

Environmental factors which influence the sink of silica in the limnetic system of the large monomictic Lake Biwa and its watershed in Japan

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Abstract Dissolved silica (DSi) and its associated biological and physicochemical factors were measured in Lake Biwa, Japan and its watershed from 2002 to 2003 in order to clarify seasonal variations in the magnitude of the sink of silica and the factors that influence it within the limnetic system. Consequently, it is concluded that Lake Biwa is a noticeable body of water where a massive sink of silica is caused. Calculated silica sedimentation in Lake Biwa was 2.0×10^7 kg Si year⁻¹ (7.1×10^8 mol Si year⁻¹) which is equivalent to about 80% of the annual inflow discharge of DSi to Lake Biwa. The magnitude of the sink varies seasonally by increasing in the winter holomictic stirring period, since it is greatly affected by the species composition of phytoplankton, the load of phosphorus and the condition of stratification. It seems reasonable to suppose that the DSi in Lake Biwa is removed mainly by biological processes, i.e.,

the assimilation of DSi by large centric diatoms and its accumulation in their frustules. Such silica sinks occur naturally in deeper stagnant waters, providing extended water residence time and supplying a certain amount of nutrients. These findings indicate that an increase in nutrient loads and abundance of stagnant water due to the construction of large dams lead to an expansion in the magnitude of the silica sink in a limnetic system.

Keywords Biogenic silica · Diatom · Dissolved silica · Silica deficiency hypothesis · Sink of silica · Stagnant waters

Introduction

An increase in nutrient loading [dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphate (DIP)] and stagnant water from dam construction in a limnetic system causes a corresponding increase in the freshwater phytoplankton biomass. Diatoms are a class of phytoplankton species that assimilates dissolved silica (DSi: Si(OH)₄) in order to build rigid diatom frustules. Diatom frustules accumulate rapidly in bottom sediments with the decrease in DSi concentration in a freshwater system, because their specific gravity is far greater than that of non-siliceous algae (Reynolds 1984). Consequently, the supply of DSi from the land to coastal seas decreases,

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and DSi : DIN and DSi : DIP ratios in coastal seas diminish (relative deficiency of silicon). Such biogeochemical changes may lead to a population shift from diatoms to non-siliceous algae, and thus greatly alter the marine ecosystem. This sequence of phenomena is known as the silica deficiency hypothesis (Schelske and Stoermer 1971, 1972) and has been recently regarded as a critical factor in any aquatic marine ecosystem (Billen et al. 1991; Conley et al. 1993; Humborg et al. 1997, 2000, 2006; Ittekkot et al. 2000; Turner et al. 2003).

Such silica deficiency constitutes a new environmental impact factor whereby the terrestrial supply of an essential material for a healthy marine ecosystem is reduced by artificial pollution and manipulation. Humborg et al. (1997) reported that the DSi discharge from the Danube River to the Black Sea decreased to about two-thirds after dam construction projects were undertaken in the early 1970s, and that phytoplankton species composition shifted dramatically from diatoms to non-siliceous algae in the Black Sea. Similar silica deficiency phenomena have been observed in various parts of the world, for example, the Great Lakes, USA (Schelske and Stoermer 1971, 1972), Funka Bay, Japan (Tsunogai and Watanabe 1983), and Rhine River-Netherlands coastal waters (Admiraal et al. 1990). In addition, Vörösmarty et al. (1997, 1998) pointed out that part of the decrease in DSi concentration in various waters is attributed to the increase in dams, with more than 36,000 large dams (more than 15 m high) in operation worldwide (Goudie 2000), representing a 700% increase in the standing stock of natural river water from 1950s to 1980s.

However, the studies mentioned above do not describe in detail seasonal fluctuations in the magnitude of silica sinks and the environmental factors, which influence them within a limnetic system. It is important for the future to accumulate detailed data on silica sinks in limnetic systems to intelligently address the silica deficiency problem including its impact on the land-ocean system. Accordingly, in this study, the dynamics of DSi in Lake Biwa and its watershed have been estimated from the viewpoint of biogeochemical cycles, and given that it is the largest monomictic lake in Japan, from its status as a major silica reservoir. Furthermore, we have evaluated the biological and physicochemical factors affecting the increase and/or decrease in DSi, and have determined

the magnitude of its silica sink in stagnant waters. Lake Biwa has one natural outflow-river, the Seta River, which is the main supply route of DSi to the coastal sea (Seto Inland Sea) via the Yodo River.

Methods

Sampling

Water and sediment samples for measurements of biogenic silica (BSi) were taken on 24 and 25 October 2002 from the littoral zone to offshore of Lake Biwa (surface area: 670 km², mean water depth: 43 m, maximum depth 104 m, mean water residence time: 5.8 years) (Fig. 1). This sampling period corresponds approximately to the intervening time of the winter when large heavily silicified diatoms predominate most and the summer when diatoms are rarely observed. Water level of Lake Biwa has been

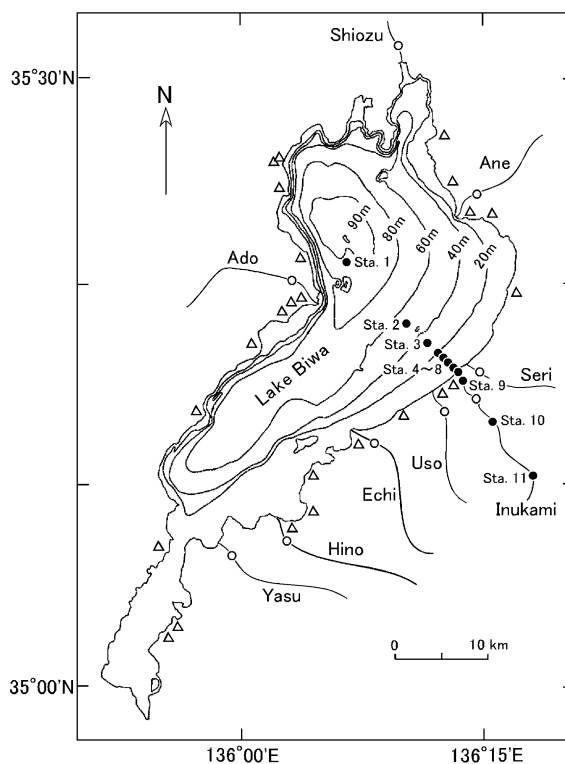


Fig. 1 General map of Lake Biwa and its catchment basin system. Sampling stations: ●-Lake Biwa (stas. 1–8), Inukami River (stas. 9–11), △-small lagoons (24 stations), and ○-rivers (nine stations)

