RESEARCH PAPER

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Seasonal variation of dissolved aluminum concentration in harmonic-type Lake Biwa, Japan

Abstract Monthly observations performed on a typical harmonic-type lake, Lake Biwa (latitude 35°15′ N, longitude 136°05′ E, Japan), showed that the particulate aluminum concentration varied around a mean value of $0.8\mu M$, with occasional extraordinarily high values, whereas the dissolved aluminum concentration varied, in the surface layer of the whole lake, between a minimum of $0.01\mu M$ and a maximum of $0.30\mu M$, depending on the season. Although the variation in dissolved aluminum paralleled the variation in the pH of the lake water, the variation in dissolved aluminum lagged behind the variation in pH by approximately 1 month. A series of laboratory incubation experiments suggested that the supply of dissolved aluminum from, and its removal by, the suspended particulate matter involved a slow, pH-dependent reaction. The stoichiometry and the apparent equilibrium constant of this reaction were evaluated by adopting a zeolite-like structure for the surfaces of the suspended particulates.

Key words Dissolved aluminum · Lake Biwa · Seasonal variation · pH

Introduction

Although aluminum is the third most abundant element in the earth's crust after oxygen and silicon, its concentration in natural waters is maintained at extremely low levels. This is attributable, on the one hand, to the low solubility of aluminosilicate minerals in natural waters (Whitfield and Turner 1987) and, on the other hand, to the high reactivity of once-dissolved aluminum toward the surfaces of particulates suspended in natural waters (Stumm and Furrer 1987). In general, it can be said that the natural levels of dissolved aluminum in terrestrial waters that are in contact with aluminosilicate minerals are maintained in a range of 0.01 to $1\mu M$ (Hydes and Liss 1976; Lum and Leslie 1983; Stabel et al. 1991; Sutheimer and Cabaniss 1995), and that levels in the water of deep lakes (such as Lake Baikal, Russia) and in deep seawater are maintained in the low range of 0.0005 to $0.005\mu M$ (Falkner et al. 1997; Bruland et al. 1994).

In seawater, the concentrations of dissolved aluminum can be explained rather simply. In deep seawater in pelagic parts of the ocean, the concentrations are balanced between input from the atmosphere and removal by adsorption to suspended particulate matter (Bruland et al. 1994). In seawater of coastal regions, concentrations are balanced between input from rivers and removal by biological activity (Moran and Moore 1988a, b; 1992). Mackin and coworkers (Mackin and Aller 1989; Mackin and Swider 1987) claimed that concentrations of dissolved aluminum in estuarine or shallow areas, where seawater contains much suspended matter ($>200\,mg\,l^{-1}$), were regulated by equilibrium reactions among dissolved silica, dissolved aluminum, and solid aluminosilicate minerals.

In acidic-type lakes, at low pH values of 4 to 5, levels of dissolved aluminum are usually higher than several micromoles per liter, and at these high concentrations, aluminum becomes hazardous to aquatic fauna (Driscoll et al. 1980). Major concerns in the study of aluminum in acidified waters are the speciation of aluminum and assessment of the toxicity of soluble aluminum (Bloom and Erich 1996).

In neutral and oligotrophic or eutrophic lakes, which are limnologically categorized as harmonic-type lakes, investigators have studied aluminum as one of the so-called trace elements. In Lake Erie in the United States, for instance, Lum and Leslie (1983) measured aluminum concentrations, along with those of eight other trace elements, and reported a steady concentration of dissolved aluminum of about

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0.1 μM. Sutheimer and Cabaniss (1995) observed concentrations of dissolved aluminum from 0.08 μM (in the epilimnion) to 0.03 μM (in the hypolimnion) in East Twin Lake, Ohio, United States. Stabel et al. (1991) suggested a possible dissolution of aluminum from gibbsite [Al(OH)$_3$] in soils when the water level of the lake rose to flood the shore and when the pH of the lake water increased above 7 due to high primary production during the warm season.

Studies of dissolved aluminum are concerned not only with its geochemical and geological behavior as a typical trace element, but also with how to preserve the inherent aquatic nature of rivers and lakes against the effects of dissolved aluminum.

As briefly reviewed above, however, geochemical and geological studies performed thus far have not sufficiently discussed the dissolved aluminum in harmonic-type lakes in relation to the total or bulk aluminum contained in particulate matter, in spite of the fact that such particulate matter is the main source and scavenger of dissolved aluminum in natural waters.

In this article, we report the seasonal variations and the distribution patterns of dissolved aluminum in harmonic-type Lake Biwa and propose a possible reaction mechanism underlying the supply and removal of the dissolved aluminum in regard to the pH of the lake water and the season.
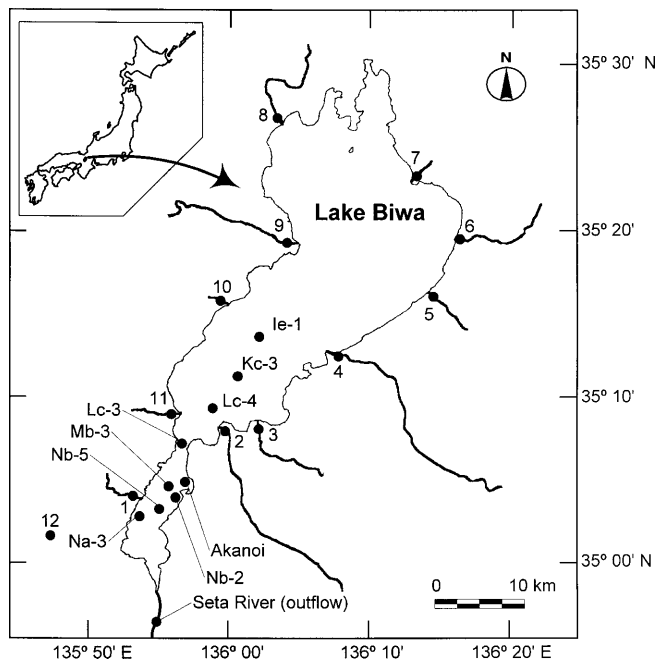
Field observations

