

1 **Title**

2 Increase in silicon concentrations and release from suspended solids and bottom  
3 sediments in Lake Kasumigaura, Japan

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5 **Authors**

6 Hiroyuki Arai • Takehiko Fukushima • Kazuhiro Komatsu

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8 **Addresses**

9 Hiroyuki Arai (✉) • Takehiko Fukushima

10 Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba,

11 Ibaraki 305-8572, Japan

12 e-mail address: [arai30312@ies.life.tsukuba.ac.jp](mailto:arai30312@ies.life.tsukuba.ac.jp)

13 Tel.: +81 298 53 6883

14 fax: +81 298 53 7189

15

16 Kazuhiro Komatsu

17 National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-8506, Japan

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19

1 **Abstract**

2       Increasing trends of dissolved Si measured by a colorimetric method and ICP (DSi<sub>col</sub>  
3 and DSi<sub>ICP</sub>, respectively) and total Si concentrations were detected at the center of Lake  
4 Kasumigaura during 1980–2006 (mean DSi<sub>col</sub> concentration in the 1980s and 2000s was  
5 1.3 mg l<sup>-1</sup> and 4.0 mg l<sup>-1</sup>, respectively). The observation of such trends is rare; therefore,  
6 the elucidation of the causes could be useful to understanding silicon dynamics in inland  
7 waters. Based on statistical analysis, we found that the increases in DSi<sub>col</sub> and lithogenic  
8 Si accounted for most of the total Si increase (44% and 45%, respectively) and that  
9 biogenic Si, consisting of diatom frustules, also increased with them. Increases in DSi<sub>ICP</sub>  
10 concentration were not detected near the mouth of the inflowing rivers, suggesting that  
11 the increase was caused by in-lake processes. Because the increase in suspended solids  
12 (SS) caused by sediment resuspension had been observed in the lake for the same period,  
13 we assumed that the Si release from SS containing diatom frustules contributed to the  
14 increase. The results of the laboratory experiments in which surface sediments were  
15 stirred in lake waters showed that the change in DSi<sub>col</sub> concentration depended mainly  
16 on SS concentration, water temperature, and the elapsed time of diatom frustules  
17 dissolution. An estimation of the released amount of Si from SS using the sediment  
18 resuspension model was  $(1.0\text{--}2.7) \times 10^9 \text{ g y}^{-1}$  in the 2000s, which was about 30–90% of  
19 the increase in the DSi<sub>col</sub> outflow of  $3.0 \times 10^9 \text{ g y}^{-1}$  from the 1980s to the 2000s. We  
20 also determined the Si release rates from bottom sediments through laboratory  
21 experiments. The Si amount released from bottom sediments in the lake in the 2000s  
22 was estimated to be  $4.3 \times 10^9 \text{ g y}^{-1}$ , which was about 2–4 times higher than the  
23 estimated Si amount released from SS. These findings suggest that the sediment  
24 resuspension might be the cause of the latest DSi increase.

25

1 **Keywords**

2 Silicon • Suspended solids • Sediment • Dissolution • Lake Kasumigaura

3

## 1 **Introduction**

2

3 Silicon (Si) is one of the most abundant elements in the biosphere, and essential  
4 nutrients for siliceous phytoplankton, i.e. diatoms, playing an important role in the  
5 global primary production (Schelske 1999; Conley et al. 2000; Kristiansen and Hoell  
6 2002; Conley et al. 2006; Harashima et al. 2006). Some plants like paddy also need Si  
7 (Derry et al. 2005). Therefore, changes in Si concentration in surface waters could affect  
8 the phytoplankton dominance, food web and biogeochemical cycling (Humborg et al.  
9 1997; Krivtsov et al. 2000; Harashima et al. 2007; Li et al. 2007; Koszelnik and  
10 Tomaszek 2008).

11 The dissolved Si (DSi) load from land to coastal areas may be declining globally  
12 (Humborg et al. 1997; Duan et al. 2007; Li et al. 2007). Humborg et al. (1997) reported  
13 that decreases in the DSi load were observed in the Danube River–Black Sea system  
14 and impacts of dam constructions on Si depletion were indicated. Teodoru et al. (2006)  
15 suggested that the large number of impoundments on the Danube and its tributaries  
16 changed Si transport to the coastal Black Sea. In Japan, a possible decrease in DSi  
17 transport was also suggested. The Foundation of River & Watershed Environment  
18 Management (2007) reported that the mean DSi concentration of 18 Japanese rivers in  
19 the 2000s was lower than that in the 1940s and 1950s, opposite to the trends of nitrogen  
20 and phosphorus. However, the scarcity of long-term Si monitoring data makes it  
21 difficult to elucidate the cause. Although few studies of long-term trends of Si  
22 concentrations in inland waters around the world exist, Vesely et al. (2005) showed the  
23 increasing trends of DSi concentration in five glacial lakes in the Bohemian Forest over  
24 the last two decades. They concluded that the higher mobility of Si from the soil to  
25 surface waters resulted from a decrease in dissolved Al and faster dissolution of

1 biogenic Si (BSi). Several studies indicated that, as a consequence of diatom  
2 sedimentation, Si was released back to the water column (Rippey 1983; Schelske et al.  
3 1988; Szczepocka and Szulc 2006).

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

1 In Lake Kasumigaura, various forms of Si have been monitored for the last 3 decades  
2 and several trends were detected. Understanding the dynamics of Si in a shallow  
3 eutrophic lake is extremely valuable. Considerable increases in turbidity and inorganic  
4 content in suspended solids (SS), due mainly to the resuspension of bottom sediments,  
5 were also observed in the lake from the mid 1990s to mid 2000s, which could cause the  
6 decline in primary production and the increase in phosphorus concentration (Fukushima  
7 et al. 2005; Seki et al. 2006). Si release rates from SS and its impact on long-term  
8 change in DSi concentrations were not assessed in previous studies. The objectives of  
9 the present paper are fourfold: (1) to detect the long-term trend of Si concentrations in  
10 Lake Kasumigaura, (2) to discuss the factors influencing this trend, (3) to estimate the  
11 Si release rates from SS and bottom sediments by laboratory experiments, and (4) to  
12 assess the contribution of these Si releases to the trend.

13

#### 14 **Study area**

15

16 Lake Kasumigaura is the second largest shallow lake in Japan, located in the Ibaraki  
17 Prefecture, approximately 50 km northeast of Tokyo. It has a surface area of 171.5 km<sup>2</sup>,  
18 a mean depth of 4 m, and a maximum depth of 7.3 m. Mean water retention time is  
19 about 200 days. The lake is so shallow that vertical stratification is easily destroyed by a  
20 moderately strong wind. The lake has two large bays, Takahama-iri and Tsuchiura-iri.  
21 The Koise and Sakura rivers are the main rivers influent into Takahama-iri and  
22 Tsuchiura-iri, respectively. Water tends to flow through the lake from the northwest,  
23 where Takahama-iri and Tsuchiura-iri are located, to the southeast, to the effluent  
24 Hitachitone River. Its catchment area of 1426 km<sup>2</sup> consists of paddy fields, plowed  
25 fields for other row crops, orchards (51%), forest (30%), and urban, industrial, and

1 residential uses (12%). Major surface geology in the catchment is loam. The climate of  
2 the area is similar to other regions on the Pacific side of Japan with the annual average  
3 air temperature of about 14°C and an annual precipitation of 1250 mm. The lake was  
4 turned from a brackish into a freshwater lake 5 years after a floodgate to the Pacific  
5 Ocean was implemented in 1963.

6 The lake is well known for eutrophication. Mean (min.–max.) chlorophyll *a*, total  
7 nitrogen (TN), and total phosphorus (TP) concentrations at the center of the lake during  
8 April 1980 – March 2007 were 53 (3–140)  $\mu\text{g l}^{-1}$ , 1.03 (0.52–1.99)  $\text{mg l}^{-1}$ , and 0.091  
9 (0.021–0.203)  $\text{mg l}^{-1}$ , respectively. Nitrogen and phosphorus load from the basin to the  
10 lake increased during the high economic growth period.

11

## 12 **Materials and methods**

13

### 14 Silicon concentrations and other water qualities in Lake Kasumigaura

15

16 The database of water quality used for this study was based on the investigation by two  
17 institutes during April 1980 – March 2007. The National Institute for Environmental  
18 Studies (NIES) collected surface waters once a month at 10 sites (A1–A4, B1–B3, and  
19 C1–C3; Fig. 1). C1 is located at the center of the lake. Water filtered through 0.45- $\mu\text{m}$   
20 glass-fiber was analyzed by inductively-coupled plasma (ICP) to determine the  
21 concentrations of DSi (expressed as  $\text{DSi}_{\text{ICP}}$  in this article) and other elements (B, Ca, K,  
22 Mg, Na, and Sr). Diatom, SS, and chlorophyll *a* concentrations taken by a  
23 column-sampler (upper 2 m) and data on basic water quality (e.g., water temperature,  
24 pH, DO, transparency observed in the field) were also used for statistical analysis.  
25 Diatoms were counted on an inverted microscope and quantified as biovolume by

1 multiplying counted cell number by mean cell volume.