regulated from 1905 by the weir in the Seta River, which is the exclusive natural outflow-river of the Lake, therefore Lake Biwa has some characteristics such as a reservoir. Samplings of the lake water (0–85 m) and surface layer sediments (0–10 cm) were carried out at eight transect points (stas. 1–8). In addition, samplings of riverbed stone and river water were conducted on the Inukami River in the Lake Biwa watershed (three stations: 9–11) on 31 October 2002 (Fig. 1). Attached materials on the surface of riverbed stones for measurement of BSi was removed using a brush, after collecting all riverbed stones within $0.5 \times 0.5 \text{ m}^2$ quadrat. At that same time, samples for measurements of DSi and chlorophyll *a* (Chl *a*) concentration were also collected at the above stations.

Water samples for measurements of DSi concentrations and other nutrients [dissolved inorganic nitrogen (DIN: sum of ammonia, nitrite and nitrate), phosphate phosphorus (DIP)] in vertical distributions (0–85 m) were taken at the north basin of Lake Biwa (sta. 1) monthly from January 2002 to May 2003 (Fig. 1), and water temperature was simultaneously measured using a CTD sensor. In addition, DSi concentrations in horizontal distribution (0.5 m depth) were investigated at all areas of the Lake on 6 and 7 June 2002. The 56 sampling stations for that investigation were located at points that divided the latitude and longitude into 2-min segments.

Dissolved silica and its associated substances (DIN, DIP, major ionic elements) in the main inflowing rivers of Lake Biwa were measured monthly or bimonthly each in 2002 and 2003 (Fig. 1). For the above investigations, we selected nine rivers with diverse geological conditions (rock types) (Table 1).

The concentrations of DSi, DIN and DIP in 24 small lagoons connected with Lake Biwa were measured monthly from January to November 2002 (Fig. 1).

Analytical methods

Water samples (in triplicate) collected for the measurement of BSi were immediately filtered through polycarbonate Nuclepore filters (0.6 μm pore size). The filters were dried at 60°C for 12 h and stored in a desiccator at room temperature until analysis. BSi concentration was analyzed by the method of Müller and Schneider (1993) with slight modifications. In this method, BSi concentration was determined based on the difference in dissolution rates between BSi and lithogenic silica using an alkaline solution (0.2 M NaOH, 80°C).

Water samples (duplicates) collected for chemical analysis of nutrients and Chl *a* were immediately filtered through glass fiber filters (Whatman GF/F) preignited at 450°C. Filtrates for the determination of DSi and other inorganic nutrients were stored at 4 and –30°C, respectively, while filters for the determination of Chl *a* were stored at –80°C until chemical analysis in the laboratory. DSi concentrations were analyzed spectrophotometrically using the molybdenum blue or yellow method of Mullin and Riley (1955). Ammonia was determined by the method of Sagi (1966), nitrite after Bendschneider and Robinson (1952), and phosphate after Murphy and Riley (1962). Nitrate was analyzed by an ion chromatographic analyzer (Dionex DX-120). Chl *a* concentration was analyzed fluorometrically using a Turner Design Fluorometer (Model 10-AU) after extraction

Table 1 Concentrations of dissolved silica in the nine inflowing rivers with diverse geological conditions

Rivers	Geologica conditions	DSi (μM : mean \pm SD)	<i>n</i>
Shiozu	granite	233 \pm 10	26
Yasu	granite, tuff and volcanic ash area	215 \pm 29	26
Uso	tuff	206 \pm 15	26
Hino	granite, tuff and volcanic ash area	189 \pm 37	12
Ane	granite, limestone and clay stone	161 \pm 10	26
Echi	granite and tuff	154 \pm 10	12
Inukami	limestone, tuff, chart and volcanic rock	147 \pm 14	26
Ado	sandstone and chart	142 \pm 5	12
Seri	limestone	98 \pm 14	26

in 90% acetone, and then ultrasonicated for 30 s (Holm-Hansen et al. 1965).

Lake sediments and attached matter on the surface of riverbed stone samples (in triplicate) collected for measurement of BSi contents were dried at 60°C for 24 h and stored in a desiccator at room temperature until analysis. Samples measured for benthic Chl *a* contents were immediately stored at –80°C. BSi contents in sediments and attached matter were analyzed by the method of Müller and Schneider (1993). Benthic Chl *a* contents were determined by the method of Holm-Hansen et al. (1965) after extraction in 90% acetone under refrigeration (–10°C) for 24 h.

The core samples (triplicates) for measurements of DSi in the interstitial water of lake sediments were taken using a core sampler. Concentrations of DSi were analyzed spectrophotometrically using the molybdenum yellow method of Mullin and Riley (1955) after extracting the interstitial water from sediment cores by centrifugation.

