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Phosphate dissolution from the sediment in Lake Biwa and decrease in dissolved oxygen in the bottom water

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琵琶湖での堆積物からのリン酸溶出と底層水中の溶存酸素濃度の減少

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Abstract

The concentration of dissolved inorganic phosphate in hypolimnion increases with depth and time during stagnation periods in a mesotrophic lake, Lake Biwa, Japan, due to the release of phosphate from the lake sediment into the bottom water. In order to elucidate the mechanism of this increase in phosphate, incubation experiments with sediment/water interface collected at the bottom of the lake were performed in a laboratory under specific conditions of water temperature (8 ºC), pH (around 7.0), and dissolved oxygen (DO) concentration (0, 2.6, and 10 mg L^{-1}). The phosphate concentration increased under all conditions, independent of the dissolved oxygen concentration. The dissolved manganese concentration increased only at a DO concentration of 0 mg L^{-1}. However, the concentration of dissolved iron did not increase under any of the conditions tested. Therefore, it was inferred that the increase in phosphate concentration in the bottom water of Lake Biwa is caused by aerobic degradation of particulate organic matter at the sediment surface. Even if DO could be depleted in the bottom water of the lake under the current conditions, hydrated iron oxide could not be quickly reduced at the sediment surface and there would be no rapid release of phosphate from the oxide. This is because hydrated manganese oxide, which exists abundantly in the bottom sediment, is reduced before iron oxide reduction and its reaction is maintained for a while.

Keywords: Phosphate dissolution, Incubation experiment, Sediment/water interface, Manganese reduction, Iron reduction, Lake Biwa

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摘　要

中栄養湖である琵琶湖北湖では，湖水停滞期に深水層の溶存態の無機リン酸濃度が水深とともに，また停滞期の進行とともに増加する．これは堆積物から湖水にリン酸が溶出するためである．この濃度増加の機構を明らかにするために，湖で採取した湖水/堆積物界面を用いてリン酸の溶出実験（水温：8 °C，pH：7.0 近傍，溶存酸素濃度：0, 2.6, 10 mg L^{-1}）を行った．すべての実験において，リン酸濃度は溶存酸素濃度とは無関係に増加した．溶存態マンガン濃度は溶存酸素濃度が 0 mg L^{-1} の条件でのみ増加した．しかし，溶存態鉄濃度はどの条件においても増加せず，低濃度のままであった．これらのことから，現在の琵琶湖深水層でのリン酸濃度の増加は，堆積物表面における粒子状有機物質の好気的分解によるものと推測された．また，たとえ現状で琵琶湖湖底の溶存酸素が涸渇したとしても，堆積物表面の水和鉄酸化物がすぐさま還元溶出するようなことにはならず，鉄酸化物の溶解に伴うリン酸放出もすぐには起こらないと判断された．これは，そのような状況下では，まず湖底堆積物中に豊富に存在する水和マンガン酸化物が還元され，鉄水和酸化物の還元に至るにはかなりの時間がかかるためである．

キーワード：リン酸溶出，溶出実験，湖水/堆積物界面，マンガン還元，鉄還元，琵琶湖

Introduction

The nutrient concentrations in a lake that has undergone eutrophication might not decrease immediately, even if the nutrient inflow from its drainage area decreases. This phenomenon is often observed in case of phosphate in particular, because it is supplied to the lake water from the bottom sediment, where it accumulates in abundance during the eutrophication period (Horne and Goldman, 1994; Petterson, 1998). This type of nutrient supply to a lake is called internal load.

Based on the supply mechanism, the internal load of phosphate is mainly classified into the following three types:

1) Phosphate dissolution through aerobic or anaerobic biodegradation of particulate organic matter,
2) Phosphate desorption from hydrated iron oxide through a pH increase in lake water,
3) Phosphate dissolution through the reduction of ferric phosphate and/or phosphate-adsorbed hydrated iron (III) oxide.

Out of these, type 1 can be observed anywhere in a lake (e.g., Fujinaga and Hori, 1982; Sugiyama et al., 2002, Hayami et al. 2006). Type 2 occurs in shallow lakes where the pH of the lake water changes from neutral to alkaline due to active biological production in summer (e.g., Horne and Goldman, 1994). Type 3 is observed at lake bottoms when dissolved oxygen (DO) becomes heavily depleted (e.g., Sholkovitz and Copland, 1982; Kawashima et al., 1985). Therefore, a decline in vertical convection of lake water during a circulation period, prolonging of a stagnation period, and increase in organic matter supply from the epilimnion to the hypolimnion during a stagnation period accelerates this type of phosphate dissolution.

