Studies on the silicon dynamics and those impacts on diatom blooms in a shallow eutrophic lake

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Abstract

Silicon (Si) is one of the essential nutrients for diatoms. In Lake Kasumigaura, a shallow eutrophic lake, increasing trends of dissolved Si (DSi) and total Si (TSi) concentration were detected during the last three decades (mean DSi concentration measured by a colorimetric method in the 1980s and 2000s was 1.3 mg l\(^{-1}\) and 4.0 mg l\(^{-1}\), respectively). The observation of such long-term trends is rare; therefore, detailed analysis could be useful to understanding Si dynamics in inland waters. The objectives of this study are fourfold: (i) to detect the long-term trend of Si concentrations and discuss the factors of the trend, (ii) to assess the contribution of DSi release from suspended solids (SS) to the increasing trend of DSi observed in the lake by laboratory experiments, (iii) to calculate the Si budgets in the lake based on the long-term database and compare with the chronological sediment information, and (iv) to assess the factors for long-term changes in diatom abundance by database analysis and model simulation, especially focusing on the relationships between diatoms and DSi.

Based on statistical analysis, we found that the increases in DSi and lithogenic Si accounted for most of the TSi increase (44% and 45%, respectively) and that biogenic Si (BSi), consisting of diatom frustules, also increased with them. Increases in DSi concentration were not detected near the mouth of the inflowing rivers, suggesting that the increase was caused by in-lake processes. Because the increase in SS caused by sediment resuspension had been observed in the lake for the same period, we considered
that DSi release from SS containing diatom frustules contributed to the increase. The results of the laboratory experiments in which surface sediments were stirred in lake waters showed that the change in DSi concentration depended mainly on SS concentration, water temperature, and the elapsed time of diatom frustules dissolution. An estimation of the released amount of DSi from SS using the sediment resuspension model was \((1.0–2.7) \times 10^9\) g y\(^{-1}\) in the 2000s, which was about 30–90% of the increase in the DSi outflow of \(3.0 \times 10^9\) g y\(^{-1}\) from the 1980s to the 2000s. We also determined the DSi release rates from bottom sediments to be \(4.3 \times 10^9\) g y\(^{-1}\), which was about 2–4 times higher than the estimated DSi amount released from SS. These findings suggest that the sediment resuspension might be the cause of the latest DSi increase.

Budgetary calculations based on the database showed that 60–70% of DSi inputs from the inflowing rivers could ultimately be accumulated as diatom frustules in bottom sediments in the lake during the 27 years. The sediment BSi analyzed in the dated cores revealed that the BSi amount accumulated in the lake from 1980–2007 was \((2.0–2.6) \times 10^{11}\) g, close to the amount based on the database of \((1.3–2.4) \times 10^{11}\) g. Although the gross sedimentation rates of BSi likely increased, the net sedimentation rates of BSi significantly decreased from \((6–10) \times 10^9\) g y\(^{-1}\) in the 1980s to \((2–6) \times 10^9\) g y\(^{-1}\) in the 2000s, suggesting fast BSi recycling in recent years caused by an increase in sediment resuspension and regeneration of DSi.

Diatom abundance increased during the last three decades. Based on the monthly dataset, N:P:Si ratios suggested that Si was the element mostly limiting diatom growth after DSi depletion. The seasonal relationships between DSi and diatoms showed a hysteresis loop, representing as follows: (i) diatom growth by uptake of DSi in a better state (e.g., at optimal temperature), (ii) rapid sinking of diatoms after DSi depletion, and
(iii) no diatoms with DSi supply from river inputs and release. The relationships were mostly characterized as a two-round loop during the 1980s (spring and autumn diatom blooms), while a one-round big loop during the 2000s (extensive winter–spring blooms). Modeling and simulation of major processes involved in DSi (inflows, outflow, uptake by diatoms, and release from bottom and SS determined by the laboratory experiments) and diatoms (outflow, sinking, and growth limited by light condition, water temperature, and DSi concentration) could reproduce a two-round and one-round loop during the 1980s and 2000s, respectively. The peaks of diatom blooms declined with the release from resuspended sediments removed, indicating the impacts of the recent release on diatom blooms in the lake. Simulation also suggested that the sediment resuspension might cause the change of the loop from two-round to one-round mainly through degradation of light condition. These findings implicate the significance of the interactions between sediments and water to phytoplankton blooms.

The products of this dissertation might be useful for lake management as basic information relevant to Si and diatoms.

**Keywords:** Silicon, Diatoms, Suspended solids, Sediments, Release, Budgetary analysis, Model simulation, Lake Kasumigaura
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Chapter 1

Introduction

1.1 Purpose of this study

Silicon (Si) is the second most common element of the earth’s crust. It occurs as silicate minerals in association with igneous, metamorphic, and sedimentary rocks. They undergo physical, chemical, and biological weathering. The products of weathering include both particulate components (e.g., clays) and dissolved silicate. The latter consists of Si(OH)$_4$ (dominant with a pH of less than 9.8), Si(OH)$_3$O$^-$ (dominant with a pH of more than 9.8), and those polymers as a result of dehydration synthesis (Alexander et al. 1954).

It is well known that part of dissolved Si (DSi) produced in weathering is used in aquatic ecosystems by diatoms, sponges, chrysophytes, radiolarians, and silicoflagellates (Conley et al. 1993). Diatoms form a major part of the aquatic food chain and play a critical role in marine biogeochemical cycles, especially in the sequestration of carbon dioxide from the atmosphere via the biological pump (Schelske 1999; Ittekkot et al. 2006). Diatoms need plentiful Si which is present in their cell walls, i.e., frustules, as amorphous silica (i.e. SiO$_2$). Freshwater diatoms have more silica per
unit of biovolume than marine species (Conley et al. 1989). Therefore, Si dynamics could affect the phytoplankton dominance, food web, and biogeochemical cycling in both marine and freshwater ecosystems (Kristiansen and Hoell 2002). In addition, terrestrial plants such as paddy rice take up a significant portion of DSi (Sommer et al. 2006). Recent evidence supports that the flux of DSi transferred from the land to the oceans is primarily leakage out of the internal terrestrial biogeochemical cycle (Derry et al. 2005; Conley et al. 2006).

While the loadings of nitrogen (N) and phosphorus (P) are enhanced by the human activities, a decreasing trend of the loadings of DSi, which tends to be taken by diatoms in the eutrophicated stagnant waters such as dammed reservoirs, has been observed globally (Humborg et al. 1997; Conley et al. 2000; Duan et al. 2007; Li et al. 2007). For example, Humborg et al. (1997) showed the decreases in the DSi load in the Danube River–Black Sea system and indicated the impacts of the construction of “Iron Gates”. In addition, Teodoru et al. (2006) suggested that the large number of impoundments on the Danube and its tributaries changed DSi transport to the coastal Black Sea. In Japan, few observational data suggested a decrease in the loadings of DSi. The Foundation of River & Watershed Environment Management (2007) reported that the mean DSi concentration of the limited 18 Japanese rivers in the 2000s was lower than that in the 1940s and 1950s, opposite to the trends of N and P. However, the report pointed out the scarcity of long-term Si monitoring data fractionated to be dissolved, biogenic, and lithogenic Si makes it difficult to elucidate the cause.

Following the DSi trapping in the eutrophicated stagnant waters, the consequent change in the N: P: Si stoichiometric ratio of the river water flowing into the coastal sea may be advantageous to nonsiliceous algae (potentially harmful such as some of
dinoflagellates) but disadvantageous to diatoms (siliceous and mostly benign). This is called as the “silica deficiency hypothesis” (Officer and Ryther 1980; Humborg et al. 1997; Ittekkot et al. 2000). For instance, Humborg et al. (1997) showed that the decrease in the DSI load of the influent rivers and the consequent changes in Si:N ratio of the Black Sea nutrient load seem to be responsible for dramatic shifts in phytoplankton species composition from diatoms to coccolithophores and flagellates in the sea. In Japan, where DSI supply by natural weathering is comparatively huge due to geological condition (mainly igneous rock) and high rainfall, Harashima et al. (2006) implied the sensitivity of the ecosystem to Si processes in the aquatic continuum composited of Lake Biwa, the Yodo River, and the Seto Inland Sea. Moreover, Harashima (2007) developed “silica deficiency hypothesis” further to the “extended silica deficiency hypothesis” as follows. While the diatoms effectively draw down the substances from the upper layer with their sinking after the spring bloom (biological pump), other algae do not. This will cause the retention of the surplus nutrient and biogenic substances in the upper layer and lead further to eutrophication of upper layer substantially. The role of Si or N: P: Si stoichiometric ratio was suggested not only in marine environment but also in freshwater ecosystems such as natural lakes (Koszelnik and Tomaszek 2008). However, evidence for significant effects of Si dynamics on aquatic ecosystems in stagnant waters is sparse in the world (Humborg et al. 1997; Harashima 2007).

This research is a case study to obtain new fundamental knowledge of a long-term Si dynamics and those impacts on diatom blooms in a shallow eutrophic lake using several biogeochemical techniques. The target area is Lake Kasumigaura, where various forms of Si have been monitored for the last three decades. With regard to the social
significance of use of lake water, detailed analysis in such a shallow eutrophic lake is important. The objectives are fourfold: (i) to detect the long-term trend of Si concentrations and discuss the factors influencing the trend, (ii) to estimate the DSI release rate from SS and bottom sediments by laboratory experiments and assess the contribution of DSI release to the trend, (iii) to calculate the Si budgets in the lake based on the long-term database and compare with the chronological sediment information, and (iv) to assess the factors for the long-term changes in diatom abundances by model simulation. The products of this dissertation might be useful for lake management as basic information relevant to Si and diatoms.

1.2 Structure of this study

This dissertation is organized from 8 chapters. Chapter 1 explains the backgrounds and objectives of this study. Chapter 2 describes the study area, Lake Kasumigaura and its catchment. Chapter 3 addresses the long-term trend of various Si concentrations and the factors influencing the trend using the water quality and meteorological data. Chapter 4 estimates the DSI release rate from SS and bottom sediments by laboratory experiments and assesses the contribution of DSI release to the observed trend. Chapter 5 calculates the Si budget in the lake based on the long-term database and discusses the budget with the chronological sediment information. Chapter 6 addresses the long-term changes in the abundance and seasonality of diatom blooms and assesses the factors using simplified box model, especially focusing on the impacts of DSI increase on diatom blooms.
Chapter 2

Study area

Lake Kasumigaura is the second largest shallow lake in Japan, located in the Ibaraki Prefecture, approximately 50 km northeast of Tokyo. Lake Kasumigaura refers group of contiguous lakes, which includes Nishiura and two smaller lakes (Kitaura and Sotonasakaura). In this study, “Lake Kasumigaura” indicates only Nishiura (Figure 2.1). It has a surface area of 171.5 km², a mean depth of 4 m, and a maximum depth of 7.3 m. Mean water retention time is about 200 days. The lake is so shallow that vertical stratification is easily destroyed by a moderately strong wind. The lake has two large bays, Takahama-iri and Tsuchiura-iri. The Koise and Sakura rivers are the main rivers influent into Takahama-iri and Tsuchiura-iri, respectively. Water tends to flow through the lake from the northwest, where Takahama-iri and Tsuchiura-iri are located, to the southeast, to the effluent Hitachitone River. Its catchment area of 1426 km² (excluding the lake area) consists of paddy fields, plowed fields for other row crops, orchards (in total of 51%), forest (30%), and urban, industrial, and residential uses (12%). Major surface geology in the catchment is loam. The climate of the area is similar to other regions on the Pacific side of Japan with the annual average air temperature of about 14°C and an annual precipitation of 1250 mm. The lake was turned from a brackish into
Figure 2.1  Lake Kasumigaura
a freshwater lake 5 years after a floodgate to the Pacific Ocean was implemented in 1963.

The lake is well known for eutrophication. Mean (min.–max.) chlorophyll $a$, total nitrogen (TN), and total phosphorus (TP) concentrations observed monthly at the center of the lake for 1980–2010 were 53 (3–140), 1040 (520–1990), and 94 (21–238) $\mu$g l$^{-1}$, respectively. Nitrogen and phosphorus load from the basin to the lake increased during the high economic growth period.

Considerable increases in turbidity and inorganic content in suspended solids (SS), due mainly to the resuspension of bottom sediments, were also observed in the lake from the late 1990s to mid 2000s, possibly causing the decline in primary production and the increase in phosphorus concentrations (Fukushima et al. 2005; Seki et al. 2006).
Chapter 3

Long-term changes of silicon concentrations in a shallow eutrophic lake

3.1 Introduction

Si is essential for diatoms, play an important role in the global primary production (Schelske 1999). In recent years, DSi load from land to coastal area may be declining globally, which are probably caused by human activities such as dam construction and N and P emission promoting diatom sinking and sedimentation in dammed reservoirs (Humborg et al. 1997; Li et al. 2007). Similar trend was observed in Japan; however, few monitoring of Si makes it difficult to elucidate the long-term Si dynamics in stagnant waters (The Foundation of River & Watershed Environment Management 2007). In fact, few studies investigated long-term trends of Si concentrations in inland waters around the world. Among the few studies, Vesely et al. (2005) showed the increasing trends of DSi concentration in five glacial lakes in the Bohemian Forest over
the last two decades. They concluded that the higher mobility of Si from the soil to surface waters resulted from a decrease in dissolved Al and faster dissolution of biogenic Si (BSi). Several studies indicated that, as a consequence of diatom sedimentation, Si was released back to the water column (Rippey 1983; Schelske et al. 1988; Szczepocka and Szulc 2006).

Annual changes in DSi concentrations and diatom abundances were assessed in many studies. Bailey-Watts (1976b) assessed the Si budget in the shallow, eutrophic Loch Leven based on the monitoring of DSi and BSi in the water column and on laboratory experiments determining diatom cell sinking rates and Si release rates from diatom frustules and sediments. The authors suggested that the incorporation of diatom frustules into the sediments and the release of DSi from the sediments were more important than the inflows and outflow in the lake. Cornwell and Banahan (1992) calculated the Si budget in shallow, ultraoligotrophic Lake Toolik based on the monitoring of DSi concentrations in streams and the water column and on estimated Si burial and release rates; these estimations were obtained through analyzing pore water and BSi concentrations in $^{210}$Pb-dated sediment, respectively. Although the internal cycling of DSi was about half of the flux through inflows, the study indicated that internal cycling can supply a significant part of the biologically utilized amount in the lake. Also, the budgets in other shallow lakes reported in previous studies suggested that Si cycling within lakes played an important role in determining the available Si for diatoms (e.g., Gibson et al. 2000; Miretzky and Cirelli 2004). On the other hand, Hoffman et al. (2002) found that the main source and export of DSi in the North basin of Lake Lugano, permanently stratified below a 100-m depth, were river input and final burial of diatom frustules in the bottom sediment, respectively, indicating that the North
basin of Lake Lugano acted as an important permanent sink for Si. Although a number of studies have assessed the annual Si budgets in shallow lakes, detailed studies analyzing the long-term Si dynamics are scarce.

In Lake Kasumigaura, various forms of Si have been monitored for the last three decades and several trends were detected. Understanding the dynamics of Si in a shallow eutrophic lake is extremely valuable. Therefore, the objectives of the present chapter are twofold: (1) to detect the long-term trend of Si concentrations in Lake Kasumigaura, and (2) to discuss the factors influencing this trend.

3.2 Materials and methods

3.2.1 Silicon concentrations and other water qualities in Lake Kasumigaura

The database of water quality used for this study was based on the investigation by two institutes during April 1980 – March 2007. The National Institute for Environmental Studies (NIES) collected surface waters once a month at 10 sites (A1–A4, B1–B3, and C1–C3; Figure 3.1). C1 is located at the center of the lake. Water filtered through 0.45-μm glass-fiber was analyzed by inductively-coupled plasma (ICP) to determine the concentrations of DSi (expressed as DSi_{ICP} in this chapter) and other elements (B, Ca, K, Mg, Na, and Sr). Diatom, SS, and chlorophyll a concentrations taken by a column-sampler (upper 2 m) and data on basic water quality (e.g., water temperature, pH, DO, transparency observed in the field) were also used for statistical analysis. Diatoms were counted on an inverted microscope and quantified as biovolume by
Figure 3.1 Sampling points in Lake Kasumigaura
multiplying counted cell number by mean cell volume.

The Kasumigaura River Office (KRO) collected surface waters once a month at 3 sites. They are relatively close to A2, B2, and C1; therefore, we call them by the same names as the NIES stations for the sake of simplicity. The concentrations of DSi were measured by silicomolybdate yellow colorimetric method JIS K 0101 after filtering the sampled water through a 0.45-μm membrane filter. In this chapter, “DSi_{col}” indicates the Si determined by the colorimetric method. Total Si (TSi) concentrations were determined by the same method as DSi_{col} after alkaline digestion of solids in water as specified by method JIS K 0101.

Monthly precipitation data at Tsukuba meteorological weather station were obtained from the web site (http://www.jma.go.jp/jma/) and used for analysis.

Particulate Si (PSi) concentrations were estimated through the subtraction of DSi_{col} from TSi at C1. PSi consists of biogenic and lithogenic one. In Lake Kasumigaura, BSi concentrations could be estimated from diatom concentrations and mean Si density of diatom frustules (1.1 \times 10^{-10} \text{ mg } \mu m^{-3}), determined by averaging the values found in Bailey-Watts (1976a) and Sicko-Goad et al. (1984). Lithogenic Si (LSi) concentrations were estimated through the subtraction of BSi from PSi.