Results

Vertical cross-section of biogenic and DSi along Lake Biwa–Inukami River transect

Concentrations of DSi ranged from 10.9 to 98.6 μM ($23.5 \pm 21.4 \mu\text{M}$, mean \pm SD) in the water column of Lake Biwa (Fig. 2). The vertical distribution of DSi offshore (stas. 1–3) increased gradually with increasing water depth, reaching their maximum value on the lake bottom. On the other hand, DSi concentrations on the shore (stas. 4–8) were approximately distributed uniformly in all layers. BSi concentrations in the water column varied from 2.21 to 3.93 μM ($2.71 \pm 0.49 \mu\text{M}$, mean \pm SD) (Fig. 2). The vertical distribution of BSi offshore was higher in the surface layer (0–20 m) and on the lake bottom. In contrast, BSi concentrations on the shore were approximately distributed uniformly in all layers and were only slightly lower than those offshore. The concentration of Chl *a* in the water column was higher in the surface layers (0–20 m) but dropped abruptly around the thermocline, ranging from 3.1 to 4.5 mg Chl *a* m^{-3} in the surface layers and 0.1–1.1 mg Chl *a* m^{-3} in the deeper layers (20–86 m) (Fig. 2). The maximum value of Chl *a* concentration was observed

in the overlying water above the sediment at station 5 (depth 13 m).

Concentrations of DSi in the interstitial water of lake sediments ranged from 114 to 1,400 μM ($704 \pm 382 \mu\text{M}$, mean \pm SD) (Fig. 3), with those in the horizontal distribution decreasing gradually from offshore to shore, and those in the vertical distribution being nearly vertically uniform at all stations. Concentrations of BSi in sediments varied widely from 0.01 to 10 wt.% Si ($3.0 \pm 2.9 \text{ wt.\% Si}$, mean \pm SD) (Fig. 3). The vertical cross-section of BSi concentration was distributed very similarly to that of DSi in sediments, decreasing from offshore to the littoral zone. However, the BSi concentration offshore (stas. 1 and 2) was particularly high in the top layer of sediments. The amount of Chl *a* in sediments was found more abundantly in the upper layer of sediments at the littoral zone, ranging from 0.1 to 3.0 $\mu\text{g Chl } a \text{ cm}^{-3}$ (Fig. 3).

Concentrations of BSi on the surface of riverbed stones and in water of the Inukami River ranged from 34.9 to 135.5 mmol m^{-2} and from 0.83 to 3.44 μM , respectively. At that same time, Chl *a* concentrations on the stones and in the water ranged from 38.9 to 46.7 mg Chl *a* m^{-2} and from 0.3 to 2.2 mg Chl *a* m^{-3} , respectively.

Seasonal and spatial distribution of DSi in Lake Biwa

The concentration of DSi in the deepest part (sta. 1) of the north basin varied from 8.1 to 95.8 μM ($38.6 \pm 13.5 \mu\text{M}$, mean \pm SD) from January 2002 to May 2003 (Fig. 4). In the surface layer (0–20 m), the lowest and highest DSi concentration was observed in October 2002 (8.1 μM) and in March 2003 (40.5 μM), respectively. The seasonal patterns of the vertical profiles were almost identical in water temperature (Fig. 4), i.e., in the stratification period (April to December), the DSi concentration in the surface layer was at a lower level, and below the thermocline it increased gradually with increasing water depth. In particular, the DSi concentration near the lake bottom increased gradually from early in the stratification period (April to May) and rose to more than 60 μM during its final phase (November–December). On the other hand, the DSi concentration in the circulation period (February) was distributed rather uniformly in all layers. The standing stock of

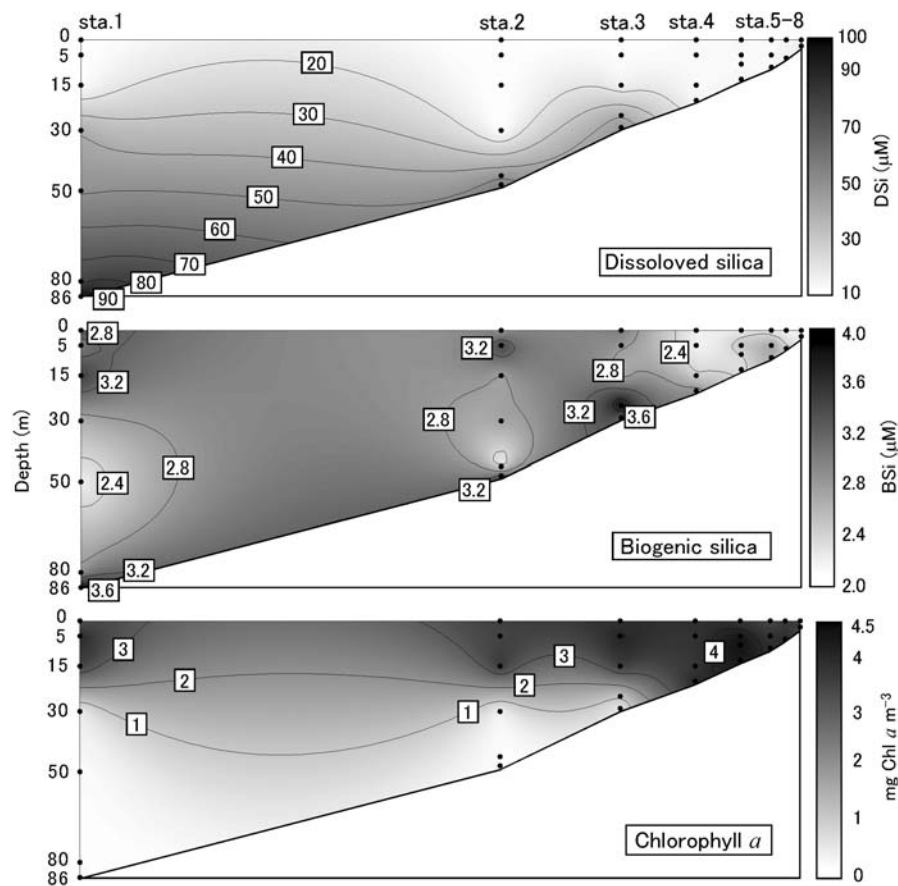


Fig. 2 Concentrations of dissolved silica, biogenic silica and chlorophyll *a* in the water column at 8 transect points (sta. 1–8) of Lake Biwa on 24 and 25 October 2002

DSi in the water column (mol m^{-2}) reached its maximum value at the end of the stratification period (December) and its minimum value during the circulation period (January–March), ranging from 3.1 to 4.0 mol m^{-2} during the entire observation period. The concentrations of DIN and DIP at the sta. 1 ranged from 2.3 to 20.4 μM [all layers: $14.3 \pm 3.5 \mu\text{M}$, surface layer (0–20 m): $12.0 \pm 3.4 \mu\text{M}$] and from 0.01 to 0.49 μM [all layer: $0.08 \pm 0.11 \mu\text{M}$, surface layer (0–20 m): $0.03 \pm 0.02 \mu\text{M}$] during the observation period, respectively.

