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Phosphorus budgetary analysis of sediment–water interface in a short-term anoxic condition in shallow Lake Kasumigaura, Japan

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Abstract To investigate the effective depth from the surface sediment, and phosphorus fractions related to phosphorus release under short-term anoxic conditions, varying lengths of sediment cores taken from Lake Kasumigaura, a large shallow polymictic lake in Japan, were incubated for a few weeks and then analyzed. Results showed few differences in total phosphorus (TP) amount per unit area in overlying waters irrespective of the core thickness, and sums of TP in both overlying water and 0- to 2-cm sediment layers were nearly equal before and after the experiment, indicating that phosphorus was released mainly from the 0- to 2-cm layer by dissolution. In contrast, phosphorus was decreased in pore water below a 2-cm depth, probably through sorption to sediment solids. The citrate-dithionite-bicarbonate total phosphorus (CBD-TP) and non-reactive phosphorus extracted by NaOH (NaOH-NRP) in sediment solids in the 0- to 2-cm layer decreased during the experiment. The decreases of CBD-TP were 10 times higher than those of NaOH-NRP, suggesting that the released phosphorus came mainly from the fraction bound to iron in Lake Kasumigaura.

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Introduction

Internal loads, such as phosphorus release from sediment, often prevent recovery of lake eutrophication even when external loads are reduced (Søndergaard et al. 1999; Jeppesen et al. 2005). Internal load is the highest in summer, and phosphorus concentration in lake water can be higher than that of the inflowing river, particularly in shallow polymictic lakes (Van Hullebusch et al. 2003). In Lake Kasumigaura, which is a shallow polymictic lake in Japan, phosphorus release from sediments occurs mostly under anoxic conditions (Ishii et al. 2009), indicating that short-term anoxic periods may have a considerable impact on recovery from eutrophication.

One of the main sources of phosphorus release under anoxic conditions is iron-bound phosphorus (Mortimer 1941; Rydin 2000; Søndergaard et al. 2003). Under oxic conditions, phosphorus is sorbed to iron (III) compounds, while iron (III) is reduced to iron (II) after nitrate and manganese reductions (Dittrich et al. 2009). Subsequently, dissolved phosphorus is transported to the overlying waters through diffusion (Rydin 2000; Søndergaard et al. 2003). The other source is organic phosphorus, which is mineralized by bacteria (Gächter and Meyer 1993; Wilson et al. 2010). A release experiment with sediments from Lake Erken showed that both organic phosphorus and iron-bound phosphorus were mobile (Rydin 2000). Furthermore, Wilson et al. (2010) suggested that organic phosphorus was mineralized in the sediment regardless of the trophic status of lakes, and that the sorption capacity of the sediment controlled the extent to which dissolved phosphorus was released to the water. Thus, it has been recognized that phosphorus release is governed by different mechanisms according to the conditions of respective lakes (Søndergaard et al. 2003). However, few studies have

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focused on the forms responsible for phosphorus release during short-term anoxic periods in polymictic lakes.

In addition, several studies have reported influence of sediment depth to phosphorus release (e.g. Søndergaard et al. 1999). In Lake Søbygaard, phosphorus in sediments from depths down to 20–25 cm decreased over 13 years by phosphorus release (Søndergaard et al. 1999). Furthermore, vertical profiles of phosphorus in sediments exhibited a decrease with depth in eutrophic lakes around the world (Carey and Rydin 2011), and higher concentrations in the surface layer might be regarded as mobile phosphorus (Rydin 2000). In Lake Kasumigaura, phosphorus concentrations in pore water are often highest several centimeters below surface sediment in summer (Hosomi and Sudo 1984), indicating that phosphorus is likely released from this layer. In contrast, phosphorus release was observed from the top millimeter of sediment in Lake Champlain (Smith et al. 2011). Also, in Lake Arendsee, phosphorus release during summer can only be explained by a substantial contribution of continuous sedimentation of particulate phosphorus and its rapid mobilization (Hupfer and Lewandowski 2005). Thus, effective depth for phosphorus release is different among lakes and little is known about this depth during short-term anoxic periods.

As mentioned above, little is known about sediment depth and forms of phosphorus related to phosphorus release in polymictic lakes where lake water is alternately oxic and anoxic for short periods of time. This is because it is difficult to conduct in situ observations under constant anoxic conditions in polymictic lakes.

We focused on the effective depths from surface sediment and forms of phosphorus related to phosphorus release from sediment during a short-term anoxic period by conducting an incubation experiment with several different lengths of sediment cores from a polymictic lake. The incubation experiment was designed as a closed system in which the sum of the phosphorus in overlying water, pore water, and sediment solids did not change during the experiment. We analyzed the amount of phosphorus in these components before and after the experiment. Increase of phosphorus in the overlying water was then compared with the decrease in the sediment.

Materials and methods

Study site

Lake Kasumiguara is located in central Japan. With a surface area of 170.1 km^2 and an average depth of 4 m (maximum depth of 7 m), it is the second largest lake in Japan. The area of watershed, excluding the lake area, is

1426 km^2, and the apparent residence time of lake water is about 200 days. Although the nutrient loads through the influent rivers were reduced due to the intensive management of the basins (Fukushima et al. 2005), the total phosphorus (TP) concentration in lake water is still high (average concentration was 0.09 mg l^{-1} in 2014). The TP concentrations in lake water increase especially in summer, even if phosphorus concentrations in influent rivers do not (Ishii et al. 2007). This is probably due to phosphorus release from sediments, because dissolved oxygen (DO) concentrations of lake water near bottom sediments decrease in summer. Since Lake Kasumiguara is a polymictic lake, the DO concentration near sediments is not always low, and the lake water is mixed from top to bottom by moderately strong winds (Komatsu et al. 2007).