### 3.2.2 Silicon concentrations of the rivers inflowing Lake Kasumigaura

Si concentrations of the main rivers inflowing Lake Kasumigaura were used in this study. In 1994, DSi_{ICP} concentrations of 10 rivers (Sakura, Koise, Sonobe, Ono, Hanamuro, Seimei, Sannou, Amano, Shin, and Takahashi Rivers) were seasonally
measured by NIES (N = 4). In 2007, DSi$_{\text{col}}$ concentrations of 5 rivers (Sakura, Ono, Seimei, Tomoe, and Hokota Rivers) were measured almost monthly by KRO (N = 11). Only 3 rivers (Sakura, Ono, and Seimei Rivers) were investigated by both institutions. In addition, we measured both DSi$_{\text{ICP}}$ and DSi$_{\text{col}}$ concentrations of 12 rivers (Sakura, Koise, Sonobe, Ono, Hanamuro, Seimei, Kajinashi, Ichinose, Hishigi, Shin, Tomoe, and Hokota Rivers) by ICP and colorimetric method, respectively, in December 2009 (Figure 3.2). There was no rainfall for 3 days before almost all samplings.

3.3 Results

3.3.1 Long-term trends of silicon concentrations in Lake Kasumigaura

Mean (min.–max.) of DSi$_{\text{col}}$, DSi$_{\text{ICP}}$, and TSi concentrations were 2.4 (0.0–9.3), 3.1 (0.0–10.3), and 4.7 (0.1–22.2) mg l$^{-1}$, respectively, at C1 during April 1980 – March 2007. Although we cannot make a fair comparison because of the difference in the sampling date, about 80% of DSi$_{\text{ICP}}$ concentrations were larger than DSi$_{\text{col}}$ concentrations at C1, which might be caused by the difference in the method for analysis. The annual average DSi$_{\text{col}}$ and TSi concentrations significantly increased ($p < 0.001$), along with DSi$_{\text{ICP}}$ concentrations ($p < 0.01$), at C1 during this period (Table 3.1; Figure 3.3). The annual maximum of each Si concentration and the minimum of TSi also significantly increased ($p < 0.001$), except in 2006, when declines were observed. From the 1980s to 2000s, the averages of DSi$_{\text{col}}$, DSi$_{\text{ICP}}$, and TSi concentrations at C1 changed from 1.3, 2.2, and 2.2 to 4.0, 4.8, and 8.4 mg l$^{-1}$, respectively, which represents
Figure 3.2  Sampling points of river water in Lake Kasumigaura Basin
Table 3.1  Mean Si concentrations in the 1980s/1990s/2000s and yearly trends detected by t-test

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean concentrations in the 1980s/1990s/2000s (mg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DS\textsubscript{icol}</td>
</tr>
<tr>
<td>A1</td>
<td>8.1/ 7.1/ 7.1</td>
</tr>
<tr>
<td>A2</td>
<td>3.0/ 4.0/ 5.1+++</td>
</tr>
<tr>
<td>A3</td>
<td>3.4/ 3.6/ 5.0++</td>
</tr>
<tr>
<td>A4</td>
<td>2.6/ 3.0/ 4.9++</td>
</tr>
<tr>
<td>B1</td>
<td>7.2/ 6.0/ 7.3</td>
</tr>
<tr>
<td>B2</td>
<td>2.1/ 3.1/ 4.6+++</td>
</tr>
<tr>
<td>B3</td>
<td>2.7/ 3.1/ 4.9+</td>
</tr>
<tr>
<td>C1</td>
<td>1.3/ 2.4/ 4.0+++</td>
</tr>
<tr>
<td>C2</td>
<td>2.2/ 2.9/ 4.9++</td>
</tr>
<tr>
<td>C3</td>
<td>2.2/ 3.0/ 5.0++</td>
</tr>
</tbody>
</table>

+, increase; -, decrease

+ or -, \( p < 0.05 \); ++ or --, \( p < 0.01 \); +++ or ---, \( p < 0.001 \)
Figure 3.3  Changes in DSi$_{col}$ (a), DSi$_{ICP}$ (b), and TSi (c) concentrations at C1 during 1980–2006. Bars indicate standard deviations. Legends (+, ++, +++, –, ––, and –––) are the same as in Table 3.1
210, 120, and 290% increases, respectively. On the other hand, ratios of change for the other dissolved elements (B, Ca, K, Mg, Na, and Sr) were within ±15% (data not shown).

Similar Si changes were also observed at A2 and B2 (Table 3.1). With the exception of DSiICP at A2, increasing trends of DSicol, DSiICP, and TSi concentrations were detected; however, these increases (37–180%) were lower than those at C1. Increasing trends of DSiICP concentrations were seen around the center of the lake, such as at A4 and B3 (Table 3.1). In contrast, DSiICP concentrations decreased at A1, near the Koise River ($p < 0.05$), and a clear trend was not detected at B1, near the Sakura River. The temporal and spatial variations of DSiICP concentrations in Figure 3.4 represent the DSi loads from inflowing rivers and progressive decreases in DSi as the flows approach the center of the lake. The concentrations at C1 were transiently higher than those at the stations near the inflowing rivers (A1 and B1) in every summer during the period of 2002–2005.

Changes in the annual averages of DSicol, BSi and LSi concentrations at C1 are shown in Figure 3.5. Increasing trends of DSicol, BSi and LSi concentrations were detected ($p < 0.001$). The increases in DSicol, BSi and LSi accounted for 44, 11 and 45%, respectively, of the TSi increase of 6.2 mg l$^{-1}$ from the 1980s to 2000s.

3.3.2 Relationships between silicon concentrations and other water quality items

DSicol concentration was positively correlated with DSiICP concentration (Table 3.2). DSicol, DSiICP, and BSi concentrations were also related to LSi concentration. In
Figure 3.4 Temporal and spatial variation of DSi\textsubscript{ICP} concentrations in Lake Kasumigaura during April 1980 – March 2007
Figure 3.5  Changes in annual averages of DSi$_{\text{col}}$ concentration (observed) and BSi and LSi concentrations (estimated) at C1 during 1980–2006. Legends (+, ++, +++, –, –, and – – –) are the same as in Table 3.1
Table 3.2  Correlation coefficient matrix of annual mean water quality items at the center of Lake Kasumiguara and annual precipitation at Tsukuba meteorological weather station during 1980–2006. \( N = 27 \) for all relationships except \( pH \) versus others \( (N = 24) \). Legends (+, ++, +++, –, ––, and –––) are the same as in Table 3.1

<table>
<thead>
<tr>
<th></th>
<th>DS(_{icol})</th>
<th>DS(_{ICP})</th>
<th>BSi</th>
<th>LSi</th>
<th>SS</th>
<th>ISS</th>
<th>Chl-a</th>
<th>WT</th>
<th>pH</th>
<th>DO</th>
<th>Transp</th>
<th>PT</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS(_{icol})</td>
<td>0.95</td>
<td>0.30</td>
<td>0.64</td>
<td>0.61</td>
<td>0.64</td>
<td>-0.27</td>
<td>-0.03</td>
<td>-0.55</td>
<td>-0.35</td>
<td>-0.61</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>DS(_{ICP})</td>
<td>++</td>
<td>0.27</td>
<td>0.60</td>
<td>0.61</td>
<td>0.63</td>
<td>-0.26</td>
<td>-0.09</td>
<td>-0.46</td>
<td>-0.35</td>
<td>-0.56</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>BSi</td>
<td></td>
<td>0.53</td>
<td>0.64</td>
<td>0.61</td>
<td>-0.05</td>
<td>0.04</td>
<td>0.16</td>
<td>0.07</td>
<td>0.59</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSi</td>
<td>++</td>
<td>++</td>
<td>0.88</td>
<td>0.88</td>
<td>-0.24</td>
<td>0.08</td>
<td>-0.21</td>
<td>-0.37</td>
<td>-0.75</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>0.97</td>
<td>-0.15</td>
<td>0.10</td>
<td>0.22</td>
<td>-0.29</td>
<td>-0.87</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>ISS</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-0.38</td>
<td>0.15</td>
<td>-0.26</td>
<td>-0.37</td>
<td>-0.78</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Chl-a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>-0.17</td>
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<td>WT</td>
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<td></td>
<td></td>
<td></td>
<td>0.33</td>
<td>0.32</td>
<td>0.13</td>
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</tr>
<tr>
<td>pH</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.16</td>
<td>-0.40</td>
<td>-0.08</td>
<td>0.20</td>
</tr>
<tr>
<td>DO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.22</td>
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</tr>
<tr>
<td>Transp</td>
<td>--</td>
<td>--</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>PT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
</tbody>
</table>

\( ISS \), inorganic suspended solids estimated by Seki et al. (2006); \( Chl-a \), chlorophyll \( a \); \( WT \), \( pH \) and \( DO \), water temperature, \( pH \) and dissolved oxygen at 0.5 m depth; \( Transp \), transparency; \( PT \), precipitation
addition, each Si concentration was significantly related to SS, inorganic content of SS, and transparency. These correlations indicate that the Si increases were related to sediment resuspension. In fact, the increase in LSi appears to be directly caused by it. In contrast, DSi, BSi, and LSi were insignificantly correlated with chlorophyll $a$, water temperature, DO, and precipitation.

3.4 Discussion

3.4.1 Potential causes of the silicon increase around the center of Lake Kasumigaura

3.4.1.1 Watershed

Contrary to the detected trends around the center of the lake, DSi$_{ICP}$ concentrations near the inflowing rivers did not increase, suggesting that the loads from the inflowing rivers had not increased. DSi loads through rivers were compared between different two years (Table 3.3). In 1994, the average (min.–max.) of annual mean DSi$_{ICP}$ concentration of the 10 NIES-monitored inflowing rivers was 12.7 (9.9–15.6) mg l$^{-1}$, with that of the 3 “overlapping” rivers (i.e., the Sakura, Ono, and Seimei Rivers) being 12.2 (10.6–13.3) mg l$^{-1}$. In 2007, the average (min.–max.) of annual mean DSi$_{col}$ concentrations of the 5 KRO-monitored rivers was 9.4 (7.8–10.9) mg l$^{-1}$, with the 3 “overlapping” rivers being 8.8 (7.8–9.8) mg l$^{-1}$. In addition, the investigation showed that the ratio of DSi$_{col}$ to DSi$_{ICP}$ concentration was 0.98 ($r^2 = 1.00$). These results suggest that DSi concentrations of inflowing rivers did not increase but rather decreased. The discharge of inflowing
Table 3.3  Mean DSi concentrations at 15 rivers inflowing Lake Kasumigaura in 1994, 2007, and 2008–2009. Standard deviations were noted in parentheses. There was no rainfall for 3 days before almost all samplings.

<table>
<thead>
<tr>
<th>Rivers</th>
<th>DS$_{\text{ICP}}$ (mg I$^{-1}$)</th>
<th>DS$_{\text{col}}$ (mg I$^{-1}$)</th>
<th>DS$_{\text{ICP}}$ (mg I$^{-1}$)</th>
<th>DS$_{\text{col}}$ (mg I$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in 1994 (N = 4)</td>
<td>in 2007 (N = 11)</td>
<td>in 2008 and 2009 (N = 2~3)</td>
<td></td>
</tr>
<tr>
<td>Amano</td>
<td>11.4 (3.5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hanamuro</td>
<td>13.7 (3.2)</td>
<td>-</td>
<td>14.9 (1.2)</td>
<td>15.2 (0.9)</td>
</tr>
<tr>
<td>Hishiki</td>
<td>-</td>
<td>-</td>
<td>11.6 (1.1)</td>
<td>11.9 (0.6)</td>
</tr>
<tr>
<td>Hokota</td>
<td>-</td>
<td>10.9 (1.5)</td>
<td>14.6 (0.9)</td>
<td>14.9 (0.4)</td>
</tr>
<tr>
<td>Ichinose</td>
<td>-</td>
<td>-</td>
<td>11.3 (0.6)</td>
<td>11.6 (0.2)</td>
</tr>
<tr>
<td>Kajinashi</td>
<td>-</td>
<td>-</td>
<td>12.8 (1.5)</td>
<td>12.9 (1.1)</td>
</tr>
<tr>
<td>Koise</td>
<td>9.9 (3.2)</td>
<td>-</td>
<td>11.6 (0.9)</td>
<td>12.0 (0.5)</td>
</tr>
<tr>
<td>Ono</td>
<td>12.6 (2.6)</td>
<td>8.8 (1.2)</td>
<td>12.0 (0.7)</td>
<td>12.2 (0.4)</td>
</tr>
<tr>
<td>Sakura</td>
<td>10.6 (2.6)</td>
<td>7.8 (1.3)</td>
<td>12.0 (0.7)</td>
<td>12.2 (0.4)</td>
</tr>
<tr>
<td>Sannou</td>
<td>15.2 (2.6)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Seimei</td>
<td>13.3 (4.5)</td>
<td>9.8 (3.0)</td>
<td>13.4 (1.3)</td>
<td>13.7 (0.8)</td>
</tr>
<tr>
<td>Shin</td>
<td>15.6 (4.9)</td>
<td>-</td>
<td>17.4 (1.5)</td>
<td>17.9 (0.7)</td>
</tr>
<tr>
<td>Sonobe</td>
<td>12.2 (4.0)</td>
<td>-</td>
<td>12.7 (1.0)</td>
<td>13.2 (0.6)</td>
</tr>
<tr>
<td>Takahashi</td>
<td>12.4 (3.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tomoe</td>
<td>-</td>
<td>9.6 (1.6)</td>
<td>13.2 (1.3)</td>
<td>13.4 (0.8)</td>
</tr>
<tr>
<td>3 rivers average$^a$</td>
<td>12.2 (3.2)</td>
<td>8.8 (2.1)</td>
<td>12.5 (1.2)</td>
<td>12.7 (1.0)</td>
</tr>
<tr>
<td>All rivers average</td>
<td>12.7 (3.5)</td>
<td>9.4 (2.0)</td>
<td>13.1 (1.9)</td>
<td>13.4 (1.7)</td>
</tr>
</tbody>
</table>

$^a$ Sakura, Ono, and Seimei River
rivers also did not increase; therefore, DSi loads through the rivers could not have caused the increase in DSi concentrations in the lake.

3.4.1.2 In-lake processes

Changes in the rate of DSi uptake by diatoms might cause the observed changes in Si concentrations. However, no decrease in volume concentrations of diatoms at C1 was detected. Bailey-Watts (1976a) and Sicko-Goad et al. (1984) suggested that the BSi contents in freshwater diatom cells are almost in the same order among species. These considerations suggest that the diatom production could not have caused the increasing trend.

BSi dissolution is one of the important process in several lakes (e.g., Bailey-Watts 1976b). For living diatoms, frustules are protected from dissolution by an organic coating (Lewin 1962; Kristiansen and Hoell, 2002), which are degraded by bacterial activity (Bidle and Azam 1999). Some diatoms also secrete macromolecules which have been suggested to protect against dissolution (Hoagland et al. 1993). In many studies, primary source of DSi release was frustules of dead diatoms accumulated in bottom sediments. DSi release rates from lake sediments were enhanced by increases in water temperature and pH (Rippey 1983; Loucaides et al. 2008). In Lake Kasumigaura, however, the annual average water temperature and pH have not significantly increased during the last three decades. On the other hand, the turbidity increase due to sediment resuspension observed in the lake from the late 1990s caused the increase in LSi concentration, and might provide the opportunity for increases in DSi concentration through regeneration of Si. DSi of sediment pore water might also be released with
resuspension. However, surface sediments less than 2 cm depth were affected by sediment resuspension (Seki et al. 2006), and DSi concentrations of those pore water were considered to be not so different from those in the water column; therefore, the DSi release from pore water might be neglected. Fukushima et al. (2005) roughly discussed the causes for the increased resuspension like the changes in meteorological condition, physical properties of sediments, benthic ecosystem, aquatic plants, and geomorphologic conditions. The plausible causes were suggested such as the changes in the organic content and water content of the sediments perhaps resulted from the recovery of the lake from hyper-eutrophicated condition and/or the transition from blackish water to freshwater; however, the authors indicated that the further investigation was needed.

3.5 Conclusions

Significant increases in Si concentrations were observed at the center of the lake over the last three decades. Dissolved and lithogenic Si accounted for 44% and 45% of the increase in total Si concentration of 6.2 mg l\(^{-1}\) from the 1980s to 2000s, respectively, and that biogenic Si, consisting of diatom frustules, also increased with them. DSi concentrations did not increase near the mouth of the inflowing rivers, suggesting that the DSi increase was caused by in-lake processes. We assumed the contribution of release from SS derived from sediments, which had increased in the lake from the late 1990s to mid 2000s, to be the cause of this DSi increase.

The final publication is available at www.springerlink.com.
Chapter 4

Silicon release from suspended solids and bottom sediments in a shallow eutrophic lake

4.1 Introduction

As a result of statistical analysis, DSi release from resuspended seiment was suspected as a major factor of DSi increase observed at the center of the lake. In fact, several studies indicated that, as a consequence of diatom sedimentation, Si was released back to the water column (Rippey 1983; Schelske et al. 1988; Szczepocka and Szulc 2006). The importance of Si cycling within a lake was indicated in several studies (Bailey-Watts 1976b; Cornwell and Banahan 1992; Gibson et al. 2000; Miretzky and Cirelli 2004); however, previous studies focused on DSi release from bottom sediments, but not on release from SS derived from sediments. Sediment resuspension tends to occur in shallow lakes by relatively strong wind. Those lakes are often used by human activities and consequently eutrophicated; therefore, it is important to assess the DSi
release from SS in such lakes.

The objectives of the present chapter are twofold: (1) to estimate the DSi release rates from SS and bottom sediments by laboratory experiments, and (2) to assess the contribution of DSi release to the increasing trend of DSi observed in the lake.

4.2 Materials and methods

4.2.1 Sampling

We sampled the surface sediments with an Ekman-Birge type bottom sampler at the center of the lake (C1) in August 2008 and June and October 2009 (Figure 4.1). Sediments at A3 and B3 were also sampled in August 2008. Lake waters were collected at A3, B3, C1, and C3 in August 2008, at B0 (located at Tsuchiura-Port) in November 2008, and at C1 in June and October 2009. Lake waters were filtered through 0.45-μm membrane filters. Filtrates and sediments were stored at 1°C under dark conditions before the incubation experiments. BSi contents of sediments were determined by colorimetric method after wet alkaline digestion according to DeMaster (1981).

