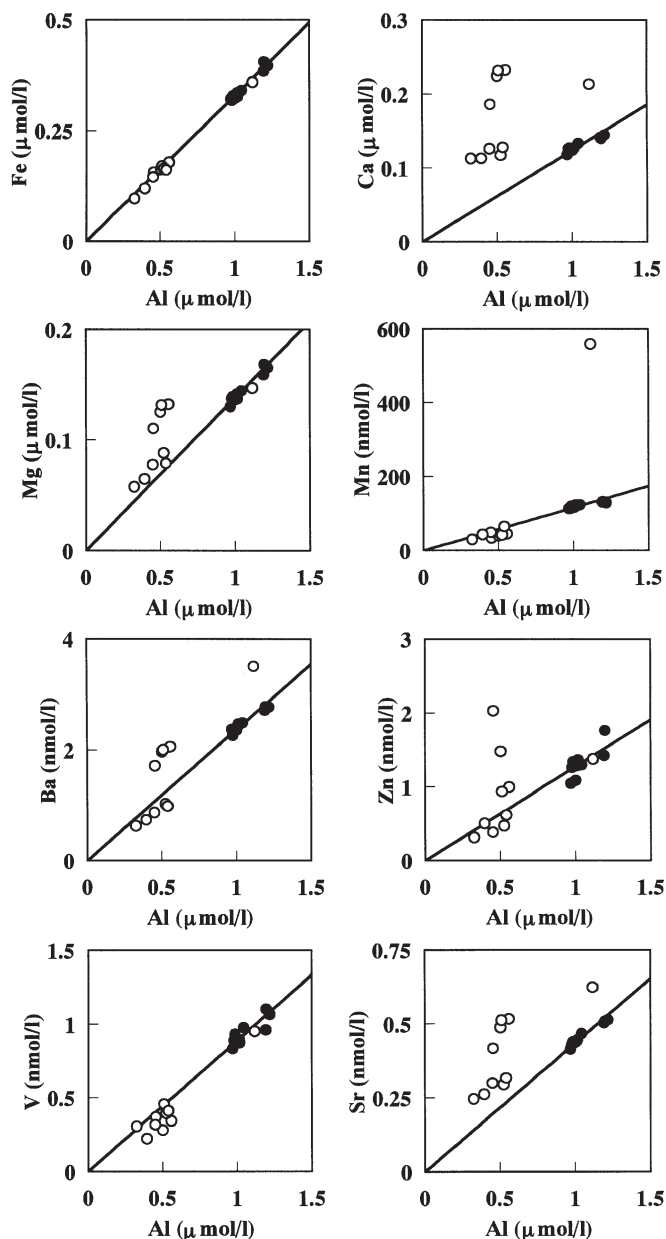
#### Geochemical behavior of trace elements

As shown in Fig. 2, Lake Biwa was in a circulation period from March 1986 to April 1986 and from February 1987 to March 1987, and in a stagnation period from May 1986 to

January 1987. In the circulation period, all trace elements showed almost uniform vertical distribution profiles for both dissolved and particulate forms at station Ie-1 (Figs. 6 and 8). These results indicate that the lake water was well mixed by vertical convection in winter and that the geochemical conditions were identical over the whole water column of the lake. In contrast, vertical profiles in the stagnation period changed with time; therefore, the stagnation period was divided into three subperiods, early (May to July), middle (August to October), and late (November to January) stages. Representative profiles of dissolved elements in each of the three stages are shown in Figs. 3–5, respectively.

Nine of the trace elements analyzed in the present work were classified into four groups based on their chemical properties and the similarity of their vertical profiles: (1) Mn and Fe; (2) Ba and Sr; (3) V and Mo; and (4) Cu, Zn, and Ni. The geochemical dynamics of these groups are discussed in the following sections.





**Fig. 9.** Correlation between particulate elements and particulate Al concentrations. October 1986 (○), February 1987 (●). The lines through the origin of the coordinates were obtained by the linear least-squares method with the data for February 1987