Incubation experiment design

Sediment cores were taken using a gravity type core sampler (converted RIGO, KB Type Core Sampler) with an acrylic tube (7.0 cm diameter and 50 cm long) at the center of Lake Kasumigaura on 28 November 2013 (Fig. 1). At the same time, lake water 50 cm above the sediment was taken using a peristaltic pump (Solinst, Model410). The thicknesses of sediment cores were adjusted to 2, 5, 10, 15 and 20 cm (named C1 to C5, respectively) and overlying waters were exchanged by the filtrate (Whatman GF/F, 0.7 μm pore size) of lake water (Fig. 2). The heights of the overlying waters were set to 20 cm for all cores, and the top and bottom sides of the columns (overlying water and sediment core) were closed with rubber stoppers to prevent oxidation. Cores C1–C5 were kept in the dark at a temperature under 25 °C, which is similar to the average sediment temperature during summer in this lake. Another core was used for measuring phosphorus concentrations in the initial state, and named C0.
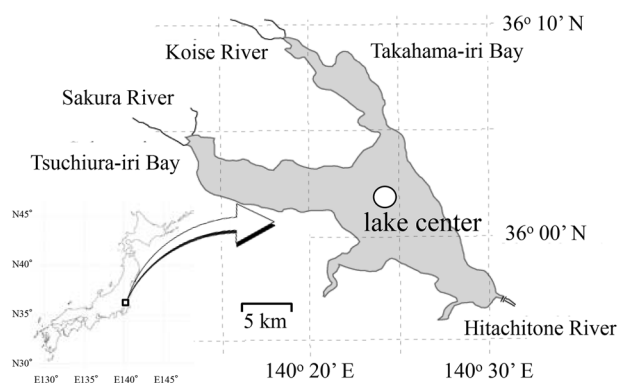
Fig. 1 Lake Kasumigaura and the sampling point
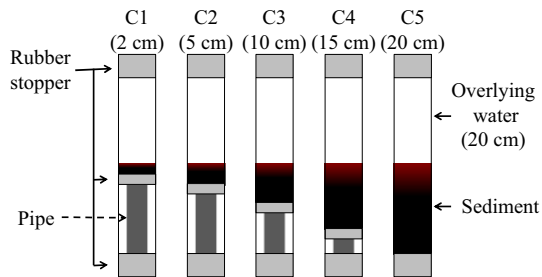
Fig. 2 Design of the incubation experiment. The thicknesses of sediment were adjusted to be 2, 5, 10, 15, and 20 cm. Pipes were used between rubber stoppers to hold the heights of the overlying water columns

Sampling of overlying water, pore water, and sediment solid

The experimental period was 23 days. A 10-ml subsample of overlying water (less than 1 % of the overlying water collected) was taken from each core after gentle mixing of overlying water by a glass rod to minimize sediment resuspension. At the same time, the DO concentration of overlying water was measured for each core using a DO concentration sensor (HACH, HQ30d). After these samplings, a 10-ml filtrate of lake water was added to each core to prevent the gas phase from occurring in the overlying water. Cores were then stored again in the dark under 25 °C after sealing with rubber stoppers. Subsamples of the overlying water were taken at days 3, 5, 7, 9, 11 and 23 after the start of the incubation experiment.

Sediment samples were taken on the 1st day for C0 and at the end of the experiment for C1–C5. After the overlying water was removed with a syphon tube, sediment cores were sliced at intervals of 2 cm, and wet sediment subsamples were inserted into centrifugation tubes under anoxic conditions. Pore water samples were collected by filtering the supernatant waters centrifuged at 10,000 rpm for 20 min through GF/F filters. Samples of sediment solids were collected by grounding the residual sediment in centrifugation tubes after freeze-drying. Subsamples of wet sediment were used to measure water content and density.

Chemical analysis

TP concentrations in overlying and pore water samples were analyzed using a continuous flow analyzer (BRAN-LUEBBE, Auto Analyzer 3), and the soluble reactive phosphorus (SRP) concentrations in pore water samples were analyzed using a continuous flow analyzer (BRAN-LUEBBE, AACS-II). TP concentrations of sediment solids were analyzed by the ascorbic acid method after digestion by potassium peroxodisulfate [standard error (SE): 1.1 %]

(Fukushima et al. 2010). The forms of phosphorus in the sediment solids were determined using a phosphorus extraction scheme (Ishii et al. 2010). The phosphorus forms were separated into four fractions based on extraction reagents of citrate-dithionite-bicarbonate (CBD-TP), NaOH (NaOH-NRP and NaOH-SRP) and HCl (HCl-TP); the respective forms are known as redox-sensitive phosphorus, such as phosphorus absorbed to iron and manganese, organic-bound phosphorus, bound to hydrated oxides of aluminum, and carbonate-bound phosphorus (Jensen and Thamdrup 1993; Rydin 2000). The SEs for chemical analyses were 2.7, 2.8, 1.4 and 2.9 %, respectively. Sediment water content and density were estimated with wet weight and dry weight (110 °C, 24 h). The mass of sediment solid (Ws) and pore water volume in sliced sediments (Ww) in an area of 1 m^2 and thickness of 2 cm were calculated as follows:

$$Ws \ (kg \ m^{-2}) = V \times \rho \times 100/(100 + W) \qquad (1)$$

$$Ww \ (1 \ m^{-2}) = Ws \times W/100 \qquad (2)$$

where V is the volume of each sediment slice in area of 1 m^2 and thickness of 2 cm (m^3), ρ is density, and W is water content (%).

Since the vertical profiles of the mass of sediment solid and pore water volume were almost the same before and after incubation, those of C0 were applied to the other cores. TP amounts per unit area (TP amounts) in overlying and pore waters were calculated as water volumes multiplied by TP concentrations, and TP amounts in sediment solids were calculated as mass of sediment solids multiplied by TP concentrations. The unit "g-P m^{-2}" is used to quantify TP amounts here as in previous studies (Søndergaard et al. 1999; Fukushima et al. 2010).