Horizontal concentrations of DSi in the surface water ranged from 15.2 to 24.1 μM ($20.4 \pm 5.4 \mu\text{M}$, mean \pm SD) in all areas of Lake Biwa on 7 and 8 June 2002. Higher DSi concentrations were observed in the northern area of the north basin, while lower DSi levels were found in the central area of the north basin.

Distribution of DSi in inflowing rivers of Lake Biwa

Mean concentrations of DSi in the nine inflowing rivers of Lake Biwa were in the range of 98 to 233 μM ($172 \pm 43 \mu\text{M}$, mean \pm SD) during the observed period (Table 1). This mean DSi concentration (172 μM) is approximately the same as the mean discharge-weighted DSi concentrations [174 μM from 1978 to 1980 (Kunimatsu 1981) and 178 μM from 2002 to 2003 (Okubo 2006)] in the inflowing rivers of Lake Biwa. The concentrations of DSi at each river were greatly unchanged in comparison with the concentrations of other nutrients (DIN concentration: $47.2 \pm 17.3 \mu\text{M}$, DIP concentration: $1.11 \pm 0.85 \mu\text{M}$). The DSi concentration in the Shiozu River, which flows through a granite area, was the highest, followed by the Yasu, Uso, and Hino Rivers, which run through granite–tuff–volcanic ash

Fig. 3 Concentrations of dissolved silica, biogenic silica and chlorophyll *a* in the sediments at eight transect points (stas. 1–8) of Lake Biwa on 24 and 25 October 2002

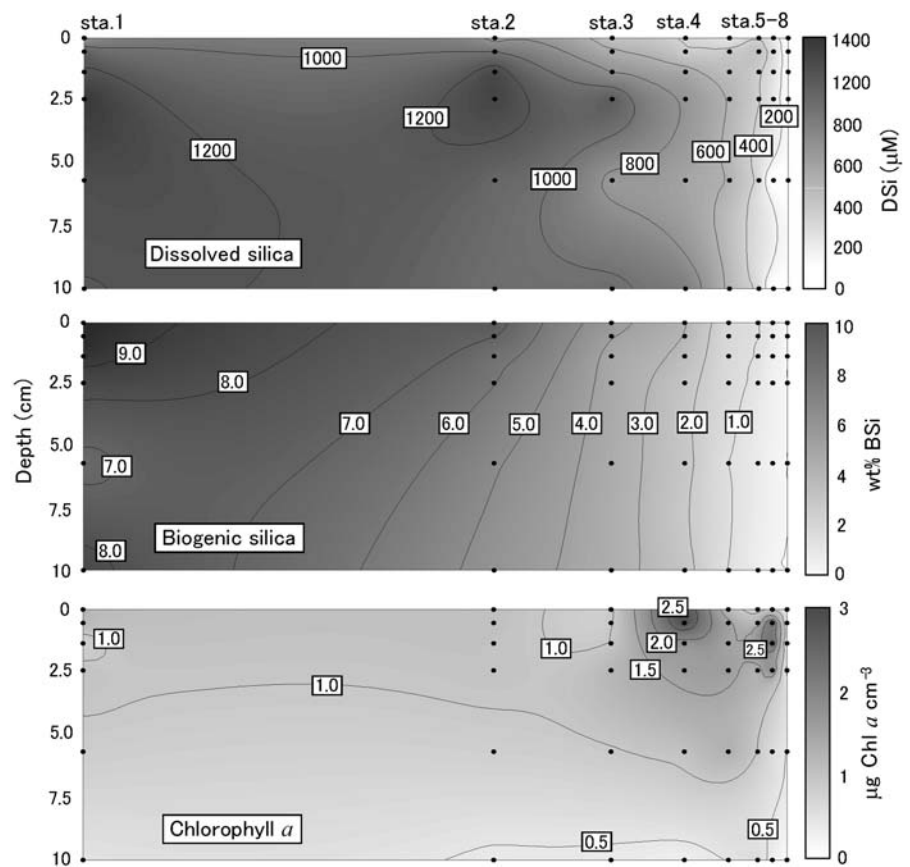
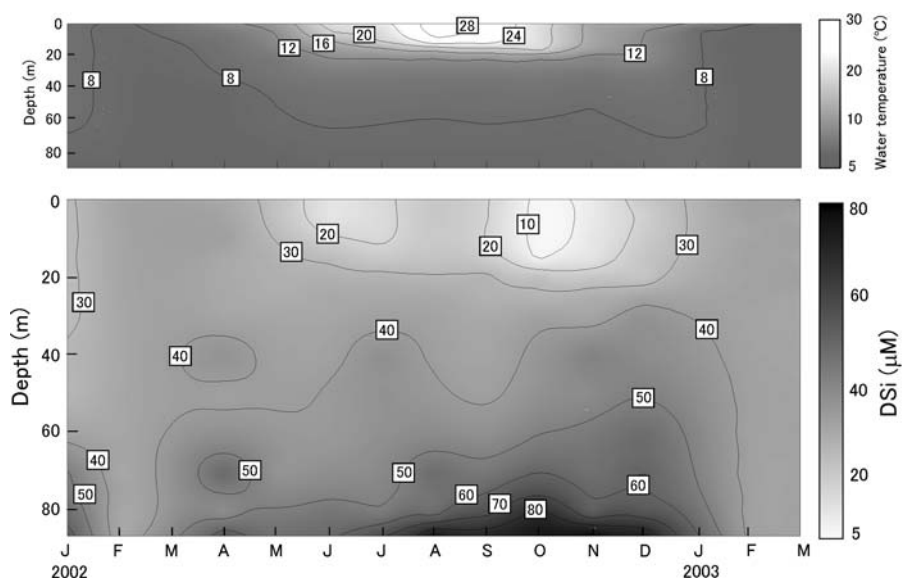


Fig. 4 Vertical distribution of dissolved silica and water temperature at station 1 of Lake Biwa from January 2002 to December 2003



areas, were high. The lowest DSi concentration was observed in the Seri River, which flows through a limestone area. At that time, the concentration of calcium ion (Ca^{2+}) in the Seri was higher than that in the other rivers.