Observation setting

Lake Biwa, the largest lake in Japan, contains 27.3 km^3 of freshwater and has been supporting the daily use of water by 14 million residents of the Kinki district. The lake consists of two basins: the northern, main basin has a surface area of 616 km^2 and a capacity of 27.1 km^3, with average and maximum depths of 44 and 104 m; the southern, sub-basin has a surface area of 58 km^2 and a capacity of 0.2 km^3, with average and maximum depths of 3.5 and 8 m. The lake water flows out through the Seta River, which is located at the south end of Lake Biwa. The water level of the lake is regulated in a range of +0.3 to −1.5 m by operating a floodgate on the Seta River.

In Lake Biwa (Fig. 1), a total of nine sampling sites were located as follows. Site Ie-1 (73 m depth) was located in the northern basin, which is now mesotrophic. In the basin, thermal stratification occurs regularly from May to December. Site Nb-5 (4 m depth) was located near the center of the southern basin. Between Ie-1 (north) and Nb-5 (south), a series of sites (Kc-3, Lc-4, Lc-3, and Mb-3) were located along the centerline of the lake. Sites Nb-2 (southeast) and Na-3 (southwest) were near the shore of the southern basin, and the Akanoi site (2 m depth) was at the mouth of Akanoi Bay (southeast), which exhibits a eutrophic nature.

In order to estimate the input of aluminum from the catchment area of Lake Biwa, sampling sites 1 through 11 (see also Fig. 1) were located at the mouths of the 11 rivers, all of which flow into Lake Biwa. In addition, we collected

Fig. 1. Map showing the sampling sites in Lake Biwa. The sampling sites to collect river water (sites 1–11) and rainwater (site 12) are also shown. Site 1, Ohmiya River; site 2, Yasu River; site 3, Hino River; site 4, Echi River; site 5, Seri River; site 6, Amano River; site 7, Ane River; site 8, Chinai River; site 9, Ado River; site 10, Ukawa River; site 11, Wani River

rainwater on the roof of a 30-m-tall building located 7 km southwest of Lake Biwa (site 12 in Fig. 1) in order to monitor the aluminum input through precipitation.

Sampling

At the nine sampling sites in the lake, we took 1-l samples directly into sampling bottles at 1-month intervals during the period from July 1992 through March 1995. At Ie-1, we also took samples with a Van Dorn sampler at depths of 1, 5, 10, 15, 20, 30, 40, 50, 60, 70, and 73 m (bottom). In addition, we took river-water samples four times during the period from March 1994 through January 1995. We collected rainwater continuously during the period from May through December 1994.

Until we analyzed the samples in the laboratory, we stored them in low-density polyethylene bottles (Nalgene, Nalge Nunc, NY, USA), which we had previously cleaned by soaking them in baths of 10% Scat and 4 M HCl, followed by thorough rinsing with water purified by a Milli-Q SP (Millipore, MA, USA) system (hereafter called MQ-water) and subsequent storage under ice-cooled, dark conditions.

Determination of dissolved and particulate aluminum

We subjected the water samples to two types of pretreatments, termed F and A. Treatment F denotes filtration with a Nuclepore (Whatman, MA, USA) membrane filter with a pore size of 0.4 μm, and treatment A denotes drying of a

20-ml aliquot of unfiltered sample in a platinum crucible with 2 ml of 12.5% Na_2CO_3, followed by alkali carbonate fusion, dissolving the resultant cake with 5 ml of 2 M HCl, and diluting the solution to 40 ml with MQ-water.

After the respective treatments, we determined the aluminum content in each sample according to the lumogallion method (Shigematsu et al. 1970): (1) We added a 0.4-ml aliquot of 4% hydroxylamine hydrochloride to an 8-ml portion of each sample and left the mixture for 30 min. (2) We then successively added 0.4 ml of 1% o-phenanthroline in 1 M HCl, 0.2 ml of 0.01% lumogallion, and 1 ml of 20% CH_3COONH_4 to the sample, and heated the mixture to 80°C for 30 min. (3) After the mixture had cooled to ambient temperature, we measured the fluorescence intensities at $\lambda = 576$ nm (Exn. $\lambda = 485$ nm) and compared the results with a calibration graph. We termed the aluminum contents after treatments F and A as Al(F) and Al(A), respectively. All of the data on Al(F) and Al(A) are reported elsewhere, along with those for silicate, phosphate, ammonia-N, nitrate-N, and dissolved organic carbon (Hori et al. 1996) and with the water temperature, pH, chlorophyll a, and dissolved oxygen, which were measured at the same time by a crew from the Center for Ecological Research of Kyoto University (Ueda et al. 1998).

According to Hydes and Liss (1976), Al(F) thus evaluated corresponds to the total concentration of all forms of aluminum dissolved in the filtered water samples, whereas Al(A) is the sum of the dissolved aluminum and the particulate aluminum which is made reactive with lumogallion after alkali carbonate fusion. By using both concentrations of aluminum, Al(F) and Al(A), and using the relations below, we obtained the concentrations of the dissolved and particulate aluminum:

Concentration of dissolved aluminum = Al(F)
Concentration of particulate aluminum = Al(A) − Al(F)

In parallel with the evaluation of Al(F) and Al(A), the detection limit and the precision (relative standard deviation) were examined by analyzing the aluminum solutions five times at concentrations of 0 (MQ-water alone), 0.01, and 0.1 μM. As a result, it was ensured that the fluorescence intensities after treatment F for 0, 0.01, and 0.1 μM aluminum solutions were, respectively, 2.9 ± 0.3, 3.8 ± 0.3, and 12.2 ± 0.5, and that the detection limit and the precision for Al(F) were 0.01 μM and 5% (at 0.1 μM level), respectively. In a similar manner, it was also ensured that the detection limit and the precision for Al(A) were 0.04 μM and 10% (at 0.2 μM), respectively.