## Mn and Fe

Both Mn and Fe are redox-sensitive elements that are easily reduced or oxidized by changes of the biogeochemical conditions of the lake. Their oxidized forms ( $\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$ ) are insoluble in natural water with neutral pH, but their reduced forms ( $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ ) are soluble in such water. Therefore, the vertical profiles of dissolved Mn (D-Mn) and D-Fe drastically changed with the progress of thermal stratification of the lake as shown in Figs. 3–6. In the circulation period, their vertical distributions were almost uniform. The profiles for February 1987 are shown in Fig. 6 as

representative examples of the period. In March 1986, the average concentrations were 11.6 nmol/l (D-Mn) and 14.7 nmol/l (D-Fe). However, the uniform profiles disappeared during the stagnation period. Figure 3 shows the results in June 1986, the early stage of the period. The average concentration of D-Mn in the epilimnion (depth: 0–10 m) was 9.9 nmol/l, nearly the same as the average value in the circulation period. In contrast, the average concentration in the hypolimnion (depth: 30–70 m) decreased to 1.7 nmol/l, much lower than that in the circulation period. On the other hand, the average concentrations of Fe were 60.7 nmol/l (epilimnion) and 9.7 nmol/l (hypolimnion) in June 1986. Compared to the average value in the circulation period, the concentration in the epilimnion increased and that in the hypolimnion decreased.

D-Fe concentrations in river waters that flow into Lake Biwa are generally higher than those in Lake Biwa itself (Itasaka 1974; Mito et al. 2004). In the stagnation period, these river waters flow into the epilimnion only. Therefore, D-Fe concentration increases only in the epilimnion. In addition, dissolved organic matter increases in the epilimnion during the stagnation period as a result of high biological activity in summer (Hori et al. 1998). Such dissolved organic matter accelerates the formation of soluble and stable organic Fe complexes and colloids in the layer (Matsunaga and Igarashi 1982; Cameron and Liss 1984). Thus, D-Fe concentration increases in the epilimnion.

D-Mn concentration in river water is also higher than that in lake water (Kawashima et al. 1988; Mito et al. 2004). However, most of the D-Mn ions in river water are quickly removed around the river estuaries through oxidation by microorganisms and adsorption onto the oxide formed (Kawashima et al. 1988). Therefore, although river waters flow only into the epilimnion in the stagnation period, the D-Mn concentration in pelagic lake water does not increase in the layer.

On the other hand, in the hypolimnion at the early stage of the stagnation period, abundant dissolved oxygen remaining in the layer oxidizes dissolved  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions to insoluble species (hydrated Mn and Fe oxides). Dissolved inorganic and organic colloids and organic complexes of  $\text{Fe}^{3+}$  ions gradually aggregate and form suspended particles of Fe (Cameron and Liss 1984). Thus, at the early stage of the stagnation period, dissolved concentrations of Mn and Fe in the hypolimnion decrease (Fig. 3).

At the middle stage of the stagnation period, both D-Mn and authigenic P-Mn concentrations increased greatly near the bottom (Figs. 4 and 7). When DO concentration decreases in the hypolimnion,  $\text{Mn}^{2+}$  ions are released into the bottom water by reductive dissolution of Mn oxides in the sediment (Kawashima et al. 1988; Davison 1993). Such  $\text{Mn}^{2+}$  ions are reoxidized by the dissolved oxygen remaining in the water and form Mn oxide particles (Davison 1993; Miyajima 1994). As a result of these processes, the vertical profiles of D-Mn and P-Mn as shown in Figs. 4 and 7 are formed. In contrast to Mn, neither D-Fe nor authigenic P-Fe levels increased in the bottom water at this stage. The standard redox potential of  $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$  is 87 mV (versus normal hydrogen electrode (NHE)),  $[\text{Fe}^{2+}] = 1.0 \mu\text{mol/l}$ ,  $\text{pH} =$

7) and that of  $\text{MnO}_2/\text{Mn}^{2+}$  is 580 mV (versus NHE,  $[\text{Mn}^{2+}] = 1.0 \mu\text{mol/l}$ ,  $\text{pH} = 7$ ) (Sugiyama 2000). Therefore, as Fe oxide is more difficult to reduce than Mn oxide (Hem 1977; Davison 1993),  $\text{Fe}^{2+}$  ions are not released from the sediment at the middle stage when DO remains at a low level in the hypolimnion.

At the late stage of the stagnation period, D-Mn concentration increased in not only the bottom water but also in the whole water column of the hypolimnion, as shown in Fig. 5. This vertical profile suggests that  $\text{Mn}^{2+}$  ions, which were released from the sediments, diffused to the upper layer. The highest value of Mn concentration was observed to be 740 nmol/l at a depth of 70 m in January 1987. However, even at this time, DO was at a level of 194  $\mu\text{mol/l}$  (51% of saturation) in the bottom water. Therefore, D-Fe concentration did not increase in the water.

When the circulation period commenced in February 1987, vertical distribution profiles of D-Mn and D-Fe became almost uniform again. D-Mn concentration in the bottom water decreased to a very low level. This is because the lake water was vigorously convected in winter. Therefore, DO was sufficiently supplied to the bottom water by the vertical convection of the lake water and dissolved  $\text{Mn}^{2+}$  ions were oxidized to insoluble Mn oxides.