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

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

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

18

19 Silicon concentrations of the rivers inflowing Lake Kasumigaura

20

21 Si concentrations of the main rivers inflowing Lake Kasumigaura were used in this  
22 study. In 1994, DSi<sub>ICP</sub> concentrations of 10 rivers (Sakura, Koise, Sonobe, Ono,  
23 Hanamuro, Seimei, Sannou, Amano, Shin, and Takahashi Rivers) were seasonally  
24 measured by NIES ( $N = 4$ ). In 2007, DSi<sub>col</sub> concentrations of 5 rivers (Sakura, Ono,  
25 Seimei, Tomoe, and Hokota Rivers) were measured almost monthly by KRO ( $N = 11$ ).

1 Only 3 rivers (Sakura, Ono, and Seimei Rivers) were investigated by both institutions.  
2 In addition, we measured both  $DSi_{ICP}$  and  $DSi_{col}$  concentrations of 12 rivers (Sakura,  
3 Koise, Sonobe, Ono, Hanamuro, Seimei, Kajinashi, Ichinose, Hishigi, Shin, Tomoe, and  
4 Hokota Rivers) by ICP and colorimetric method, respectively, in December 2009. There  
5 was no rainfall for 3 days before almost all samplings.

6

7 Silicon release experiments in the laboratory

8

9 *Sampling*

10

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

19

20 *Experiment design*

21

22 Si release rates from SS were assessed in the laboratory (Table 1). The sediments  
23 were mixed with lake water or distilled water at various SS concentrations (about  
24 50–500 mg  $\Gamma^{-1}$ ) in a polycarbonate bottle (500 ml or 1 l) and stirred continuously by  
25 magnetic stirrer under dark conditions at room temperature (25°C). Two additional

1 water temperature conditions, 1 and 15°C, were used, for which the samples were not  
2 stirred continuously but mixed once a day by hand. Aliquots of 3–10 ml were taken  
3 from the bottles at the beginning of the experiment, every day or every second day in  
4 the first week, and then every other week. pH, EC, and DO were measured to be 8.0–8.3,  
5 290–330  $\mu\text{S cm}^{-1}$ , and 5–8  $\text{mg l}^{-1}$ , respectively, for the experiments using lake waters.

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

17

### 18 *Analysis*

19

20 All aliquots were filtered through 0.45- $\mu\text{m}$  membrane filters and kept at 1°C, under dark  
21 conditions. DSi concentrations were determined by silicomolybdate yellow or blue  
22 colorimetric method.

23 For checking the budget in the system, aliquots of 30 ml were taken at the start and  
24 end of experiments S4-3 and S5-4, respectively. Aliquots of 20 ml were filtered through  
25 0.45- $\mu\text{m}$  membrane filters for analyzing BSi by the method according to DeMaster

1 (1981). Aliquots of 10 ml were used for analyzing TSi by silicomolybdate yellow  
2 colorimetric method after alkaline digestion according to JIS K 0101.

## 3 4 **Results**

### 5 6 Long-term trends of silicon concentrations in Lake Kasumigaura

7  
8 Mean (min.–max.) of  $DSi_{col}$ ,  $DSi_{ICP}$ , and TSi concentration were 2.4 (0.0–9.3), 3.1  
9 (0.0–10.3), and 4.7 (0.1–22.2)  $mg\ l^{-1}$ , respectively, at C1 during April 1980 – March  
10 2007. Although we cannot make a fair comparison because of the difference in the  
11 sampling date, about 80% of  $DSi_{ICP}$  concentrations were larger than  $DSi_{col}$   
12 concentrations at C1, which might be caused by the difference in the method for  
13 analysis. The annual average  $DSi_{col}$  and TSi concentrations significantly increased ( $p <$   
14  $0.001$ ), along with  $DSi_{ICP}$  concentrations ( $p < 0.01$ ), at C1 during this period (Table 2;  
15 Fig. 2). The annual maximum of each Si concentration and the minimum of TSi also  
16 significantly increased ( $p < 0.001$ ), except in 2006, when declines were observed. From  
17 the 1980s to 2000s, the averages of  $DSi_{col}$ ,  $DSi_{ICP}$ , and TSi concentrations at C1  
18 changed from 1.3, 2.2, and 2.2 to 4.0, 4.8, and 8.4  $mg\ l^{-1}$ , respectively, which represents  
19 210, 120, and 290% increases, respectively. On the other hand, ratios of change for the  
20 other dissolved elements (B, Ca, K, Mg, Na, and Sr) were within  $\pm 15\%$  (data not  
21 shown).

22 Similar Si changes were also observed at A2 and B2 (Table 2). With the exception of  
23  $DSi_{ICP}$  at A2, increasing trends of  $DSi_{col}$ ,  $DSi_{ICP}$ , and TSi concentrations were detected;  
24 however, these increases (37–180%) were lower than those at C1. Increasing trends of  
25  $DSi_{ICP}$  concentrations were seen around the center of the lake, such as at A4 and B3

1 (Table 2). In contrast,  $DSi_{ICP}$  concentrations decreased at A1, near the Koise River ( $p <$   
2  $0.05$ ), and a clear trend was not detected at B1, near the Sakura River. The temporal and  
3 spatial variations of  $DSi_{ICP}$  concentrations in Fig. 3 represent the Si loads from  
4 inflowing rivers and progressive decreases in Si as the flows approach the center of the  
5 lake. The concentrations at C1 were transiently higher than those at the stations near the  
6 inflowing rivers (A1 and B1) in every summer during the period of 2002–2005.

7 Changes in the annual averages of  $DSi_{col}$ , BSi, and LSi concentrations at C1 are  
8 shown in Fig. 4. Increasing trends of  $DSi_{col}$ , BSi, and LSi concentrations were detected  
9 ( $p < 0.001$ ). The increases in  $DSi_{col}$ , BSi, and LSi accounted for 44, 11, and 45%,  
10 respectively, of the TSi increase of  $6.2 \text{ mg l}^{-1}$  from the 1980s to 2000s.

11

## 12 Silicon release rates from suspended solids

13

14 The BSi contents of sediments sampled at A3, B3, and C1 in August 2008 and at C1 in  
15 June and October 2009 were 23, 29, 38, 40, and  $43 \text{ mg g}^{-1}$ , respectively. Si release rates  
16 from the sediments sampled at A3 and B3 were within  $\pm 20\%$  of the rate at C1 (Table 1,  
17 S1). C1 is representative of the center area of the lake; therefore, we applied the rates  
18 obtained at C1 to the whole lake.  $DSi_{col}$  concentrations were approximately proportional  
19 to SS concentrations at the same condition in the experiment S2 and S3 ( $r^2 = 0.90\text{--}1.00$ ,  
20 Fig. 5). This result means that Si release rates from SS were independent of SS  
21 concentrations in this experiment. Si release rates in lake water were higher than those  
22 in distilled water (Fig. 5). Loucaides et al. (2008) suggested that such an enhancement  
23 of the Si release rate was due to the catalytic effect of seawater cations, which may  
24 cause the difference in the rates in this study. In addition, Si release rates strongly  
25 depended on water temperature (Table 1, S4).

1 Changes in  $DSi_{col}$  concentrations from Day 0 for various combinations of sediment  
2 and lake water are shown in Fig. 6. Concentration changes could be largely divided into  
3 two parts, until and after Day 1. Until Day 1, Si release rates were quite different among  
4 used lake waters.  $DSi_{col}$  concentrations increased in S3 using C1 lake water in June  
5 2009 ( $1.10 \pm 0.16 \text{ mg g}^{-1} \text{ day}^{-1}$ ), remained almost constant in S5-4 using C1 lake water  
6 in October 2009 ( $-0.09 \text{ mg g}^{-1} \text{ day}^{-1}$ ), and decreased in S5-1 using B0 lake water ( $-0.36$   
7  $\text{mg g}^{-1} \text{ day}^{-1}$ ). On the other hand, after Day 1, Si release rates were not so different  
8 among the waters, but gradually decreased with time. Si release rates of S3 during Days  
9 0–1, 1–7, and 7–28 were  $1.10 \pm 0.16$ ,  $0.29 \pm 0.04$ , and  $0.24 \pm 0.03 \text{ mg g}^{-1} \text{ day}^{-1}$ ,  
10 respectively. Loucaides et al. (2008) determined the Si release rates from fresh diatom  
11 frustules and two diatomaceous lake sediments in freshwater at 25°C under stirred,  
12 flow-through conditions, which were 0.6, 0.9, and 1.6  $\text{mg g}^{-1} \text{ day}^{-1}$ , respectively. They  
13 used BSi-rich materials; therefore, our results were lower than those values but of the  
14 same order.