Results

Characteristics of the variations of dissolved aluminum and particulate aluminum

In Fig. 2, we show the monthly variations of particulate and dissolved aluminum, which were observed at the surface layer of Ie-1. The particulate aluminum (Fig. 2A) varied rather simply around a mean concentration of 0.8 μM, with
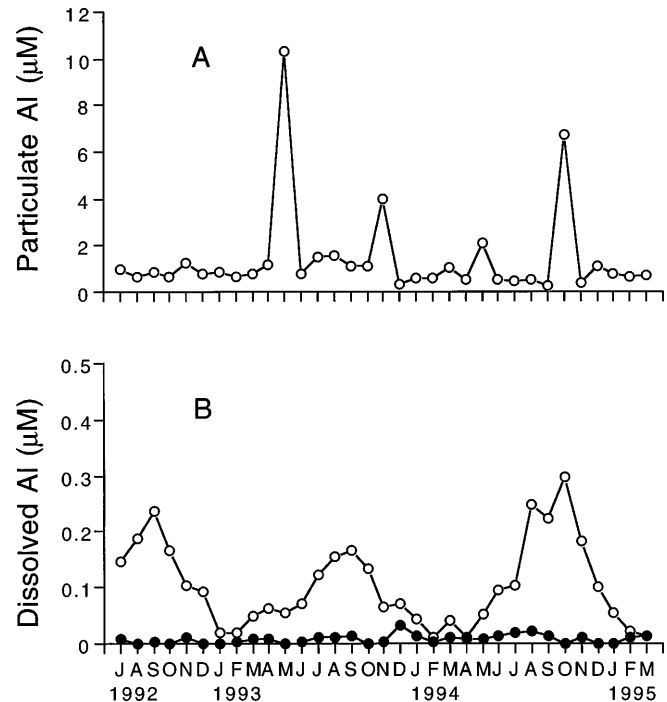

Fig. 2. Monthly variations (○) in (**A**) particulate aluminum concentration and (**B**) dissolved aluminum concentration observed in the surface layer (0 m depth) at site Ie-1 of Lake Biwa, Japan, from July 1992 through March 1995. Variation in dissolved aluminum (●) in the bottom layer (73 m) at the same site

a few extraordinarily high values. Although we do not yet fully understand why, we observed such high values four times during the observation period of 2 yeas and 9 months, with magnitudes of 10.3 μM (May 1993), 4.0 μM (November 1993), 2.1 μM (May 1994), and 6.7 μM (October 1994).

In contrast, the variation of the dissolved aluminum (Fig. 2B) was periodic with a 1-year cycle; the concentration of dissolved aluminum started to increase from 0.01 μM in April, reached a maximum in the range of 0.15 to 0.30 μM in September or October, and then decreased to 0.01 μM in February.

We observed similar variations at sites Kc-3, Lc-3, Lc-4, Mb-3, Nb-5, Na-3, Nb-2, and Akanoi (Fig. 3). One can easily see by comparing Fig. 2B with Fig. 3A and B that these variations in dissolved aluminum followed basically the same pattern, irrespective of the wide differences in the geological or limnological natures of the observation sites. In other words, the seasonal variations in dissolved aluminum in the surface layer occurred quite similarly over the whole lake.

In contrast, the dissolved aluminum in the hypolimnion at site Ie-1 varied little and remained at steady concentrations below 0.03 μM, exhibiting a maximum of only 0.03 μM in December 1993 and several minimal values below 0.01 μM in August, October, and December 1992; in January, May, and October 1993; and in October and December 1994 (closed circles in Fig. 2B). We observed no sign of seasonal variations in dissolved aluminum in the hypolimnion.
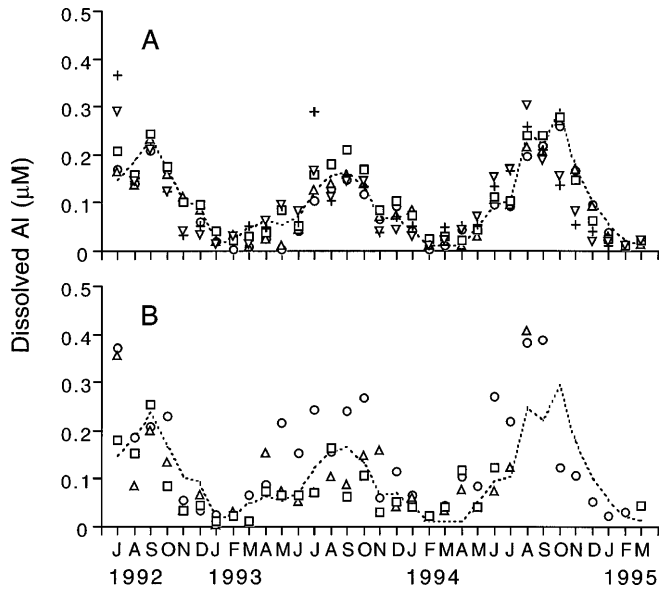
Fig. 3. Monthly variations in dissolved aluminum observed in the surface layers at sites (**A**) Kc-3 (○), Lc-4 (△), Lc-3 (□), Mb-3 (+), and Nb-5 (▽); and (**B**) Na-3 (○), Nb-2 (△), and Akanoi (□). For comparison, the variation in dissolved aluminum at Ie-1 (0 m) is transferred from Fig. 2B and shown by the *dotted lines*