#### Ba and Sr

These two elements are alkaline earth elements and their chemical properties are very similar. However, their geochemical behaviors in a lake are very different (Sugiyama et al. 1992; Sugiyama and Hori 1994). The vertical distribution profile of D-Sr is almost uniform in a mesotrophic lake, but D-Ba concentration decreases with depth in the stagnation period. In a eutrophic lake with a seasonally anoxic hypolimnion, both D-Ba and P-Ba concentrations show a maximum value at a depth near the oxycline. Such specific behaviors of Ba are controlled by the redox cycle of Mn and selective adsorption of D-Ba onto Mn oxides.

In the present work, D-Sr showed a uniform vertical profile in all seasons and its concentration was almost constant throughout the year. On the other hand, D-Ba decreased with depth in the stagnation period (Figs. 4 and 5). D-Ba concentrations in the surface (0–10 m) and bottom (70 m) waters in December 1986 were 58.8 nmol/l and 54.7 nmol/l, respectively (Fig. 5). D-Ba concentration in the bottom water decreased further to 52.6 nmol/l in January 1987. This is because dissolved  $\text{Ba}^{2+}$  ions were adsorbed onto Mn oxides which were produced by the reoxidation of  $\text{Mn}^{2+}$  ions released from the sediments as discussed in the above section (Sugiyama et al. 1992). The validity of this process is demonstrated well in the results in October 1986. As shown in Figs. 4 and 7, D-Ba decreased greatly in the bottom water and authigenic P-Ba increased in the same water. In contrast, both D-Mn and authigenic P-Mn increased in the bottom water. Decrease of D-Ba in the bottom water corresponded closely to the increase of authigenic P-Ba and P-Mn.

From the concentrations of authigenic P-Ba and P-Mn and D-Ba in the bottom water in October 1986, the distribution ratio (enrichment factor) of Ba between lake water and authigenic Mn oxide was calculated. In the calculation, it was assumed that the authigenic P-Mn was suspended Mn oxides in the bottom water and that all authigenic P-Ba was included in the oxides. The distribution ratio,  $D$ , was thus calculated according to the following equation:

$$D(\text{ml/g-Mn}) = \left\{ \frac{[\text{authigenic P-Ba}(\text{mol/l})]}{[\text{authigenic P-Mn}(\text{g-Mn/l})]} \right\} / [\text{D-Ba}(\text{mol/ml})]$$

Concentrations of authigenic P-Ba, P-Mn, and D-Ba were  $8.8 \times 10^{-10}$  mol/l,  $3.05 \times 10^{-5}$  g-Mn/l, and  $4.82 \times 10^{-11}$  mol/ml, respectively. Based on these values,  $D$  was estimated to be  $6.0 \times 10^5$  ml/g-Mn. This value agreed well with the  $D$  values of Ba from the Lake Biwa water to the Mn fraction in Mn nodules formed in the lake,  $1.13 \times 10^6$  ml/g-Mn, and experimentally synthesized Mn oxide,  $3.24 \times 10^6$  ml/g-Mn (Sugiyama et al. 1992). These results suggest that the geochemical behavior of Ba is regulated by the process mentioned above.

Dissolved  $\text{Sr}^{2+}$  ions are also adsorbed onto Mn oxides, but the affinity of  $\text{Sr}^{2+}$  for these oxides is much weaker than that of Ba (Murray 1975; Sugiyama et al. 1992). Therefore, because only a very small portion of D-Sr is adsorbed, its vertical profile is not affected by adsorption onto Mn oxides.

Both authigenic P-Ba and P-Sr concentrations were high in the epilimnion of October 1986, as shown in Fig. 7. Authigenic P-Mg, and P-Ca also showed similar profiles to P-Ba and P-Sr. However, the authigenic P-Mn concentration was very low and was almost constant between depths of 0 and 40 m. Therefore, these increases of authigenic P-Ba, P-Sr, P-Mg, and P-Ca concentrations are not the result of adsorption onto Mn oxides. Sagi et al. (1997) reported that total P-Ca concentration correlated well with total P-P concentration in the northern basin of Lake Biwa. Mito et al. (2002) also pointed out a good correlation between total P-Ca and P-P concentrations and a similarity in seasonal changes of authigenic P-Ca and P-P concentrations in the basin. These previous works and our present results suggest that the increase of authigenic particulate concentrations of alkaline earth elements in the epilimnion is caused by biological uptake.