Results
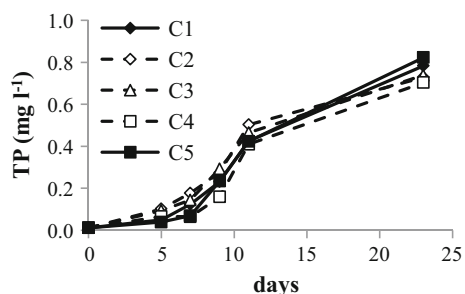
Concentrations of overlying water

DO concentration in the overlying water was 6.7 mg l^{-1} at the beginning of the incubation period, and was depleted on day 5 in all cores, regardless of sediment thickness (Fig. 3). TP concentrations increased with time, and at the end of the anoxic incubation there was little difference in TP concentrations between cores, which were all around 0.76 mg l^{-1} (average of C1–C5; Fig. 4).

SRP concentration in pore waters

The SRP concentrations, which were almost the same as TP concentrations in pore waters, are shown in Fig. 5. Before the experiment, the SRP concentrations increased
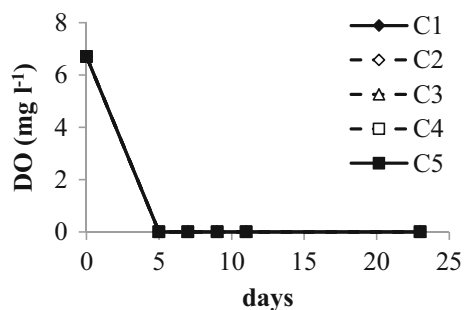
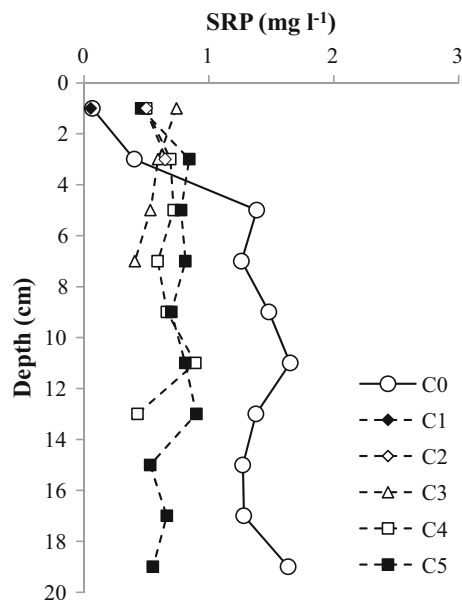Fig. 3 Time course of DO concentrations in overlying waters

Fig. 4 Time course of TP concentrations in overlying waters. *Solid lines* with *closed diamonds* are C1, which was the thinnest, and those with *closed squares* are C5, which was the thickest of the cores

Fig. 5 SRP concentrations in pore waters before and after the experiment. The *solid line* with *closed circles* is the initial concentration. *Broken lines* indicate concentrations after the incubation period

with sediment depth from 0.07 mg l^{-1} in the 0- to 2-cm layer to 1.38 mg l^{-1} in the 4- to 6-cm layer. Below 6 cm, the SRP concentrations were nearly constant at about 1.42 mg l^{-1}.
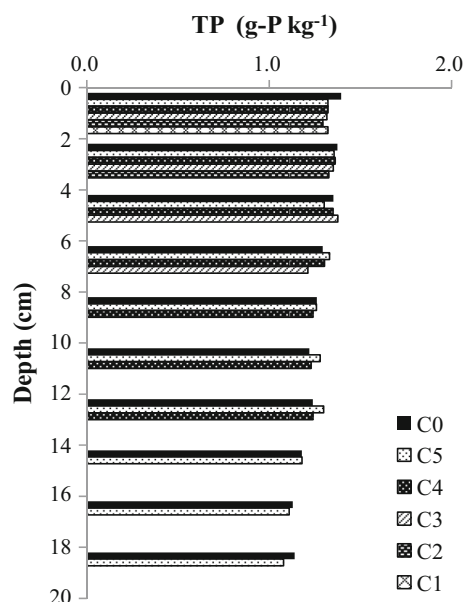
At the end of the incubation period, the SRP concentrations were relatively constant in the range of 0.41–0.90 mg l^{-1} in all pore waters except for C1. Therefore, compared to the initial state, increases in the SRP concentrations in pore waters were observed in the 0- to 4-cm layer, and decreases were found below the 4- to 6-cm layer. The SRP concentration in the 0- to 2-cm layer of C1 was nearly same as that of C0.

Phosphorus concentrations in sediment solids

In the initial state (C0), the concentration of sediment solids in the 0- to 2-cm layer was highest in the core (1.39 g-P kg^{-1}), and TP concentrations decreased with sediment depth (1.14 g-P kg^{-1} in the 18- to 20-cm layer) (Fig. 6). At the end of the incubation period, the TP concentration of sediment solids in the 0- to 2-cm layer in all cores was 1.32 ± 0.01 g-P kg^{-1}, a decrease of around 5 % from C0. Meanwhile, the averaged TP concentrations of sediment solids in the 2- to 4-cm and 4- to 6-cm layers were highest in the cores (1.35 ± 0.02 g-P kg^{-1}).