According to the calculation given in Appendix 1, we estimated the increasing (or decreasing) rate with time (months) of dissolved aluminum in the whole lake. In the calculation, by using the dissolved aluminum concentration in the epilimnion and the volume of the epilimnion, the amount of dissolved aluminum in the epilimnion in each month was obtained, followed by its addition to the corresponding amount of aluminum in the hypolimnion to obtain the amount of aluminum in the whole lake. It is seen from the bottom row of Appendix 1 that the dissolved aluminum contained in the whole lake increased at an average rate of 414×10^3 mol month^{-1} during the period from March 1994 through October 1994, and decreased at an average rate of 580×10^3 mol month^{-1} during the period from October 1994 through March 1995. It is temporarily inferred here that such variation (increase and decrease) of the dissolved aluminum would be caused by its material balance between the input from rivers and rain and the outflow through the Seta River or by the interactions with dissolved silica and/or the siliceous walls of diatoms. These factors can be examined as follows.

Effect of river water and rainwater on the variation in dissolved aluminum in the lake

According to the calculation in Appendix 2, on average, rivers and rain brought dissolved aluminum into Lake Biwa at respective rates of 22×10^3 and 32×10^3 mol month^{-1}, whereas dissolved aluminum flowed out of the lake through the Seta River at a rate of 21×10^3 mol month^{-1}. As the balance between input and outflow, the net amount of dissolved aluminum remaining in the lake was estimated to be 33×10^3 mol month^{-1}, which is 8% in the increase in the

dissolved aluminum in the lake (414×10^3 mol month^{-1}, Appendix 1). Thus, river water and rainwater seemed to have minor effects on the variation in dissolved aluminum in the lake.

Weak correlation between dissolved aluminum and dissolved silica in Lake Biwa

Mackin and coworkers (Mackin and Aller 1989; Mackin and Swider 1987) conducted a study on the dissolution–precipitation equilibrium of various kinds of aluminosilicates, including standard minerals and natural sediments; the concentration of dissolved aluminum was measured against the varying concentration of dissolved silica (ranging from 0.002 to 1.6 mM Si) in the presence of the minerals. They found that the product of the concentrations of dissolved aluminum and dissolved silica became a constant [Al/μM][Si/mM] = 0.01. In the present observations on Lake Biwa, however, the concentration of dissolved silica always remained below 0.03 mM (see the third column of Table 1), and the product of [Al][Si] in the lake varied

Table 1. Correlations of dissolved Al with Si, chlorophyll *a* (Chl *a*), and diatom abundance at Ie-1

Month and year	Dissolved Al (μM)	Dissolved Si[a] (mM)	Chl *a*[b] (μg L^{-1})	Diatoms[c] (cells ml^{-1})
Jul 92	0.15	0.013	8.05	120
Aug 92	0.19	0.020	2.15	4
Sep 92	0.24	0.030	1.92	10
Oct 92	0.17	0.027	2.48	85
Nov 92	0.11	0.021	4.16	126
Dec 92	0.09	0.017	5.89	159
Jan 93	0.02	0.019	4.11	52
Feb 93	0.02	0.023	2.97	52
Mar 93	0.03	0.023	2.88	93
Apr 93	0.02	0.023	1.72	53
May 93	0.05	0.027	9.29	67
Jun 93	0.07	0.021	4.01	309
Jul 93	0.12	0.013	6.49	1019
Aug 93	0.16	0.020	2.16	18
Sep 93	0.17	0.025	6.95	137
Oct 93	0.13	0.022	5.72	237
Nov 93	0.07	0.009	3.36	280
Dec 93	0.07	0.007	2.51	147
Jan 94	0.04	0.016	2.34	nd[d]
Feb 94	0.01	0.016	2.26	nd
Mar 94	0.01	0.018	2.02	nd
Apr 94	0.01	0.011	1.69	2605
May 94	0.05	0.003	2.99	67
Jun 94	0.10	0.008	1.24	5
Jul 94	0.10	0.009	1.32	0
Aug 94	0.25	0.013	0.55	10
Sep 94	0.22	0.016	0.42	17
Oct 94	0.30	0.012	2.52	730
Nov 94	0.18	0.009	1.18	44
Dec 94	0.10	0.005	3.04	390
Jan 95	0.05	0.005	2.47	160
Feb 95	0.02	0.013	1.32	23
Mar 95	0.01	0.013	1.15	41

[a] From Hori et al. (1996)
[b] From Ueda et al. (1998)
[c] Sum of the cell numbers of the dominant species; *Stephanodiscus carconensis* var. *pusilla* and *Fragilaria crotonensis* (Shiga Prefectural Institute of Public Health and Environmental Science 1995, 2000)
[d] nd, Not determined

Appendix 1. Increase of dissolved Al in Lake Biwa

Measurement	Mar 94	Apr 94	May 94	Jun 94	Jul 94	Aug 94	Sep 94	Oct 94	Nov 94	Dec 94	Jan 95	Feb 95	Mar 95
Dissolved Al concentration in epilimnion (μM)	0.01	0.01	0.05	0.10	0.10	0.25	0.22	0.30	0.18	0.10	0.05	0.02	0.01
Volume of epilimnion ($\times 10^9\,m^3$)[a]	0.0	2.5	7.5	7.5	7.5	7.5	7.5	10.0	14.5	14.5	15.5	25.5	25.5
Dissolved Al content in epilimnion ($\times 10^3\,mol$)[b]	0	25	375	750	750	1875	1650	3000	2610	1450	775	510	255
Dissolved Al content in hypolimnion ($\times 10^3\,mol$)[c]	273	248	198	198	198	198	198	173	128	128	118	18	18
Dissolved Al content in lake ($\times 10^3\,mol$)	273	273	573	948	948	2073	1848	3173	2738	1578	893	528	273
Average rate of increase in the dissolved Al in lake ($\times 10^3\,mol\,month^{-1}$)	414 (Average increase rate during the 7 months from Mar 94 to Oct 94)								−580 (Average increase rate during the 5 months from Oct 94 to Mar 95)				