#### Mo and V

Results for V in the present survey were reported previously (Sugiyama 1989). D-V in the surface layer changed seasonally at all stations in the northern and southern basins: it started to increase in May, reached a maximum in late summer, and decreased in autumn. In contrast, in the deep layer, D-V concentration was almost constant throughout the year. Such a seasonal variation of D-V can be revealed more clearly by drawing the time–depth profile

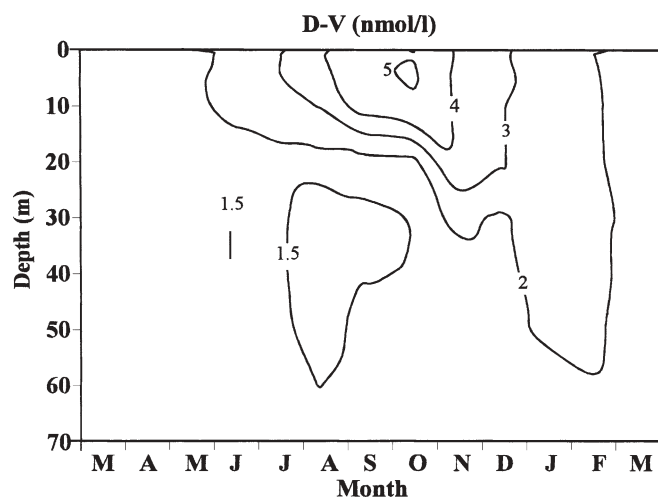


Fig. 10. Time–depth profile of dissolved vanadium (*D-V*) at station Ie-1 from March 1986 to March 1987

of *D-V* at station Ie-1, as shown in Fig. 10. We can easily recognize that *D-V* concentration changed seasonally only in the epilimnion and that the marked changes in *D-V* concentration as shown in Figs. 3–5 were observed at the thermocline. This time–depth profile is very similar to those of water temperature and pH, suggesting that the geochemical behavior of *D-V* is affected by the formation of the thermocline and the change of pH in the epilimnion. Harita et al. (2005) reported that *D-V* concentration changes seasonally in the oxygenated surface layer in response to the pH variation in the epilimnion. They concluded that *D-V* increases as a result of the release from littoral sediments and suspended particulate matter in response to the pH rise induced by high biological production during spring and summer, and that *D-V* decreases through adsorption onto the sediments and suspended matter in response to the pH drop caused by the decline of biological activity during autumn and winter. The present results shown in Figs. 2 and 10 agree well with this process proposed by Harita et al.

Most of the authigenic *P-V* concentrations were negative in October 1986 (Fig. 7). In addition, the total *P-V* concentrations in this month showed a good linear relationship with those of *P-Al*, as shown in Fig. 9, similar to the results in February 1987. The correlation coefficient between total *P-V* and *P-Al* concentrations was 0.983 for all data sets in October 1986 and February 1987. These results suggest that suspended particulate matter at station Ie-1 in Lake Biwa do not contain significant biological and geochemical fractions for *V*. Therefore, it is inferred that the increase of *D-V* in the epilimnion of station Ie-1 was mainly supplied by release from the sediments.

As with *V*, *Mo* dissolves as an oxyanion in natural waters with neutral pH. However, in contrast to *D-V*, *D-Mo* concentration remains seasonally unchanged, as shown in Fig. 11. This figure shows the seasonal distributions of *D-Mo* in the surface and bottom waters at stations Ie-1, Nb-5, and Na-3. The vertical profile of *D-Mo* at station Ie-1 was