15 TSi concentrations of S4-3 and S5-4 were not so different between the start and end  
16 of the experiment ( $\pm 10\%$ , within the measurement error); therefore, the closed system  
17 was confirmed. The sum of  $DSi_{col}$  and BSi concentrations was nearly the same between  
18 them ( $\pm 8\%$ ; for example,  $DSi_{col}$  and BSi concentrations in the experiment S5-4 were  
19 4.3 and 10.2  $\text{mg l}^{-1}$  at Day 0 and 5.3 and 8.5  $\text{mg l}^{-1}$  at Day 28, respectively), suggesting  
20 that the main source of DSi was BSi, mostly consisting of diatom frustules. In addition,  
21 Si release rates from LSi are typically five orders of magnitude slower than those from  
22 BSi (Hurd 1983), and as such, we expected a negligible influence of LSi on Si release.  
23 The estimated degradation ratios of BSi of S3 at Days 1, 7, and 28 were  $2.7 \pm 0.4$ ,  $7.1 \pm$   
24  $0.5$ , and  $20.0 \pm 2.0\%$ , respectively. The ratios of S5-1 at Day 32 and S5-4 at Day 28  
25 were 7.3% and 6.5%, respectively, and they were lower than those of S3. The variability

1 may be affected by diatom frustules. Bailey-Watts (1976b) determined the degradation  
2 ratio of BSi using dead diatom frustules at 20°C under dark conditions, which were 17%  
3 after 38 days and 19% after 50 days, and our values at Day 28 were not far from those.

4

5 Silicon release rates from bottom sediments

6

7 Si release rates from bottom sediments were not significantly different between distilled  
8 water and lake water (initial concentration was 0.1 mg-Si l<sup>-1</sup>), indicating that the  
9 catalytic effect of cation was saturated by release from sediments in this experiment  
10 (Table 1, B1 and B2). The release rates were also independent of sediment thickness in  
11 the range of this experiment (Table 1, B3). On the other hand, they largely depended on  
12 water volume (B1 and B2) and temperature (B3). The rates during Days 0–8 at 1, 15,  
13 and 25°C were 0.020 ± 0.006, 0.051 ± 0.001, and 0.084 ± 0.002 g m<sup>-2</sup> day<sup>-1</sup>,  
14 respectively. Also, they gradually decreased with time (Fig. 7a). In series B3, Si release  
15 rates at 25°C during Days 0–8, 8–15, and 15–25 were 0.084 ± 0.002, 0.039 ± 0.002, and  
16 0.023 ± 0.001 g m<sup>-2</sup> day<sup>-1</sup>, respectively. DSi<sub>col</sub> concentrations gradually reached  
17 constant values, depending on water temperature. After replacing the old water with  
18 distilled water in the experiments of B3-2, -5, and -6, Si release rates were much  
19 enhanced (Fig. 7b). This result suggests that the decrease in the rates with time was not  
20 caused by a change in sediment qualities, such as aging of diatom frustules, but caused  
21 by the change in overlying water qualities, such as DSi concentration. The variance of  
22 the rates among the three water volumes in the experiments of B1 and B2 also supports  
23 this consideration because the rates were independent of sediment thickness.  
24 Bailey-Watts (1976b) and Rippey (1983) measured Si release rates in laboratory cores  
25 sampled at shallow eutrophic lakes (0.02–0.10 and 0.05–0.39 g m<sup>-2</sup> day<sup>-1</sup>, respectively),

1 and our results in the first week were within those values.

2

### 3 **Discussion**

4

5 Relationship between silicon concentrations and other water quality items

6

7  $DSi_{col}$  concentration was positively correlated with  $DSi_{ICP}$  concentration (Table 3).  
8  $DSi_{col}$ ,  $DSi_{ICP}$ , and  $BSi$  concentrations were also related to  $LSi$  concentration. In  
9 addition, each Si concentration was significantly related to SS, inorganic content of SS,  
10 and transparency. These correlations indicate that the Si increases were related to  
11 sediment resuspension. In fact, the increase in  $LSi$  appears to be directly caused by it. In  
12 contrast,  $DSi$ ,  $BSi$ , and  $LSi$  were insignificantly correlated with chlorophyll *a*, water  
13 temperature, DO, and precipitation.

14

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

16

17 Contrary to the detected trends around the center of the lake,  $DSi_{ICP}$  concentrations near  
18 the inflowing rivers did not increase, suggesting that the loads from the inflowing rivers  
19 had not increased. Si loads through rivers were compared between different two years as  
20 follows. In 1994, the average (min.–max.) of annual mean  $DSi_{ICP}$  concentration of the  
21 10 NIES-monitored inflowing rivers was 12.7 (9.9–15.6)  $mg\ l^{-1}$ , with that of the 3  
22 “overlapping” rivers (i.e., the Sakura, Ono, and Seimei Rivers) being 12.2 (10.6–13.3)  
23  $mg\ l^{-1}$ . In 2007, the average (min.–max.) of annual mean  $DSi_{col}$  concentrations of the 5  
24 KRO-monitored rivers was 9.4 (7.8–10.9)  $mg\ l^{-1}$ , with the 3 “overlapping” rivers being  
25 8.8 (7.8–9.8)  $mg\ l^{-1}$ . In addition, our investigation showed that the ratio of  $DSi_{col}$  to

1 DSi<sub>ICP</sub> concentration was 0.98 ( $r^2 = 1.00$ ). These results suggest that DSi concentrations  
2 of inflowing rivers did not increase but rather decreased. The discharge of inflowing  
3 rivers also did not increase; therefore, Si loads through the rivers could not have caused  
4 the increase in DSi concentrations in the lake.

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

11 In other studies, the Si release rates from lake sediments were enhanced by increases  
12 in water temperature and pH (Rippey 1983; Loucaides et al. 2008). In Lake  
13 Kasumigaura, however, the annual average water temperature and pH have not  
14 significantly increased during the last 3 decades. On the other hand, the turbidity  
15 increase due to sediment resuspension observed in the lake from the mid 1990s caused  
16 the increase in LSi concentration, and might provide the opportunity for increases in  
17 DSi concentration through regeneration of Si. DSi of sediment pore water might also be  
18 released with resuspension. However, surface sediments less than 2 cm depth were  
19 affected by sediment resuspension (Seki et al. 2006), and DSi concentrations of those  
20 pore water were considered to be not so different from those in the water column;  
21 therefore, the Si release from pore water might be neglected. Fukushima et al. (2005)  
22 roughly discussed the causes for the increased resuspension like the changes in  
23 meteorological condition, physical properties of sediments, benthic ecosystem, aquatic  
24 plants, and geomorphologic conditions. The plausible causes were suggested such as the  
25 changes in the organic content and water content of the sediments perhaps resulted from

1 the recovery of the lake from hyper-eutrophicated condition and/or the transition from  
2 blackish water to freshwater; however, the authors indicated that the further  
3 investigation was needed.

4

5 Factors influencing the silicon release rates

6

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

20 
$$\frac{dC}{dt} = -\frac{d\alpha}{dt} SS - \frac{dB}{dt} \quad (1)$$

21 where  $C$  is the  $DSi_{col}$  concentration (mg  $\Gamma^{-1}$ ),  $t$  is the time (day),  $\alpha$  is the Si adsorbed on  
22 the surface of SS (mg  $g^{-1}$ ),  $SS$  is the suspended solids concentration (g  $\Gamma^{-1}$ ), and  $B$  is the  
23 BSi concentration (mg  $\Gamma^{-1}$ ).  $\alpha$  can be described as following equation:

24 
$$\alpha = \alpha'X \quad (2)$$

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

$$5 \quad \alpha = \gamma C \quad (3)$$

6 where  $\gamma$  is a constant ( $\text{l g}^{-1}$ ). Using Eq. 3, the change in  $C$  can be determined by the  
 7 following equation:

$$8 \quad \frac{dC}{dt} = -\frac{1}{1 + \gamma SS} \frac{dB}{dt} \quad (4)$$

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

11 Experimental results suggested that the Si dissolved in water and adsorbed on the  
 12 surface of SS might not have been at equilibrium on Day 0, but had reached equilibrium  
 13 by Day 1 at the latest. Therefore, we can assume that  $\alpha$  was independent of  $C$  on Day 0  
 14 and dependent on it on Day 1 ( $\alpha_1 = \gamma C_1$ ). Applying this assumption to Eq. 1, the  
 15 following equation was obtained:

$$16 \quad \frac{C_1 - C_0}{SS} = -(\alpha_1 - \alpha_0) - \frac{B_1 - B_0}{SS} = \alpha_0 - \frac{B_1 - B_0}{SS} - \gamma C_1 \quad (5)$$

17 where the subscripts indicate the days since the experiment started. The values of  $\alpha_0$  are  
 18 specific to the used sediments, and  $B_1 - B_0$  is subject to the Si dissolution rate of diatom  
 19 frustules, which might be independent of  $C$ . Thus, the left part of Eq. 5 was linearly  
 20 correlated with  $C_1$ ; as a result,  $\gamma$  was determined through a regression analysis to be 0.12  
 21 by assuming that the  $\alpha_0$  and  $B_1 - B_0$  are not so different among the used sediments (Fig.  
 22 8).