[a] Obtained from the observed depth of the thermocline and the depth–volume diagram of Okamoto (1992)
[b] Calculated from the product of [dissolved Al concentration in epilimnion] and [volume of epilimnion]
[c] Calculated from the product of [dissolved Al concentration in hypolimnion = 0.01 μM] and [volume of hypolimnion]

between a minimum of 0.0001 and a maximum of 0.007, suggesting that the water of the lake was not saturated with aluminosilicate minerals.

Weak correlation of dissolved aluminum with chlorophyll *a* and diatom abundance

In coastal seawater, Moran and Moore (1988a,b) observed decreases in dissolved aluminum accompanying diatom blooms. Moran and Moore (1992) concluded that the removal of dissolved aluminum from the seawater was due to its adsorption onto diatom frustules. As can be seen from data on chlorophyll *a* and the cell numbers of the two dominant species of diatom (Table 1), diatom abundance in Lake Biwa became high in early summer (June 1992; June and July 1993) and late autumn (October, November, and December 1992; October, November, and December 1993; October and December 1994), whereas dissolved aluminum showed no tendency to decrease in early summer. In other words, in Lake Biwa, diatom blooms were not the main factor in the decrease in dissolved aluminum.

Strong correlation of dissolved aluminum with pH and water temperature

Figure 4A and B shows the variations in water temperature and pH that we observed at the surface of site Ie-1. In Fig. 4A, one can see at a glance that the variation in water temperature coincided with the variation in dissolved aluminum, and a high correlation coefficient (0.85) was obtained. Figure 4B shows a similar relationship between pH and dissolved aluminum, but the correlation coefficient was
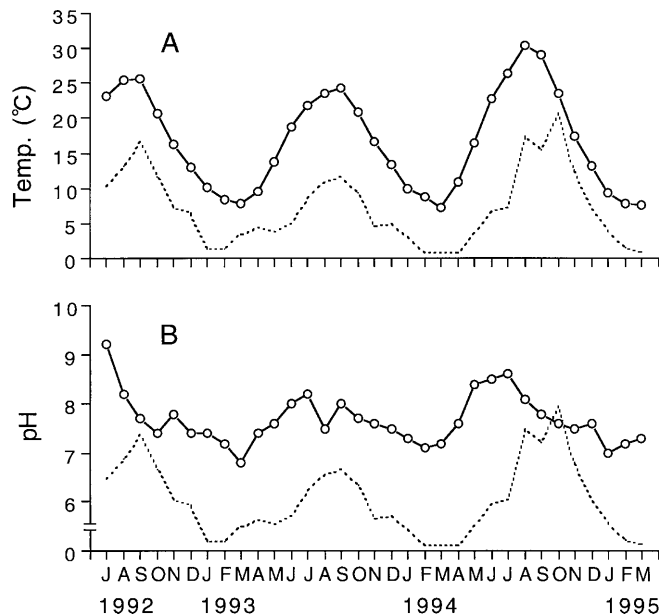

Fig. 4. Monthly variations in (**A**) water temperature and (**B**) pH observed in the surface layer at Ie-1. For comparison, the variation in dissolved aluminum in the surface at Ie-1 (0 m) is superimposed and shown by *dotted lines* in both panels

low (0.39). This low correlation coefficient, however, was due to the time lag of approximately 1 month between the variation in dissolved aluminum and the variation in pH. During the period from July through August in 1992, 1993, and 1994, when the pH tended to decrease, the dissolved aluminum tended to increase, and during the period from March through May in 1993 and 1994, the increase in pH was rather steeper than the increase in dissolved aluminum (see Fig. 4B). As a consequence, the maximal value of dissolved aluminum appeared approximately 1 month behind the maximal value of pH. When we recalculated the correlation coefficient by pairing dissolved aluminum values with the pH values observed on the date 1 month prior to the observation of dissolved aluminum, the correlation coefficient increased to 0.65.

As we describe below, a series of incubation experiments in our laboratory confirmed that the correlation between dissolved aluminum and water temperature was a matter of secondary importance, but the correlation between dissolved aluminum and pH had geochemical significance with respect to aluminum circulating in natural waters.

Laboratory incubation experiments

For the incubation experiments to characterize the aluminum in Lake Biwa, we took an additional five samples (samples 1–5) at selected sites in the lake. We list the sampling sites and dates, water temperatures, pH values, aluminum contents, and Al/Si ratios in particulate matter of these samples in the second to sixth columns of Table 2. We chose sample 1 (Ie-1, 0 m depth, April) and sample 2 (Na-3, 0 m depth, April) to represent the lake water under conditions in which the dissolved aluminum was minimal in both the northern and the southern basins. We took sample 3 (Ie-1,

0 m depth, September) and sample 4 (Ie-1, 60 m depth, September) to represent the lake under conditions in which the dissolved aluminum was highest, and we used sample 5 (Akanoi, 0 m depth, September) to characterize the aluminum contained in highly eutrophic water.

Effect of water temperature on dissolved aluminum

Without filtration, we transferred 100-ml aliquots of samples 1 to 5 into low-density polyethylene bottles (capacity 125 ml, Nalgene) with screw caps and incubated them at 30°C (which represented a summer water temperature) with shaking at a stroke rate of 1 Hz. After 1 week, we evaluated the dissolved aluminum concentration in an approximately 15-ml aliquot of each sample. We then incubated the same samples for another week at 10°C (a winter temperature) and evaluated dissolved aluminum again. Irrespective of the difference in the incubating temperatures, the dissolved aluminum concentrations before and after the incubation remained unchanged within a ±5% experimental error. Thus, water temperature had little effect on the variations in dissolved aluminum in the lake water.