4.2.2 Experiment design

4.2.2.1 Silicon release experiments from suspended solids

DSi release rates from SS were assessed in the laboratory (Table 4.1A). The sediments were mixed with lake water or distilled water at various SS concentrations (about 50–
Figure 4.1  Sampling points in Lake Kasumigaura
<table>
<thead>
<tr>
<th>Sediment</th>
<th>SS conc. (mg l⁻¹)</th>
<th>Water</th>
<th>Sampling day</th>
<th>DSi₄₋₉ (mg l⁻¹)</th>
<th>Si release rate (mg g⁻¹ day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>500</td>
<td>DW</td>
<td>25°C</td>
<td>0.10</td>
<td>0.64</td>
</tr>
<tr>
<td>B1</td>
<td>500</td>
<td>DW</td>
<td>25°C</td>
<td>0.05</td>
<td>0.61</td>
</tr>
<tr>
<td>C1</td>
<td>700 ml</td>
<td>DW²</td>
<td>25°C</td>
<td>0.09</td>
<td>0.63</td>
</tr>
<tr>
<td>S1-1</td>
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<td>DW</td>
<td>25°C</td>
<td>0.01</td>
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</tr>
<tr>
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<td>DW</td>
<td>25°C</td>
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<tr>
<td>S1-2</td>
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<td>120</td>
<td>LW</td>
<td>25°C</td>
<td>0.14</td>
<td>0.23</td>
</tr>
<tr>
<td>S3-2</td>
<td>190</td>
<td>LW</td>
<td>25°C</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>S4-2</td>
<td>340</td>
<td>LW</td>
<td>25°C</td>
<td>0.19</td>
<td>0.15</td>
</tr>
<tr>
<td>S1-3</td>
<td>530</td>
<td>LW</td>
<td>25°C</td>
<td>1.10</td>
<td>0.36</td>
</tr>
<tr>
<td>S2-3</td>
<td>1600</td>
<td>LW²</td>
<td>25°C</td>
<td>4.71</td>
<td>0.23</td>
</tr>
<tr>
<td>S3-3</td>
<td>820</td>
<td>LW²</td>
<td>25°C</td>
<td>6.01</td>
<td>0.10</td>
</tr>
<tr>
<td>S4-3</td>
<td>230</td>
<td>LW</td>
<td>25°C</td>
<td>4.26</td>
<td>0.18</td>
</tr>
</tbody>
</table>

**Type (Sampled on):**
- **A**: From suspended solids
- **B**: From bottom sediments
- **C**: From other sources

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Water</th>
<th>Sampling day</th>
<th>DSi₄₋₉ (mg l⁻¹)</th>
<th>Si release rate (mg g⁻¹ day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>9.9 cm</td>
<td>700 ml</td>
<td>25°C</td>
<td>1.6</td>
</tr>
<tr>
<td>B2</td>
<td>9.9 cm</td>
<td>700 ml</td>
<td>25°C</td>
<td>1.6</td>
</tr>
<tr>
<td>B3</td>
<td>9.9 cm</td>
<td>700 ml</td>
<td>25°C</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Notes:**
- DW and LW indicate distilled water and lake water, respectively.
- Mixture of lake waters sampled at A3, B3, C1, and C3 on August 7th, 2008.
- Mixture of lake waters sampled at A3 on August 7th and at B0 on November 13th, 2008.
- After replacing the overlying water by distilled water.

---

**Table 4.1** Summary of experimental design and results of DSi release experiments from SS (A) and bottom sediments (B)
500 mg l\(^{-1}\)) in a polycarbonate bottle (500 ml or 1 l) and stirred continuously by magnetic stirrer under dark conditions at room temperature (25°C). Two additional water temperature conditions, 1 and 15°C, were used, for which the samples were not stirred continuously but mixed once a day by hand. Aliquots of 3–10 ml were taken from the bottles at the beginning of the experiment, every day or every second day in the first week, and then every other week. pH, EC, and DO were measured to be 8.0–8.3, 290–330 μS cm\(^{-1}\), and 5–8 mg l\(^{-1}\), respectively, for the experiments using lake waters.

### 4.2.2.2 Silicon release experiments from bottom sediments

DSi release rates from bottom sediments were also assessed in the laboratory (Table 4.1B). Distilled or lake water was added to the sediments gradually in polyethylene bottles under dark conditions. In the series of experiments on B1 and B2, three sediment-water volume ratios were used at 25°C. In the series of experiments on B3, various sediment thicknesses and three water temperature conditions (1, 15, and 25°C) were used. Aliquots of 3–10 ml were taken from the bottles at the beginning of the experiment, every 2–7 days in the first month, and several times later. Before sampling, the water was stirred softly. In the experiments B3-2, -5, and -6, almost all of the water was siphoned, and the same volumes of new distilled water were replaced at Days 90 and 104. pH, EC, and DO were measured to be 6.7–7.8, 290–410 μS cm\(^{-1}\), and 1–8 mg l\(^{-1}\), respectively, for the experiments using lake water.
4.2.3 Analysis

All aliquots were filtered through 0.45-μm membrane filters and kept at 1°C, under dark conditions. DSi concentrations were determined by silicomolybdate yellow or blue colorimetric method. In the DSi release experiments from SS, the rate of change in DSi concentration was divided by SS concentration to estimate DSi release rate from SS as Table 4.1A, calculated in mg g⁻¹ day⁻¹. Meanwhile, in the DSi release experiments from bottom sediments, the rate of change in DSi concentration was divided by the cross-sectional area to estimate DSi release rate from bottom sediments as Table 4.1B, calculated in g m⁻² day⁻¹.

For checking the budget in the system, aliquots of 30 ml were taken at the start and end of experiments S4-3 and S5-4, respectively. Aliquots of 20 ml were filtered through 0.45-μm membrane filters for analyzing BSi by the method according to DeMaster (1981). Aliquots of 10 ml were used for analyzing TSi by silicomolybdate yellow colorimetric method after alkaline digestion according to JIS K 0101.

4.3 Results

4.3.1 Silicon release rates from suspended solids

The BSi contents of sediments sampled at A3, B3, and C1 in August 2008 and at C1 in June and October 2009 were 23, 29, 38, 40, and 43 mg g⁻¹, respectively. DSi release rates from the sediments sampled at A3 and B3 were within ± 20% of the rate at C1 (Table 4.1, S1). C1 is representative of the center area of the lake; therefore, we applied
the rates obtained at C1 to the whole lake. DSi$_{col}$ concentrations were approximately proportional to SS concentrations at the same condition in the experiment S2 and S3 ($r^2 = 0.90$–$1.00$, Figure 4.2). This result means that DSi release rates from SS were independent of SS concentrations in this experiment. DSi release rates in lake water were higher than those in distilled water (Figure 4.2). Loucaides et al. (2008) suggested that such an enhancement of the DSi release rate was due to the catalytic effect of seawater cations, which may cause the difference in the rates in this study. In addition, DSi release rates strongly depended on water temperature (Table 4.1, S4).

Changes in DSi$_{col}$ concentrations from Day 0 for various combinations of sediment and lake water are shown in Figure 4.3. Concentration changes could be largely divided into two parts, until and after Day 1. Until Day 1, DSi release rates were quite different among used lake waters. DSi$_{col}$ concentrations increased in S3 using C1 lake water in June 2009 ($1.10 \pm 0.16$ mg g$^{-1}$ day$^{-1}$), remained almost constant in S5-4 using C1 lake water in October 2009 ($-0.09$ mg g$^{-1}$ day$^{-1}$), and decreased in S5-1 using B0 lake water ($-0.36$ mg g$^{-1}$ day$^{-1}$). On the other hand, after Day 1, DSi release rates were not so different among the waters, but gradually decreased with time. DSi release rates of S3 during Days 0–1, 1–7, and 7–28 were $1.10 \pm 0.16$, $0.29 \pm 0.04$, and $0.24 \pm 0.03$ mg g$^{-1}$ day$^{-1}$, respectively. Loucaides et al. (2008) determined the DSi release rates from fresh diatom frustules and two diatomaceous lake sediments in freshwater at 25°C under stirred, flow-through conditions, which were 0.6, 0.9, and 1.6 mg g$^{-1}$ day$^{-1}$, respectively. They used BSi-rich materials; therefore, the results in this study were lower than those values but of the same order.

TSi concentrations of S4-3 and S5-4 were not so different between the start and end of the experiment ($\pm 10\%$, within the measurement error); therefore, the closed system
Figure 4.2  Relationship between SS concentrations and DSi\textsubscript{col} concentrations using the sediments sampled at C1 in June 2009. Distilled water and lake water sampled at C1 in June 2009 were used. DSi\textsubscript{col} concentrations at Day 0 were subtracted from those at each day. Details are shown in Table 4.1 (S2 and S3)
Figure 4.3  Changes in DSi\textsubscript{col} concentrations released from SS. DSi\textsubscript{col} concentrations at Day 0 were subtracted from those at each day. Details are shown in Table 4.1 (S3-3, S5-1, and S5-4)
was confirmed. The sum of DS$_{\text{col}}$ and BSi concentrations was nearly the same between them (± 8%; for example, DS$_{\text{col}}$ and BSi concentrations in the experiment S5-4 were 4.3 and 10.2 mg l$^{-1}$ at Day 0 and 5.3 and 8.5 mg l$^{-1}$ at Day 28, respectively), suggesting that the main source of DSi was BSi, mostly consisting of diatom frustules. In addition, DSi release rates from LSi are typically five orders of magnitude slower than those from BSi (Hurd 1983), and as such, we expected a negligible influence of LSi on DSi release. The estimated degradation ratios of BSi of S3 at Days 1, 7, and 28 were 2.7 ± 0.4, 7.1 ± 0.5, and 20.0 ± 2.0%, respectively. The ratios of S5-1 at Day 32 and S5-4 at Day 28 were 7.3% and 6.5%, respectively, and they were lower than those of S3. The variability may be affected by diatom frustules. Bailey-Watts (1976b) determined the degradation ratio of BSi using dead diatom frustules at 20°C under dark conditions, which were 17% after 38 days and 19% after 50 days, and my values at Day 28 were not far from those.

4.3.2 Silicon release rates from bottom sediments

DSi release rates from bottom sediments were not significantly different between distilled water and lake water (initial concentration was 0.1 mg-Si l$^{-1}$), indicating that the catalytic effect of cation was saturated by release from sediments in this experiment (Table 4.1, B1 and B2). The release rates were also independent of sediment thickness in the range of this experiment (Table 4.1, B3). On the other hand, they largely depended on water volume (B1 and B2) and temperature (B3). The rates during Days 0–8 at 1, 15, and 25°C were 0.020 ± 0.006, 0.051 ± 0.001, and 0.084 ± 0.002 g m$^{-2}$ day$^{-1}$, respectively. Also, they gradually decreased with time (Figure 4.4a). In series B3, DSi release rates at 25°C during Days 0–8, 8–15, and 15–25 were 0.084 ± 0.002, 0.039 ±
Figure 4.4  DSi$_{\text{col}}$ concentrations in the series of the experiment B3 with no water replacement (a) and with replacing the overlying water by distilled water at Days 90 and 104 (b)
0.002, and 0.023 ± 0.001 g m$^{-2}$ day$^{-1}$, respectively. DSi$_{col}$ concentrations gradually reached constant values, depending on water temperature. After replacing the old water with distilled water in the experiments of B3-2, -5, and -6, DSi release rates were much enhanced (Figure 4.4b). This result suggests that the decrease in the rates with time was not caused by a change in sediment qualities, such as aging of diatom frustules, but caused by the change in overlying water qualities, such as DSi concentration. The variance of the rates among the three water volumes in the experiments of B1 and B2 also supports this consideration because the rates were independent of sediment thickness. Bailey-Watts (1976b) and Rippey (1983) measure DSi release rates in laboratory cores sampled at shallow eutrophic lakes (0.02–0.10 and 0.05–0.39 g m$^{-2}$ day$^{-1}$, respectively), and my results in the first week were within those values.

4.4 Discussion

4.4.1 Factors influencing the silicon release rates from suspended solids

The experimental conditions were aerobic, as was the field condition; therefore, no anaerobic biodegradation of diatom frustules should have occurred. DSi uptake by diatoms (that might be alive in the sediments) can be neglected under dark conditions. Therefore, inorganic processes are the focus of the following discussion. Experimental results revealed that DSi release rates from SS depended mainly on water temperature and used lake waters whose DSi$_{col}$ concentrations had a large variability (0.1–11.4 mg l$^{-1}$). The latter was observed only at the beginning of the experiment, but the rates were
nearly constant among lake waters after Day 1. Notably, the rate during Day 0–1 was negative in B0 lake water, whose DSi\textsubscript{col} concentration was the highest. These results suggested that the DSi\textsubscript{col} concentrations were not only affected by dissolution of diatom frustules, but also by the transport of adsorbed Si on SS. The dissolution of LSi can be neglected (Hurd 1983). From these considerations, the change in DSi\textsubscript{col} concentration in the DSi release experiment from SS can be expressed as follows:

\[
\frac{dC_{\text{DSi}}}{dt} = -\frac{d\alpha}{dt}_{\text{SS}} - \frac{dC_{\text{BSi}}}{dt} \quad (4.1)
\]

where \(C_{\text{DSi}}\) is the DSi\textsubscript{col} concentration (mg l\(^{-1}\)), \(t\) is the time (day), \(\alpha\) is the Si adsorbed on the surface of SS (mg g\(^{-1}\)), SS is the suspended solids concentration derived from sediments (g l\(^{-1}\)), and \(C_{\text{BSi}}\) is the BSi concentration (mg l\(^{-1}\)). \(\alpha\) can be described as following equation:

\[
\alpha = \alpha'X \quad (4.2)
\]

where \(\alpha'\) is the Si adsorbed on the carrier (mg mg\(^{-1}\)) and \(X\) is the carrier content of SS (mg g\(^{-1}\)). \(X\) was assumed to be constant in this experiment. Therefore, when the Si dissolved in water comes to equilibrium with the Si adsorbed on SS, \(\alpha\) depends only on the surrounding DSi\textsubscript{col} concentration and can be expressed as following formula:

\[
\alpha = \gamma C_{\text{DSi}} \quad (4.3)
\]
where $\gamma$ is a constant (1 g$^{-1}$). Using Eq. 4.3, the change in the DSi concentration $C_{\text{DSi}}$ can be determined by the following equation:

$$\frac{dC_{\text{DSi}}}{dt} = \frac{1}{1 + \gamma SS} \frac{dC_{\text{BSi}}}{dt} \quad (4.4).$$

In the field, the adsorption equilibrium can be assumed. The constant $\gamma$ and the change in BSi concentrations ($dC_{\text{BSi}}/dt$) are unknown and can be determined as described below.

Experimental results suggested that the Si dissolved in water and adsorbed on the surface of SS might not have been at equilibrium on Day 0, but had reached equilibrium by Day 1 at the latest. Therefore, we can assume that $\alpha$ was independent of $C_{\text{DSi}}$ on Day 0 and dependent on it on Day 1 ($\alpha_1 = \gamma C_{\text{DSi},1}$). Applying this assumption to Eq. 4.1, the following equation was obtained:

$$\frac{C_{\text{DSi},1} - C_{\text{DSi},0}}{SS} = (\alpha_1 - \alpha_0) - \frac{C_{\text{BSi},1} - C_{\text{BSi},0}}{SS} = \alpha_0 - \frac{C_{\text{BSi},1} - C_{\text{BSi},0}}{SS} - \gamma C_{\text{DSi},1} \quad (4.5)$$

where the subscripts indicate the days since the experiment started. The values of $\alpha_0$ are specific to the used sediments, and $C_{\text{BSi},1} - C_{\text{BSi},0}$ is subject to the Si dissolution rate of diatom frustules, which might be independent of $C$. Thus, the left part of Eq. 4.5 was linearly correlated with $C_{\text{DSi},1}$; as a result, $\gamma$ was determined through a regression analysis to be 0.12 by assuming that the $\alpha_0$ and $C_{\text{BSi},1} - C_{\text{BSi},0}$ are not so different among the used sediments (Figure 4.5).
Figure 4.5  Relationship between DSi_{col} concentrations (C_1) and (C_1-C_0) / SS in the experiment S3 (averaged), S5-1, -2, -3, and -4
Figure 4.6 shows the changes in the Si dissolution rates, \( D \) (mg g\(^{-1}\) day\(^{-1}\)), calculated by the following equation derived from Eq. 4.4:

\[
D = -\frac{1}{SS} \frac{dC_{BSi}}{dt} = 1 + \gamma SS \frac{dC_{PSi}}{dt} \quad (4.6).
\]

The rates decreased exponentially, which suggests that the following reaction rate equations can be applied to the experimental results:

\[
C_{BSi} = C_{BSi,0} e^{-kt} \quad (4.7)
\]

\[
\frac{dC_{BSi}}{dt} = -kC_{BSi,0} e^{-kt} \quad (4.8)
\]

where \( k \) is the dissolution rate constant (day\(^{-1}\)) and the subscript indicates the initial value \( (t = 0) \). The rates decreased notably within about a first week, but were almost constant after that (Figure 4.6). It suggests the decrease in the BSi amount of comparatively fresh diatom frustules which is dissolved more rapidly than old diatom frustules due to alternations of the bulk structure and surface chemistry (Van Cappellen et al. 2002; Gendron-Badou et al. 2003). Now, we assumed that the BSi can be divided into two parts, contained in fresh and old diatom frustules with same temperature dependence of dissolution, and the dissolution rates of old ones were approximately constant on the time scale of this experiment. Defining \( \beta \) as the BSi content of SS (\( = C_{BSi}/SS, \) mg g\(^{-1}\)), the dissolution rate can be described as following equation:
Figure 4.6  Change in Si dissolution rate of SS at 25°C in the experiment S3 (averaged) and S5-4

\[ y = 1.4 \exp(-1.2x) + 0.24 \]
\[ r^2 = 0.91 \]

\[ y = 1.1 \exp(-1.3x) + 0.16 \]
\[ r^2 = 0.87 \]
\[ D = -\frac{dB}{dt} = k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0} e^{-k_o t} \approx k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0} \]  \hspace{1cm} (4.9) \\

where the subscripts f and o indicate the fresh and old diatom frustules, respectively (\( \beta = \beta_f + \beta_o, k_f > k_o \)). The equation could fit well to the experimental results (Figure 4.6). The initial BSi content, \( \beta_0 \) was 40 mg g\(^{-1}\) in the experiment S3 and 43 mg g\(^{-1}\) in the experiment S5-4; therefore, \( \beta_{f0}, \beta_{o0}, k_f, \) and \( k_o \) were determined to be 1.2, 39, 1.2, and \( 6.2 \times 10^{-3} \) in the experiment S3 and 0.8, 42, 1.3, and \( 3.8 \times 10^{-3} \) in the experiment S5-4, respectively. It suggests that the dissolution rate constants, \( k_f \) and \( k_o \), were almost constant for the diatom frustules in the lake. In addition, the experimental period of about 30 days was sufficiently smaller than \( 1/k_o \) of 160–260 days, suggesting that the assumption is reasonable. The mean values of \( k_f \) and \( k_o \) (1.3 and \( 5.0 \times 10^{-3} \), respectively) were used to the estimation for the field as described later. The dissolution rates also correlated positively with water temperature (Figure 4.7). Finally, the rates and the change in DSi\(_{col}\) concentration can be expressed as follows:

\[ D = \left( k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0} \right) e^{\left( \frac{a}{T - T_a} \right)} \]  \hspace{1cm} (4.10) \\

\[ \frac{dC_{DSi}}{dt} = \frac{SS}{1 + \dot{\gamma}SS} \left( k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0} \right) e^{\left( \frac{a}{T - T_a} \right)} \]  \hspace{1cm} (4.11) \\

where \( T \) is the water temperature (K), \( T_a \) is a constant (298.15 K), and \( a \) is a constant (K). The value of \( a \) was determined from the experiment of S4 to be \((4.1–4.4) \times 10^3 \) (Figure 4.7). We applied the mean value of \( a \) of \( 4.2 \times 10^3 \) to the estimation for the field.
Figure 4.7 Relationship between water temperature and Si dissolution rate of SS in distilled water in the experiment S4
as described later.