Fig. 6 TP concentrations in sediment solids before and after the experiment

Both before and after incubation, CBD-TP concentrations were the highest (0.47–0.66 g-P kg^{-1}), followed in order by NaOH-SRP (0.25–0.35 g-P kg^{-1}), NaOH-NRP(0.15–0.26 g-P kg^{-1}) and HCl-TP (0.08–0.14 g-P kg^{-1}) (Fig. 7). Vertical profiles of phosphorus concentration of CBD-TP and NaOH-NRP were highest in the 2- to 4-cm and 4- to 6-cm layers, respectively. On the other

Fig. 7 Concentrations of CBD-TP (**a**), NaOH-NRP (**b**), NaOH-SRP (**c**), and HCl-TP (**d**) in sediment solids before and after the experiment
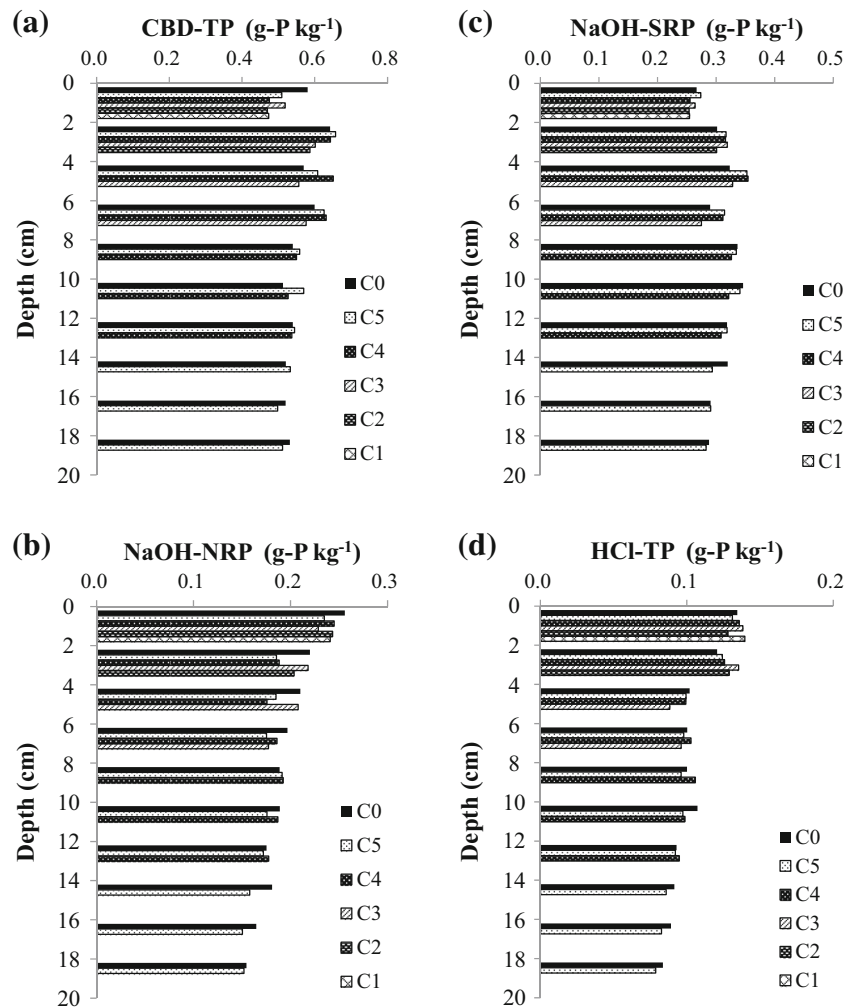
hand, those of NaOH-SRP and HCl-TP decreased with sediment depth. Compared to the initial state, concentrations of CBD-TP and NaOH-NRP in the 0- to 2-cm layer were 15 and 7 %, respectively, lower than those of C0.

Changes in amount of TP in overlying water, pore water, and sediment solids

TP amounts in overlying water, pore water, and sediment solids are shown in Table 1. Total The TP amount in overlying water and sediment (pore water and sediment solid) of 0–20 cm in C0 was 28.465 g m^{-2}. That in C5 was 28.412 g m^{-2}, a difference of only 0.2 % of the total amount in C0. The differences between total TP amounts in the sediments at depths 0–2 cm (C0 and C1), 0–4 cm (C0 and C2), 0–8 cm (C0 and C3) and 0–14 cm (C0 and C4) were 2.8 % of C0 in C2, 2.0 % of C0 in C3 and less than 1.0 % of C0 in C1 and C4, respectively.

Changes in TP amounts in overlying water, pore water, and sediment solids before and after the incubation experiment were calculated for each core, based on the assumption that the respective initial TP amounts of C1 to C5 were the same as those of C0 (Table 2). The TP amounts in the overlying water increased comparably in all the cores (0.149 ± 0.009 g-P m^{-2} on average), even though the thicknesses of cores were different. TP amounts in pore water of C1 and C2 increased, whereas those of C3–C5 decreased. In sediment solids, TP amounts were decreased by 0.235 ± 0.106 g-P m^{-2} on average, and most of the decreases were observed in the 0- to 2-cm layers. In the 0- to 2-cm layer, CBD-TP decreased by 0.200 ± 0.050 g-P m^{-2}, and NaOH-NRP decreased by 0.038 ± 0.014 g-P m^{-2} (Table 3).