In Lake Biwa, the largest lake in Japan, although DO in the bottom water is never totally depleted throughout stagnation periods, the phosphate concentration in the hypolimnion increases with depth and time due to its dissolution from the sediment during this period every year (Fujinaga and Hori, 1982; Koyama et al., 1984; Fujii, 2000). Vertical convection of the lake water in winter has also been reported to have declined due to the influence of global warming in recent decades (Kumagai et al., 2006). Therefore, phosphate dissolution by type 3 mechanism might occur in Lake Biwa in the future. In this study, we examine the present mechanism of phosphate dissolution at the bottom of Lake Biwa by incubation experiments with sediment/water interface collected from the lake and discuss the potential for type 3 phosphate dissolution in the future.

Study area

The limnological features of Lake Biwa have been summarized previously (Sugiyama et al., 2005). It is located at 35°15’ N and 136°05’ E and is geometrically and limnologically divided into two parts, the mesotrophic northern basin and the eutrophic southern basin. The northern basin is the main basin and has a surface area of 616 km^2 and a capacity of 27.3 km^3. Its average and maximum depths are 44 m and 104 m, respectively. The residence time of lake water is estimated to be 5.5 years. Thermal stratification typically occurs from May to January, and vertical convection of lake water in the whole water column occurs regularly from February to April. DO concentration in the bottom water reaches a minimum in early winter but is never totally depleted during the stagnation period.

The southern basin of the lake has a surface area of 58 km^2 and a capacity of 0.2 km^3, with average and maximum depths of 3.5 m and 8 m, respectively. The residence time of water is calculated to be 0.04 years. The water in this basin is not thermally stratified and is mostly saturated with atmospheric oxygen throughout the year.

Sampling and analytical method

Sampling

Lake water and sediment/water interface were collected in 2005 – 2006 at station Ie-1 (35°12.97' N and 135°59.92' E; Sugiyama et al, 2005) located in the northern basin at a depth of 73 m using a Niskin water sampler and a core sampler (HR type, Rigo-sha, Japan), respectively. Lake water samples were taken at various depths and were filtered through 0.4-μm Nuclepore® filters immediately after collection. The filtrate was acidified to pH <2 by adding ultrapure nitric acid (Kanto Kagaku, Japan) and was used to determine the concentrations of dissolved inorganic phosphate (DIP) and other elements. Water temperatures and DO concentrations were measured onboard using a water quality multichannel sensor (SBE911, SeaBird, USA).

The samples of sediment/water interface were transported to our laboratory under dark and cold conditions within 4 h after collection and were subjected to an incubation experiment. Sediment samples for chemical analysis were also collected and treated in the same manner as the sediment/water interface sample.

Incubation experiment

Two or three samples of sediment/water interface collected in cylindrical containers (50 cm height, 11 cm internal diameter) were placed in a dark refrigerator, regulated at 8 ºC, and were incubated under the same conditions. The pH and DO concentration of the lake water were controlled by bubbling mixture of CO_2 and N_2 gases and the mixture of N_2 gas and air, respectively, as shown in Fig. 1. The pH, DO concentration, and oxidation-reduction potential (ORP) were monitored continuously using pH, DO, and ORP electrodes, respectively (Fig.1). Lake water samples collected during the experiment were filtered through the 0.4-μm Nuclepore® filters. The filtrates were used to determine the dissolved concentrations of inorganic phosphate and other elements. In the following sections, we discuss the average value for two or three samples incubated under the same conditions.