Annual mean concentrations of DSi in 24 small lagoons connected with Lake Biwa ranged from 118 to 351 μM ($190 \pm 61 \mu\text{M}$, mean \pm SD), with the concentration in each lagoon remaining largely unchanged throughout the year. The concentrations of DIN and DIP ranged from 0.4 to 260 μM ($56.8 \pm 48.6 \mu\text{M}$) and from 0.09 to 6.61 μM ($0.89 \pm 0.87 \mu\text{M}$) during the observation period, respectively.

Discussion

Distributions of DSi in Lake Biwa and its inflowing rivers

The vertical concentration of DSi at station 1 in Lake Biwa was lower than that of nine inflowing rivers throughout the sampling period, except for the deepest layer at the end of the stratification period (October–December) (Table 1 and Fig. 4). This station, located in the northern area of the north basin, has a relatively high concentration of DSi abundantly supplied by rivers, which flow through the granite area. This clearly indicates that DSi concentrations in most areas of Lake Biwa are lower than those of inflowing rivers throughout the year, thus enabling the lake to function as a sink of DSi.

Humborg et al. (1997, 2000) reported that, following construction of a dam in the early 1970s, DSi concentrations in the Danube River were reduced to less than half of that in the predam era. Moreover, DSi concentrations in Black Sea into which the Danube flows similarly decreased. Schelske (1988) indicated that epilimnetic DSi concentrations in Lake Michigan were greatly diminished from the 1950s to the 1970s, thus increasing the load of dissolved inorganic phosphate. In common with the waters mentioned above, Lake Biwa is a globally renowned silica trap water area, moreover, the DSi concentration in the Seta River, which is the exclusive natural outflow-river of Lake Biwa, was about 30–40 μM (Harashima 2003), which is about a quarter that of the inflowing rivers. However, in the small lagoons of

stagnant water in our study, the annual mean concentration of DSi was about 190 μM , which is almost the same as that of the inflowing rivers (about 170 μM) (Table 1). These results can be attributed to the difference between the water depth and hydraulic residence time in small lagoons (mean water depth: several meters, mean residence time: several days to months) and in Lake Biwa (mean water depth: 43 m, mean residence time: 5.8 years). These findings indicate that the sink of silica occurs naturally in stagnant waters of some depth, with sufficient water residence time, and an adequate supply of certain nutrients.

Biogeochemical silica mass balance in Lake Biwa was calculated based on this finding using the input/output model of Schelske (1985) (Fig. 5). The sink calculation shows that $2.0 \times 10^7 \text{ kg Si year}^{-1}$ ($7.1 \times 10^8 \text{ mol Si year}^{-1}$) was retained in Lake Biwa sediments. This estimate for Si sedimentation is equivalent to about 80% of the annual inflow discharge of DSi in Lake Biwa. Schelske (1985) and Schelske et al. (2006) calculated silica mass balances for Lake Michigan during the post-1970 and Lake Erie in the 1970s of the Great Lakes and estimated that Si sedimentation in Lake Michigan and Lake Erie was $8.1 \times 10^7 \text{ kg Si year}^{-1}$ ($29 \times 10^8 \text{ mol Si year}^{-1}$, equivalent to 80% of annual inflow discharge) and $7.5 \times 10^7 \text{ kg Si year}^{-1}$ ($26 \times 10^8 \text{ mol Si year}^{-1}$, equivalent to 80% of annual inflow discharge), respectively. Although the volume of Lake Biwa ($2.75 \times 10^{10} \text{ m}^3$) is very small compared to that of Lake Michigan ($487 \times 10^{10} \text{ m}^3$) and Lake Erie ($45.8 \times 10^{10} \text{ m}^3$), the magnitude of the silica sink in Lake Biwa reaches approximately a quarter of that in the two Lakes. This fact suggests that Si sedimentation occurs very promptly in Lake Biwa.

The annual accumulation of BSi to the bottom sediments of Lake Biwa was approximated from the contents of BSi in the bottom sediments (Fig. 3) and the mean sedimentation rate of Lake Biwa ($0.033 \text{ g cm}^{-2} \text{ year}^{-1}$, Nakamura et al. 1987). As a result, the basin-wide BSi accumulation in Lake Biwa becomes $1.2 \times 10^7 \text{ kg Si year}^{-1}$ ($4.3 \times 10^8 \text{ mol Si year}^{-1}$), and this estimate is equivalent to 60% of the Si sedimentation in Lake Biwa (Fig. 5). It is assumed that the remaining fractions were removed from the water by the outflow of BSi from Lake Biwa to Seta River and/or

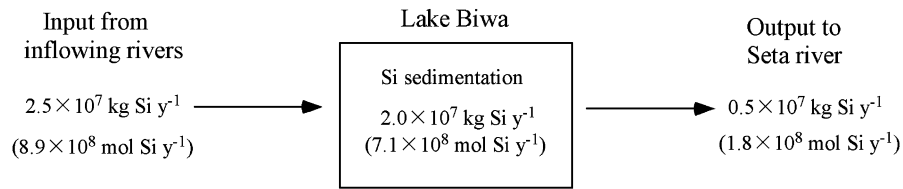


Fig. 5 Si mass balance in Lake Biwa. Inflow discharge of Si was calculated with the following date: inflow discharge $52 \times 10^8 \text{ m}^3 \text{ year}^{-1}$ (a), DSi concentration $4.8 \times 10^{-3} \text{ kg Si m}^{-3}$ (b). Outlet flow of Si was calculated

with the following date: $49 \times 10^8 \text{ m}^3 \text{ year}^{-1}$ (c), DSi concentration $1.0 \text{ kg} \times 10^{-3} \text{ kg Si m}^{-3}$ (b). ^(a) Kawabata (1981), ^(b) this study, ^(c) Kunimatsu (2000)

physicochemical processes. In following section we describe on the silica dynamics in Lake Biwa.