Discussion

Relation between depth and phosphorus release

In this experiment, the released TP amount was 0.149 ± 0.009 g-P m^{-2}, calculated from the increase in overlying waters. We concluded that the released TP

Table 1 TP amounts in overlying waters, pore waters, and sediment solids before and after the incubation period

Amounts of phosphorus (g-P m^{-2})

	C0		C1		C2		C3		C4		C5	
	Water	Sediment solid	Water	Sediment solid	Water	Sediment solid	Water	Sediment solid	Water	Sediment solid	Water	Sediment solid
Overlying water (cm)	0.002	–	0.157	–	0.146	–	0.148	–	0.141	–	0.164	–
0–2	0.001	3.068	0.001	2.910	0.009	2.848	0.014	2.896	0.010	2.909	0.009	2.912
2–4	0.008	3.575	–	–	0.013	3.453	0.011	3.515	0.013	3.541	0.016	3.526
4–6	0.026	2.974	–	–	–	–	0.010	3.032	0.014	2.970	0.015	2.864
6–8	0.024	2.847	–	–	–	–	0.008	2.669	0.011	2.867	0.015	2.930
8–10	0.028	2.774	–	–	–	–	–	–	0.012	2.728	0.013	2.772
10–12	0.031	2.684	–	–	–	–	–	–	0.017	2.706	0.015	2.816
12–14	0.026	2.728	–	–	–	–	–	–	0.008	2.728	0.017	2.882
14–16	0.024	2.596	–	–	–	–	–	–	–	–	0.010	2.596
16–18	0.024	2.486	–	–	–	–	–	–	–	–	0.012	2.442
18–20	0.031	2.508	–	–	–	–	–	–	–	–	0.010	2.376

Quantity of overlying water was 200 l m^{-2} and that of pore water in each layer was 18.3–19.0 l m^{-2}. Weight of sediment solids in each layer was 2.2–4.2 kg m^{-2}

Table 2 Changes in phosphorus amounts in overlying water, pore water, and sediment solids before and after the incubation experiment

	Changes in phosphorus amounts before and after the incubation experiment (g-Pm^{-2})			
	Overlying water	Pore water	Sediment solid	
			All layers	Only in the 0- to 2-cm layer
C1 (0–2 cm)	0.155	0.000	−0.158	−0.158
C2 (0–4 cm)	0.144	0.013	−0.342	−0.220
C3 (0–8 cm)	0.146	−0.016	−0.352	−0.172
C4 (0–14 cm)	0.139	−0.059	−0.201	−0.159
C5 (0–20 cm)	0.162	−0.091	−0.124	−0.156

Positive and negative values indicate increases and decreases, respectively, from the initial state. We assumed that the initial phosphorus amounts for C1 to C5 were the same as those of C0

amount was independent of sediment thickness, due to negligible difference in TP amounts in overlying waters irrespective of sediment thickness. It can also be supposed that TP was released from the layers below 2 cm, because the results indicated a decrease in TP amounts in pore waters below 2 cm. We discuss this in detail below.
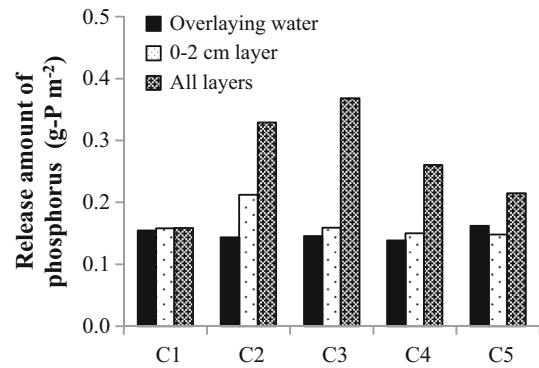
The amount of phosphorus released from the 0- to 2-cm layer was calculated to be 0.165 g-P m^{-2} on average, since the average decrease in the sediment solids was 0.173 ± 0.024 g-P m^{-2}, and the average increase in pore water was 0.008 ± 0.004 g-P m^{-2}. These decreases were nearly the same as the TP increases in overlying waters (Fig. 8). In contrast, the amounts of TP released from sediments based on the calculation of decreased TP amounts in all the layers were estimated as 0.158 g-P m^{-2} in C1, 0.329 g-P m^{-2} in C2, 0.368 g-P m^{-2} in C3, 0.260 g-P m^{-2} in C4, and 0.215 g-P m^{-2} in C5 (Table 2), and these decreases were rather larger than the TP increases in

overlying water. This overestimation probably resulted from estimation errors of TP amounts in the sediment solids. The estimation error in the 0- to 2-cm and the 0- to 20-cm layers were about 0.03 and 0.3 g-P m^{-2}, respectively, due to the SE being 1.1 %, and TP amounts in sediment solids were 2.910 and 28.116 g-P m^{-2}, respectively. Thus, the estimation errors were proportional to the TP amounts in sediment solids. To determine the amount of released phosphorus, it is essential to take the decreases of TP amounts between the sediment surface and the stabilization depth at which phosphorus concentration does not change into account (Carey and Rydin 2011). TP amounts in the overlying water and in sediments in the 0- to 2-cm layer before and after the incubation experiment were nearly equal, and decreases in the sediment solids were also equal to increases in the overlying water (Fig. 9). Based on these results, it is likely that the stabilization depth is 2 cm below the surface sediment, and that

Table 3 Amounts of respective phosphorus forms in sediment solids before and after the incubation period