4.4.2 Factors influencing the silicon release rates from bottom sediments

The results of DSI release experiment from bottom sediments fit well to the equation described in Figure 4.4 (a). DSicol concentrations reached constant values, which could be regarded as the equilibrium concentration, \( C_e \). \( C_e \) was correlated with water temperature (11.7, 14.9, and 25.3 mg l\(^{-1}\) at 1, 15, and 25°C, respectively), and fit to the equation in Figure 4.8 \((r^2 = 0.86)\). Assuming that the concentration close to the surface of the sediments was equal to \( C_e \), and that the concentration adequately far from the sediments was equal to the observed concentration \( (C_{DSi}) \), Si diffusion can be limited by the concentration difference, that is, the subtraction of \( C_{DSi} \) from \( C_e \). Figure 4.9 shows that the rates were linearly correlated with this difference, suggesting that the above assumptions could be applied to DSI release rates from bottom sediments, \( R_{bottom} \) (g m\(^{-2}\) day\(^{-1}\)) and the change in DSI concentration can be written as follows:

\[
R_{bottom} = K \left( C_e - C_{DSi} \right) \quad (4.12)
\]

\[
\frac{dC_{DSi}}{dt} = \frac{R_{bottom}}{h} \quad (4.13)
\]

where \( K \) is the rate constant (m day\(^{-1}\)) and \( h \) is the water depth (m). In this experiment, a temperature dependence of \( K \) was not clearly seen, but it was determined to be \( 4.9 \times 10^{-3} \) \((r^2 = 0.73, \text{ Figure 4.9})\). We applied this equation to the estimation for the field as
Figure 4.8  Relationship between water temperature and the equilibrium concentration of DSi\text{\textsubscript{col}}, \(C_e\) in the experiment B3

\[ y = 4.9 \times 10^{-4} \exp(0.036x) \]

\( r^2 = 0.86 \)
Figure 4.9  Relationship between the difference between DSi$_{\text{col}}$ and equilibrium concentrations ($C_e - C_{\text{DSi}}$) and DSi release rate in the experiment B3

$$y = 4.9 \times 10^{-3} x, \quad r^2 = 0.73$$
4.4.3 Estimation of silicon release rate in Lake Kasumigaura

The annual amount of DSi released from SS in Lake Kasumigaura in 2004 was estimated by assuming that: (1) the particle size distribution of SS in the entire lake is the same as that of this experiment, (2) \( X \) is constant, (3) the influence of variance in the concentrations of cations in lake water can be neglected, (4) SS concentrations contributing to the DSi release are subject to sediment resuspension driven by a critical wind, and (5) SS remaining constantly in the water column (mainly consisting of clay minerals; called as “background SS” in this study) does not affect the DSi release. Using Eq. 4.11, the amount of DSi released from SS can be estimated by following equation:

\[
Y = V_{\text{total}} \int \frac{\text{d}C_{\text{DSi}}}{\text{d}t} \, \text{d}t = V_{\text{total}} \int \frac{SS}{1 + \gamma SS} \left( k_i \beta_{i0} e^{-k_i \tau} + k_a \beta_{a0} e^{-\left(\frac{\alpha - \alpha}{\tau}\right)} \right) \, \text{d}t \quad (4.14)
\]

where \( Y \) is the total amount of DSi released from SS in the entire lake (g \( \text{y}^{-1} \)), \( V_{\text{total}} \) is the water volume of the lake (\( 6.6 \times 10^8 \) m\(^3\)) and \( \tau \) is the time (day). The hourly concentrations of SS derived from sediment resuspension at C1 in 2004 were simulated in the range of 10–299 mg l\(^{-1}\) by a numerical model with wind speed and sediment parameters such as the critical bottom shear stress (Seki et al. 2006). A minimum value of simulated concentrations could be regarded as “background SS”. According to the assumption (2), the difference between simulated SS concentrations and background SS
concentrations was applied to SS in Eq. 4.14. In addition, the hourly water temperature at C1 measured by KRO was also used in Eq. 4.14. Y was estimated by two scenarios. The first scenario assumes that the initial BSi contents of SS were constant to be experimentally determined as the average of experiment S3 and S5-4, that is, $\beta_{t0} = 1.0$ and $\beta_{o0} = 40$. The time since the latest resuspension event (wind speed above 12 m s$^{-1}$) was applied to $\tau$ at each $t$ in Eq. 4.14. This estimated value was regarded as a maximum one. The second scenario assumes that the dissolution of BSi is only of old diatom frustules, that is, $\beta_{t0} = 0$ and $\beta_{o0} = 40$. This estimated value was regarded as a minimum one. As a result, the minimum and maximum values of $Y$ were $1.0 \times 10^9$ and $2.7 \times 10^9$ g y$^{-1}$, respectively.

The annual amount of DSI released from bottom sediments at C1 in 2004 was also estimated from Eqs. 4.12 and 4.13. DSI$_{col}$ concentrations at C1 observed monthly by KRO were interpolated to hourly values and used in the estimation. As a result, the annual amount of DSI released from bottom sediments was estimated to be $4.3 \times 10^9$ g y$^{-1}$. These results suggest that the DSI released from SS accounted for about 20–40% of the total DSI amount released in the lake in 2004.

Recent DSI release rate from SS determined by the experiments in this chapter were compared with the observed increase in the DSI load through the outflow over the last three decades. The amount of DSI released from SS in 2004 was assumed to be representative of those in the 2000s. The amount of DSI released from SS in the 1980s was assumed to be zero because mean concentration of SS derived from sediment resuspension in the 1980s was estimated to be 5.5 mg l$^{-1}$ by the method of Seki et al. (2006), about half of the background SS concentration in 2004. The increases in DSI load from the 1980s to the 2000s were $3.0 \times 10^9$ g y$^{-1}$, based on the DSI concentration at
C1, the lake volume of $6.9 \times 10^8$ m$^3$, the mean water residence time of 200 days, and the mean annual precipitation of 1250 mm. The DSi release from SS could account for about 30–90% of the increases in DSi load through the outflow.

4.5 Conclusions

Laboratory experiments, suspending the sediments in filtered lake water, provided the formula of change in DSi concentration as a function of SS concentration, water temperature, and the elapsed time of dissolution of diatom frustules. The annual amount of DSi released from SS in the 2000s accounted for 30–90% of the increase in DSi load through outflow over the last three decades, as well as 20–40% of the total amount of DSi released in the lake. These findings suggest that the sediment resuspension might be the cause of the latest DSi increase.

The final publication is available at www.springerlink.com.
Chapter 5

Silicon budget in a shallow eutrophic lake

5.1 Introduction

In chapter 3, monitoring data could provide long-term trends of Si concentration in Lake Kasumigaura. To obtain the information on these historical changes, analyzing the vertical distribution of Si in sediments is also useful. In fact, BSi is commonly determined in lake sediments as an indicator of diatoms (Conley 1998).

Several paleolimnological studies have analyzed the stratigraphy of BSi in dated lake sediments to estimate long-term changes in the trophic condition (Schelske et al. 1986; Newberry and Schelske 1986; Schelske et al. 1987) and the BSi retention (Teodoru et al. 2006). Schelske et al. (1986) studied the eutrophication in the lower Great Lakes using the peaks in BSi contents and BSi:phosphorus ratios in the sediment cores from the lakes. Newberry and Schelske (1986) found that BSi contents in sediment stratigraphy corresponded to the trophic history of Little Round Lake, Ontario. The authors qualitatively indicated that the evaluation of siliceous microfossils, excluding diatoms,
and the dissolution of BSi should be considered to make a precise estimate of past diatom abundances. Teodoru et al. (2006) analyzed the sedimentary records of BSi to elucidate DSi retention in Iron Gate I Reservoir on the Danube River. The authors also compared the vertical profiles of sediment BSi with the long-term changes in DSi concentrations observed in the Black Sea coastal waters, suggesting that the construction of the Iron Gate I Reservoir was not solely responsible for decreasing the DSi loads downstream. Several researchers have also examined short sediment cores and measured water quality to calculate the annual DSi and BSi budgets from river inputs, outputs, BSi sedimentation and DSi release from sediments in lakes (Cornwell and Banahan 1992; Hoffman et al. 2002; Triplett et al. 2008). However, very few studies have assessed the long-term DSi and BSi budgets by both analyzing the sediment cores and monitoring water quality.

The purposes of this chapter are twofold: (1) to assess the DSi and BSi budgets in Lake Kasumigaura during the last three decades based on both the chronological sediment information, such as a vertical distribution of BSi content in the sediment cores, and the existing data of water quality, such as DSi concentrations and diatom abundances in the lake and DSi concentrations of the inflowing rivers, and (2) to discuss the Si cycling during the period, focusing on the recent DSi release from SS due to sediment resuspension, by comparing the historical changes of the gross sedimentation (using several diatom sinking rates), net sedimentation (by subtraction of river output from input) and apparent accumulation of BSi (based on the vertical profile of BSi in dated sediment cores). In Lake Kasumigaura, Si dynamics have been clearly changed during a last few decades; therefore, it might provide valuable findings to elucidate the long-term Si dynamics in shallow eutrophic lakes.
5.2 Materials and methods

5.2.1 Sampling of sediment cores and chemical analysis

5.2.1.1 Sampling

Multiple sediment cores were collected at the center of the lake (see Figure 5.1; site C) on 17 June 2005 (three cores), 19 June 2007 (two cores) and 14 July 2009 (two cores) by scuba divers using acrylic tubes of 10 cm in diameter and 100 cm long. Fukushima et al. (2010) indicated that the sedimentation process in the central basin is represented by the values obtained from the sediment taken from the center of the lake. Additional sediment cores were also collected at 2 other sites (see Figure 5.1; site A and B) on 19 June 2007. The sediment cores were sliced at intervals of 2 cm and those slices were composited. The water contents and apparent density were estimated from wet and dry weight (110°C, 12 hours). The mass sedimentation rates during the last 7 decades were estimated using the chronological information (such as the $^{137}$Cs peak depth and the distribution of apparent density) of the sediment cores taken in 2005 and 2007, respectively. Details of dating and calculations can be found in Fukushima et al. (2010). In addition, the vertical distribution of apparent density of the cores taken in 2009 was used to calculate the mass sedimentation rate by the same method as Fukushima et al. (2010).
Figure 5.1 Sampling sites in Lake Kasumigaura
5.2.1.2 Chemical analysis

After freeze-drying the sediment samples, BSi was extracted for the samples taken in 2005 and 2007 by a single-step wet alkaline digestion (Mortlock and Froelich 1989). The sediments of 12–15 mg were digested in 60 ml of 1% Na$_2$CO$_3$ solution for 2 h at 85°C in an oven and the solutions were sub-sampled. These sub-samples were filtered through a 0.45-μm membrane filter. The concentrations of DSi were then analyzed by silicomolybdate blue colorimetric method JIS K 0101. However, this method has been reported to possibly overestimate BSi concentrations due to mineral dissolution; therefore, a time-step digestion (DeMaster 1981; Conley and Schelske 2001) was applied to the samples taken in 2009. Sediments of 13–19 mg were digested in 60 ml of 1% Na$_2$CO$_3$ solution for 5 h at 85°C in an oven and were sub-sampled after 3-, 4- and 5-h. These sub-samples were then filtered and analyzed following the same method as the 2005 and 2007 sub-samples. DSi concentrations at the 3-, 4- and 5-h were graphed to chart the progressive Si dissolution over time in order to correct for DSi contributed by mineral silicates. The precision of the method was 10%. The apparent accumulation rate of BSi, $Z$ (g m$^{-2}$ y$^{-1}$), was defined by the following equation:

$$Z = BSi \cdot S_M$$  \hspace{1cm} (5.1)

where $BSi$ is the BSi content in the sediments (g kg$^{-1}$) and $S_M$ is the mass sedimentation rate (kg m$^{-2}$ y$^{-1}$).
5.2.2 Budgetary calculation

5.2.2.1 Estimation of the inflows, outflow, and net sedimentation rate

Si in lake water is composed of dissolved and particulate one, and the latter consists of BSi and lithogenic Si (LSi). The dissolution of LSi is typically five orders of magnitude slower than that of BSi (Hurd 1983). Therefore, the Si budgets were calculated concentrating on DSi and BSi in the lake. The sum of DSi and BSi was expressed as (D + B) Si in this paper.

DSi concentrations and diatom abundances were observed by the Kasumigaura River office (KRO) and the National Institute for Environmental Studies (NIES), respectively, during April 1980 – March 2007. Surface waters were collected at site C and filtered through 0.45-μm glass-fiber to analyze DSi concentration by the colorimetric method (JIS K 0101). Diatom abundances were taken by a column-sampler (upper 2 m), counted on an inverted microscope, and quantified as biovolume by multiplying counted cell number by mean cell volume. BSi concentrations were estimated by multiplying the diatom abundances by the mean BSi content of freshwater diatom frustules of $1.1 \times 10^5$ g m$^{-3}$. The mean BSi content was determined by averaging the values found in Bailey-Watts (1976a) and Sicko-Goad et al. (1984).

Mass balances of (D + B) Si in the lake can be defined by the following equation:

$$I - O + (R - S)A = M \quad (5.2)$$

where $I$ is the (D + B) Si loads from the inflows (g y$^{-1}$), $O$ is the (D + B) Si loads from
the outflow (g y\(^{-1}\)), \( R \) is the area-averaged DSI release rate (g m\(^{-2}\) y\(^{-1}\)), \( S \) is the area-averaged gross sedimentation rate of BSi (g m\(^{-2}\) y\(^{-1}\)), \( A \) is the lake area (m\(^2\)), and \( M \) is the rate of change in the (D + B) Si amounts in water (g y\(^{-1}\)). The DSI input through atmospheric precipitation was estimated using the annual mean precipitation and the DSI concentration of precipitation in Tsukuba, as averaged over 4 years by Hirata and Muraoka (1991). It was \( 2.2 \times 10^7 \) g y\(^{-1}\), two orders of magnitude lower than other fluxes; therefore, it could be neglected. The subtraction of \( R \) from \( S \) represents the area-averaged net sedimentation rate of BSi, \( N \) (g m\(^{-2}\) y\(^{-1}\)), calculated by the following equation:

\[
N = S - R = (I - O - M)/A \quad (5.3)
\]

Inflows of BSi were not observed, but considered to be negligible. Temporal variation of DSI concentrations of the rivers depends mostly on the dilution by rainfall (Muraoka and Hirata 1988; Neal et al. 2005). Muraoka and Hirata (1988) measured the hydrochemistry of streams during four rainfall runoff events in the experimental forested area in the Lake Kasumigaura basin. The authors showed that the concentration of DSI decreased until the peak flow due to a dilution effect by the surface runoff water, whereas the concentration increased to approximately the same concentration around the end of the runoff period as the base flow level prior to the runoff event. Therefore, the maximum and minimum DSI loads through the inflows, \( I_{\text{max}} \) and \( I_{\text{min}} \), respectively, were determined by the following equations:

\[
I_{\text{max}} = DSI_{\text{base}}Q'_{\text{total}} \quad (5.4)
\]

\[
I_{\text{min}} = [DSI_{\text{base}}/q_{\text{mean}} + DSI_{\text{min}}(1 - q_{\text{base}}/q_{\text{mean}})]Q'_{\text{total}} \quad (5.5)
\]
where $DSi_{\text{base}}$ is the DSi concentration of the base flows which is the inflows when there was no rainfall (g m$^{-3}$), $Q'_{\text{total}}$ is the annual total discharge of the inflows (m$^3$ y$^{-1}$), $q_{\text{base}}$ is the daily discharge of the base flows (m$^3$ day$^{-1}$), $q_{\text{mean}}$ is the annual mean daily discharge of the inflows (m$^3$ day$^{-1}$), and $DSi_{\text{rain}}$ is the DSi concentration of rainwater (g m$^{-3}$). $I_{\text{min}}$ was calculated by assuming the dilution effect at a maximum. $DSi_{\text{base}}$ was determined to be 11.8 g m$^{-3}$, which is the mean DSi concentration of the 5–12 rivers inflowing the lake during 1994, 2007 and 2009 (details are shown in Chapter 3). There was no rainfall for 3 days before almost all samplings. $Q'_{\text{total}}$ was estimated to be $1.0 \times 10^9$ m$^3$ y$^{-1}$, using the lake volume, the mean water residence time and the mean annual precipitation. $q_{\text{base}}$ was estimated as the ordinary water discharge; that is, the daily discharge is not less than $q_{\text{base}}$ for just 185 days during a year. $q_{\text{base}}$ and $q_{\text{mean}}$ were averaged among the main 5 rivers (Sakura, Koise, Sonobe, Ono and Seimei Rivers) inflowing the lake observed by KRO during the last decade, respectively. As a result, $q_{\text{base}}/ q_{\text{mean}}$ was estimated to be 0.65. The $DSi_{\text{rain}}$ value of 0.097 g m$^{-3}$ was reported by Hirata and Muraoka (1991) as the observed value in the Lake Kasumigaura basin. Finally, $I$ was estimated from these calculations to be $(0.8–1.2) \times 10^{10}$ g y$^{-1}$. The (D + B) Si loads through the outflow $O$ were determined by multiplying (D + B) Si concentrations observed at site C by the annual discharge through the outflow ($1.1 \times 10^9$ m$^3$ y$^{-1}$; estimated using the volume, water residence time and the mean annual evaporation of the lake). Assuming that the water quality at the center of the lake is representative of the whole lake, the changes in (D + B) Si concentrations at site C were used to calculate $M$.