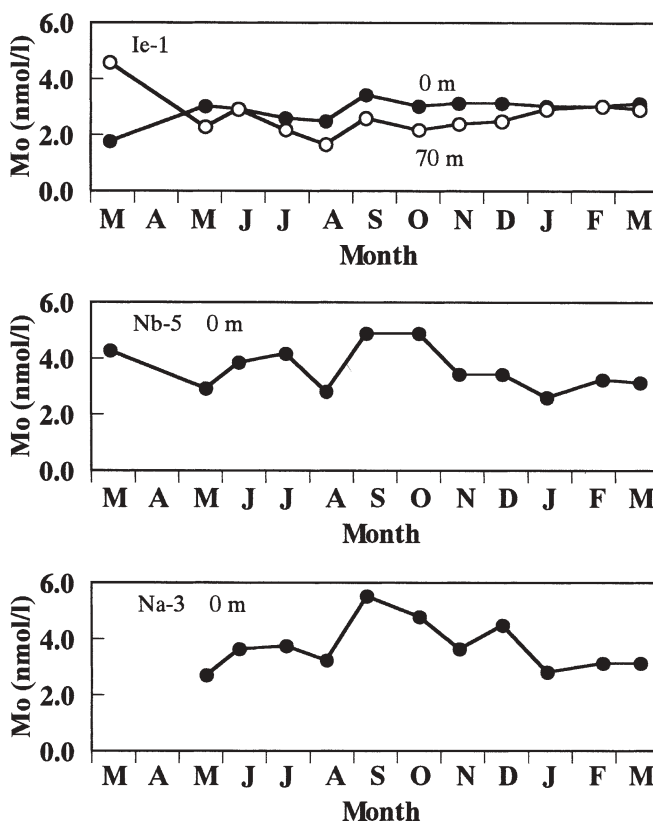


Fig. 11. Seasonal distribution of dissolved *Mo* at stations Ie-1, Nb-5, and Na-3 from March 1986 to March 1987

almost uniform for all seasons (Figs. 3–6). It is well known that *Mo* promotes the growth of various kinds of algae (Henry and Tundisi 1982; Horne and Goldman 1994) and is classified as a so-called bio-element. However, the *D-Mo* distribution in the ocean is also not affected by biological activity and is vertically constant (Morris 1975). This may be because *Mo* is present in natural water at very high levels compared to the biological demand from living organisms in lakes and in the ocean. Therefore, even if some portion of *D-Mo* in lake water is assimilated by limnetic microorganisms, the *D-Mo* concentration is not affected because of the small quantity removed in such processes. In addition, because *D-Mo* has little tendency to adsorb onto limnetic sediments and suspended particulate matter at neutral pH levels (Harita et al. 2005), the sediments and particulate matter only release tiny amounts of *D-Mo* into lake water in response to the pH rise in the epilimnion. Therefore, the *D-Mo* concentration does not change like that of *D-V* does. These views are supported by the following results for *Mo* concentrations in suspended particulate matter and sediments. Total *P-Mo* concentration was measured in October 1986 and February 1987, but its concentration in all samples was lower than the detection limit (0.15 nmol/l), i.e., 1/20 of *D-Mo* concentration. These results contrast with those for *V*. Total *P-V* concentration ranged from 0.2 to 6.8 nmol/l, from 1/17 to 3 times the *D-V* concentration. Also, in the sediments, *Mo* concentration was much lower than that of *V*. The *Mo* concentration was less than 0.16  $\mu\text{mol/g}$  at all

**Table 6.** Distribution ratio between lake water and manganese nodules in Lake Biwa

Element	Concentration		Distribution ratio (ml/g)
	Lake water (mol/l)	Mn nodule <sup>a</sup> (mol/g)	
Na	$2.84 \times 10^{-4}$	$3.7 \times 10^{-4}$	$1.3 \times 10^3$
Ca	$2.75 \times 10^{-4}$	$1.1 \times 10^{-4}$	$4.0 \times 10^2$
Mg	$8.59 \times 10^{-5}$	$4.2 \times 10^{-4}$	$4.9 \times 10^3$
K	$4.10 \times 10^{-5}$	$3.4 \times 10^{-4}$	$8.3 \times 10^3$
Si	$2.19 \times 10^{-5}$	$9.7 \times 10^{-3}$	$4.4 \times 10^5$
Sr	$4.85 \times 10^{-7}$	$1.2 \times 10^{-6}$	$2.5 \times 10^3$
Ba	$5.62 \times 10^{-8}$	$1.0 \times 10^{-5}$	$1.8 \times 10^5$
Mn	$8.1 \times 10^{-9}$	$3.0 \times 10^{-3}$	$3.7 \times 10^8$
Fe	$1.86 \times 10^{-8}$	$5.6 \times 10^{-4}$	$3.0 \times 10^7$
Cu	$7.5 \times 10^{-9}$	$9.4 \times 10^{-7}$	$1.3 \times 10^5$
Zn	$4.2 \times 10^{-9}$	$2.9 \times 10^{-6}$	$6.9 \times 10^5$
Ni	$3.0 \times 10^{-9}$	$5.8 \times 10^{-6}$	$1.9 \times 10^6$
Mo	$3.0 \times 10^{-9}$	—	—
V	$1.9 \times 10^{-9}$	—	—

<sup>a</sup>Takamatsu et al. (1985)

stations and V concentrations at stations Ie-1 and Nb-5 were 2.3 and 2.1  $\mu\text{mol/g}$ , respectively.