	C0	C1	C2	C3	C4	C5
Amounts of CBD-TP (g-P m^{-2}, cm)						
0–2	1.276	1.041	1.034	1.140	1.044	1.120
2–4	1.412	–	1.290	1.324	1.414	1.446
4–6	1.254	–	–	1.223	1.432	1.338
6–8	1.319	–	–	1.267	1.389	1.376
8–10	1.187	–	–	–	1.209	1.229
10–12	1.128	–	–	–	1.159	1.253
12–14	1.188	–	–	–	1.181	1.198
14–16	1.145	–	–	–	–	1.172
16–18	1.144	–	–	–	–	1.096
18–20	1.169	–	–	–	–	1.125
Amounts of NaOH-NRP (g-P m^{-2}, cm)						
0–2	0.563	0.530	0.535	0.503	0.539	0.516
2–4	0.484	–	0.448	0.480	0.414	0.408
4–6	0.462	–	–	0.457	0.386	0.407
6–8	0.433	–	–	0.390	0.409	0.386
8–10	0.415	–	–	–	0.423	0.421
10–12	0.416	–	–	–	0.411	0.386
12–14	0.403	–	–	–	0.391	0.379
14–16	0.398	–	–	–	–	0.347
16–18	0.362	–	–	–	–	0.331
18–20	0.340	–	–	–	–	0.334
Amounts of HCl-TP (g-P m^{-2}, cm)						
0–2	0.587	0.560	0.558	0.581	0.561	0.602
2–4	0.664	–	0.662	0.702	0.695	0.697
4–6	0.711	–	–	0.722	0.780	0.776
6–8	0.638	–	–	0.605	0.686	0.692
8–10	0.740	–	–	–	0.718	0.736
10–12	0.762	–	–	–	0.707	0.750
12–14	0.701	–	–	–	0.679	0.701
14–16	0.704	–	–	–	–	0.646
16–18	0.639	–	–	–	–	0.640
18–20	0.634	–	–	–	–	0.622
Amounts of HCl-TP (g-P m^{-2}, cm)						
0–2	0.296	0.307	0.282	0.304	0.299	0.289
2–4	0.266	–	0.284	0.298	0.277	0.273
4–6	0.224	–	–	0.194	0.219	0.219
6–8	0.221	–	–	0.212	0.226	0.215
8–10	0.220	–	–	–	0.233	0.211
10–12	0.236	–	–	–	0.217	0.214
12–14	0.205	–	–	–	0.209	0.203
14–16	0.201	–	–	–	–	0.189
16–18	0.196	–	–	–	–	0.182
18–20	0.184	–	–	–	–	0.173

CBD-TP, NaOH-NRP, NaOH-SRP, HCl-TP are explained in the text

Fig. 8 Release amounts of phosphorus calculated by the increases in overlying water and amount of change in pore waters and sediment solids in the 0- to 2-cm layer and all layers. Details are explained in the text

phosphorus is released only from the 0- to 2-cm layer. Subsequently, the TP concentrations in the 2- to 6-cm layers became the highest in all layers at the end of the experiment.

Phosphorus release from the surface portion of sediments was also observed in Lake Champlain, where the change in the amount of reactive phosphorus in the surface sediment could explain the TP increase in the water column (Smith et al. 2011). The reasons why phosphorus was released from the surface sediment would be the high concentration of reactive phosphorus in the surface sediment due to the high capacity of iron to bind phosphorus under oxic conditions (Søndergaard et al. 2003), and the continuous flux of settling phosphorus from lake water (Hupfer and Lewandowski 2005). Therefore, the phosphorus concentration in the pore water of the surface sediment becomes high during the phosphorus dissolution period in the oxidized surface sediment by reduction (Enell and Löfgren 1988). Also, in Lake Arendsee, phosphorus release during summer can only be explained by a substantial contribution from a continuous sedimentation of particulate phosphorus and its rapid mobilization (Hupfer and Lewandowski 2005).

Phosphorus behavior below the 0- to 2-cm layer

There are studies reporting phosphorus release from tens of centimeters of sediment depth in Lake Kasumigaura (Fukushima et al. 2010) and other lakes (Søndergaard et al. 1999; Rydin 2000; Carey and Rydin 2011). Phosphorus release from deeper sediment results from phosphorus diffusion upward from the layer with the highest phosphorus concentration in pore water (Hupfer et al. 1998;
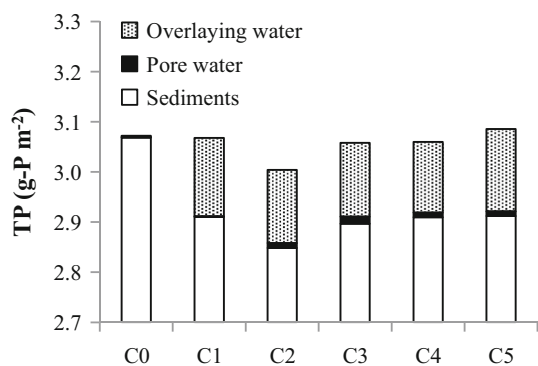
Fig. 9 TP amounts in overlying water, pore water, and sediment in the 0- to 2-cm layer before and after the experiment

Wilson et al. 2010). In the present study, there was the possibility of upward diffusion from the 10- to 12-cm layer where the SRP concentration in pore water was the highest throughout the core in the initial state. The amount of released TP calculated by the decrease in the pore water of C5 was larger than that of C1 (Table 2). This difference, however, was not observed in the overlying water (Fig. 8). Additionally, TP amounts in overlying water and in the 0- to 2-cm sediment layer before and after the incubation period were nearly equal (Fig. 9). These results indicate that the decrease of TP in pore water did not move to the overlying water.

No interaction of TP amounts between the overlying water and various sediment depths can be due to the different time scale for phosphorus release. Many studies that have reported phosphorus release from tens of centimeters of sediment depth were the result of several-year experiments. Generally, vertical profiles of phosphorus concentrations in pore water show seasonal changes (Amirbahman et al. 2013), including in Lake Kasumigaura (Hosomi and Sudo 1984). Such findings indicate the gradual upward transport from the deeper layer where the phosphorus concentration is the highest via a diffusion-mediated concentration gradient (Hupfer et al. 1998; Søndergaard et al. 2003; Wilson et al. 2010). Therefore, it seems that phosphorus releases from the sediment surface occur during short-period anoxic conditions, whereas phosphorus releases from deeper layers of sediment occur over a longer time scale.