23 Figure 9 shows the changes in the Si dissolution rates,  $R$  ( $\text{mg g}^{-1} \text{ day}^{-1}$ ), calculated by

1 the following equation derived from Eq. 4:

$$2 \quad R = -\frac{1}{SS} \frac{dB}{dt} = \frac{1 + \gamma SS}{SS} \frac{dC}{dt} \quad (6)$$

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

$$5 \quad B = B_0 e^{-kt} \quad (7)$$

$$6 \quad \frac{dB}{dt} = -k B_0 e^{-kt} \quad (8)$$

7 where  $k$  is the dissolution rate constant ( $\text{day}^{-1}$ ) and the subscript indicates the initial  
8 value ( $t = 0$ ). The rates decreased notably within about a first week, but were almost  
9 constant after that (Fig. 9). It suggests the decrease in the BSi amount of comparatively  
10 fresh diatom frustules which is dissolved more rapidly than old diatom frustules due to  
11 alternations of the bulk structure and surface chemistry (Van Cappellen et al. 2002;  
12 Gendron-Badou et al. 2003). Now, we assumed that the BSi can be divided into two  
13 parts, contained in fresh and old diatom frustules with same temperature dependence of  
14 dissolution, and the dissolution rates of old ones were approximately constant on the  
15 time scale of this experiment. Defining  $\beta$  as the BSi content of SS ( $= B/SS$ ,  $\text{mg g}^{-1}$ ), the  
16 dissolution rate can be described as following equation:

$$17 \quad R = -\frac{d\beta}{dt} = k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0} e^{-k_o t} \approx k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0} \quad (9)$$

18 where the subscripts f and o indicate the fresh and old diatom frustules, respectively ( $\beta$   
19  $= \beta_f + \beta_o$ ,  $k_f > k_o$ ). The equation could fit well to the experimental results (Fig. 9). The  
20 initial BSi content,  $\beta_0$  was  $40 \text{ mg g}^{-1}$  in the experiment S3 and  $43 \text{ mg g}^{-1}$  in the  
21 experiment S5-4; therefore,  $\beta_{f0}$ ,  $\beta_{o0}$ ,  $k_f$ , and  $k_o$  were determined to be 1.2, 39, 1.2, and  
22  $6.2 \times 10^{-3}$  in the experiment S3 and 0.8, 42, 1.3, and  $3.8 \times 10^{-3}$  in the experiment S5-4,

1 respectively. It suggests that the dissolution rate constants,  $k_f$ , and  $k_o$ , were almost  
 2 constant for the diatom frustules in the lake. In addition, the experimental period of  
 3 about 30 days was sufficiently smaller than  $1/k_o$  of 160–260 days, suggesting that the  
 4 assumption is reasonable. The mean values of  $k_f$  and  $k_o$  ( $1.3$  and  $5.0 \times 10^{-3}$ , respectively)  
 5 were used to the estimation for the field as described later. The dissolution rates also  
 6 correlated positively with water temperature (Fig. 10). Finally, the rates and the change  
 7 in  $DSi_{col}$  concentration can be expressed as follows:

$$8 \quad R = (k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0}) e^{-\left(\frac{a}{T} - \frac{a}{T_a}\right)} \quad (10)$$

$$9 \quad \frac{dC}{dt} = \frac{SS}{1 + \gamma SS} R = \frac{SS}{1 + \gamma SS} (k_f \beta_{f0} e^{-k_f t} + k_o \beta_{o0}) e^{-\left(\frac{a}{T} - \frac{a}{T_a}\right)} \quad (11)$$

10 where  $T$  is the water temperature (K),  $T_a$  is a constant (298.15 K), and  $a$  is a constant  
 11 (K). The value of  $a$  was determined from the experiment of S4 to be  $(4.1\text{--}4.4) \times 10^3$   
 12 (Fig. 10). We applied the mean value of  $a$  of  $4.2 \times 10^3$  to the estimation for the field as  
 13 described later.

14 Our results of Si release experiment from bottom sediments fit well to the equation  
 15 described in Fig. 7 (a).  $DSi_{col}$  concentrations reached constant values, which could be  
 16 regarded as the equilibrium concentration,  $C_e$ .  $C_e$  was correlated with water temperature  
 17 (11.7, 14.9, and 25.3 mg  $\Gamma^{-1}$  at 1, 15, and 25°C, respectively), and fit to the equation in  
 18 Fig. 11 ( $r^2 = 0.86$ ). Assuming that the concentration close to the surface of the sediments  
 19 was equal to  $C_e$ , and that the concentration adequately far from the sediments was equal  
 20 to the observed concentration ( $C$ ), Si diffusion can be limited by the concentration  
 21 difference, that is, the subtraction of  $C$  from  $C_e$ . Figure 12 shows that the rates were  
 22 linearly correlated with this difference, suggesting that the above assumptions could be  
 23 applied. Si release rates from bottom sediments,  $J$  ( $\text{g m}^{-2} \text{ day}^{-1}$ ) and the change in  $DSi_{col}$

1 concentration can be written as follows:

$$2 \quad J = K(C_e - C) \quad (12)$$

$$3 \quad \frac{dC}{dt} = \frac{J}{h} \quad (13)$$

4 where  $K$  is the rate constant ( $\text{m day}^{-1}$ ) and  $h$  is the water depth (m). In this experiment, a  
5 temperature dependence of  $K$  was not clearly seen, but it was determined to be  $4.9 \times$   
6  $10^{-3}$  ( $r^2 = 0.73$ , Fig. 12). We applied this equation to the estimation for the field as  
7 described later.

8

9 Estimation of silicon release rate in Lake Kasumigaura

10

11 The annual amount of Si released from SS in Lake Kasumigaura in 2004 was estimated  
12 by assuming that: (1) the particle size distribution of SS in this experiment is the same  
13 as that of the entire lake, (2)  $X$  is constant, (3) the influence of variance in the  
14 concentrations of cations in lake water can be neglected, (4) SS concentrations  
15 contributing to the Si release are subject to sediment resuspension driven by a critical  
16 wind, and (5) background SS remaining constantly in the water column (mainly  
17 consisting of clay minerals) does not affect the Si release. Using Eq. 11, the annual  
18 amount of Si released from SS,  $Y$  ( $\text{g y}^{-1}$ ), can be estimated by following equation:

$$19 \quad Y = V \int \frac{dC}{dt} dt = V \int \frac{SS}{1 + \gamma SS} (k_f \beta_{f0} e^{-k_f \tau} + k_o \beta_{o0}) e^{-\left(\frac{a}{T} - \frac{a}{T_a}\right)} dt \quad (14)$$

20 where  $V$  is the water volume of the lake ( $\text{m}^3$ ) and  $\tau$  is the time (day). The hourly  
21 concentrations of SS derived from sediment resuspension at C1 in 2004 were simulated  
22 in the range of 10–299  $\text{mg l}^{-1}$  by a numerical model with wind speed and sediment  
23 parameters such as the critical bottom shear stress (Seki et al. 2006). A minimum value

1 of simulated concentrations could be regarded as background SS. The difference  
2 between simulated concentrations and background concentrations was applied to SS in  
3 the Eq. 14. The hourly water temperature at C1 measured by KRO was also used in Eq.  
4 14.  $Y$  was estimated by two methods. The first method assumes that the initial BSi  
5 contents of SS were constant to be experimentally determined as the average of  
6 experiment S3 and S5-4, that is,  $\beta_{f0} = 1.0$  and  $\beta_{o0} = 40$ . The time since the latest  
7 resuspension event (wind speed of above  $12 \text{ m s}^{-1}$ ) was applied to  $\tau$  at each  $t$  in Eq. 14.  
8 This estimated value was regarded as a maximum one. The second method assumes that  
9 the dissolution of BSi is only of old diatom frustules, that is,  $\beta_{f0} = 0$  and  $\beta_{o0} = 40$ . This  
10 estimated value was regarded as a minimum one. As a result, the minimum and  
11 maximum values of  $Y$  were  $1.0 \times 10^9$  and  $2.7 \times 10^9 \text{ g y}^{-1}$ , respectively.

12 The annual amount of Si released from bottom sediments at C1 in 2004 was also  
13 estimated from Eq. 12 and 13.  $\text{DSi}_{\text{col}}$  concentrations at C1 observed monthly by KRO  
14 were interpolated to hourly values and used in the estimation. As a result, the annual  
15 amount of Si released from bottom sediments was estimated to be  $4.3 \times 10^9 \text{ g y}^{-1}$ . These  
16 results suggest that the Si released from SS accounted for about 20–40% of the Si  
17 recycling in the lake in 2004.