#### Cu, Zn, and Ni

D-Cu concentration was almost constant throughout the year. Although total P-Cu was analyzed, reliable data were not obtained because of the very low concentrations. It was reported that Cu is adsorbed more easily onto Mn oxides than Ba is (Murray et al. 1975). The average concentration of D-Cu was one-eighth that of D-Ba (Table 3). Therefore, if D-Ba in the bottom water decreases through adsorption onto Mn oxides, as mentioned above, D-Cu in the water should also decrease at the same time. However, the D-Cu concentration scarcely changed even at the late stage of the stagnation period (Fig. 6). This difference is inferred to be caused by most D-Cu in Lake Biwa water forming stable complexes (which are not easily adsorbed onto Mn oxides) with dissolved organic compounds in lake water. More than 50% of D-Cu in lake water was reported to be dissolved as organic complexes (Matsunaga and Igarashi 1982).

Vertical profiles of D-Zn and D-Ni were almost uniform in all seasons. However, markedly high concentrations of these metals were occasionally measured in the surface water during the stagnation period (Fig. 3). Some kinds of trace metals are enriched at very high concentrations in a thin layer at the surface (the surface microlayer) of a lake and the ocean through atmospheric input of the metals (Elzerman and Armstrong 1979; Hardy et al. 1985). The high values of Ni and Zn in the present work may have been related to such a surface microlayer. The vertical profile of P-Ni levels was not obtained because of its low concentration. Authigenic P-Zn concentration in October 1986 was highest at the surface of the lake and decreased with depth as shown in Fig. 7. This high concentration in the epilimnion corresponded to a low concentration of D-Zn in the layer (1–5 m, Fig. 4) and may have been caused by biological uptake, as seen for alkaline earth elements.

Distribution ratio of trace elements with respect to limnetic Mn nodules

Mn nodules are found on the sediment surface of the northern basin of Lake Biwa, as is also the case for other lakes and pelagic oceans. Many kinds of elements are accumulated in these nodules (Takamatsu et al. 1985). Based on the concentrations of major and trace elements in both lake water and manganese nodules, we calculated the apparent distribution ratios of the elements between these two phases. The values are tabulated in Table 6. Average dissolved concentrations at station Ie-1 in the circulation period of February and March 1987 were used as the concentrations in lake water for the calculation. As shown in the table, the order of their distribution ratios was:

$\text{Mn} > \text{Fe} > \text{Ni} > \text{Zn} > \text{Si} > \text{Ba} > \text{Cu} > \text{K} > \text{Mg} > \text{Sr} > \text{Na} > \text{Ca}$ .

Ni had the highest value of all elements studied except for Mn, Fe, and Si, which were host elements of the nodule, and was concentrated most preferentially in the nodule. Murray (1975) reported that the selectivity order of the elements for their adsorption onto synthesized hydrous Mn oxide was:

$\text{Cu} > \text{Zn} > \text{Ni} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$ .

On the other hand, the selectivity order in an adsorption experiment onto synthesized hydrous Fe oxide (Kinniburgh et al. 1976) was:

$\text{Cu} > \text{Zn} > \text{Ni} > \text{Sr} > \text{Mg}$  and  $\text{Ba} > \text{Ca} > \text{Sr} > \text{Mg}$ .

This difference between the selectivities in accumulation into natural limnetic nodules and in the adsorption experiment may have been caused by the difference in dissolved concentrations among the elements in Lake Biwa water, the coexistence of other elements and dissolved organic matter, and partial oxidation of the element after adsorption. The distribution ratio of an element onto Mn or Fe oxides de-



creases with an increase of equilibrium concentration in the aqueous phase (Duval and Kurbatov 1952; Glay and Malati 1979). Therefore, elements that dissolve at a low concentration in Lake Biwa water may have high distribution ratios. Because the adsorption reaction is competitive (Kinniburgh et al. 1976), the distribution ratio is affected by the chemical species and the concentration of coexisting elements. Dissolved organic matter may form dissolvable and stable complexes and colloids with some metals such as Cu and Fe (Matsunaga and Igarashi 1982; Cameron and Liss 1984), decreasing the distribution ratios of the metals. Some metals, such as Ni, are partially oxidized at the oxide-solution interface after their adsorption onto Mn oxide and are preferentially accumulated in the oxide (Takamatsu et al. 1993). Thus, Ni had a higher distribution ratio than Cu and was concentrated most preferentially in the nodules of the elements studied.

The distribution ratio is a very significant index in the study of the scavenging mechanism of dissolved elements from lake water to Mn nodules. When we have acquired the ratios for many other elements in addition to those studied in the present work, we will be able to discuss the mechanism in more detail.