The decreases of TP amounts in the pore water over the course of the experiment were probably due to phosphorus being sorbed to sediment solids. One possible reason for the sorption may be precipitation as vivianite (Hupfer et al. 1998). Vivianite, for which the chemical formula is $Fe_3(PO_4)_2 \cdot 8H_2O$ (Dodd et al. 2003), is a kind of iron-bound phosphorus and is formed under mildly reducing conditions and under high concentrations of available iron and phosphate (Nriagu and Dell 1974). Vivianite dissolves in

sulfide-rich sediment and is stable as long as the iron concentration exceeds sulfide formation (Murphy et al. 2001). Sulfide concentration in 0- to 20-cm sediment in Lake Kasumigaura is almost equal to that in Lake Biwa (Terashima et al. 1991), where vivianite exists (Murphy et al. 2001).

Phosphorus forms related to its release

At the end of the experiment, phosphorus amounts of CBD-TP and NaOH-NRP decreased in the 0- to 2-cm layer, and NaOH-SRP and HCl-TP were nearly the same as in the initial state. This result is in agreement with previous studies. CBD-TP and NaOH-NRP are known to be releasable phosphorus (Mortimer 1941; Rydin 2000; Carey and Rydin 2011) and NaOH-SRP and HCl-TP are permanently buried (Rydin 2000). Thus, CBD-TP and NaOH-NRP can release from sediment solids during a short-term anoxic period in Lake Kasumigaura. Since CBD-TP and NaOH-NRP include redox-sensitive phosphorus and organic phosphorus, respectively (Ishii et al. 2010), anoxic conditions in lake water and mineralization of organisms in the surface sediment should be the important processes for phosphorus release in Lake Kasumiguara.

In the 0- to 2-cm layer, the sum of decreases of CBD-TP and NaOH-NRP was 0.238 g-P m^{-2} on average in each core, larger than the decrease of TP (0.173 g-P m^{-2} on average). The difference was due to the average increase of 0.080 g-P m^{-2} in residual TP, which was calculated as TP minus total extracted phosphorus (Jensen and Thamdrup 1993; Rydin 2000). Residual TP is considered a refractory organic phosphorus, as well as an inert inorganic phosphorus (Jensen and Thamdrup 1993; Rydin 2000) and is permanently buried in the sediment (Rydin 2000; Søndergaard et al. 2003). One of the origins of residual TP is as a resolvent of organic phosphorus (Gächter and Meyer 1993). Additionally, CBD-TP is supposed to transform into other forms during diagenesis (Hupfer et al. 1998). Thus, it is likely that decreases of CBD-TP and NaOH-NRP were not all released into overlying water, but that some was buried in the sediment as residual TP. The combined values in the 0- to 2-cm layers summed up the decreases of CBD-TP and NaOH-NRP, and increases of residual TP were 0.151 g-P m^{-2} on average, corresponding to the TP decreases in sediment solids and increases in overlying waters. Thus, estimation of the amount of phosphorus released by decreases of respective forms of phosphorus is a useful approach for accurate estimation, but it should account not only for the decreased forms but also for increased forms such as residual TP.

Redox-sensitive phosphorus and organic phosphorus would be the releasable phosphorus forms during a short-term anoxic period in Lake Kasumigaura. Both phosphorus

forms are considered as bioavailable phosphorus, and higher concentrations of these forms are important for an internal source of phosphorus (Wang and Morrison 2014). Therefore, understandings of these contributions are necessary to estimate the amount of phosphorus release in Lake Kasumigaura. The decreases of CBD-TP were 10 times higher than that of NaOH-NRP, indicating that the main source of released phosphorus during the short anoxic period in Lake Kasumigaura was CBD-TP. One of the reasons for this would be the difference in the amount of each form of phosphorus in sediment solids. In Lake Kasumigaura, the amount of CBD-TP was larger than that of NaOH-NRP. In contrast, in lakes of Maine, USA, concentrations of phosphorus forms extracted with bicarbonate-dithionite (Fe and Mn hydroxides and associated phosphorus) were lower than that of NaOH-NRP where mineralization of organic phosphorus controls the phosphorus release (Wilson et al. 2010). Furthermore, iron-bound phosphorus showed a rapid decrease, while organic phosphorus decreased slowly in Lake Erken (Rydin 2000), indicating that degradation rates of organic phosphorus controlled by biotic mineralization is slower than that of iron-bound phosphorus controlled by redox reaction. The main forms of phosphorus contributing to the release from the sediment would vary according to the phosphorus amounts in sediment solids and degradation rates of the respective phosphorus forms. In Lake Kasumiguara, an investigation of the origin of CBD-TP is necessary to prevent further eutrophication.

Conclusions

An incubation experiment was conducted with several different lengths of sediment cores. Results showed that the increase of phosphorus amounts in both overlying water and pore water in the 0- to 2-cm layer were almost the same as the decrease of phosphorus in sediment solids in the 0- to 2-cm layer. It is likely that phosphorus was released only from surface sediment during the short period (around 2 weeks) of anoxic conditions. In contrast, the amount of phosphorus in pore water below the 2-cm layer that moved to overlying water was negligible, even though the amount of this phosphorus decreased over the experiment. Phosphorus amounts of CBD-TP and NaOH-NRP in sediment solids decreased during the experiment. The decreases in CBD-TP were around 10 times higher than those of NaOH-NRP, indicating the main source of released phosphorus was iron-bound phosphorus in Lake Kasumigaura. It seems that the main forms of phosphorus released during a short anoxic period would vary, depending on the amount of phosphorus in sediment solids and the degradation rate of each phosphorus form.

Generally, it is difficult to investigate the stabilization depth by in situ observations under short-term anoxic conditions. One advantage with this approach is that it allows investigation of the stabilization depth by comparing increases in phosphorus amounts in overlying water with decreases in sediment. Analyses of forms of phosphorus are also useful for estimating the stabilization depth rather than that of TP. However, it must be noted that not only the decreased forms, such as CBD-TP and NaOH-NRP, but also increased forms such as residual TP must be analyzed for an accurate estimation of amounts of phosphorus released.