Biotic and abiotic effects on a silica sink

It seems reasonable to suppose that most of the DSi in Lake Biwa is removed from the water column by biological rather than physicochemical processes. In fact, the adsorption of DSi by sediment particles and/or the formation of colloidal silica by polymerization of DSi almost never develop over the DSi concentration range in Lake Biwa (Hori et al. 1969). Therefore, planktonic and benthic diatoms are thought to play a major role in the sink of silica in Lake Biwa. We found an inverse relationship between BSi and DSi concentrations in the water column of Lake Biwa (Fig. 2). In addition, we confirmed that large quantities of diatom frustules (dead shells) had accumulated in the bottom sediments of the lake (Fig. 3). It thus may be supposed that, while one part of BSi recurs to DSi within a period of its sedimentation, the other part of BSi is accumulated on the lake bottom.

In this study, the amount of diatom frustules (BSi) in sediments was particularly high in the offshore sediments (Fig. 3). This distribution is thought to result from diatoms being transported by waves and/or lake currents from the littoral zone to offshore and from the fact that diatom frustules in those offshore sediments are less susceptible to dissolution since the water temperature in the hypolimnion offshore is low ($7\text{--}8^\circ\text{C}$) throughout the year (Fig. 4). The dissolution of diatom frustules that accumulate in bottom sediments is controlled by both biological factors (bioturbation by zoobenthos, bacterial attacks of hydrolytic enzymes) and physicochemical ones (water temperature, pH, salinity, oxidation-reduction

potential) (Beucher et al. 2004; Bidle and Azam 1999; Bidle et al. 2003; Brzezinski et al. 1997; Kamatani 1982; Kato 1969; Nriagu 1978). In this study, BSi and DSi concentrations in bottom sediments offshore were nearly vertically uniform (Fig. 3), suggesting that the dissolution of diatom frustules does not proceed much in offshore sediments, except for the upper few millimeters, and that the regeneration of DSi into interstitial or overlying water on bottom sediments is limited by several factors.

More than 97% of diatom frustules (cell numbers) that accumulate in the surface layer sediments (0–6 m) of the north basin of Lake Biwa is comprised of two species of centric diatoms, *Aulacoseira solida* and *Stephanodiscus carconensis* (Negoro 1960, 1967). Similarly, we observed large quantities of *A. solida* and *S. carconensis* frustules in the lake bottom sediments. Since these large diatoms have a heavy, thick siliceous cell wall, they are not ingested by most zooplankton (Horne and Goldman 1994). These findings indicate that since these large and heavy diatoms, *A. solida* and *S. carconensis*, sink so rapidly, they soon settle to the hypolimnion where the water temperature is lower ($7\text{--}8^\circ\text{C}$) before suffering biological and physicochemical degradation in the epilimnion (Reynolds 1984; Ryves et al. 2003). On the other hand, other diatoms are thought to be decomposed by biological and physicochemical factors in the water column where their frustules are recurred to DSi through colloidal silica in the water. Bidle and Azam (1999) reported that the dissolution rates of diatom silica markedly differed depending on the species, perhaps reflecting differences in the degree of cell wall silicification. The above findings confirm that only certain species of large centric diatoms contribute to the sink of silica in Lake Biwa.

The DSi and other nutrients are supplied from the hypolimnion to the epilimnion of the lake during the winter holomictic stirring period (from January to March) (Fig. 4). In this period of low water temperature, large diatoms such as *Aulacoseira*, *Fragilaria*, and *Stephanodiscus* become dominant in Lake Biwa (Kawabata 1987). Those diatoms settle rapidly to the bottom sediments because of the disruption of the thermocline in the circulation period. Our recent observations have confirmed that the sinking flux of those diatom species at 30- and 70-m depths was at its highest in February (unpublished). It has been shown in many lakes that the genus *Aulacoseira* is the winter species most abundant among the phytoplankton (Lund 1971). On the other hand, during the period of thermal stratification in Lake Biwa, large diatoms are rarely observed, while green algae and cyanobacteria dominate. At this time, although small diatom species are occasionally found, it is assumed that their frustules undergo almost total dissolution before reaching the bottom sediments. Thus, we conclude that the magnitude of a silica sink in lakes depends on seasonality, which reaches its height in the winter holomictic stirring period. This finding is supported by the fact that the standing stock of DSi per square meter in Lake Biwa was at its lowest during February of the circulation period in the present study. The sequence of events described above may apply to other lakes, i.e., mixing patterns of a lake greatly influence the silica trapping efficiency. Schelske et al. (1986) described based on nutrient enrichment experiments at low light and low temperature that significant Si uptake by diatoms in the Great lakes occurred during the period of winter-spring convective mixing.