18

#### 19 Budgetary analysis

20

21 Table 4 summarizes the DSi and BSi budgets in Lake Kasumigaura. The DSi load  
22 through inflows was estimated using the mean DSi concentration of rivers in 1994 and  
23 2007, which might be overestimated because the dilution effect on the concentration by  
24 rainfall was not considered (Muraoka and Hirata 1988; Neal et al. 2005). Inflows of BSi  
25 were not observed, but considered to be negligible. The amount of Si released from SS

1 and bottom sediments in 2004 were assumed to be representative of those in the 2000s.  
2 The amount of Si released from SS in the 1980s was assumed to be zero because mean  
3 concentration of SS derived from sediment resuspension in the 1980s was estimated to  
4 be  $5.5 \text{ mg l}^{-1}$  by the method of Seki et al. (2006), about half of the background  
5 concentration of it in 2004. The DSi input through atmospheric precipitation was also  
6 estimated using the annual mean precipitation and the DSi concentration of precipitation  
7 in Tsukuba, as averaged over 4 years by Hirata and Muraoka (1991). It was  $2.2 \times 10^7 \text{ g}$   
8  $\text{y}^{-1}$ , two orders of magnitude lower than other fluxes; therefore, it could be neglected.  
9 Table 4 suggests that the primary source of DSi in the lake is river inflow, but Si  
10 recycling plays a significant role. The main export is diatom sedimentation. The  
11 increases in DSi load over the last 3 decades were estimated to be  $3.0 \times 10^9 \text{ g y}^{-1}$ , based  
12 on the change in the outflow loads. The Si release from SS could account for about  
13 30–90% of the increases in DSi load through outflow.

14

## 15 **Conclusions**

16

17 Significant increases in  $\text{DSi}_{\text{col}}$ ,  $\text{DSi}_{\text{ICP}}$ , and TSi concentrations were observed at the  
18 center of the lake over the last 3 decades.  $\text{DSi}_{\text{ICP}}$  concentrations did not increase near the  
19 mouth of the inflowing rivers, suggesting that the Si increase was caused by in-lake  
20 processes. We assumed the contribution of Si release from SS, which had increased in  
21 the lake lately, to be the cause of this Si increase. Our laboratory experiments,  
22 suspending the sediments in filtered lake water, provided the formula of change in DSi  
23 concentration as a function of SS concentration, water temperature, and the elapsed time  
24 of dissolution of diatom frustules. The annual amount of Si released from SS in the  
25 2000s accounted for 30–90% of the increase in DSi load through outflow over the last 3

1 decades, as well as 20–40% of the total recycling of Si in the lake. These findings  
2 suggest that the sediment resuspension might be the cause of the latest DSi increase. Si  
3 budgets in the lake were estimated; however, we have to analyze dated sediment core  
4 and estimate the sedimentation rate of BSi in the past and present to determine the Si  
5 retention more quantitatively.

6

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13

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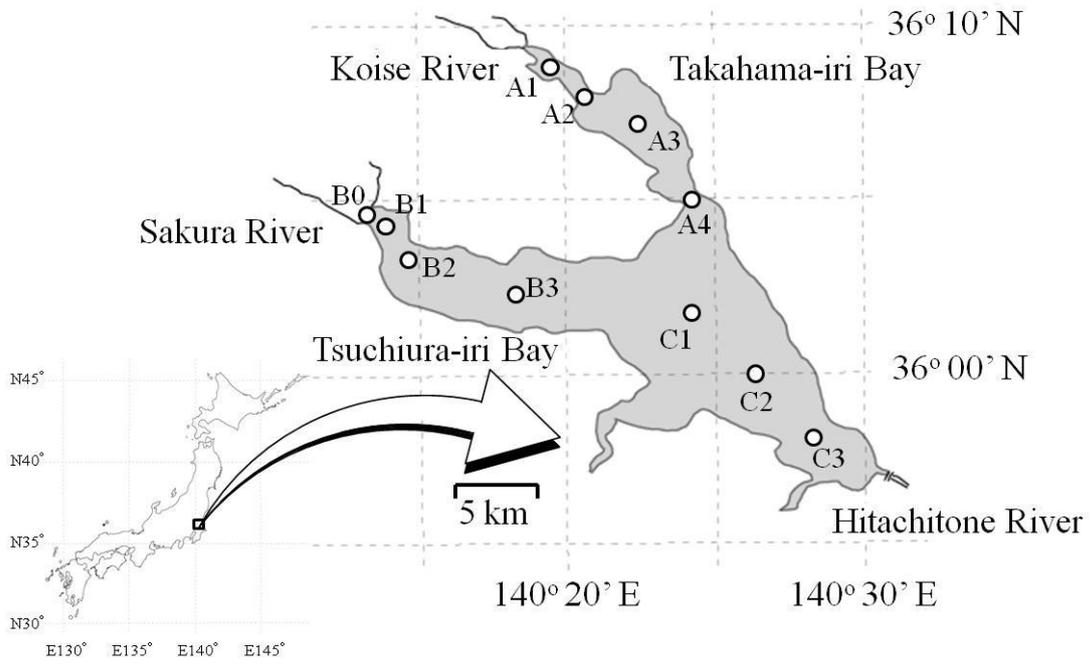
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3

1 **Figures and Tables**

2

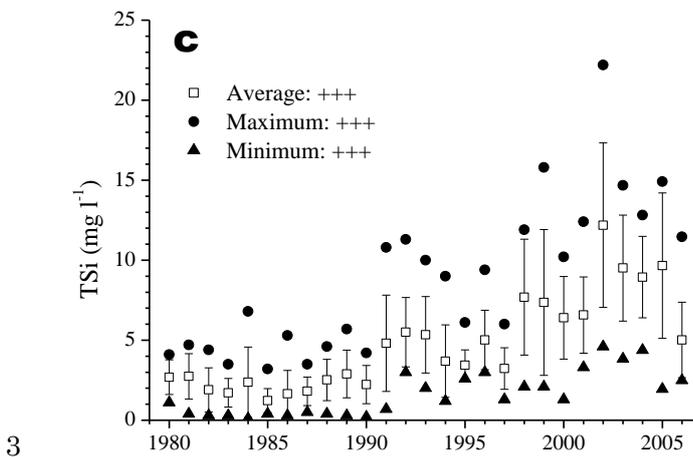
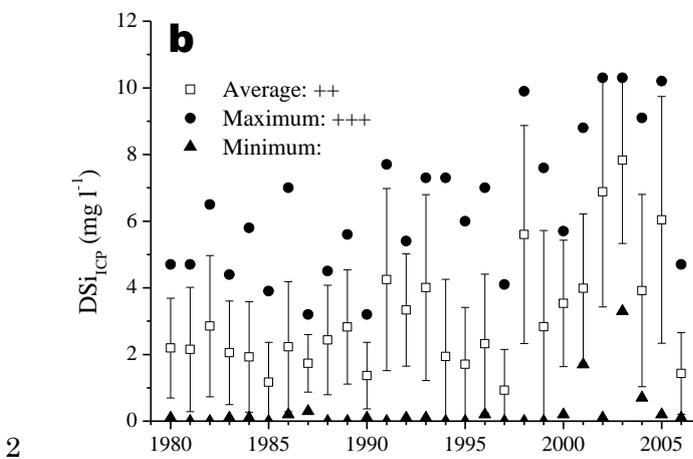
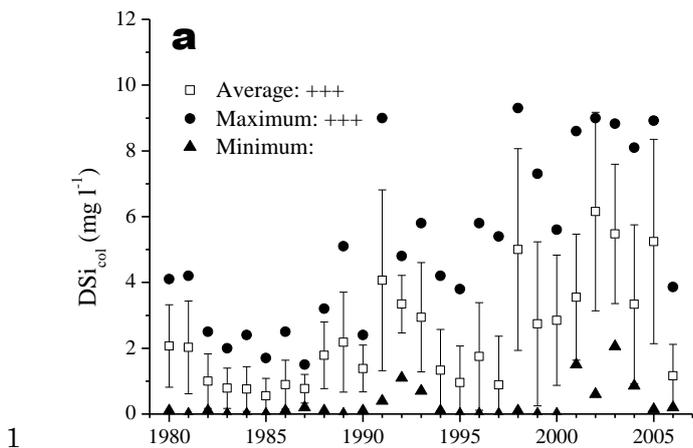


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4 **Fig. 1** Sampling points in Lake Kasumigaura