5.2.2.2 Estimation of the gross sedimentation rate

The gross sedimentation rates of BSi were estimated by the following equation:
where \( c \) is the diatom sinking rate (m day\(^{-1}\)) and \( BSi_w \) is the concentration of BSi in lake water (g m\(^{-3}\)). The diatom sinking rate is not constant but depends mostly on diatom species and their growing stages. Laboratory measurements in previous studies reported the diatom sinking rates in lake water to be 0.2–0.7 m day\(^{-1}\) (Bailey-Watts 1976b; Gibson 1984; Ferris and Lehman 2007). In this study, 0.2 and 0.7 m day\(^{-1}\) were used for the calculation as the minimum and maximum diatom sinking rate \( c \), respectively.

### 5.3 Results

#### 5.3.1 Spatial distributions of sediment BSi

Mean (min.–max.) concentrations of BSi in the dated sediments taken at site A, B and C in 2007 were 24 (19–30), 9 (6–11) and 32 (18–51) g kg\(^{-1}\), respectively. The mass sedimentation rates at site A, B and C were estimated to be 1.5, 4.1 and 1.3 kg m\(^{-2}\) y\(^{-1}\), respectively (Fukushima et al. 2010). Therefore, mean (min.–max.) apparent accumulation rates of BSi at site A, B and C were calculated to be 36 (29–45), 37 (25–45) and 42 (23–66) g m\(^{-2}\) y\(^{-1}\), respectively. These rates were relatively consistent among the sites (Figure 5.2); therefore, the results obtained at site C were regarded as representative of the lake.

Mean (min.–max.) contents of BSi in the dated sediments taken at site C in 2005, 2007 and 2009 were 31 (22–40), 32 (18–51) and 40 (20–51) g kg\(^{-1}\), respectively. Although the difference between these values was not large, the analytical method applied to the sediments taken in 2009 was more reliable than the others (Conley 1998);
**Figure 5.2** Historical plots of the apparent accumulation rate of BSi from the sediment cores taken in 2007
therefore, the contents of BSi in the sediments taken in 2009 were mainly used as described later.

5.3.2 (D + B) Si budgets over 27 years in Lake Kasumigaura

Table 5.1 shows the (D + B) Si budgets from 1980–2007 in Lake Kasumigaura. The DSi amount transported through the inflowing rivers for this 27-year time period was calculated to be \((2.2-3.3) \times 10^{11}\) g. The amounts of DSi and BSi transported through the outflow for this time period were calculated to be \(0.7 \times 10^{11}\) and \(0.2 \times 10^{11}\) g, respectively. Therefore, 60–70% of the DSi transported through the inflows was taken by diatoms and ultimately accumulated in the bottom sediments. The BSi amounts accumulated for the 27-year period in the lake were estimated to be \((2.0-2.6) \times 10^{11}\) g by analyzing the sediment cores taken in 2007 and 2009, which is slightly higher but close to the BSi amounts of \((1.3-2.4) \times 10^{11}\) g estimated by the budgetary calculation. The gross accumulated amount of BSi was estimated using Eq. 5.6 to be \((2.3-8.0) \times 10^{11}\) g, higher than the other results but of the same order of magnitude.

5.3.3 Long-term changes of net sedimentation, apparent accumulation and gross sedimentation rate of BSi

Figure 5.3 shows the changes in the net sedimentation, apparent accumulation and gross sedimentation rates of BSi in the lake. The net sedimentation rates of BSi were calculated by Eq. 5.3 to be a minimum of 6–39 g m\(^{-2}\) y\(^{-1}\) and a maximum of 31–65 g m\(^{-2}\) y\(^{-1}\) during 1980–2007, which were close to the apparent accumulation rates of BSi of 49–67 g m\(^{-2}\) y\(^{-1}\) estimated by the sediment analysis. Although a clear trend of the
Table 5.1  (D + B) Si budgets from 1980–2007 in Lake Kasumigaura. The rate of change in the (D + B) Si amounts in water column was not shown because those values were one order of magnitude smaller than other budgets in a decadal time scale.

<table>
<thead>
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<td>8–12</td>
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<tr>
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<td>4–8</td>
<td>2–6</td>
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<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
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<td>9–32</td>
<td>13–46</td>
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</tr>
<tr>
<td>from bottom sediments</td>
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<td></td>
<td>5.3–7.0</td>
<td></td>
</tr>
<tr>
<td>from SS</td>
<td></td>
<td></td>
<td>4.3</td>
<td>1.0–2.7</td>
</tr>
</tbody>
</table>

a estimated by the laboratory experiments in chapter 4
Figure 5.3  Historical plots of the net sedimentation, apparent accumulation and gross sedimentation rates of BSi. The apparent accumulation rates of BSi were estimated using the sediment cores taken at C1 in 2009. Time resolution was adjusted to the apparent accumulation rates.
apparent accumulation rates was not detected, the decreasing trend of the net sedimentation rates of BSi was statistically significant \((p < 0.05)\). The gross sedimentation rates of BSi were calculated by Eq. 5.6 to be a minimum of \(14–120 \text{ g m}^{-2} \text{ y}^{-1}\) and a maximum of \(50–420 \text{ g m}^{-2} \text{ y}^{-1}\) during the same period. The increasing trend of those rates was observed \((p < 0.05)\). These rates were mostly larger than both the net sedimentation and apparent accumulation rates of BSi.

### 5.4 Discussion

#### 5.4.1 Gross sedimentation rate of BSi

The gross sedimentation rates of BSi increased due to the increase in the diatom abundance in lake water during 1980–2007, which might be caused by the increase in the lake concentration of DSi (see Figure 5.3; Table 5.1). However, those rates have a large uncertainty derived from the diatom sinking rates and the BSi content of diatoms used in this study. Conley (1988) suggested that the size range and the BSi content of different diatom species make it difficult to discuss the relationship between diatom abundance and BSi contents in sediments. The diatoms observed in Lake Kasumigaura by NIES for the 27 years were mainly composed of 4 dominant species, that is, *Cyclotella* spp., *Fragilaria* spp., *Aulacoseira* spp. and *Actinocyclus* spp., accounting for about 80% of the total diatom abundance. About 60% of the increase in the diatom abundance was attributed to the increase in *Cyclotella* spp., which might influence both the diatom sinking rate and the BSi content of the diatoms in the lake. The gross sedimentation rates could be better determined using sediment traps if the exposure time is short and the traps located sufficiently above the bottom to reduce resuspension. Moreover, the resuspension may be calculated based on the difference in organic
content of the tripton and that of the re-suspended matter (Gasith 1975).

5.4.2 Net sedimentation rate of BSi

Most of the net sedimentation rates of BSi were smaller than the gross sedimentation rates of BSi (see Figure 5.3), indicating the dissolution of BSi comprised in diatom frustules in the water column and/or in the sediments. The net sedimentation rates of BSi decreased due to the significant increase in (D + B) Si loads through the outflow during the time period (see Table 5.1). Those rates were calculated by Eq. 5.3 with the assumption of constant (D + B) Si loads through the inflows, which might include an error such as a long-term increase in the DSi loads. However, a increasing trend of annual precipitation was not seen at Tsukuba meteorological weather station from 1980–2007 (http://www.jma.go.jp/jma/). In addition, there was no increasing trend of both DSi concentrations of lake water near the rivers inflowing the lake for the 27 years and those of the main inflows during 1994, 2007 and 2009, suggesting that the DSi loads through the inflows did not increase. This supports the theory of a decreasing trend of the net sedimentation rates of BSi. The decrease in those rates could be explained by a decrease in the gross sedimentation rate of BSi and/or an increase in the DSi release rate from sediments to overlying water. However, a decrease in the gross sedimentation rates of BSi is inconsistent with the trend of the gross sedimentation rates of BSi in Figure 5.3. On the other hand, an increase in the DSi release rates from sediments could be due to the increasing sediment resuspension from the late 1990s to mid 2000s (mean concentration of inorganic SS during the 1980s and the 2000s, estimated by the method of Seki et al. (2006) using the monthly concentrations of SS and chlorophyll a, was 5 and 21 mg l⁻¹, respectively). The DSi release rates from re-suspended sediment in 2004 were estimated to be (1–3) × 10⁹ g y⁻¹ by the laboratory experiments in Chapter 4,
which could account for about 30–80% of the decrease in the net sedimentation rate of BSi from the 1980s to the 2000s of $4 \times 10^9$ g y$^{-1}$ (see Table 5.1). The DSi release rate could have also been enhanced by an increase in temperature, pH and salinity (Loucaides et al. 2008). However, increasing trends of those factors were not clearly seen in the lake.

### 5.4.3 Apparent accumulation rate of BSi

Although the net sedimentation rates of BSi significantly decreased, a corresponding trend of the apparent accumulation rates of BSi was not detected from 1980–2007 (see Figure 5.3, Table 5.1), suggesting that some mechanism balanced the recent higher DSi release rate derived from sediment resuspension. Those rates were determined by analyzing the BSi contents in the cores, affected by sinking and sedimentation of diatom frustules and a disappearance of BSi contained in those frustules through dissolution. The solubility and reactivity of BSi decrease with aging of diatom frustules, due mainly to alternations of the bulk structure and surface chemistry (Loucaides et al. 2008). BSi might be dissolved for a few decades after accumulation; therefore, the larger part of BSi in old sediments might already be dissolved than that in recent sediments, in the absence of an increase in the DSi release from re-suspended sediment. It suggests that the apparent accumulation rates of BSi in past years were strongly influenced by a long-term dissolution of sediment BSi and the rates in recent years were influenced by the recent higher DSi release rate derived from sediment resuspension.
5.5 Conclusions

We calculated the (D + B) Si budgets from 1980–2007 in Lake Kasumigaura, based on the chronological sediment information and the database of water quality. The BSi amount accumulated in the lake for the 27-year time period determined by analyzing the sediment cores was close to the amount based on the database of water quality, about 60–70% of DSi inputs from the inflowing rivers. Although the gross sedimentation rates of BSi might have increased during these 27 years, the net sedimentation rates of BSi decreased, suggesting the fast BSi recycling in recent years. This suggestion was consistent with the increase in the DSi release from re-suspended sediment. On the other hand, the decreasing trend could not be detected in the apparent accumulation rates of BSi based on the sediment information. Comparison between the apparent accumulation and net sedimentation rates suggested that the time scale of dissolution of sediment BSi might be a few decades. However, the apparent accumulation rates of BSi were estimated by assuming the constant mass sedimentation rate, and the errors caused by the assumption make it difficult to assess those rates quantitatively. To assess the long-term dissolution of sediment BSi, a measurement of the pore water distribution of DSi and/or analyzing the BSi content in the cores taken over a much greater time span is necessary.

The final publication is available at www.springerlink.com.
Chapter 6

Impacts of long-term increase in silicon concentrations on diatom blooms in a shallow eutrophic lake

6.1 Introduction

Diatoms, most abundant phytoplankton on Earth, play an important role in the global primary production and carbon cycling (Schelske 1999; Kristiansen and Hoell 2002; Conley et al. 2006). They take up DSi as silicate, which they mainly incorporate as BSi in their frustules. They are the dominating primary producers in the world, and Si is therefore a key factor in the ecosystem.

It was often reported that DSi acts as a factor limiting diatom growth. Kilham (1971) suggested that lake eutrophication might promote a decrease in diatom abundance due to DSi limitation. Schelske (1985) showed the decreasing trend of DSi in Lake Michigan during 1955–1970, with the increase in P load, and Barbiero et al. (2002) demonstrated the increasing trends of DSi and diatoms in summer after P load dropping
by half from the late 1970s to the 1990s in the lake. These observations indicate a shift of a factor limiting diatom growth from P to Si by eutrophication and a decline in spring diatom blooms after P emission constraint which might cause summer residual DSi. On the other hand, Takano and Hino (1994) reported that the dense water blooms of blue-green algae had been disappeared and diatoms had been dominated in Japanese hypertrophic Lake Barato during 1990–1992, suggesting that diatoms adapted to higher phosphorus limitation under conditions of low water temperature and high silicate concentration.

Following recent global trends of decline in DSi load from land to sea, a long-term influence of DSi dynamics on the phytoplankton dominance, food web and biogeochemical cycling was deeply concerned (e.g., Humborg et al. 1997; Li et al. 2007; Conley et al. 2008). However, most modeling studies simulated DSi and diatoms just in a year or few years. Ferris and Lehman (2007) reported that the spring development of diatoms in Ford Lake, Michigan, USA was markedly different in 2004 (diatom biovolume above 15 mm$^3$ l$^{-1}$) from 2005 and 2006 (less than 5 mm$^3$ l$^{-1}$), whereas DSi concentration fell below 0.14 mg l$^{-1}$ in 2004 and remained above 0.84 mg l$^{-1}$ in 2005 and 2006. Their model simulations of Si uptake, washout rates, and sinking implicated hydrologic differences among years as the cause of differential success by diatom populations in April of each year.

Chapter 3 showed the increasing trends of DSi concentration in Lake Kasumigaura during the last three decades and Chapter 4 indicated the influence of the recent sediment resuspension enhancing DSi release in the lake. Although the lake has a valuable database and showed the increasing trend of DSi concentration which is rare in the world, the influence of the DSi increase on the magnitude and seasonality of diatom
blooms was not assessed. The purposes of this chapter are threefold: (1) to detect the long-term trends of diatom abundance in Lake Kasumigaura during the last three decades, (2) to assess the relationships between diatom abundance and other items based on the long-term monitoring data, especially focusing on DSi concentration, and (3) to assess the impact of the long-term increase in DSi concentration on magnitude and seasonality of diatom blooms using a simple model.

6.2 Materials and methods

6.2.1 Observation data for statistical analysis

The database of monthly water quality used for this chapter was based on the NIES investigation at site C during 1981–2010 (Figure 6.1). The analytical period was coincided with the model simulation period described later. Surface waters were collected and filtered through 0.45-μm glass-fiber to analyze DSi concentration by ICP. Surface waters were also taken by a column-sampler of 2 m length, providing for analyzing NH$_4$-N, NO$_2$-N, NO$_3$-N, PO$_4$-P by auto-analyzer after filtering the collected waters through 0.45-μm glass-fiber. Dissolved inorganic nitrogen (DIN) and phosphorus (DIP) was defined as the sum of NH$_4$-N, NO$_2$-N, and NO$_3$-N and solely PO$_4$-P, respectively. Unfiltered samples were treated in an autoclave under 120°C for 30 minutes after adding potassium peroxodisulfate under alkaline pH for the measurement of total nitrogen (TN) and under acidic pH for total phosphorus (TP). Filtered water samples were provided for analyzing dissolved total nitrogen (DTN) and phosphorus (DTP) by the same method of TN and TP, respectively. Phytoplankton were also taken.
Figure 6.1 Observation sites in Lake Kasumigaura and box division on the model
by a column-sampler, counted on an inverted microscope, and quantified as biovolume by multiplying counted cell number by mean cell volume. BSi concentrations were estimated by multiplying diatom abundances by the BSi content of freshwater diatom frustules of 0.11 g cm$^{-3}$ determined by averaging the values found in Bailey-Watts (1976a) and Sicko-Goad et al. (1984). The sum of DSi and BSi was expressed as (D + B) Si in this chapter. Monthly water temperature, pH, and DO were used also for correlation analysis.