Effects of pH and incubation time on dissolved aluminum

Without filtration, we placed a series of 200-ml aliquots of each sample listed in Table 2 into low-density polyethylene bottles (250 ml) as described above and adjusted the pH values of the samples within a range from 6 to 11 by adding small volumes of NaOH or HCl solution. After we adjusted the pH, we set the clock to $t = 0$ and evaluated the dissolved aluminum concentration in an approximately 15-ml aliquot of each sample; we incubated the sample remaining in the bottle at 25°C for succeeding measurements of pH and dissolved aluminum.

Appendix 2. Input of dissolved Al into Lake Biwa and outflow of dissolved Al from Lake Biwa

Measurement	Minimum	Maximum	Average
Total input of dissolved Al from all rivers ($\times 10^3$ mol month^{-1})[a]	4	44	22
Input of dissolved Al from rain ($\times 10^3$ mol month^{-1})[b]	1	93	32
Outflow of dissolved Al through the Seta River ($\times 10^3$ mol month^{-1})[c]	2	56	21

[a] By knowing (1) the concentration of dissolved Al in river water (observed at sampling sites 1 through 11 in March, July, and December 1994 and January 1995 in this study) and (2) the flow rate of the rivers (Shiga Prefecture 1995), we were able to estimate (3) the total input of dissolved Al through the rivers per month, for the 11 main rivers that flow into the lake. Since we knew that the sum of the water of the 11 rivers accounts for 56% of the total inflow of river water into Lake Biwa (Kunimatsu 1981), the total input of dissolved Al from all of the rivers could be estimated at {(3)/0.56}

[b] By knowing the concentration of dissolved Al in rainwater (observed at sampling site 12 in May, June, July, and December 1994 in this study) and the amount of rain that fell on Lake Biwa, which was calculated from the surface area of Lake Biwa and the record of precipitation (River Bureau, Japan Ministry of Construction 1996b, 1997b), we calculated the input of dissolved Al from rainwater per month

[c] By knowing the dissolved Al concentration at the surface layer of the lake (this study) and the outflow rate of the lake water through the Seta River (River Bureau, Japan Ministry of Construction 1996a, 1997a), we estimated the outflow of dissolved Al from the lake per month, during the period from March 1994 through March 1995

Table 2. Specification of lake-water samples 1–5 and results of the incubation experiment

Sample no.	Sampling site and date	Before incubation				After incubation			
		Temp (°C)	pH	$Al_{int}{}^{a}$ (μM)	Al/Si^{b} (mol mol^{-1})	n^{c}	$\log K + n \log K_{W}{}^{d}$	$\log K^{e}$	$Al_{fin}{}^{f}$
1	Ie-1 (0–m depth), 13 Apr 95	9.6	7.4	0.02	0.38	1.77	−14.5	10.3	0.09
2	Na-3 (0–m depth), 13 Apr 95	13.7	7.6	0.12	0.36	1.73	−13.6	10.7	0.26
3	Ie-1 (0–m depth), 13 Sep 95	24.6	8.2	0.23	0.004	0.14	−1.73	0.23	0.26
4	Ie-1 (60–m depth), 13 Sep 95	8.0	7.0	0.02	0.008	0.72	−6.76	3.32	0.06
5	Akanoi (0–m depth), 13 Sep 95	26.0	8.2	0.04	0.077	3.18	−23.9	20.6	0.20

[a] Dissolved aluminum concentration before incubation
[b] Atomic ratio of Al/Si found in the suspended particulate matter
[c] Slope value evaluated from the regression line in Fig. 6
[d] Intercept value from the regression line in Fig. 6
[e] Equilibrium constant expressed by Eq. 2
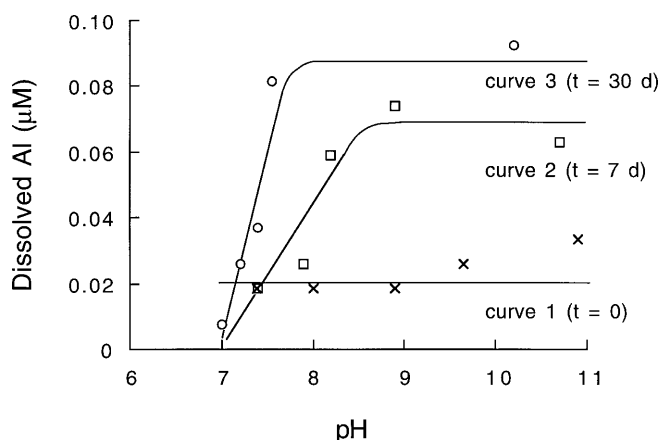[f] Dissolved aluminum concentration after incubation at pH > 8

Fig. 5. Dependence of dissolved aluminum on pH as shown by incubation experiments performed using the lake water (sample 1) specified in Table 2. The plot of dissolved aluminum concentration vs. pH changed from curve 1 ($t = 0$) to curve 2 ($t = 7$ days) and converged ultimately to curve 3 ($t = 30$ days) upon incubation at 25°C

Fig. 6. Relationships of log{dissolved Al/μM} vs. pH attained with samples 1–5 (listed in Table 2) incubated for $t > 30$ days at 25°C. (□) Sample 1 (Ie-1, 0 m, Apr); (◇) sample 2 (Na-3, 0 m, Apr); (△) sample 3 (Ie-1, 0 m, Sept); (×) sample 4 (Ie-1, 60 m, Sept); (○) sample 5 (Akanoi, 0 m, Sept)

We repeated measurements of dissolved aluminum and pH at $t = 7$, 30, and 40 days and plotted the values of dissolved aluminum against the corresponding pH values. The values of dissolved aluminum in sample 1 are plotted against pH as a function of the incubation time in Fig. 5. Curve 1 in the figure shows the relationship between dissolved aluminum and pH measured immediately after pH adjustment ($t = 0$) and indicates that dissolved aluminum was little changed from its initial value (before pH adjustment) of 0.02 μM, even though the pH varied from 7.4 to 9.0 in the presence of the suspended particulate matter that was present in the original sample.