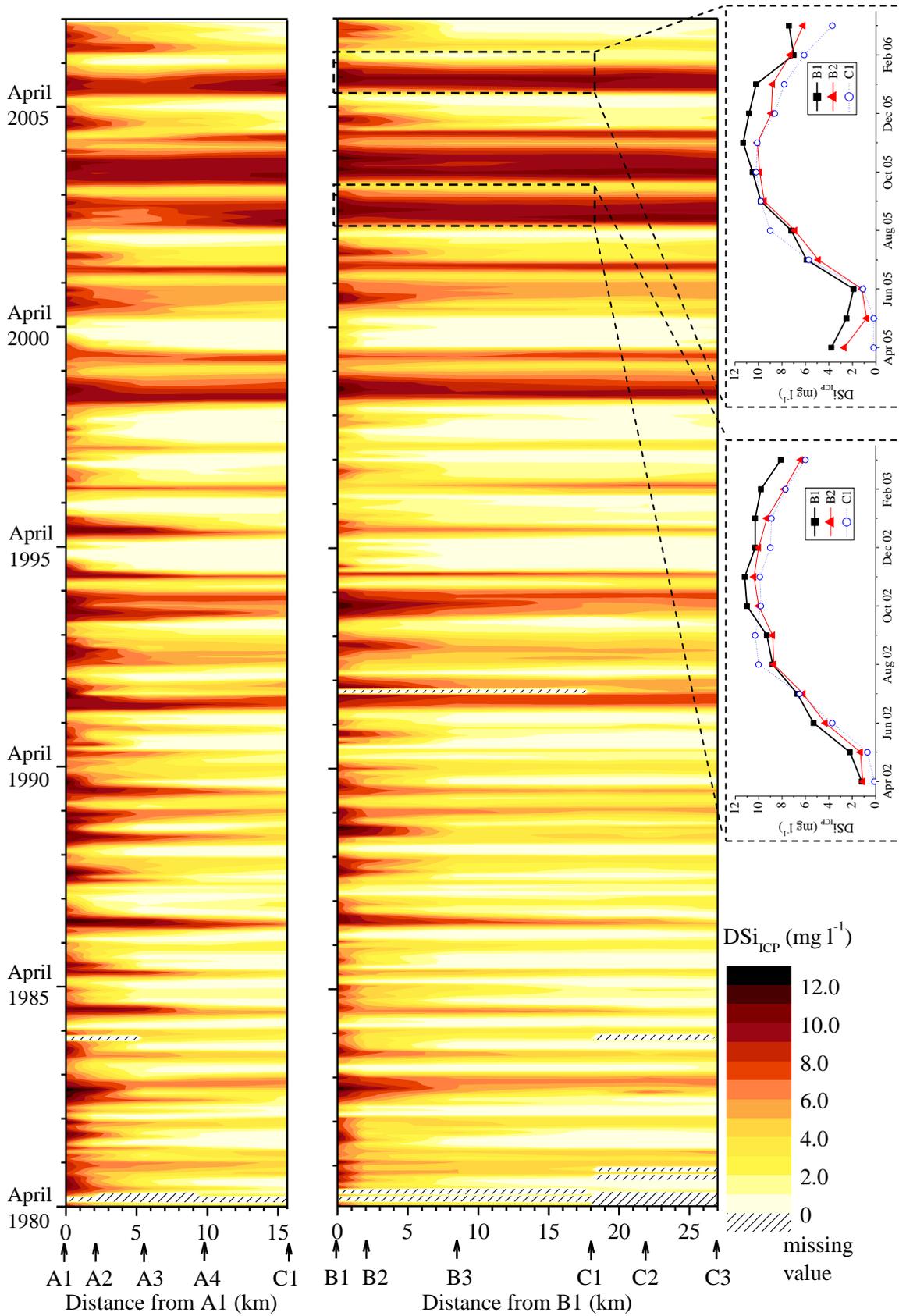
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4 **Fig. 2** Changes in DSi<sub>col</sub> (a), DSi<sub>ICP</sub> (b), and TSi (c) concentrations at C1 during  
 5 1980–2006. Bars indicate standard deviations. Legends (+, ++, +++, -, --, and ---)  
 6 are the same as in Table 2

7

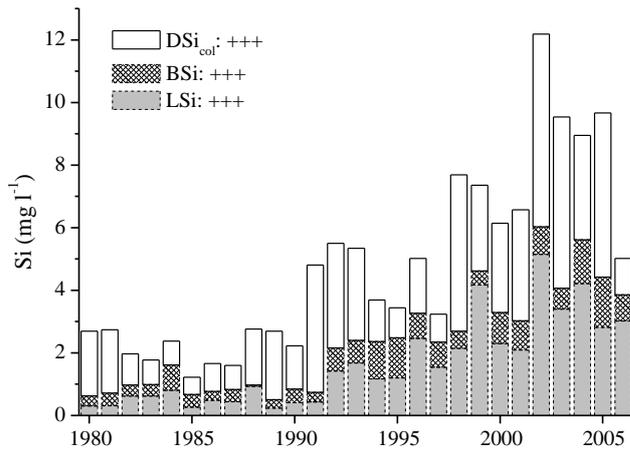


2 **Fig. 3** Temporal and spatial variation of DSi<sub>ICP</sub> concentrations in Lake Kasumigaura

1 during April 1980 – March 2007

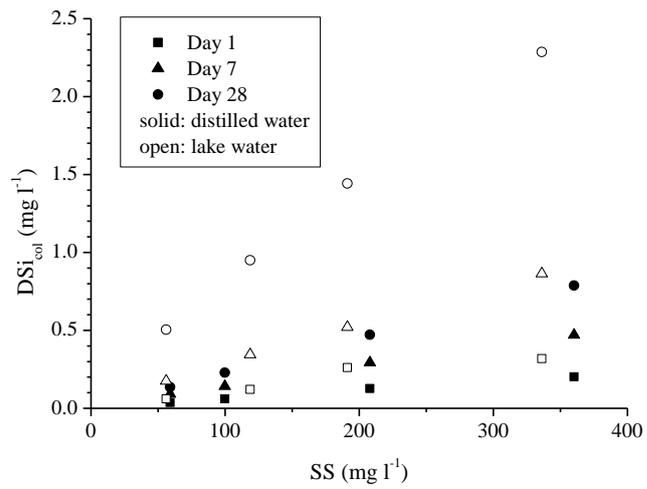
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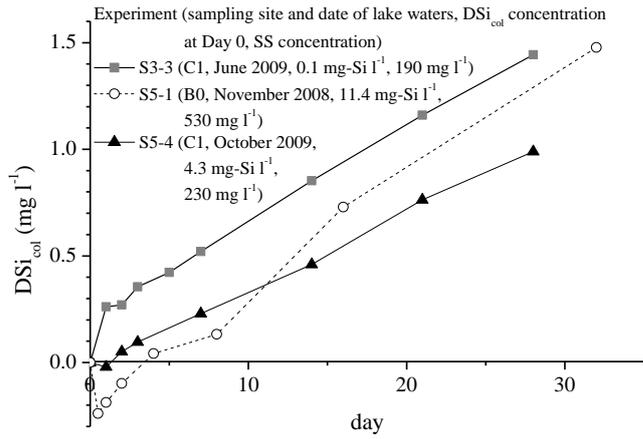
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**Fig. 4** Changes in annual averages of DSi<sub>col</sub> concentration (observed) and BSi and LSi concentrations (estimated) at C1 during 1980–2006. Legends (+, ++, +++, -, --, and ---) are the same as in Table 2



1  
2  
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7

**Fig. 5** Relationship between SS concentrations and DSi<sub>col</sub> concentrations using the sediments sampled at C1 in June 2009. Distilled water and lake water sampled at C1 in June 2009 were used. DSi<sub>col</sub> concentrations at Day 0 were subtracted from those at each day. Details are shown in Table 1 (S2 and S3)



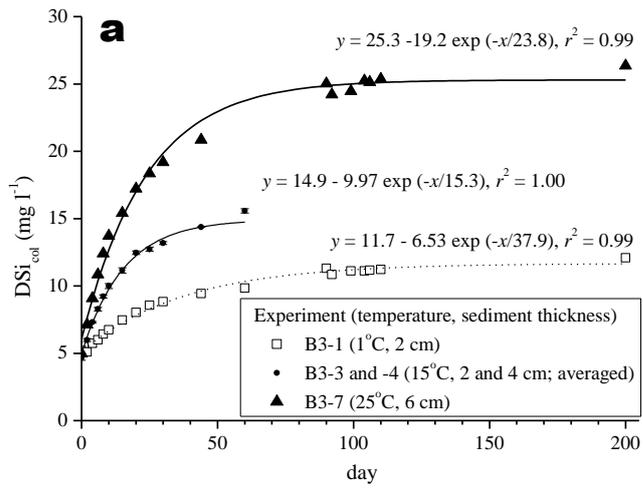
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2 **Fig. 6** Changes in  $DSi_{col}$  concentrations from SS.  $DSi_{col}$  concentrations at Day 0 were

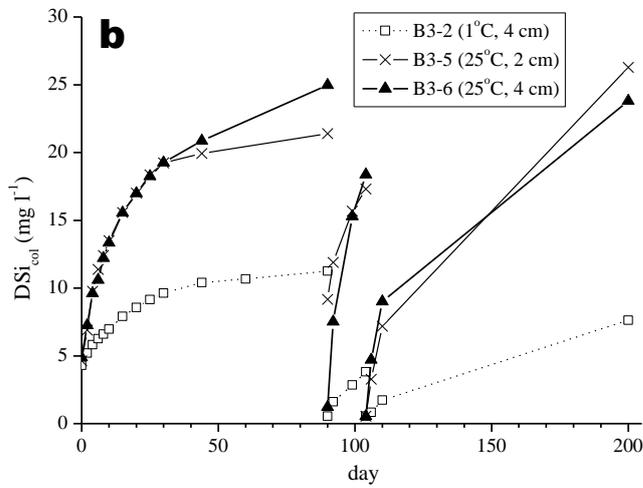
3 subtracted from those at each day. Details are shown in Table 1 (S3-3, S5-1, and S5-4)