A typical N : P : Si molar ratio in diatom cells is 16:1:[16–50], and any significant deviation from such ratios threatens to be growth limiting for diatoms (Brzezinski 1985; Levine et al. 1997; Schelske et al. 1983, 1986; Sommer 1986; Teubner and Dokulil 2002). We determined the means of DSi : DIP and DIN : DIP molar ratios at the surface layer (0–20 m) in Lake Biwa to be 1,646 (range: 457–2,700) and 446 (range: 214–802), respectively, during our observation period. These results indicate that the growth of diatoms in the lake was severely limited by phosphorus throughout the year. Tsunogai (1979) proposed that, among all phytoplankton species, diatoms are predominant when all physical and chemical

conditions are adequate for phytoplankton growth. Tsunogai and Watanabe (1983) later verified that hypothesis in Funka Bay, Japan. Egge and Aksnes (1992) indicated that diatoms dominate as long as the silicate concentration exceeds 2 μM . On the basis of the aforementioned studies, it is highly probable that in Lake Biwa an increase in the load of phosphorus first causes the growth of diatoms, as a result of which silica sink expands. A contrary opinion holds that the magnitude of a silica sink is most likely reduced when the load of phosphorus decreases. In fact, the concentration of DSi in the outflowing Seta River of Lake Biwa was around 40 μM in the 1950s but had fallen to around 30 μM by the 1970s, possibly because of the enhancement of the silica trap due to an increased inflow of phosphorus during the period of rapid economic growth from the 1960s to the 70s (Harashima 2003). Conversely, after the regulation of phosphorus discharges into Lake Biwa in the 1990s, DSi concentrations showed a tendency to increase (Harashima 2003). A similar phenomenon was observed in the Great Lakes, USA (Conley et al. 1993; Schelske and Stoermer 1971, 1972). Schelske et al. (1986) demonstrated in laboratory experiments that Si uptake by diatoms increased to several times by relatively small P enrichments and explained that biogeochemical silica depletion in the Great Lakes was induced by increased phosphorus loading. Judging from the above, it seems reasonable to suppose that imbalances between P and Si supplies have a profound effect on Si dynamics in Lake Biwa.

It is concluded that Lake Biwa is a body of water known worldwide for its massive sink of silica. This sink can be attributed mainly to biological activity, i.e., the assimilation of DSi by large centric diatoms and the descent of their frustules to the bottom sediments. The magnitude of the silica sink is affected by seasonality, becoming highest in the winter holomictic stirring period, and is also significantly influenced by the load of phosphorus from the watershed of Lake Biwa. It follows, then, that the sink of silica occurs naturally in stagnant waters of some depth, with sufficient water residence time, and an adequate supply of certain nutrients. These findings indicate that an increase in nutrient loads into stagnant waters from the construction of dams leads to an expansion in the silica sink with a subsequent alteration of the aquatic ecosystem.

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References

- Admiraal W, Breugem P, Jacobs DMLHA, de Ruyter van Steveninck ED (1990) Fixation of dissolved silicate and sedimentation of biogenic silicate in the lower river Rhine during diatom blooms. *Biogeochemistry* 9:175–185
- Bendschneider K, Robinson RJ (1952) A new spectrophotometric method for the determination of nitrite in sea water. *J Mar Res* 11:87–96
- Bidle KD, Azam F (1999) Accelerated dissolution of diatom silica by marine bacterial assemblages. *Nature* 397:508–512
- Bidle KD, Brzezinski MA, Long RA, Jones JL, Azam F (2003) Diminished efficiency in the oceanic silica pump caused by bacterial-mediated silica dissolution. *Limnol Oceanogr* 48:1855–1868
- Billen G, Lancelot C, Meybeck M (1991) N, P, and Si retention along the aquatic continuum from land to ocean. In: Matoura RFC, Martin JM, Wollast R (eds) *Ocean margin processes in global change*. Wiley, Chichester, pp 19–44
- Brzezinski MA (1985) The Si : C : N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. *J Phycol* 21:347–357
- Brzezinski MA, Phillips DR, Chavez FP, Friederich GE, Dugdale RC (1997) Silica production in the Monterey, California upwelling system. *Limnol Oceanogr* 42:1694–1705
- Beucher C, Tréguer P, Corvaisier R, Hapette AM, Elskens M (2004) Production and dissolution of biosilica, and changing microphytoplankton dominance in the Bay of Brest (France). *Mar Ecol Progr Ser* 267:57–69
- Conley DJ, Schelske CL, Stoermer EF (1993) Modification of the biogeochemical cycle of silica with eutrophication. *Mar Ecol Progr Ser* 101:179–192
- Egge JK, Aksnes DL (1992) Silicate as regulating nutrient in phytoplankton competition. *Mar Ecol Progr Ser* 83:281–289
- Goudie A (2000) *The human impact on the natural environment*, 5th edn. Blackwell Publishers, Oxford
- Harashima A (2003) Silica deficiency in the aquatic continuum and its effect to the marine ecological change. *J Jpn Soc Water Environ* 26:621–625
- Holm-Hansen O, Lorenzen CJ, Holmes RW, Strickland JDH (1965) Fluorometric determination of chlorophyll. *J Cons Int Explor Mer* 30:3–15
- Hori T, Itasaka O, Mitamura O (1969) The removal of dissolved silica from freshwater in the Lake Biwa-ko. *Mem Fac Liberal Arts Educ Shiga Univ* 19:45–51 (in Japanese with English summary)
- Horne AJ, Goldman CR (1994) Phytoplankton and periphyton. In: Horne AJ, Goldman CR (eds) *Limnology* 2nd edn. McGraw-Hill, New York, pp 226–264
- Humborg C, Conley DJ, Rahm L, Wulff F, Cociasu A, Ittekkot V (2000) Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *Ambio* 29:45–50
- Humborg C, Ittekkot V, Cociasu A, Bodungen B (1997) Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature* 386:385–388
- Humborg C, Pastuszak M, Aigars J, Siegmund H, Mörtz CM, Ittekkot V (2006) Decreased silica land-sea fluxes through damming in the Baltic sea catchment—significance of particle trapping and hydrological alterations. *Biogeochemistry* 77:265–281
- Ittekkot V, Humborg C, Schäfer P (2000) Hydrological alterations and marine biogeochemistry: a silicate issue? *BioScience* 50:776–782
- Kamatani A (1982) Dissolution rate of silica from diatoms decomposing at various temperatures. *Mar Biol* 68:91–96
- Kato K (1969) Behavior of dissolved silica in connection with oxidation-reduction cycle in lake water. *Geochem J* 3:87–97
- Kawabata H (1981) Inflow of groundwater from the watershed of Kusatsu River to the South basin of Lake Biwa. *Environmental dynamics in Lake Biwa and its watershed*. Environmental Science Research Report (B105-R12-12), Education Ministry, pp 12–20 (in Japanese)
- Kawabata K (1987) Ecology of large phytoplankton in Lake Biwa: population dynamics and food relations with zooplankters. *Bull Plankton Soc Jpn* 34:165–172
- Kunimatsu T (1981) Water quality of the river water, groundwater, precipitation in the watershed of Lake Biwa and the outflowing water of Lake Biwa. The report collection on Environmental Science (B105-R12-12), the Education Ministry, pp 82–105 (in Japanese)
- Kunimatsu T (2000) Water budget in Lake Biwa. In: Somiya I (ed) *Biwako*. Gihodou Shuppan, Tokyo, pp 95–99 (in Japanese)
- Levine SN, Shambaugh AD, Pomeroy SE, Braner M (1997) Phosphorus, nitrogen, and silica as controls on phytoplankton biomass and species composition in Lake Champlain (USA-Canada). *J Great Lakes Res* 23:131–148
- Lund JWG (1971) An artificial alternation of the seasonal cycle of the plankton diatom *Melosira italica* in an English lake. *J Ecol* 59:521–533
- Müller PJ, Schneider R (1993) An automated leaching method for the determination of opal in sediments and particulate matter. *Deep Sea Res, Part 1*, 40:425–444
- Mullin JB, Riley JP (1955) The colorimetric determination of silicate with special reference to sea and natural waters. *Anal Chim Acta* 12:162–176
- Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Anal Chim Acta* 27:31–36
- Nakamura T, Nakai N, Kimura M, Kojima S, Maeda H (1987) Geological studies on radionuclides distributed in the bottom sediments of Lake Biwa. *Research Report from*