On continuing incubation, the relationship between dissolved aluminum and pH changed gradually from curve 1 to curve 2 ($t = 7$ days) and converged ultimately to curve 3 ($t = 30$ days). Because we had previously confirmed that both the contaminating elution of aluminum from, and the adsorptive removal of aluminum to, the walls of the sample containers were negligible under the existing conditions, the increase and decrease in dissolved aluminum could be attributed to the dissolution of aluminum from, and the adsorption of aluminum to, suspended particulate matter.
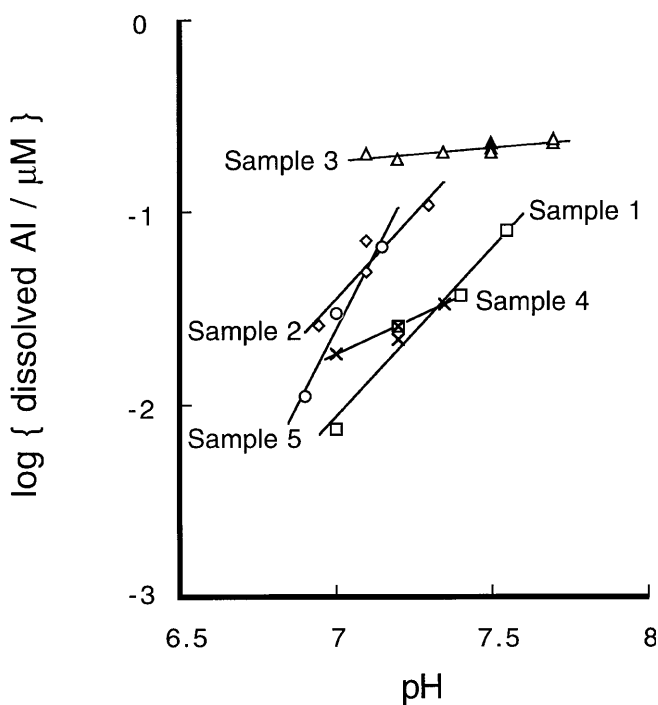
Comparison of curve 1 ($t = 0$) with curve 3 ($t = 30$ days) indicates that the initial concentration of dissolved aluminum had a tendency to decrease with time at pH < 7.2 and a tendency to increase with time at pH > 7.2. The comparison also shows that the final concentration of dissolved aluminum attained after $t = 30$ days was dependent on pH in the region of pH < 8, but independent of pH at pH > 8. The pH-independent values of dissolved aluminum, found in the plateau region of curve 3, were termed Al_{fin} and are listed in the tenth column of Table 2.

Along with this result, we replotted the pH-dependent part of curve 3 at pH < 8 on a graph of log{dissolved Al/μM} vs. pH (Fig. 6). Regression analysis of the plot yielded a straight line expressed as

$$\log\{\text{dissolved Al}/\mu M\} = 1.77 \cdot \text{pH} - 14.5$$

The regression line is superimposed in Fig. 6. We created similar plots for the other four samples; their regression lines are also shown in Fig. 6. We used the values of the slopes and intercepts for the respective lines to evaluate the characteristics of aluminum in the lake, as discussed in the next section.

Discussion

The increase and decrease in dissolved aluminum in the lake-water samples were dependent not only on the pH but also on how long we incubated the samples with the suspended particulate matter. To understand the characteristics of dissolved aluminum, we show one of the possible reactions schematically in Fig. 7, in which we adopted a zeolite-like structure for the surface of the particulate matter (Sauer et al. 1994). In the scheme, n denotes the number of OH^- ions that release $[Al(OH)_4]^-$, which we assumed to be the main form of dissolved aluminum, from the surfaces of the particulate matter. According to the scheme, the stoichiometry of the reaction can be given as

$$[Al - SS]^- + n \cdot OH^- \rightleftarrows [Al(OH)_4]^- + [SS]^{-n} \qquad (1)$$
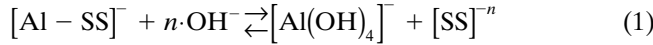
Here, SS denotes suspended solid.
The equilibrium constant K and the dependence of dissolved aluminum on pH are given as
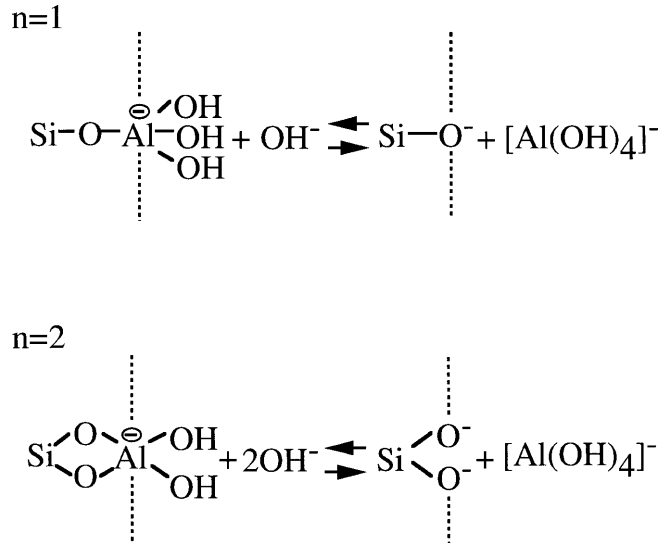
n=1