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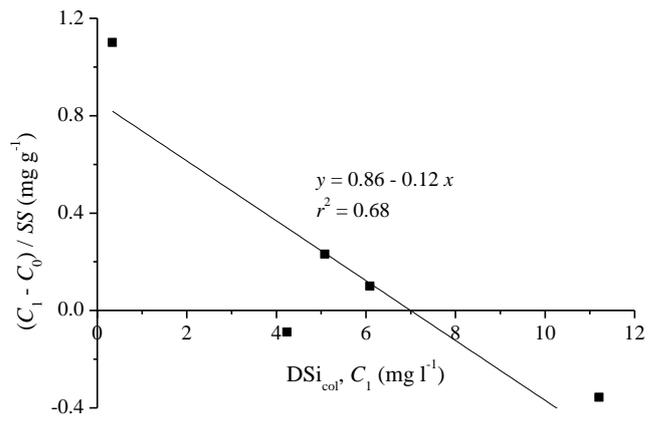


2

3 **Fig. 7** DSi<sub>col</sub> concentrations in the series of the experiment B3 with no water  
 4 replacement (a) and with replacing the overlying water by distilled water at Days 90 and  
 5 104 (b)

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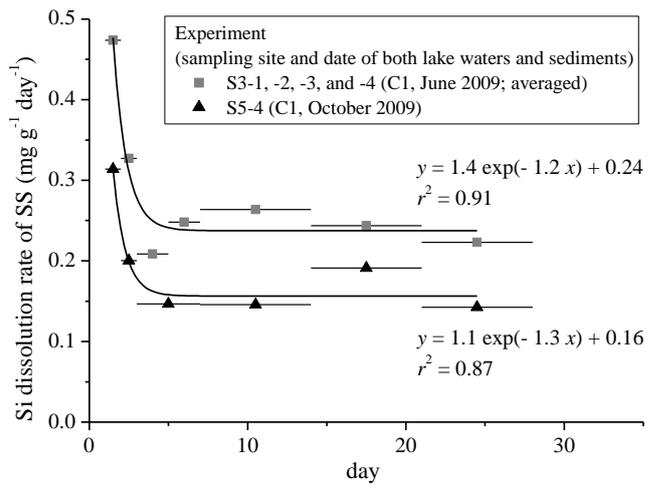


1

2 **Fig. 8** Relationship between DSi<sub>col</sub> concentrations (C<sub>1</sub>) and (C<sub>1</sub>-C<sub>0</sub>) / SS in the  
 3 experiment S3 (averaged), S5-1, -2, -3, and -4

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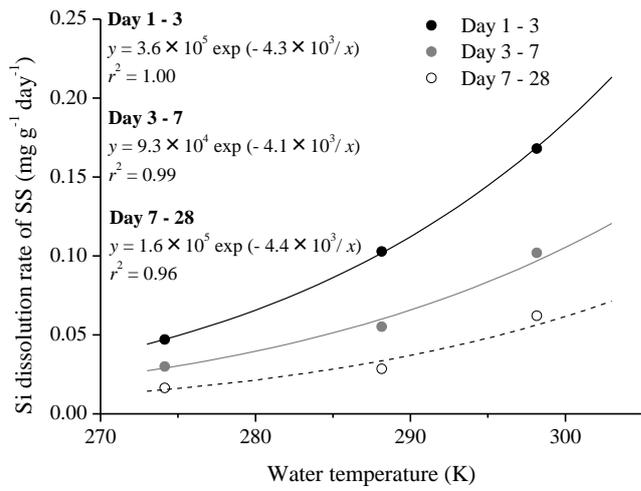
1

2 **Fig. 9** Change in Si dissolution rate of SS at 25°C in the experiment S3 (averaged) and

3 S5-4

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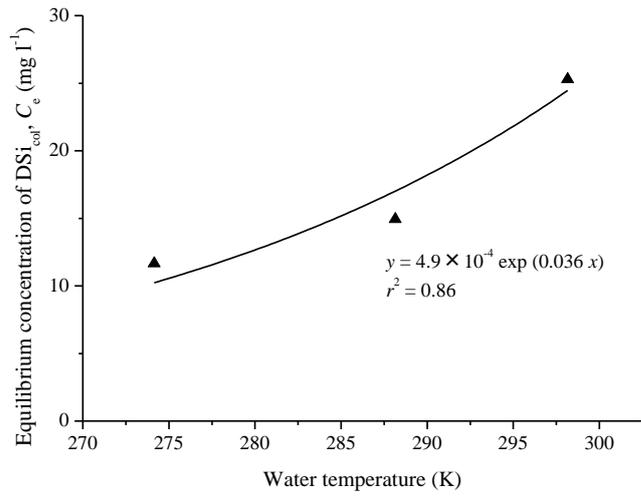


1

2 **Fig. 10** Relationship between water temperature and Si dissolution rate of SS in distilled  
 3 water in the experiment S4

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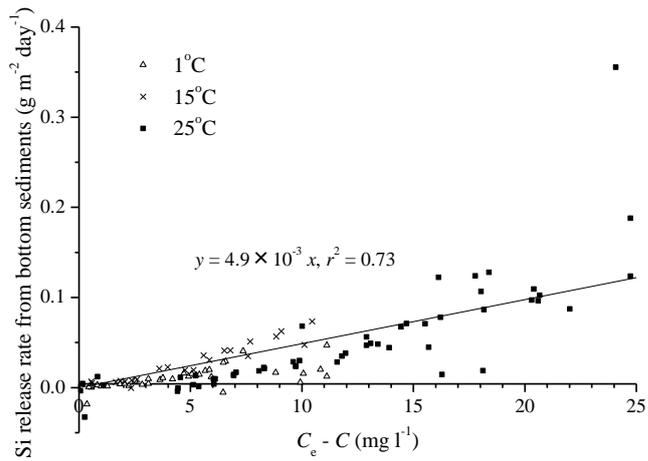
1

2 **Fig. 11** Relationship between water temperature and the equilibrium concentration of

3  $DSi_{col} (C_e)$  in the experiment B3

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1

2 **Fig. 12** Relationship between the difference between  $\text{DSi}_{\text{col}}$  and equilibrium  
 3 concentrations ( $C_e - C$ ) and Si release rate in the experiment B3

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1 **Table 1** Summary of experimental design and results of Si release experiments from SS  
 2 (A) and bottom sediments (B)

**(A) From suspended solids**

Label	Sediment		Water			Sampling day	DSi <sub>col</sub> (mg l <sup>-1</sup> )				Si release rate (mg g <sup>-1</sup> day <sup>-1</sup> )		
	Site	SS conc. (mg l <sup>-1</sup> )	Type <sup>d</sup>	Site	Temp.		Day 0	Day 1	Day 7 (or 8)	Day 28 (or 32)	Days 0-1	Days 1-7 (or 8)	Days 7 (or 8)-28 (or 32)
S1-1	A3 <sup>a</sup>	500	DW		25°C	Day 0, 0.5, 1, 3, 8, 16, 32	0.11	0.43	0.81	1.59	0.64	0.11	0.06
S1-2	B3 <sup>a</sup>	500	DW		25°C		0.06	0.38	0.84	1.55	0.63	0.13	0.06
S1-3	C1 <sup>a</sup>	500	DW		25°C		0.09	0.35	0.80	1.47	0.53	0.13	0.06
S2-1	C1 <sup>b</sup>	59	DW		25°C	Day 0, 1, 2, 3, 5, 7, 14, 21, 28	0.01	0.05	0.11	0.15	0.61	0.16	0.03
S2-2	C1 <sup>b</sup>	100	DW		25°C		0.02	0.08	0.16	0.25	0.61	0.13	0.04
S2-3	C1 <sup>b</sup>	210	DW		25°C		0.03	0.16	0.32	0.50	0.61	0.13	0.04
S2-4	C1 <sup>b</sup>	360	DW		25°C		0.05	0.25	0.52	0.84	0.56	0.12	0.04
S3-1	C1 <sup>b</sup>	56	LW	C1 <sup>b</sup>	25°C	Day 0, 1, 2, 3, 5, 7, 14, 21, 28	0.12	0.18	0.30	0.63	1.07	0.34	0.28
S3-2	C1 <sup>b</sup>	120	LW	C1 <sup>b</sup>	25°C		0.14	0.26	0.48	1.09	1.01	0.32	0.24
S3-3	C1 <sup>b</sup>	190	LW	C1 <sup>b</sup>	25°C		0.14	0.40	0.66	1.58	1.37	0.23	0.23
S3-4	C1 <sup>b</sup>	340	LW	C1 <sup>b</sup>	25°C		0.19	0.51	1.05	2.47	0.95	0.27	0.20
S4-1	C1 <sup>c</sup>	260	DW		1°C	Day 0, 1, 2, 3, 5, 7, 14, 21, 28	0.03	0.07	0.12	0.21	0.15	0.03	0.02
S4-2	C1 <sup>c</sup>	240	DW		15°C		0.03	0.11	0.21	0.35	0.34	0.07	0.03
S4-3	C1 <sup>c</sup>	240	DW		25°C		0.03	0.17	0.34	0.64	0.58	0.12	0.06
S5-1	C1 <sup>a</sup>	530	LW	B0 <sup>g</sup>	25°C	Day 0, 0.5, 1, 2, 4, 8, 16, 32	11.40	11.21	11.53	12.87	-0.36	0.09	0.11
S5-2	C1 <sup>a</sup>	1600	LW <sup>e</sup>		25°C	Day 0, 1	4.71	5.08	-	-	0.23	-	-
S5-3	C1 <sup>a</sup>	820	LW <sup>f</sup>		25°C		6.01	6.09	-	-	0.10	-	-
S5-4	C1 <sup>c</sup>	230	LW	C1 <sup>c</sup>	25°C	Day 0, 1, 2, 3, 7, 14, 21, 28	4.26	4.24	4.49	5.25	-0.09	0.18	0.16