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## References

- Batley GE, Farrar YJ (1978) Irradiation techniques for the release of bound heavy metals in natural waters and blood. *Anal Chim Acta* 99:283–292
- Borg H (1994) Trace elements in lakes. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC Press, Boca Raton, pp 177–201
- Brewer PG, Nozaki Y, Spencer DW, Fleer AP (1980) Sediment trap experiment in the deep North Atlantic: isotopic and elemental fluxes. *J Mar Res* 38:703–728
- Cameron AJ, Liss PS (1984) The stabilization of “dissolved” iron in freshwaters. *Water Res* 18:179–185
- Campbell NJ, Dengel AC, Edwards CJ, Griffith WP (1989) Studies on transition metal peroxo complexes. Part 8. The nature of peroxomolybdates and peroxotungstates in aqueous solution. *J Chem Soc Dalton Trans* 1203–1207
- Davison W (1993) Iron and manganese in lakes. *Earth-Sci Rev* 34:119–163
- Donat JR, Bruland KW (1994) Trace elements in the ocean. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC Press, Boca Raton, pp 247–281
- Duval JE, Kurbatov MH (1952) The adsorption of cobalt and barium ions by hydrous ferric oxide at equilibrium. *J Phys Chem* 56:982–984
- Elzerman AW, Armstrong DE (1979) Enrichment of Zn, Cd, Pb, and Cu in the surface microlayer of Lakes Michigan, Ontario, and Mendota. *Limnol Oceanogr* 24:133–144
- Falkner KK, Church M, Measures CI, LeBarron G, Thouron D, Jeandel C, Stordal MC, Gill GA, Mortlock R, Froelich P, Chan L-H (1997) Minor and trace element chemistry of Lake Baikal, its tributaries, and surrounding hot springs. *Limnol Oceanogr* 42:329–345
- Fujinaga T, Hori T (1982) Environmental chemistry on Lake Biwa (in Japanese). Japan Society for the Promotion of Science, Tokyo
- Glay MJ, Malati MA (1979) Adsorption from aqueous solution by  $\delta$ -manganese dioxide I. Adsorption of the alkaline-earth cations. *J Chem Tech Biotechnol* 29:127–134
- Haraguchi H, Itoh A, Kimata C, Miwa H (1998) Speciation of yttrium and lanthanides in natural water by inductively coupled plasma mass spectrometry after preconcentration by ultrafiltration and with a chelating resin. *Analyst* 123:773–778
- Hardy JT, Apts CW, Creselius EA, Fellingham GW (1985) The sea-surface layer: fate and residence times of atmospheric metals. *Limnol Oceanogr* 30:93–101
- Harita Y, Hori T, Sugiyama M (2005) Release of trace oxyanions from littoral sediments and suspended particles induced by pH increase in the epilimnion of lakes. *Limnol Oceanogr* 50:636–645
- Hem JD (1977) Reactions of metal ions at surfaces of hydrous iron oxide. *Geochim Cosmochim Acta* 41:527–538
- Henry R, Tundisi JG (1982) Evidence of limitation by molybdenum and nitrogen on the growth of the phytoplankton community of the Lobo Reservoir (Sao Paulo, Brazil). *Rev Hydrobiol Trop* 15:201–208
- Hori T, Sugiyama Y, Sugiyama M (1998) Chemical and physicochemical characteristics of dissolved organic carbon circulating in harmonic Lake Biwa, Japan. *Jpn J Limnol* 59:39–52
- Horie S (1984) Lake Biwa. DW Junk, Dordrecht
- Horne AJ, Goldman CR (1994) Limnology. McGraw-Hill, New York
- Irgolic KJ (1991) Determination of organometallic compounds in environmental samples with element-specific detectors. In: Krull IS (ed) Trace metal analysis and speciation. Elsevier, Amsterdam, pp 21–48
- Itasaka O (1974) Water quality of Lake Biwa (in Japanese). In: Limnological Institute, Shiga University (ed) Lake Biwa I. Sankyō Shuppan, Tokyo, pp 97–146
- Kawashima M, Takamatsu T, Koyama M (1988) Mechanisms of precipitation of manganese (II) in Lake Biwa, a freshwater lake. *Water Res* 22:613–618
- Kinniburgh DG, Jackson ML, Syers JK (1976) Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum. *Soil Sci Soc Am J* 40:796–799
- Lake Biwa Research Institute, National Institute for Research Advancement (1984) Data book of world lakes. LECS '84, Otsu
- Matsunaga K, Igarashi K (1982) Heavy metals and organic complexes (in Japanese). *Kaiyo Kagaku* 14:286–291
- 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
- Mito S, Sohrin Y, Norisuye K, Matsui M, Hasegawa H, Maruo M, Tsuchiya M, Kawashima M (2004) The budget of dissolved trace metals in Lake Biwa, Japan. *Limnology* 5:7–16
- Miyajima T (1994) Mud-water fluxes of inorganic nitrogen and manganese in the pelagic region of Lake Biwa: seasonal dynamics and impact on the hypolimnetic metabolism. *Arch Hydrobiol* 130:303–324
- Morris AW, (1975) Dissolved molybdenum and vanadium in the northeast Atlantic Ocean. *Deep-Sea Res* 22:49–54
- Murray JW (1975) The Interaction of metal ions at the manganese dioxide-solution interface. *Geochim Cosmochim Acta* 39:505–519
- Nakayama E, Okazaki S (1987) Marine electroanalytical chemistry (in Japanese). Bunseki, 296–302
- Nojiri Y (1992) Trace metals in freshwater (in Japanese). In: Chemical Society of Japan (ed) Chemistry of terrestrial water. Gakkai Shuppan Center, Tokyo, pp 45–55
- Nozaki Y (1992) Trace elements in sea water: their mean concentrations and North Pacific profiles (in Japanese). *Chikyū Kagaku* 26:25–39
- Otsu Hydrobiological Station (1988) Seventh report of the regular limnological survey of Lake Biwa during 1972–1987. Contr Otsu Hydrobiol Stn, Kyoto Univ No. 327:1–56
- Riley JP, Chester R (1983) Chemical oceanography. Academic, London
- Sagi K, Endo S, Kawashima M, Okumura Y, Hattori T, Nakayama S (1997) Seasonal variation of benthic nepheloid layer in Lake Biwa (in Japanese). *Jpn J Limnol* 58:27–44
- Sholkovitz ER, Copland D (1982) The chemistry of suspended matter in Esthwaite Water, a biologically productive lake with seasonally anoxic hypolimnion. *Geochim Cosmochim Acta* 46:393–410