n=2

Fig. 7. Schematic representation of the dissolution of aluminum from, and the adsorption of aluminum to, the surfaces of particulate matter suspended in lake water. It was assumed that the coordination sphere of aluminum is hexagonal and the cleavage of Si-O-Al bonding(s) occurs by one ($n = 1$) or two ($n = 2$) equivalent amounts of OH^-

$$K = \left\{[Al(OH)_4]^-\right\}\left\{[SS]^{-n}\right\} \bigg/ \left\{[Al - SS]^-\right\}[OH^-]^n$$

$$= \left\{[Al(OH)_4]^-\right\}\left\{[SS]^{-n}\right\}\left\{H^+\right\}^n \bigg/ \left\{[Al - SS]^-\right\}(K_w)^n$$

$$(2)$$

$$\log\left\{[Al(OH)_4]^-\right\} = n \cdot \text{pH} + \log K + n \cdot \log K_w$$

$$+ \log\left\{[Al - SS]^-\right\}\bigg/\left\{[SS]^{-n}\right\} \qquad (3)$$

In Eq. 1, $[Al - SS]^-$ denotes the aluminum contained in the particulate matter. By applying Eq. 3 to the plots of $\log\{\text{dissolved Al}/\mu M\}$ vs. pH and by using the intercept, $\log K + n \cdot \log K_w + \log\{[Al - SS]^-\}/\{[SS]^{-n}\}$ and the slope, n, of the straight lines (in Fig. 6), we were able to calculate the sets of n and $\log K$, because $\log K_w$ is known to be -14 and the activities of the solid phase, $[Al - SS]^-$ and $[SS]^{-n}$, were assumed to be unity. Table 2 lists the results obtained from samples 1 to 5 (seventh and ninth columns).

Referring to the values of n in Table 2, the character of the aluminum contained in the particulate matter could be categorized into three groups: the first group ($n < 1$) included samples 3 and 4, the second ($n \approx 2$) included samples 1 and 2, and the third ($n > 3$) included sample 5. Since n is the number of OH^- ions needed for the cleavage of Si–O–Al bonds on the solid surfaces, we concluded that the smaller n was, the weaker was the bonding of aluminum to the solid, and vice versa. In other words, stronger bonds between dissolved aluminum and particulate matter were formed in samples 1 and 2, which we took at Ie-1 and Na-3 in April, than in samples 3 and 4, which we took at Ie-1 in September. Similarly, we expected much stronger bonding in sample 5, which we took at Akanoi Bay. The strengths of the bonds thus estimated from the values of n were well in accord with those of $\log K$ evaluated by using Eq. 3. These findings may indicate that the dissolution and adsorption of aluminum were closely related to the nature of the suspended particulate matter. Actually, the atomic ratios of Al/Si in the suspended particulate matter (in the sixth column of Table 2) varied according to the values of n and $\log K$. For instance, the Al/Si ratios for samples 1 and 2 were 0.38 and 0.36, respectively, and were closer to those known for clay minerals. It seems that the dissolved aluminum in these samples was controlled by the suspended matter composed mainly of clay minerals. In contrast, the ratios in samples 3 and 4 were 0.004 and 0.008, respectively, and such small ratios indicate that the suspended matter in these samples was composed of materials such as opals or skeletons of diatoms, to which relatively small amounts of aluminum were bonded rather loosely.

Although we did not fully understand the nature of sample 5, taken at Akanoi Bay, regarding the Al/Si ratio, we suspected that the suspended particulate matter consisted of complex mixtures of clay minerals and opals. In addition, the effects of large amounts of particulate organic matter on aluminum cannot be negligible. In any case, the value of n for sample 5 ($n = 3.18$) was unusually high in comparison with that of each of the other four samples.
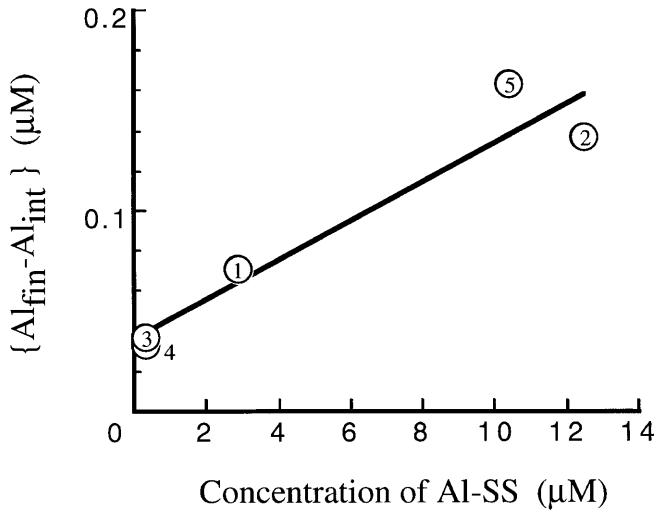
Fig. 8. Dependence of $\{Al_{fin} - Al_{int}\}$ on the concentration of Al-SS confirmed by incubation experiments using the lake water (samples 1–5) specified in Table 2

The values of $\{Al_{fin} - Al_{int}\}$, which is the difference between the ultimate concentration of dissolved aluminum attained during incubation for $t > 30$ days at pH > 8 and the initial concentration of dissolved aluminum, clearly show a linear relation to the concentration of $[Al - SS]^-$ (Fig. 8). This finding also suggests that suspended particulate matter is the principal origin of dissolved aluminum in harmonic-type lake waters.

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