**(B) From bottom sediments**

Label	Sediment		Water			Sampling day	DSi <sub>col</sub> (mg l <sup>-1</sup> )				Si release rate (g m <sup>-2</sup> day <sup>-1</sup> )		
	Site	Thickness	Volume	Site	Temp.		Day 0	Day 7	Day 14	Day 28	Days 0-7	Days 7-14	Days 14-28
B1-1	C1 <sup>b</sup>	3.3 cm	750 ml	DW <sup>d</sup>	25°C	Day 0, 7, 14, 21, 28, 35, 42	0.5	6.9	11.6	15.9	0.089	0.064	0.030
B1-2	C1 <sup>b</sup>	6.6 cm	500 ml	DW <sup>d</sup>	25°C		0.8	10.1	14.1	17.8	0.090	0.038	0.017
B1-3	C1 <sup>b</sup>	9.9 cm	250 ml	DW <sup>d</sup>	25°C		1.6	16.6	17.7	19.5	0.070	0.005	0.004
B2-1	C1 <sup>b</sup>	3.3 cm	750 ml	C1 <sup>b</sup>	25°C	Day 0, 7, 14, 21, 28, 35, 42	0.5	6.9	9.9	14.2	0.099	0.047	0.033
B2-2	C1 <sup>b</sup>	6.6 cm	500 ml	C1 <sup>b</sup>	25°C		0.8	9.5	13.3	16.9	0.081	0.035	0.017
B2-3	C1 <sup>b</sup>	9.9 cm	250 ml	C1 <sup>b</sup>	25°C		1.6	17.4	18.1	19.2	0.074	0.003	0.003
B3-1	C1 <sup>c</sup>	2 cm	700 ml	C1 <sup>c</sup>	1°C	Day 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 44, 60 (90, 92, 99, 104, 106, 110, 200)	5.2	6.4	11.1	11.2	0.014	0.013	0.001
B3-2	C1 <sup>c</sup>	4 cm	700 ml	C1 <sup>c</sup>	1°C		4.3	6.6	0.6 <sup>h</sup>	1.7 <sup>h</sup>	0.026	0.016	0.018 <sup>h</sup>
B3-3	C1 <sup>c</sup>	2 cm	700 ml	C1 <sup>c</sup>	15°C		4.8	9.3	-	-	0.051	0.024	-
B3-4	C1 <sup>c</sup>	4 cm	700 ml	C1 <sup>c</sup>	15°C		4.5	9.1	-	-	0.052	0.023	-
B3-5	C1 <sup>c</sup>	2 cm	700 ml	C1 <sup>c</sup>	25°C		4.6	12.4	0.6 <sup>h</sup>	7.2 <sup>h</sup>	0.086	0.038	0.099 <sup>h</sup>
B3-6	C1 <sup>c</sup>	4 cm	700 ml	C1 <sup>c</sup>	25°C		4.9	12.2	0.6 <sup>h</sup>	9.0 <sup>h</sup>	0.083	0.041	0.127 <sup>h</sup>
B3-7	C1 <sup>c</sup>	6 cm	700 ml	C1 <sup>c</sup>	25°C		5.0	12.4	25.2	25.4	0.082	0.036	0.002

<sup>a</sup> August 7th, 2008, <sup>b</sup> June 10th, 2009, <sup>c</sup> October 7th, 2009, <sup>d</sup> DW and LW indicate distilled water and lake water, respectively, <sup>e</sup> Mixture of lake waters sampled at A3, B3, C1, and C3 on August 7th, 2008, <sup>f</sup> Mixture of lake waters sampled at A3 on August 7th and at B0 on November 13th, 2008, <sup>g</sup> November 13th, 2008, <sup>h</sup> After replacing the overlying water by distilled water

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1 **Table 2** Mean Si concentrations in the 1980s/1990s/2000s and yearly trends detected by

2 t-test

Site	Mean concentrations in the 1980s/1990s/2000s (mg l <sup>-1</sup> )		
	DSi <sub>col</sub>	DSi <sub>ICP</sub>	TSi
A1		8.1/ 7.1/ 7.1 <sup>-</sup>	
A2	3.0/ 4.0/ 5.1 <sup>+++</sup>	5.4/ 4.9/ 5.8	4.8/ 7.2/ 9.4 <sup>+++</sup>
A3		3.4/ 3.6/ 5.0 <sup>++</sup>	
A4		2.6/ 3.0/ 4.9 <sup>++</sup>	
B1		7.2/ 6.0/ 7.3	
B2	2.1/ 3.1/ 4.6 <sup>+++</sup>	4.5/ 4.5/ 6.2 <sup>+</sup>	3.7/ 6.9/ 10.4 <sup>+++</sup>
B3		2.7/ 3.1/ 4.9 <sup>+</sup>	
C1	1.3/ 2.4/ 4.0 <sup>+++</sup>	2.2/ 2.8/ 4.8 <sup>++</sup>	2.2/ 4.8/ 8.4 <sup>+++</sup>
C2		2.2/ 2.9/ 4.9 <sup>++</sup>	
C3		2.2/ 3.0/ 5.0 <sup>++</sup>	

+, increase; -, decrease

3 + or -,  $p < 0.05$ ; ++ or --,  $p < 0.01$ ; +++ or ---,  $p < 0.001$

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1 **Table 3** Correlation coefficient matrix of annual mean water quality items at the center  
 2 of Lake Kasumiguara and annual precipitation at Tsukuba meteorological weather  
 3 station during 1980–2006.  $N = 27$  for all relationships except pH versus others ( $N = 24$ ).  
 4 Legends (+, ++, +++, -, --, and ---) are the same as in Table 2

	DSi <sub>col</sub>	DSi <sub>lCP</sub>	BSi	LSi	SS	ISS	Chl-a	WT	pH	DO	Transp	PT
DSi <sub>col</sub>		0.95	0.30	0.64	0.61	0.64	-0.27	-0.03	-0.55	-0.35	-0.61	0.27
DSi <sub>lCP</sub>	+++		0.27	0.60	0.61	0.63	-0.26	-0.09	-0.46	-0.35	-0.56	0.23
BSi				0.53	0.64	0.61	-0.05	0.04	0.16	-0.07	-0.59	-0.22
LSi	+++	+++	++		0.88	0.88	-0.24	0.08	-0.21	-0.37	-0.75	0.01
SS	+++	+++	+++	+++		0.97	-0.15	0.10	-0.22	-0.29	-0.87	0.13
ISS	+++	+++	+++	+++	+++		-0.38	0.15	-0.26	-0.37	-0.78	0.08
Chl-a								-0.17	0.33	0.32	-0.13	0.20
WT									0.16	-0.40	-0.08	0.20
pH	--	-								0.22	0.11	-0.21
DO								-			0.08	-0.21
Transp	---	--	--	---	---	---						-0.22
PT												

5 *ISS*, inorganic suspended solids estimated by Seki et al. (2006); *Chl-a*, chlorophyll *a*; *WT*, *pH* and *DO*, water  
 6 temperature, pH and dissolved oxygen at 0.5 m depth; *Transp*, transparency; *PT*, precipitation

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1 **Table 4** DSi and BSi budgets in Lake Kasumigaura

Processes	Si fluxes ( $\times 10^9$ g $y^{-1}$ )	
	1980s	2000s
<b>Inputs</b>		
Inflows <sup>a,b</sup>	11.3	11.3
Release		
from bottom sediments <sup>c</sup>	4.3	4.3
from SS <sup>c</sup>	0 ?	1.0–2.7
Atmospheric precipitation <sup>d</sup>	0.0	0.0
<b>Outputs</b>		
Outflow		
DSi <sup>b,e</sup>	1.4	4.4
BSi <sup>b,e</sup>	0.4	1.2
Diatom sedimentation <sup>f</sup>	13.8	11.0–12.7

<sup>a</sup> Estimated using the mean DSi concentration of inflowing rivers in 1994 and 2007, <sup>b</sup> Flow rate was estimated using lake area, mean water depth, annual mean precipitation or evaporation, and mean water residence time, <sup>c</sup> Experimental estimation in this study, <sup>d</sup> Muraoka and Hirata (1991), <sup>e</sup> Estimated using DSi<sub>col</sub> and BSi concentrations at C1, <sup>f</sup> Estimated by residual analysis

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