References

Amirbahman A, Lake BA, Norton SA (2013) Seasonal phosphorus dynamics in the surficial sediment of two shallow temperate lakes: a solid-phase and pore-water study. Hydrobiologia 701:65–77

Carey CC, Rydin E (2011) Lake trophic status can be determined by the depth distribution of sediment phosphorus. Limnol Oceanogr 56(6):2051–2063

Dittrich M, Wehrli B, Reichert P (2009) Lake sediments during the transient eutrophication period: reactive-transport model and identifiability study. Ecol Model 220:2751–2769

Dodd J, Large DJ, Fortey NJ, Kemp S, Styles M, Wetton P, Milodowski A (2003) Geochemistry and petrography of phosphorus in urban canal bed sediment. Appl Geochem 18:259–267

Enell M, Löfgren S (1988) Phosphorus in interstitial water: methods and dynamics. Hydrobiologia 170:103–132

Fukushima T, Kawamura S, Seki T, Onda Y, Matsushige K (2005) Why has Lake Kasumigaura become turbid? Verh Internat Verein Limnol 29:732–737

Fukushima T, Kamiya K, Onda Y, Imai A, Matsushige K (2010) Long-term changes in lake sediments and their influences on lake water quality in Japanese shallow lakes. Fundam Appl Limnol Arch Hydrobiol 177(3):177–188

Gächter R, Meyer JS (1993) The role of microorganisms in mobilization and fixation of phosphorus in sediments. Hydrobiologia 253:103–121

Hosomi M, Sudo R (1984) Release of nitrogen and phosphorus from sediments of Lake Kasumigaura (in Japanese). Res Rep Natl Inst Environ Stud Jpn 51:191–217

Hupfer M, Lewandowski J (2005) Retention and early diagenetic transformation of phosphorus in Lake Arendsee (Germany)—consequences for management strategies. Archiv für Hydrobiol 164(2):143–167

Hupfer M, Fischer P, Friese K (1998) Phosphorus retention mechanisms in the sediment of an eutrophic mining lake. Water Air Soil Pollut 108:341–352

Ishii Y, Kitamura T, Watanabe K, Komatsu N (2007) Classification of rivers flowing into Lake Kasumigaura based on land use in their watershed (in Japanese). Annu Rep Ibaraki Kasumigaura Environ Sci Cent 3:118–123

Ishii Y, Yabe T, Nakamura M, Amano Y, Komatsu N, Watanabe K (2009) Effect of nitrate on phosphorus mobilization from bottom sediment in shallow eutrophic lakes. J Water Environ Technol 7(3):163–176

Ishii Y, Harigae S, Tanimoto S, Yabe T, Yoshida T, Taki K, Komatsu N, Watanabe K, Negishi M, Tasumoto H (2010) Spatial variation of phosphorus fractions in bottom sediments and the potential contributions to eutrophication in shallow lakes. Limnology 11:5–16

Jensen HS, Thamdrup B (1993) Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. Hydrobioloigia 253:47–59

Jeppesen E, Søndergaard M, Jensen JP, Havens KE, Anneville O, Carvalho L, Coveney MF, Deneke R, Dolulil MT, Foy B, Gerdeaux D, Hampton SE, Hilt S, Kangur K, Köhler J, Lammens EHHR, Lauridsen TL, Manca M, Miracle MR, Moss B, Nõges P, Person G, Phillips G, Portielje R, Romo S, Schelske CL, Straile D, Tatrai I, Willèn E, Winder M (2005) Lake responses to reduced nutrient loading—an analysis of contemporary long-term data from 35 case studies. Freshw Biol 50:1747–1771

Komatsu N, Kitamura T, Ishii Y, Kitazawa D (2007) Observation of the oxygen-deficient water mass in Kasumigaura (in Japanese). Annu Rep Ibaraki Kasumigaura Environ Sci Cent 3:83–92

Mortimer CH (1941) The exchange of dissolved substances between mud and water in lakes. J Ecol 29:280–329

Murphy T, Lawson A, Kumagai M (2001) Release of phosphorus from sediments in Lake Biwa. Limnology 2:119–128

Nriagu JO, Dell CI (1974) Diagenetic formation of iron phosphates in recent lake sediments. Am Min 59:934–946

Rydin E (2000) Potentially mobile phosphorus in Lake Erken sediment. Water Res 34(7):2037–2042

Smith L, Watzin MC, Druschel G (2011) Relating sediment phosphorus mobility to seasonal and diel redox fluctuations at the sediment-water interface in a eutrophic freshwater lake. Limnol Oceanogr 56(6):2251–2264

Søndergaard M, Jensen JP, Jeppesen E (1999) Internal phosphorus loading in shallow Danish lakes. Hydrobiologia 408(409):145–152

Søndergaard M, Jensen JP, Jeppesen E (2003) Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia 506–509:135–145

Terashima S, Inouchi Y, Saito Y, Miyata Y, Katayama H, Terashima M (1991) Vertical variation and chemical characteristics of elements in bottom sediments from the dredged hollow of Lake Biwa and Lake Kasumigaura, Japan (in Japanese). Bull Geol Surv Jpn 42(8):387–407

Van Hullebusch E, Auvray F, Deluchat V, Chazal P, Baudu M (2003) Phosphorus fractionation and short-term mobility in the surface sediment of a polymictic shallow lake treated with a low dose of alum (Courtille laké, France). Water Air Soil Pollut 146:75–91

Wang C, Morrison RJ (2014) Phosphorus speciation and changes with depth in the sediment of Lake Illawarra, New South Wales, Australia. Environ Earth Sci 71(8):3529–3541

Wilson TA, Amirbahman A, Notron SA, Voytek MA (2010) A record of phosphorus dynamics in oligotrophic lake sediment. J Paleolimnol 44:279–294