6.2.2 Modeling

6.2.2.1 Box-model structure

The lake is so shallow that stratigraphy is easily broken by wind; therefore, it could be assumed that the water qualities are constant along water depth direction. Annual variation of both DSi concentration and diatom abundance were simultaneously simulated using the simple four-box model. The lake was divided into four which was developed by Fukushima (1984) (Figure 6.1; Table 6.1). In this study, it was assumed that each box has a constant water depth. The changes in DSi concentration and diatom abundance were simulated as following equations:

$$\frac{dC_{\text{DSi,}j}}{dt} = \frac{I_{\text{DSi,}j} - O_{\text{DSi,}j}}{V_j} + \frac{R_{\text{SS,}j} S_{\text{sed,}j}}{1000} + \frac{R_{\text{bottom,}j}}{h_j} - b_\mu j C_{\text{diatoms,}j}$$  \hspace{1cm} (6.1)

$$\frac{dC_{\text{diatoms,}j}}{dt} = \frac{I_{\text{diatoms,}j} - O_{\text{diatoms,}j}}{V_j} + \left(\mu_j - c \right) \frac{C_{\text{diatoms,}j}}{h_j}$$  \hspace{1cm} (6.2)
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<th>Value</th>
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<th>BOX2</th>
<th>BOX3</th>
<th>BOX4</th>
</tr>
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<tr>
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</tr>
<tr>
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<td>0.32</td>
<td>0.17</td>
<td>0.22</td>
<td></td>
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<tr>
<td>inflowing to the entire lake (^a)</td>
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<tr>
<td>BSi concentration of SS (mg g⁻¹) (^b)</td>
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<td>23</td>
<td>29</td>
<td>41</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Fukushima (1984)

\(^b\) BSi concentrations of surface sediments determined in Chapter 4 were used.
where $C$ is the concentration in the water column (DSi amount in g m$^{-3}$; diatom cell volume in cm$^3$ m$^{-2}$), $t$ is the time (day), $I$ and $O$ are the inflow and outflow, respectively (DSi in g day$^{-1}$; diatoms in cm$^3$ day$^{-1}$), $V$ is the lake volume (m$^3$), $R_{SS}$ is the DSi release rate from SS (mg g$^{-1}$ day$^{-1}$), $SS_{sed}$ is the concentration of SS derived from sediment resuspension (g m$^{-3}$), $R_{bottom}$ is the DSi release rate from bottom sediments (g m$^{-2}$ day$^{-1}$), $h$ is the water depth (m), $b$ is the BSi content of freshwater diatom frustules (g cm$^{-3}$, calibrated), $\mu$ is the growth rate of freshwater diatoms (day$^{-1}$), and $c$ is the diatom sinking rate (m day$^{-1}$, calibrated). The subscript $j$ indicates the box number. The values of $h$ and $V$ in each box are shown in Table 6.1.

**Inflow**

The loads flowing to the box $j$ were expressed by:

$$I_j = (L_{river,j} + L_{piston,j} + L_{exch,j}) \times 60 \times 60 \times 24$$

(6.3)

where $L_{river}$ is the load from the inflowing rivers (DSi amount in g s$^{-1}$; diatom cell volume in cm$^3$ s$^{-1}$), $L_{piston}$ is the load by extrusion flows from the upper boxes, and $L_{exch}$ is the load by exchange flows from the adjacent boxes. The loads by groundwater input and precipitation could be negligible. $L_{river}$ for diatoms was also regarded as zero. $L_{river}$ for DSi was calculated by the following formula:

$$L_{river,j} = \frac{Q_{total}(Q_{Sakura} + Q_{Ono})}{(Q_{Sakura} + Q_{Ono})} r_j$$

(6.4)

$$Q_{total} = \frac{A'_t(1 + A'_{Sakura} + A'_{Seimei} + A'_{Ono})}{(A'_Sakura + A'_{Seimei} + A'_Ono)}$$

(6.5)
where $Q$ is the river discharge ($m^3/s$) and $A'$ is the watershed area ($km^2$). $Q_{\text{total}}$ is the total river discharge inflowing to the entire lake and $A'_{\text{total}}$ is the watershed area of Lake Kasumigaura of 1426 km$^2$. $r_j$ is the mean ratio of the river discharge inflowing to the box $j$ to the total river discharge inflowing to the entire lake which determined by water budgets in the lake investigated by Fukushima (1984). $Q_{\text{Sakura}}$, $Q_{\text{Seimei}}$, $Q_{\text{Ono}}$ were hourly observed discharge at the monitoring station on R. Sakura, Seimei, and Ono by KRO, respectively (Table 6.2). $L_{\text{sakura}}$ and $L_{\text{Ono}}$ were estimated by L-Q equation based on the monitoring data in 6 rainfall events taken by KRO in 2007 ($L_{\text{sakura}} = 8.9 Q_{\text{sakura}}^{0.88}$, $r^2 = 0.98$, $N = 50$; $L_{\text{Ono}} = 8.4 Q_{\text{Ono}}^{0.80}$, $r^2 = 0.94$, $N = 50$). $L_{\text{piston}}$ was calculated by multiplying the concentration $C$ of the upper box by the flow rate determined on the assumption of steady state of water level. $L_{\text{exch}}$ was calculated by multiplying $M$ of the adjacent box and exchange flow discharge $Q_{\text{exch}}$ ($3.0 m^3/s$ between BOX 1 and BOX 3, $21.4 m^3/s$ between BOX 2 and BOX 3, and $13.9 m^3/s$ between BOX 3 and BOX 4; Fukushima 1984).

**Outflow**

The outflow load was calculated by multiplying the mass in the water column $M$ by the flow rate on the assumption of steady state of water level on each box.

**DSi release**

The DSi release rate $R$ was determined by laboratory experiments (see Chapter 4). The rate could be divided into two processes; DSi release from re-suspended sediments and that from bottom sediments. $R_{\text{SS}}$ was expressed as the following equation:
### Table 6.2 Model input variables

<table>
<thead>
<tr>
<th>Hourly input variables</th>
<th>Symbol</th>
<th>Used data</th>
<th>How to estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>River discharge (m³ s⁻¹)</td>
<td>Q</td>
<td>Hourly discharge at the sites in R. Sakura, Ono, and Koise during 1981–2010 (KRO)</td>
<td>directly used</td>
</tr>
<tr>
<td>Solar irradiation (MJ m² h⁻¹)</td>
<td>IRR</td>
<td>(i) Daily irradiation at Tsukuba weather station during 1981–2010 (JMA) (ii) Hourly irradiation at Kasumigaura Water Research Station during 1998–2010 (NIES)</td>
<td>multiplying the daily irradiation by α to estimate hourly values (α was the ratio of hourly to daily irradiation averaged during 1998–2010 using data by NIES; CV of RMSE is 42%)</td>
</tr>
<tr>
<td>Water temperature (°C)</td>
<td>WT</td>
<td>Monthly water temperatures at the depth of 0.5 m at site A, B, C, and D during 1981–2010 (NIES)</td>
<td>linearly-interpolating the monthly water temperatures to hourly values</td>
</tr>
<tr>
<td>SS concentration derived from sediment resuspension (g m⁻³)</td>
<td>SS₆ₑᵈ</td>
<td>(i) Automatic-monitored hourly turbidity and chlorophyll a concentration at site A, B, C, and D during 1998–2010 (KRO) (ii) Monthly SS and chlorophyll a concentrations at site A, B, C, and D during 1998–2010 (NIES)</td>
<td>1981–1997: simulated by Seki et al. (2006) at site C in 1997 1998–2010: Hourly SS and chlorophyll a concentration were estimated from the data (i) and the linear regression model between the monthly-sorted data (i) and (ii) in each year (CV of RMSE for SS, 29–38%; chlorophyll a., 33–42%). Hourly SS₆ₑᵈ was calculated by the method in Seki et al. (2006) using SS and chlorophyll a. except site D: Monthly K₆ was calculated by the Lambert-Beer's law using the light intensity profiles. Hourly K₆ was estimated from NPSS and the linear regression model of monthly NPSS and K₆ (r² = 0.36–0.50). site D: estimated from K₆ at site C and the linear regression model of K₆ at site C and D</td>
</tr>
<tr>
<td>Light attenuation coefficient (m⁻¹)</td>
<td>K₆</td>
<td>(i) Monthly light intensity in water at the depth of 0, 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0, and 4.0 m at site A, B, and C during 1981–2010 (NIES) (ii) Hourly NPSS concentration estimated as seen above</td>
<td>1981–1997: simulated by Seki et al. (2006) at site C in 1997 1998–2010: Hourly SS and chlorophyll a concentration were estimated from the data (i) and the linear regression model between the monthly-sorted data (i) and (ii) in each year (CV of RMSE for SS, 29–38%; chlorophyll a., 33–42%). Hourly SS₆ₑᵈ was calculated by the method in Seki et al. (2006) using SS and chlorophyll a. except site D: Monthly K₆ was calculated by the Lambert-Beer's law using the light intensity profiles. Hourly K₆ was estimated from NPSS and the linear regression model of monthly NPSS and K₆ (r² = 0.36–0.50). site D: estimated from K₆ at site C and the linear regression model of K₆ at site C and D</td>
</tr>
</tbody>
</table>
\[ R_{SS,j} = \frac{1}{1 + \gamma \cdot SS_{sed,j}} \left[ k_f \beta_{0f,j} \exp(-k_i \tau_j) + k_o \beta_{0o,j} \right] \exp \left[ -\left( \frac{a_i}{WT_j + 273.15} - \frac{a_i}{298.15} \right) \right] \quad (6.6) \]

where \( \gamma \) is a constant \((m^3 \text{ g}^{-1})\), \( k \) is the dissolution rate constant of diatom frustules \((\text{day}^{-1})\), \( \beta_0 \) is the initial BSi content of SS \((\text{mg g}^{-1})\), \( \tau \) is the elapsed time of dissolution of diatom frustules \((\text{day})\), \( a_1 \) is a constant \((K)\), and \( WT \) is the water temperature \(^{\circ}\text{C}\). The subscripts \( f \) and \( o \) indicate the fresh and old diatom frustules, respectively \((k_f > k_o)\). The laboratory experiments determined the values of \( \gamma, k_f, k_o, \) and \( a_1 \) to be \( 1.2 \times 10^{-4} \text{ m}^3 \text{ g}^{-1} \), \( 1.3 \text{ day}^{-1} \), \( 5.0 \times 10^{-3} \text{ day}^{-1} \), and \( 4.2 \times 10^3 \text{ K} \), respectively (see chapter 4). The ratios \( \beta_{0f}/\beta_0 \) and \( \beta_{0o}/\beta_0 \) were found to be 0.024 and 0.98, respectively. Therefore, those ratios were multiplied by \( \beta_0 \) determined in chapter 4 \((\text{Table 6.1})\) to calculate \( \beta_{0f} \) and \( \beta_{0o} \), respectively. Method for estimating \( SS_{sed} \) was different between before 1997 and since 1998. Before 1997, no trend of inorganic SS concentration was obtained, based on the estimation technique of Seki et al. (2006) using monthly observed SS and chlorophyll \( a \). Therefore, I assumed that \( SS_{sed} \) did not change among the years during the period. The concentrations of resuspended sediments in 1997 were simulated by sediment resuspension model driven by wind developed by Seki et al. (2006), and they were applied to \( SS_{sed} \) before 1997. On the other hand, \( SS_{sed} \) was estimated by method of Seki et al. (2006) using the automatically-monitored hourly turbidity and chlorophyll \( a \) concentrations by KRO and monthly SS and chlorophyll \( a \) concentrations taken by NIES at site A, B, C, and D since 1998 (details are shown in \( \text{Table 6.2} \)). A minimum value of the SS concentrations in 2004 simulated by Seki et al. (2006), 10 g m\(^{-3}\), were subtracted from estimated \( SS_{sed} \) by assuming that SS remaining constantly in the water column (mainly consisting of clay minerals) might not attribute to DSi release.
\( R_{\text{bottom}} \) was also determined by:

\[
R_{\text{bottom},j} = k_{\text{bottom}} \left[ a_2 \exp\left( a_1 W T_j \right) - C_{\text{DSi}_j} \right]
\]

(6.7)

where \( k_{\text{bottom}} \) is the rate constant (m day\(^{-1}\)), \( a_1 \) is a constant (g m\(^{-3}\)), and \( a_2 \) is a constant (K\(^{-1}\)). The parameters \( k_{\text{bottom}}, a_1 \) and \( a_2 \) were experimentally determined to be \( 4.9 \times 10^{-3} \) m day\(^{-1}\), \( 4.9 \times 10^{-4} \) g m\(^{-3}\) and \( 3.6 \times 10^{-2} \) K\(^{-1}\), respectively. \( WT \) was estimated by linear-interpolation of the monthly water temperature at the depth of 0.5 m at site A, B, C, and D observed by NIES (Table 6.2).

**Diatom growth**

Assuming that the limiting factors of growth of diatoms are light condition, water temperature or DSi concentration in the lake, the growth rate of diatoms \( \mu \) was calculated by the following equation:

\[
\mu_j = \mu_{\text{max}} f_{I,j} f_{T,j} f_{\text{DSi},j}
\]

(6.8)

where \( \mu_{\text{max}} \) is the maximum growth rate of freshwater diatoms (day\(^{-1}\), calibrated) and \( f_I, f_T, \) and \( f_{\text{DSi}} \) are the function representing the influence of irradiance, temperature, and DSi concentration on the growth of diatoms, respectively.

In this model, \( f_I \) at a certain depth was expressed as the following equation:
\[ f_{i,j} = \frac{IRR_j}{K_i + IRR_j} \]  

(6.9)

where \( IRR \) is the irradiance in water at a certain depth (MJ m\(^{-2}\) h\(^{-1}\)) and \( K_i \) is the half-saturation constant of irradiance (MJ m\(^{-2}\) h\(^{-1}\), calibrated). \( IRR \) was subject to the Lambert-Beer’s law as the following equation:

\[ IRR = IRR_0 \exp(-K_d z) \]  

(6.10)

where \( IRR_0 \) is the solar irradiance at the water surface, \( K_d \) is the vertically-averaged light attenuation coefficient (m\(^{-1}\)) and \( z \) is the water depth (m). Using Eq. 6.9 and 6.10, the vertically-averaged light influence function \( f'_{i} \) could be expressed by:

\[ f'_{i} = \frac{1}{h_j} \int_{h_j}^{0} f_{i,j} \, dz = \frac{1}{K_{d_j} \cdot h_j} \ln \left[ \frac{IRR_0 + K_i}{IRR_0 \exp(-K_{d_j} \cdot h_j) + K_i} \right] \]  

(6.11).

The hourly \( IRR \) was estimated by multiplying the daily \( IRR \) at Tsukuba weather station by the ratio of hourly to daily irradiance averaged during 1998–2010 using data at Kasumigaura Water Research Station by NIES (details are shown in Table 6.2). The hourly \( K_d \) was estimated from \( SS_{sed} \) using the relationships between \( SS_{sed} \) and monthly-observed \( K_d \) in all sites except site D where the correlation coefficient was low (Figure 6.2). Therefore, \( K_d \) at sited D was estimated from that at site C \((y = 1.06 \, x, r^2 = 0.36\)). Monthly \( K_d \) shown in Figure 6.2 was determined by the Lambert-Beer’s law applying to the profiles of light intensity in water column taken by NIES (Table 6.2).
**Figure 6.2** Relationships between $SS_{\text{sed}}$ and $K_d$ at each site during 1998–2010 in Lake Kasumigaura. $K_d$ was determined using the monthly profiles of light intensity in water column observed by NIES.
The temperature influence function \( f_T \) was expressed as the following formula by reference to Matsuoka (1984):

\[
f_{T,j} = \begin{cases} 
\frac{(W_T - d_{WT})}{14} & (W_T < 14 + d_{WT}) \\
1 & (14 + d_{WT} \leq W_T < 20 + d_{WT}) \\
2 - \frac{(W_T - d_{WT})}{20} & (20 + d_{WT} \leq W_T)
\end{cases} 
\]  
(6.12)

where \( d_{WT} \) is constant (°C, calibrated).

The influence function of DSi concentration \( f_{Si} \) was expressed as the Monod equation as the following equation:

\[
f_{Si,j} = \frac{C_{DSi,j}}{K_{Si} + C_{DSi,j}} 
\]  
(6.13)

where \( K_{Si} \) is the half-saturation constant of DSi concentration for diatoms (g m\(^{-3}\), calibrated).

### 6.2.2.2 Parameter calibration

The BSi content of freshwater diatom frustules \( b \), the maximum growth rate of diatoms \( \mu_{max} \), the half-saturation constant of irradiance \( K_i \), the water temperature constant \( d_{WT} \), the half-saturation constant of DSi concentration for diatoms \( K_{Si} \), and the diatom sinking rate \( c \) were calibrated in every 5 year (1981, 1986, 1991, 1996, 2001, and 2006). The parameter sets were determined by random sampling and the least squares method.
(Komatsu et al. 2006). For random sampling, the ranges of $b$, $\mu_{\text{max}}$, and $K_{\text{Si}}$ were assigned based on the literature values (Table 6.3). The sufficient ranges of $K_{\text{f}}$, $d_{\text{WT}}$, and $K_{\text{Si}}$ were determined after sensitive analysis.

The object function $OFUNC$ was calculated as following equations:

$$OFUNC = \bar{E}_{\text{DSi}} \bar{E}_{\text{diatoms}}$$

$$E = \frac{\sum E_j V_j}{\sum V_j}$$

where $\bar{E}$ is the volume-weighted root mean squared error (RMSE; DSi in g m$^{-3}$, diatoms in cm$^3$ m$^{-3}$), $E$ is the RMSE, and $V$ is the water volume of the box (m$^3$; Table 6.1). DSi concentrations were calibrated in all boxes using the observation data at sites A, B, C, and D. On the other hand, diatom abundances were just monitored at sites A and C; therefore, parameters were calibrated in BOX 1 and 3. While $E_{\text{DSi}}$ was determined as RMSE of monthly DSi concentration, $E_{\text{diatoms}}$ was calculated by 3 different methods as: (1) RMSE of monthly diatom abundance ($N = 12$ months $\times$ 6 years), (2) RMSE of annual maximum diatom abundance ($N = 6$), and (3) average of RMSE of annual maximum diatom abundance and RMSE of annual minimum diatom abundance ($N = 6$). In this study, the above 3 calibration methods were called as CM1, CM2, and CM3, respectively.