- Lake Biwa Research Institute No. 86-A05:75–85 (in Japanese with English summary)
- Negoro K (1960) Studies on the diatom-vegetation of Lake Biwa-ko. *Jpn J Limnol* 21:200–220 (in Japanese)
- Negoro K (1967) An analytical study of diatom shells in the bottom deposits of Lake Biwa-ko, based on a new core-sample. *Jpn J Limnol* 28:132–135 (in Japanese)
- Nriagu JO (1978) Dissolved silica in pore waters of Lakes Ontario, Erie, and Superior sediments. *Limnol Oceanogr* 23:53–67
- Okubo K (2006) Modeling of the silica sink and the loading of P and N in watershed of Lake Biwa, Study on determination of marine environment due to the loading of N and silica decline in the global aquatic continua. *Glob Environ Res* (Ministry of the Environment) D-3: 60–79 (in Japanese)
- Reynolds CS (1984) *The ecology of freshwater phytoplankton*. Cambridge University Press, New York
- Ryves DB, Jewson DH, Sturm M, Battarbee RW, Flower RJ, Mackay AW, Granin NG (2003) Quantitative and qualitative relationships between planktonic diatom communities and diatom assemblages in sedimenting material and surface sediments in Lake Balk, Siberia. *Limnol Oceanogr* 48:1643–1661
- Sagi T (1966) Determination of ammonia in sea water by the indophenol method and its application to the coastal and off-shore waters. *Oceanogr Mag* 18:43–51
- Schelske CL (1985) Biogeochemical silica mass balances in Lake Michigan and Lake Superior. *Biogeochemistry* 1:197–218
- Schelske CL (1988) Historical trends in Lake Michigan silica concentrations. *Internationale Revue der gesamten Hydrobiologie* 73:559–591
- Schelske CL, Stoermer EF (1971) Eutrophication, silica depletion, and predicted changes in algal quality in Lake Michigan. *Science* 173:423–424
- Schelske CL, Stoermer EF (1972) Phosphorus, silica and eutrophication in Lake Michigan. In: Likens GE (ed) *Nutrients and eutrophication*. American Society of Limnology and Oceanography, Kansas, pp 157–171
- Schelske CL, Stoermer EF, Conley DJ, Robbins JA, Glover R (1983) Early eutrophication in the lower Great Lakes: new evidence from biogenic silica in sediments. *Science* 222:320–322
- Schelske CL, Stoermer EF, Fahnenstiel GL, Haibach M (1986) Phosphorus enrichment, silica utilization, and biogeochemical silica depletion in the Great Lakes. *Can J Fish Aquat Sci* 43:407–415
- Schelske CL, Stoermer EF, Kenney WF (2006) Historical low-level phosphorus enrichment in the Great Lakes inferred from biogenic silica accumulation in sediments. *Limnol Oceanogr* 51:728–748
- Sommer U (1986) Nitrate- and silicate-competition among antarctic phytoplankton. *Mar Biol* 91:345–351
- Teubner K, Dokulil MT (2002) Ecological stoichiometry of TN : TP : SRSi in freshwaters: nutrient ratios and seasonal shifts in phytoplankton assemblages. *Arch Hydrobiol* 154:625–646
- Tsunogai S (1979) Dissolved silica as the primary factor determining the composition of phytoplankton classes in the ocean. *Bull Fac Fish, Hokkaido Univ* 30:314–322
- Tsunogai S, Watanabe Y (1983) Role of dissolved silicate in the occurrence of a phytoplankton bloom. *J Oceanogr Soc Jpn* 39:231–239
- Turner RE, Rabalais NN, Justic D, Dortch Q (2003) Global patterns of dissolved N, P and Si in large Rivers. *Biogeochemistry* 64:297–317
- Vörösmarty CJ, Li C, Sun J, Dai Z (1998) Drainage basins, river systems, and anthropogenic change: the Chinese example. In: Galloway JN, Melillo JM (eds) *Asian change in the context of global climate change*. Cambridge University Press, Cambridge, pp 210–244
- Vörösmarty CJ, Sharma KP, Fekete BM, Copeland AH, Holden J, Marble J, Lough JA (1997) The storage and aging of continental runoff in large reservoir systems of the world. *Ambio* 26:210–219