- Sohrin Y, Matsui M, Kawashima M, Hojo M, Hasegawa H (1997) Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. *Environ Sci Technol* 31:2712–2720
- Somiya I (2000) Lake Biwa (in Japanese). Giho-do, Tokyo
- Stumm W, Morgan JJ (1996) *Aquatic chemistry* 3rd edn. Wiley Interscience, New York
- Sugiyama M (1989) Seasonal variation of vanadium concentration in Lake Biwa, Japan. *Geochem J* 23:111–116
- Sugiyama M (1996) Simultaneous multi-element analysis of aquatic suspended particulate matter (in Japanese). *Bunseki Kagaku* 45:667–675
- Sugiyama M (2000) Biological activity and environmental change (in Japanese). In: Tsuda K, Ogawa T (eds) *Life and environment*. Kyoto University Academic Press, Kyoto, pp 117–142
- Sugiyama M (2004) Suspended particulate matter in a freshwater (in Japanese). *Bunseki*, 412–414
- Sugiyama M, Hori T (1994) Geochemical behavior of barium in the vicinity of a  $\text{MnO}_2/\text{Mn}^{2+}$  redox front formed in a eutrophic lake. *Jpn J Limnol* 55:27–37
- Sugiyama M, Hori T (1996) Suspended particulate elements in anoxic hypolimnion of a eutrophic lake. *Trans Res Inst Oceanochem* 9:8–22
- Sugiyama M, Fujino O, Kihara S, Matsui M (1986) Preconcentration by dithiocarbamate extraction for determination of trace elements in natural waters by inductively-coupled plasma atomic emission spectrometry. *Anal Chim Acta* 181:159–168
- Sugiyama M, Hori T, Kihara S, Matsui M (1992) A geochemical study on the specific distribution of barium in Lake Biwa, Japan. *Geochim Cosmochim Acta* 56:597–605
- Takaku Y, Akiba S, Hayashi T, Kano M, Ohtsuka Y (2003) Development of “all-ium” analytical method for water samples at Lake Biwa. In: Holland G, Tanner SD (eds) *Plasma source mass spectrometry*. The Royal Society of Chemistry, Cambridge, pp 105–111
- Takamatsu T, Kawashima M, Matsushita R, Koyama M (1985) General distribution profiles of thirty-six elements in sediments and manganese concretions of Lake Biwa. *Jpn J Limnol* 46:115–127
- Takamatsu T, Kawashima M, Takada J, Matsushita R (1993) Characteristics in elemental composition of ferromanganese concretions from Lake Biwa. *Jpn J Limnol* 54:281–291
- Tanaka M (1992) *The lakes of Japan* (in Japanese). Nagoya Daigaku Shuppankai, Nagoya
- Taylor SR, McLennan SM (1985) *The continental crust*. Blackwell Scientific Publications, Oxford