Calibrated parameters were shown in Table 6.4. After parameter identification, the parameter sets were not changed during model validation for the whole period. Half
### Table 6.3  Values of the model parameters in the previous studies

<table>
<thead>
<tr>
<th>Paper</th>
<th>Mean (min.–max.)</th>
<th>Diatom species</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BSi content of diatom frustules, ( b ) (g cm(^{-3} ))</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bailey-Watts (1976a)</td>
<td>0.10 (0.08–0.12)</td>
<td><em>Asterionella formosa, Cyclotella pseudostelligera, C. pseudostelligera, C. comta, and S. rotula</em></td>
</tr>
<tr>
<td>Sicko-Goad et al. (1984)</td>
<td>0.10 (0.07–0.41)</td>
<td><em>Cyclotella spp., Fragilaria spp., Melosira spp., and Stephanodiscus spp.</em></td>
</tr>
<tr>
<td>Takano and Hino (1996)</td>
<td>0.07</td>
<td><em>Cyclotella meneghiniana mostly</em></td>
</tr>
<tr>
<td>Conley et al. (1989)</td>
<td>0.13 (0.10–0.15)</td>
<td>nano- and netplanktonic diatoms</td>
</tr>
<tr>
<td><strong>Maximum growing rate of diatoms, ( \mu ) (day(^{-1} ))</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matsuoka (1984)</td>
<td>1.7</td>
<td><em>Asterionella formosa</em></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td><em>Cyclotella spp.</em></td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td><em>Skeletonema costatum</em></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td><em>Synedra spp.</em></td>
</tr>
<tr>
<td><strong>Sinking rate of diatoms, ( c ) (m day(^{-1} ))</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bailey-Watts (1976b)</td>
<td>0.25</td>
<td>diatoms existed in lake water</td>
</tr>
<tr>
<td>Gibson (1984)</td>
<td>0.3 (0.2(^a)–0.4(^b))</td>
<td>Fitting an exponential regression to observatins</td>
</tr>
<tr>
<td>Ferris and Lehman (2007)</td>
<td>0.66</td>
<td>diatoms existed in lake water, mainly of <em>Asterionella, Cyclotella, Fragilaria, Aulacoseira, and Synedra spp.</em></td>
</tr>
<tr>
<td><strong>Range</strong></td>
<td>0.07–0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6–2.5</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) growing period, \(^b\) depletion period
Table 6.4  Values of the parameters calibrated by the various methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CM1</td>
</tr>
<tr>
<td>BSi content of diatom frustules, $b$ (g cm$^{-3}$)</td>
<td>0.13</td>
</tr>
<tr>
<td>Maximum growth rate of diatoms, $\mu$ (day$^{-1}$)</td>
<td>2.3</td>
</tr>
<tr>
<td>Half-saturation constant of irradiance, $K_I$ (MJ m$^{-2}$ h$^{-1}$)</td>
<td>0.071</td>
</tr>
<tr>
<td>Water temperature constant, $d_{WT}$ ($^o$C)</td>
<td>-3.8</td>
</tr>
<tr>
<td>Half-saturation constant of DSi, $K_{Si}$ (g m$^{-3}$)</td>
<td>6.5</td>
</tr>
<tr>
<td>Sinking rate of diatoms, $c$ (m day$^{-1}$)</td>
<td>0.20</td>
</tr>
</tbody>
</table>
saturation constant of DSi $K_{Si}$ was larger than the experimental value of about 0.9 at 20°C reported by Takano and Hino (1996).

6.3 Results

6.3.1 Field observations
6.3.1.1 Dominant phytoplankton species

In Lake Kasumigaura, diatoms and cyanobacteria were most dominant during the last three decades. They occupied about 80% of all phytoplankton cell volume on average. Although the trends of chlorophyll $a$ concentration and total phytoplankton abundance were not significantly detected (Figure 6.3a), dominant phytoplankton species changed remarkably (Figure 6.3b). Mean proportion of diatom abundance was increased from less than 40% during 1981–2000 to 66% during 2001–2010, with the decrease in mean proportion of cyanobacteria abundance from over 40% to about 20%.

Dominant diatom species in the lake, Actinocyclus spp., Aulacoseira spp., Cyclotella spp., Fragilaria spp., and Synedra spp., occupied about 90% of all diatom cell volume on average. Shift of dominant diatom species was also observed during the last three decades (Figure 6.4). Actinocyclus spp., blooming often in autumn before 1991, vanished and Cyclotella spp. was remarkably dominant during the 2000s.
Figure 6.3 Long-term change in phytoplankton abundances and chlorophyll \( a \) concentrations (a) and mean proportion of cell volumes of the respective phytoplankton groups during 1981–1990, 1991–2000, and 2001–2010 (b) at site C in Lake Kasumigaura
Figure 6.4  Long-term and seasonal change in the most dominant diatom species at site C in Lake Kasumigaura. Open area indicate the period when the phytoplankton except diatoms were dominant
6.3.1.2 Nutrient limitation

Marine diatoms take up N, P, and Si in an atomic ratio of 1 for Si/N and 16 for Si/P which is well known as Redfield ratio (Redfield et al. 1963; Brzezinski 1985). On the other hand, freshwater diatoms usually need more Si than marine diatoms. Nagai et al. (2001) reported that the Si/N and Si/P atomic ratios of diatoms collected in Japanese Lake Biwa were 3–14 times higher than Redfield ratio. These ratios could be used for analyzing a limiting nutrient for diatoms. Therefore, Si:N:P atomic ratios were investigated in the lake during the last three decades (Figure 6.5). (D + B)Si was compared with TP and TN since LSi was not attribute to nutrient for diatoms. DSi/DTP, (D + B)Si/TP, DSi/DTN, and (D + B)Si/TN atomic ratios mostly declined to below those ratios of freshwater diatoms and occasionally less than the ratios of marine diatoms when annual maximum diatom abundance was observed. DSi/DIP atomic ratios were often more than Si/P ratio of freshwater diatoms, but in the range of it at few years when a blooming occurred. DSi/DIN atomic ratios were frequently less than Si/N ratio of freshwater diatoms, but significantly increased during the last three decades ($p < 0.01$). However, usually N might not limit diatom growth compared with P from the viewpoint of N/P ratios. These findings suggest that DSi might be one of the main factors limiting growth of diatoms in the lake during a bloom season.

6.3.1.3 Long-term trends of diatom abundance

Increasing trend of diatom abundances was detected during 1981–2010 (12 months moving average, $p < 0.001$; Figure 6.6). Mean abundance of diatoms during 1981–
Figure 6.5  Long-term changes in the nutrient atomic ratios when annual maximum
diatom abundance was observed at site C during 1981–2010. The gray zone and broken
line indicates the nutrient atomic ratios of freshwater diatoms reported by Nagai et al.
(2001) and of marine diatoms (Redfield ratio), respectively
Figure 6.6  Long-term change in diatom abundances at site C in Lake Kasumigaura
1990, 1991–2000, and 2001–2010 was 6.0, 8.4, and 9.2 cm$^3$ m$^{-3}$, respectively. Massive blooming was seen during 1994–1995 and 2005–2006, which consists mainly of *Synedra* spp. and *Cyclotella* spp., respectively.

Mean seasonal changes of diatom abundances in Figure 6.7 showed that spring and autumn diatom blooms were confirmed during 1981–1990, but autumn blooms decreased and spring blooms were beginning since last winter during 2001–2010. As results of monthly t-test, diatom abundance significantly increased in January ($p < 0.01$), February, and March ($p < 0.05$) and decreased in in November ($p < 0.01$). The characteristics of periodic blooms were clearly shown by Fourier analysis (Figure 6.8).

Seasonal relationships between DSi and diatoms were investigated due to the role of DSi as a factor limiting diatom growth. Many relationships between DSi concentration and diatom abundance during the last three decades showed a counterclockwise loop (Figure 6.9). These hysteresis loops represent as follows: (i) diatom growth by uptake of DSi under preferable condition (e.g., at optimal temperature), (ii) rapid sinking of diatoms after DSi depletion, and (iii) almost no diatom with DSi supply by inflowing DSi-rich river water and release from sediments. The relationships were mostly characterized as a two-round loop during the 1980s with spring and autumn diatom blooms (e.g., 1983, 1986, and 1987), while a one-round big loop during the 2000s with extensive winter–spring blooms (e.g., 2002, 2003 and 2005).
Figure 6.7  Monthly change in decadal statistics of diatom abundances at site C during 1981–1990 (a), 1991–2000 (b), and 2001–2010 (c)
Figure 6.8  Power spectrums of diatom abundance at site C during 1981–2010 (a) and 1981–1990, 1991–2000, and 2001–2010 (b)
Figure 6.9  Seasonal changes of DSi concentration and diatom abundance at site C during 1981 –2010
Figure 6.9  (continued)
6.3.1.4 Long-term relationships between DSi concentration and diatom abundance

DSi concentration significantly increased at the center of the lake (see Chapter 3). Long-term change in DSi concentration was compared with diatom abundance (Figure 6.10). Annual statistics were calculated for the year from August to July because recent diatom blooms often occurred in winter and because about 60% of annual minimum diatom abundance was observed in July and August during the period. Annual maximum diatom abundance was significantly related to annual maximum DSi concentration ($r^2 = 0.16, p < 0.05$) and (D + B)Si concentration ($r^2 = 0.59, p < 0.001$; Figure 6.10a, b). Significant correlation was also detected between DSi concentration and two year-lagged diatom abundance, but a correlation coefficient was lower than no lagged diatom abundance ($p < 0.05$; Figure 6.10c). Correlation coefficient between DSi concentration and diatom abundance was not so high, which might be caused by daily fluctuation of diatom abundance and other factors influencing diatom growth such as N and P concentrations, light condition, and water temperature. However, annual maximum diatom abundance was not significantly related to annual mean values of other nutrients such as DIP, TP, DIN, and TN ($r^2 < 0.07$) and those of potential factors influencing diatom blooms such as water temperature, pH, DO ($r^2 < 0.01$), and transparency ($r^2 = 0.07$).
Figure 6.10  Long-term changes in annual maximum diatom abundance (left axis) and annual maximum (D + B)Si concentration (right axis) at site C in Lake Kasumigaura (a), comparisons of annual maximum DSi or (D + B)Si concentration with diatom abundance (b), and distributions of cross-correlation coefficient between annual maximum DSi or (D + B)Si concentration and diatom abundance lagging $\Delta t$ years behind DSi or (D + B)Si concentration (c). Annual maximum values were determined for the period from August to July. * and *** indicate a significant level $p < 0.05$ and 0.001, respectively in (c)
6.3.2 Simulation

6.3.2.1 Comparison of different calibration methods

Different shapes of diatom bloom patterns were obtained among the various calibration methods (Figure 6.1). Some model predictions by CM1 and 2 represented relatively flat peaks of diatom blooms which were different from field observations (e.g., in 2003 and 2004). On the other hand, predictions calibrated by CM3 showed sharp peaks of blooms which were similar to observations. Therefore, the results calibrated by CM3 were used as described later.

6.3.2.2 Accuracy of the model

Model predictions for DSi and diatoms were shown in Figure 6.12 and 6.13. Focusing on BOX 3, including the center of the lake, the validation results showed that RMSE was 2.6 g m\(^{-3}\) for DSi and 13 cm\(^3\) m\(^{-3}\) for diatoms, respectively (Figure 6.14). The coefficient of variation (CV) of RMSE was calculated as the ratio of RMSE to the mean of the observation values, to be 85\% for DSi and 170\% for diatoms. The coefficient of determination \(R^2\) was also calculated to be 0.22 \((p < 0.001)\) for DSi and 0.0061 \((p = 0.14)\) for diatoms.

Annual statistics of DSi and diatoms observed at site C were compared with model predictions in BOX 3 (Figure 6.15, 6.16). CV of annual mean, standard deviation, and maximum DSi concentration was less than 50\%. In addition, model predictions of annual mean and maximum DSi concentration were significantly related to the observed
Figure 6.11 Long-term changes in DSi concentration and diatom abundance calculated by the model whose parameters were calibrated by the various methods (CM1, 2, and 3) in BOX 3 and observed at site C in Lake Kasumigaura during 1981–2010
Figure 6.12  Model predictions in BOX 1, 2, 3, and 4 (solid lines) and observed data at site A, B, C, and D (broken lines and points) for DSi in Lake Kasumigaura during 1981–2010. The model was calibrated by CM3.
Figure 6.12  (continued)
Figure 6.13  Model predictions in BOX 1, 2, 3, and 4 (solid lines) and observed data at site A, B, C, and D (broken lines and points) for diatoms in Lake Kasumigaura during 1981–2010. The model was calibrated by CM3
Figure 6.13 (continued)
Figure 6.14 Comparisons of monthly observation data at site C with model predictions in BOX3 for DSi (a) and diatoms (b) during 1981–2010.
Figure 6.15  Long-term changes in annual statistics of DSi concentration calculated by model simulation in BOX 3 and observed at site C (a) and comparisons of them (b) during 1981–2010. Annual statistics were calculated for the year from August to July. Model predictions on the observation date were used to calculate annual statistics.
Figure 6.16  Long-term changes in annual statistics of diatom abundance of model predictions in BOX 3 and observed data at site C (a) and comparisons of them (b) during 1981–2010. Annual statistics were calculated for the year from August to July. Model predictions on the observation date were used to calculate annual statistics.
data ($p < 0.001$). On the other hand, CV of annual standard deviation, maximum, and minimum diatom abundance was more than 80%, while CV of annual mean diatom abundance was 59%. Model prediction was not significantly related to the observation data except annual standard deviation ($p < 0.05$). These results suggest that the long-term changes in DSi concentrations were reproduced with more sufficient accuracy than diatom abundances. Although peaks of diatom blooms were underestimated in some years (e.g., 1994, 2005, and 2006), long-term increasing trends of both DSi and diatoms were detected for model predictions as well as observed data (12 month moving average; $p < 0.001$).

Seasonal changes in DSi concentration were relatively well-simulated (Figure 6.17). RMSE (CV) of decadal average during 1981–1990, 1981–1990, and 2001–2010 were 1.2 g m$^{-3}$ (56%), 1.4 g m$^{-3}$ (46%), and 1.4 g m$^{-3}$ (34%), respectively. In addition, decadal average of model predictions were significantly related to observation data during 2001–2010 ($r^2 = 0.37$, $p < 0.05$) and close to significant level during 1981–1990 ($r^2 = 0.30$, $p = 0.063$) and 1991–2000 ($r^2 = 0.30$, $p = 0.064$).

Seasonal changes in diatom abundance were shown in Figure 6.18. RMSE (CV) of decadal average during 1981–1990, 1981–1990, and 2001–2010 were 3.9 cm$^3$ m$^{-3}$ (65%), 8.1 cm$^3$ m$^{-3}$ (96%), and 8.5 cm$^3$ m$^{-3}$ (92%), respectively. Decadal averages of model predictions were significantly related to observation data during 1981–1990 ($r^2 = 0.71$, $p < 0.001$), but no significant correlation during 1991–2000 ($r^2 = 0.063$, $p = 0.43$) and 2001–2010 ($r^2 = 0.048$, $p = 0.49$). In spring, model predictions of diatom blooms might have a lag time of a month compared to observation data during 1991–2000. Although the peak of diatom blooms were underestimated in some years, observed change in a seasonality of diatom blooms, from spring and autumn during 1981–1990 to
Figure 6.17  Monthly changes in decadal statistics of DSi concentration calculated in BOX 3 and observed at site C during 1981–1990 (a), 1981–1990 (b), and 2001–2010 (c). Model predictions on the observation date were used to calculate decadal statistics.
Monthly changes in decadal statistics of diatom abundance calculated in BOX 3 and observed at site C during 1981–1990 (a), 1991–2000 (b), and 2001–2010 (c). Model predictions on the observation date were used to calculate decadal statistics.
winter–spring period during 2001–2010, was comparatively reproduced by the model. Moreover, Fourier analysis showed that model predictions of diatom abundance had a cyclic period of 6 and 12 months, same as observation data (Figure 6.19a). Change in frequency of diatom blooms, twice a year during 1981–1990 and once a year during 2001–2010, was also obtained by model simulation (Figure 6.19b, c, d).

The shift of seasonal relationships between DSi concentration and diatom abundance, from two-round loop during 1981–1990 with spring and autumn diatom blooms to one-round big loop during the 2001–2010 with extensive winter–spring blooms, was nearly reproduced by model simulation (Figure 6.20).

6.4 Discussion

6.4.1 Causes for error of simulation

Most high peaks of diatom blooms were underestimated by model simulation (Figure 6.13, 6.16), which might be attributed in part by time intervals of observation data used in calibration. Monthly observation data was used for parameter calibration in the model; however, diatom abundance varied enormously in a month (e.g., 5.0 cm$^3$ m$^{-3}$ on 20th September 1984, 24 cm$^3$ m$^{-3}$ on 4th October 1984, and 5.5 cm$^3$ m$^{-3}$ on 24th October 1984; NIES observation at site C). Moreover, constant diatom parameters might cause an error due to several species existing in the field. For example, diatom abundance was not simulated well during 1994 and 1995 (Figure 6.13), when significant blooms consisting of *Synedra* spp. were observed transiently (Figure 6.3, 6.4). Additionally, peaks of diatom abundance were lower than observed ones in the first half of 2005 and
**Figure 6.19**  Power spectrums of model predictions of diatom abundance in BOX 3 during the entire period (a), 1981–2010 (b), 1991–2000 (c), and 2001–2010 (d). Model predictions on the observation date were used for Fourier analysis.
Figure 6.20  Mean seasonal changes of DSi concentration and diatom abundance observed at site C (a) and calculated in BOX 3 (b) during 1981–1990, 1991–2000, and 2001–2010
2006 even though beginning of blooms was relatively well simulated (Figure 6.13, BOX 3). Several studies indicated that diatom sinking rate was different between growing season and depletion season; that is, rapid sinking of diatoms occurs under nutrient limitation in fresh water (Titman and Kilham 1976; Sommer and Stabel 1983; Conley et al. 1989) and in physically stable water columns (Reynolds 1973; Scavia and Fahnstenstiel 1987). These reports suggest that the model with constant sinking rate of diatoms could not reproduce the observed peaks in these years.

6.4.2 Influence of DSi release and degradation of light condition on long-term changes in diatom blooms

Among the input variables of the model, increasing trend was detected only for SS concentration derived from sediment resuspension $SS_{sed}$ (Figure 6.21). Sediment resuspension, pronouncedly increased in the early 2000s, probably caused not only an increase in DSi release amount but also degradation of light condition. For investigating those impacts on diatom blooms, DSi concentration and diatom abundance were calculated by assuming no recent intense resuspension of bottom sediments (Table 6.5, Case-1) to be compared with the results of the simulation shown in Figure 6.12 and 6.13. Now, the simulation shown in Figure 6.12 and 6.13 is called as “standard simulation”. The calculated DSi concentrations and diatom abundances of Case-1 were usually lower than the “standard simulation” during the 2000s (Figure 6.22). In fact, there was no significant trend for DSi concentration and diatom abundance of Case-1 during 1981–2010. Seasonal relationships between DSi and diatoms of Case-1 showed two-round loop on average during 2001–2010 (Figure 6.23b), being difference from the “standard simulation” (Figure 6.23a). On the other hand, DSi concentration and diatom
Figure 6.21  Annual averages of model input variables such as discharge of the rivers inflowing the entire lake (a), daily solar irradiance (b), water temperature in BOX 3 (c), and SS concentration derived from sediment resuspension $SS_{sed}$ in BOX 3 (d) and annual total amount of DSi released from $SS_{sed}$ and annual mean light attenuation coefficient in water $K_d$ estimated from $SS_{sed}$ in BOX 3 (e)
Table 6.5  Difference of the input variables and parameters between the “standard simulation”, simulation of Case-1, and of Case-2

<table>
<thead>
<tr>
<th>Input variables or parameters</th>
<th>Symbol</th>
<th>“standard simulation”</th>
<th>Case-1</th>
<th>Case-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(simulation in Figure 6.12 and 6.13)</td>
<td>(no recent intense sediment resuspension)</td>
<td>(no DSi release from SS)</td>
</tr>
<tr>
<td>SS derived from sediments SS_{sed}</td>
<td></td>
<td>simulated values in 1997^a</td>
<td>simulated values in 1997^a</td>
<td>estimates from monitoring data in each year^b</td>
</tr>
<tr>
<td>1981–1997</td>
<td></td>
<td>estimates from monitoring data in each year^b</td>
<td>estimates from monitoring data in each year^b</td>
<td></td>
</tr>
<tr>
<td>1998–2010</td>
<td></td>
<td>1.3</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>Dissolution rate constant (day^{-1})</td>
<td></td>
<td>5 × 10^{-3}</td>
<td>5 × 10^{-3}</td>
<td>0</td>
</tr>
<tr>
<td>Fresh diatom frustules k_f</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Old diatom frustules k_o</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Change from the period 1981–1990 to 2001–2010^c

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DSi amount released from SS_{sed}</td>
<td>↑</td>
<td>→</td>
<td>→</td>
</tr>
<tr>
<td>Light attenuation coefficient K_d</td>
<td>↑</td>
<td>→</td>
<td>↑</td>
</tr>
<tr>
<td>Diatom abundance</td>
<td>↑</td>
<td>→</td>
<td>↓</td>
</tr>
<tr>
<td>Frequency of blooms per year</td>
<td>1</td>
<td>2</td>
<td>approximately 1</td>
</tr>
<tr>
<td>during 2001–2010</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a Seki et al. (2006)

^b see Table 6.2

^c ↑, increase; ↓, decrease; →, no trend
Figure 6.22  Model predictions for DSi and diatoms in BOX 3 calculated by the "standard simulation", simulation of Case-1, and of Case-2
abundance were calculated by assuming that the recent sediment resuspension occurred but DSi release rate from SS was zero during the entire period (Table 6.5, Case-2). The results of Case-2 represented diatom blooms at once a year during some years (e.g., 2003 and 2004) (Figure 6.22, 6.23c). Therefore, DSi release from SSsed alone could never explain the observed change in seasonality of diatom blooms. These results suggested that degradation of light condition by resuspension might play an important role in the changes of a seasonality of diatom blooms. As a result of Case-2, annual maximum diatom abundance in BOX 3 were 20–50% lower than those by the “standard simulation” for 2002–2006 (Figure 6.22), nearly same as Case-1, indicating the impacts of the recent release on diatom blooms in the lake. Although annual maximum DSi concentrations of Case-2 were about 20–30% lower than those by the “standard simulation” for the same period, an increasing trend of DSi concentration was detected ($p < 0.001$), suggesting the impacts of a weakening of diatom blooms due to degradation of light condition on DSi concentration.

6.4.3 Comparison among budgetary calculations

(D + B) Si budgets calculated by the “standard simulation” and simulation of Case-1 were compared with those by budgetary analysis based on the long-term database shown in chapter 5 (Table 6.6). The values of the “standard simulation” were close to those described in chapter 5, on average during the last three decades. Based on the simulation the “standard simulation”, the river input and release account for about 60% and 40% of total (D + B) Si inputs, which are close to the percentages 70% and 30% estimated in chapter 5, respectively. In addition, the river output and BSi gross sedimentation account for 30% and 70% of total output, which are within to the ranges 70–90% and 10–30% estimated by the budgetary analysis in chapter 5, respectively.
Table 6.6  (D + B) Si budgets in Lake Kasumigaura estimated by budgetary analysis based on the long-term database (see chapter 5) and calculated by the “standard simulation” and the simulation of Case-1

<table>
<thead>
<tr>
<th>(10^9 g year⁻¹)</th>
<th>Budgetary analysis</th>
<th>“standard simulation”</th>
<th>Case-1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River input of DSi</td>
<td>12–17</td>
<td>12–16</td>
<td>13–19</td>
</tr>
<tr>
<td>DSi release</td>
<td>8–12</td>
<td>8–12</td>
<td>8–12</td>
</tr>
<tr>
<td>from bottom sediments</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>from SS</td>
<td>0.3–0.9</td>
<td>0?</td>
<td>1.0–2.7</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River output</td>
<td>11–33</td>
<td>7–18</td>
<td>19–52</td>
</tr>
<tr>
<td>DSi</td>
<td>3</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>BSi</td>
<td>2.6</td>
<td>1.4</td>
<td>4.4</td>
</tr>
<tr>
<td>BSi gross sedimentation</td>
<td>0.7</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Apparent accumulation</strong></td>
<td>8–30</td>
<td>5–16</td>
<td>13–46</td>
</tr>
</tbody>
</table>

(determined by core analysis)
Although the recent amount of DSi released from SS by the “standard simulation” was close to the maximum estimation by budgetary analysis during the 2000s, the increase in river output of (D + B) Si was not so much as the results of budgetary analysis. It might be caused by DSi uptake by diatoms and their rapid sinking in the model. The BSi gross sedimentation by the “standard simulation” was lower than that by budgetary analysis; however, close to BSi apparent accumulation rate calculated by analyzing sediment cores (Table 6.6). It suggests the underestimation of gross sedimentation by the “standard simulation” due to inaccuracy in peaks of diatom blooms and/or overestimation of that by budgetary analysis in chapter 5 due to an incompatibility of the parameters such as diatom sinking rate.

6.4.4 Factors influencing seasonality of diatom blooms

Although only physical environment was considered for estimating diatom abundances in the model, daily changes in diatom abundance were probably influenced by physiological and/or ecological factors such as other phytoplankton appearance and predation pressure. Laboratory experiments by Bienfang et al. (1982) demonstrated the rapid sinking of some diatom species after DSi depletion, and they did not come back soon in water column after addition of nutrients. This report was consistent with the hysteresis loop of DSi and diatoms seasonally observed in Lake Kasumigaura (Figure 6.9). However, the typical seasonality could be nearly simulated by the box model with only considering physical condition and constant diatom parameters such as sinking rate (Figure 6.20). This result suggests that physical condition is one of the causes for the observed hysteresis loop.

The influence function of irradiance $f_I$, temperature $f_T$, and DSi concentration $f_{Si}$ on diatom growth are shown for 1982–1984 (Figure 6.24) and 2002–2004 (Figure 6.25),
Figure 6.24  Model predictions and observation data for diatoms (a), influence functions of irradiance $f_i$ (b), temperature $f_T$ (c), and DSi concentration $f_{Si}$ (d) on diatom growth at 12:00 noon, and products of multiplication of $f_i$, $f_T$, and $f_{Si}$ (e) in BOX 3 during 1982–1984. They were calculated by the “standard simulation” or simulation of Case-1. The gray zones through (a) to (e) indicate the growing season of diatoms in the “standard simulation”. Observation was missing in March and December 1983.
Figure 6.25  Model predictions and observation data for diatoms (a), influence functions of irradiance $f_I$ (b), temperature $f_T$ (c), and DSi concentration $f_{Si}$ (d) on diatom growth at 12:00 noon, and products of multiplication of $f_I$, $f_T$, and $f_{Si}$ (e) in BOX 3 during 2002–2004. The gray zones through (a) to (e) indicate the growing season of diatoms in the “standard simulation”. They were calculated by the “standard simulation” or simulation of Case-1.
as a representative of the year spring and autumn blooms and winter–spring blooms observed, respectively. During each period, while short fluctuation range of $f_i$ in a year, $f_T$ and $f_{Si}$ changed substantially. During 1982–1984, an increase in diatom abundance was not obtained during the increase in $f_{Si}$, but obtained when $f_T$ approaching optimal temperatures (e.g., in the second half of 1982). Therefore, timing of the beginning of diatom blooms probably depends mainly on water temperature. On the other hand, a timing of the ending of diatom blooms probably depends mainly on DSi concentration due to radical decline of $f_{Si}$ during blooming. Seasonal patterns of $f_{Si}$ in 1982–1984 were similar to those of Case-1 during 2002–2004, but not of the “standard simulation”. For instance, autumn blooms were not observed in 2002 and winter–spring blooms were observed in the first half of 2003, which was well reproduced by the “standard simulation” but not the simulation of Case-1. During autumn in 2002, the products of multiplication of $f_i$, $f_T$, and $f_{Si}$ of the “standard simulation” were less than those of Case-1 in spite of larger $f_{Si}$ of the “standard simulation” than the simulation of Case-1. During the same period, $f_i$ of the “standard simulation” was less than that of Case-1; therefore, degradation of light condition might prevent autumn diatom blooms. Peaks of diatom blooms of the “standard simulation” were higher than that of Case-1. It could be derived from high $f_{Si}$ which lasted a long time until bloom ending, probably caused by high DSi concentration at the beginning of blooms.

As results, I propose the following scenario about winter–spring blooms observed in recent years: (1) beginning of autumn blooms got delay due to degradation of light condition, (2) blooms lasted for several months due to DSi concentration which were sufficient for diatom growth. Diatom blooms were observed during winter–spring
period but not in summer–autumn, which might be related to lower $f_T$ remaining for several months during summer than winter.

### 6.4.5 Other factors influencing long-term trends in diatom abundance

In Lake Kasumigaura, a shift of dominant diatom species was observed during the last three decades (Figure 6.4). During the 2000s, *Cyclotella* spp., especially *C. meneghiniana*, was most dominant. Their growth rate is relatively fast (Table 6.3); therefore, they could form extend blooms under better condition for them such as high DSi concentration. It might be related the underestimation of peaks of recent diatom abundance based on the model simulated (Figure 6.13, 6.16).

In the light of nutrient for diatoms, the increase in phosphorus (P) concentration, observed in the lake during the last three decades, might also be related to diatom blooms. However, nutrient atomic ratios indicated that Si is one of the most crucial factors limiting diatom growth (Figure 6.5).

### 6.5 Conclusions

In Lake Kasumigaura, diatom abundance significantly increased during the last three decades. Seasonality of diatom blooms shifted from spring and autumn to winter–spring period; therefore, the relationships between DSi and diatoms changed from two-round during the 1980s to one-round during the 2000s. Nutrient limitation for diatoms was analyzed by nutrient atomic ratios N:P:Si, which provided a suggestion of Si limitation during blooms in most years. Modeling and simulation of major processes involved in
DSi and diatoms reproduced spring and autumn blooms during the 1980s and winter–spring blooms during the 2000s. Peaks of diatom blooms were underestimated in some years, suggesting an influence of the observed shift of diatom species and other physiological and/or ecological factors. Peaks of diatom blooms declined by removal of DSi release from resuspended sediments removed, which indicated the impacts of the recent release on diatom blooms in the lake. Seasonality of diatom blooms did not changed by removal of DSi release from SS; however, it changed by removal of sediment resuspension causing both DSi release and degradation of light condition, suggesting the contribution of degradation of light condition by resuspension to the observed change of the loop from two-round to one-round. These findings implicate the significance of the interactions between sediments and water to phytoplankton blooms.
Chapter 7

General Conclusions

7.1 Significance of Si regeneration by sediment resuspension in a shallow eutrophic lake

In shallow lakes, sediment resuspension had been often observed (Amano et al. 2002; Seki et al. 2006). Regeneration of N and P was indicated in several studies (Amano et al. 2002). On the other hand, Si was focused only on release from bottom sediments in the previous studies. In this dissertation, I found a significance of DSI release from SS in a shallow lake, which explained the increasing trend of DSI in Lake Kasumigaura during the last three decades.

In Lake Kasumigaura, the amount of DSI released from SS was 20–40% of the total amount of DSI released during high sediment resuspension period. Total amount of DSI released from SS and bottom sediments for this period might be about two-third of the loads from inflows. These results suggested that DSI release from SS might not be neglected for budgetary analysis of Si in some shallow lakes where sediments are resuspended by wind easily and contains BSI plentifully.
7.2 Application of information of Si dynamics on management of water quality in a shallow eutrophic lake

Diatoms form a major part of the aquatic food web. From the viewpoint of prevention of harmful algal blooms (HABs), diatom species have been preferred. In addition, diatoms play a critical role in marine biogeochemical cycles, especially in the sequestration of carbon dioxide from the atmosphere via the biological pump (Schelske 1999; Ittekkot et al. 2006). Therefore, management and prediction of diatom blooms were important, especially in lakes and estuaries subjected by intense human activities.

In Lake Kasumigaura, cyanobacteria abundance declined when diatoms were dominant during the 2000s (Figure 6.3). Although other factors might cause a decrease in cyanobacteria abundance, small-scale blooms remained for the last decade, indicating that a possibility of preventing harmful algae by regulating diatom blooms. Tsunogai (1979) suggested that diatoms could be predominant under an ideal environmental condition for growth of phytoplankton in the ocean. Figueiras (2003) also indicated that diatoms have faster growth rate than others with adequate nutrient supply, but upward advection or turbulent mixing is required. These suggestions imply that shallow lakes suffering HABs have potentiality of occurrence of diatom blooms due to high nutrient loads from inflows and high turbulence condition by a wind.

The statistical analysis of observation data (Figure 6.10) and model simulations (Figure 6.22) in chapter 6 suggested that the scale of diatom blooms were mainly dependent on DSi concentration before blooms starting in Lake Kasumigaura. The significance of Si for diatoms was suggested both in marine and freshwater ecosystems.
(Koszelnik and Tomaszek 2008); however, evidence for significant effects of Si dynamics on aquatic ecosystems in stagnant waters is sparse in the world (Humborg et al. 1997; Harashima 2007). In addition, the long-term changes in the dominant season of diatoms could be explained by model simulation with considering an effect of resuspension of bottom sediments, which promoted DSi release and degraded light condition in water column (Figure 6.24, 6.25). The results of this study suggested that not only N and P but also Si should be monitored regularly for management of algal occurrence in eutrophic lakes. N: P: Si stoichiometric ratio should also be investigated. In shallow lakes, the variance of turbidity is usually large; therefore, light condition should also be taken consideration for predicting diatom blooms.

7.3 Summary

Si dynamics and its impacts on diatom blooms were assessed in Lake Kasumigaura as a representative of shallow lakes, using various biogeochemical methods such as statistical analysis, laboratory experiment, budgetary analysis comparing with sediment core information, and simulation by a numerical model. Knowledge and information obtained by this dissertation was summarized as follows:

(i) Previous studies indicated an importance of Si cycling through release from bottom sediments. However, in a shallow lake, a significance of Si release from resuspended sediment was suggested in this study.

(ii) Long-term budgets of Si were calculated in a shallow lake and got consistency with the recent increase in a release amount from resuspended sediments.
determined by laboratory experiments.

(iii) Model simulation suggested that DSi supply rate to lake water could be a crucial factor determining a scale of diatom blooms in a eutrophic lake. On the other hand, a seasonality of blooms might be influenced by a degradation of light condition in water column caused by sediment resuspension.

(iv) Significance of water-sediment interaction and its impacts on ecosystems were implied in a shallow eutrophic lake.

The above information suggested a complexity of Si dynamics in inland waters. Importance of taking considerable care in Si was implied for management in a shallow eutrophic lake, especially focusing on Si cycling and its influence on diatom blooms.

### 7.4 Further research

This dissertation focused on Si dynamics and relationships with diatom blooms in a shallow eutrophic lake. However, a part of role of Si for aquatic ecosystems remains poorly understood, such as effects of bacteria on BSi dissolution, long-term dissolution of sediment BSi, and impacts of Si dynamics on shift of dominant phytoplankton species. Especially, the last problem is intricately related to biogeochemistry and physiology. Global decreasing trend of DSi load from land to coastal area may become more acute in the near future, especially around a developing country such as in South East Asia where dam construction is active. For this reason, a continuous monitoring may be of more significance. For interpreting a long-term change, analyzing sediment cores can also bring useful information; however, still accumulated sediments should be
preferred for analyzing stratigraphy of BSi.

As for Lake Kasumigaura, the causes for sediment resuspension observed during the early 2000s are still unclear. Wind speed did not increase in that region. The sediment properties might become susceptible to resuspending by a wind, such as an increase in water content and a decrease in organic content (Seki et al. 2006); however, the external factors were not elucidated. In this study, the influence of sediment resuspension on Si dynamics and phytoplankton dominance was suggested. Therefore, the detailed studies approaching the mechanisms of intense sediment resuspension in the lake during the early 2000s is needed in future.
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I spent about six worthwhile years in my laboratory, and thank every member for...
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Tsunogai S (1979) Dissolved silica as a primary factor determining the composition of phytoplankton classes in the ocean (in Japanese with English abstract). Bull Faculty Fisheries Hokkaido Univ 30:314–322

# Glossary

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