Analytical method

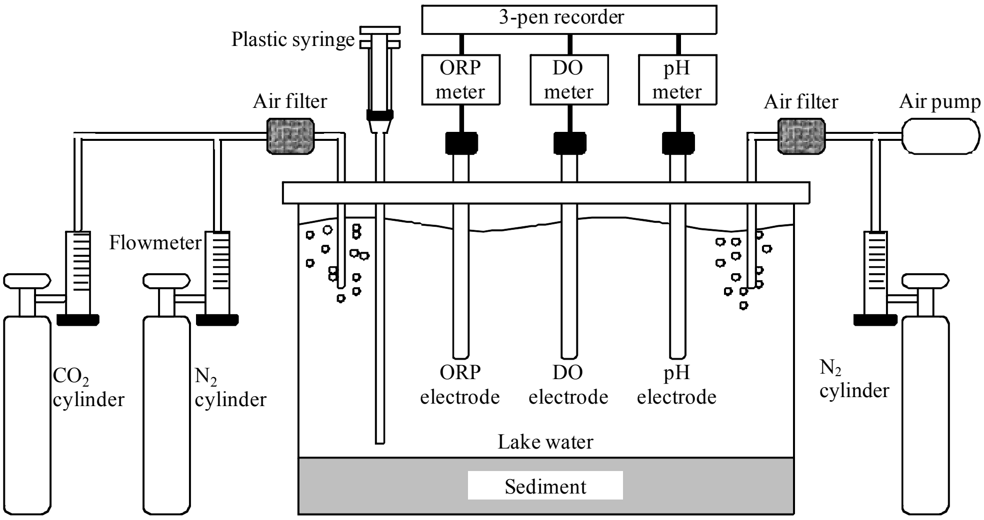

Fig. 1 Experimental setup for the examination of phosphate dissolution at the sediment water interface.
図１ 湖水/堆積物界面におけるリン酸溶出実験装置の概要.

The concentration of DIP was determined colorimetrically, with an air-segmented continuous-flow analysis system (Auto-Analyzer II, BL Tech, Japan), using the ascorbic acid - molybdenum blue method (Hansen and Koroleff, 1999). Dissolved manganese and iron concentrations were measured with a graphite furnace atomic absorption spectrophotometer (Analyst 600, Perkin Elmer, Japan). Carbon and nitrogen concentrations in the sediment samples were determined with a CHN analyzer (CHN 2400II, Perkin Elmer, Japan). Inorganic phosphate and total phosphate in a sediment sample were extracted by hydrochloric acid treatment, without and with ignition of the sample, respectively (Aspia et al., 1976). Their concentrations were determined using the air-segmented continuous-flow analysis system described above. Organic phosphate concentration was obtained by subtracting the inorganic phosphate from the total phosphate concentrations.

Results and discussion

Vertical distribution in Lake Biwa

Figure 2 shows the vertical distribution profiles of water temperature, DIP, and DO. The DIP concentrations were low in the whole water column during the circulation period (April), and the difference between its surface and bottom water concentrations was very small compared with that during the stagnation period (August or November), because of the vigorous convection of the lake water. On the other hand, during the stagnation period, the DIP concentration increased with depth; the increase was abrupt near the bottom. The concentration of DIP in the bottom water increased with time and was 23 nmol L^{-1} (0.70 μg-P L^{-1}) in April, 93 nmol L^{-1} (2.9 μg-P L^{-1}) in August, and 150 nmol L^{-1} (4.7 μg-P L^{-1}) in November. These results suggest that DIP was supplied from the bottom sediment. However, DO was not depleted and was at 45 % saturation (5.3 mg L^{-1}) in the bottom water in November. Dissolved manganese and iron concentrations were very low and did not increase near the bottom (data not shown in the figure; Mn at 30 nmol L^{-1} and Fe at <1 nmol L^{-1} in November). Therefore, we infer that the DIP increase in the bottom water is caused by

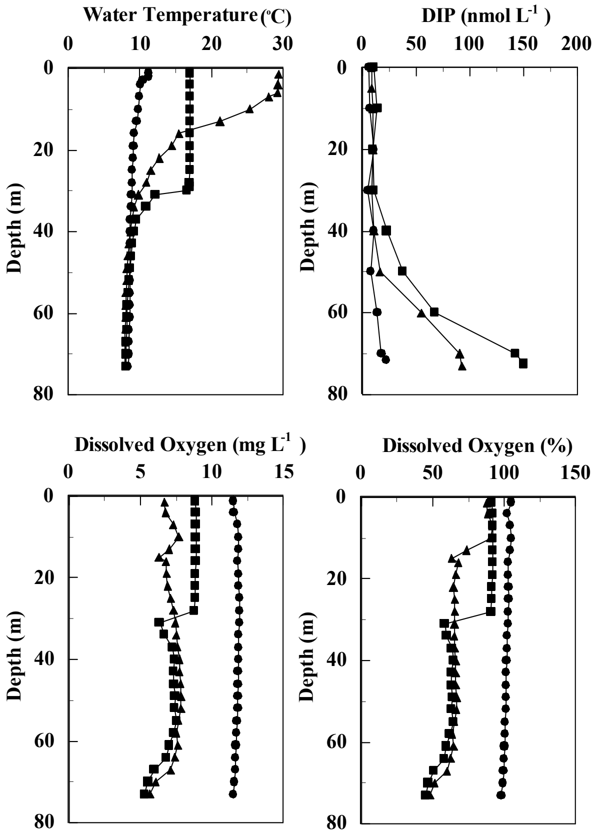

Fig. 2 Vertical distribution profile in Lake Biwa.
●: 12 April, 2005; ▲: 9 August, 2005; ■: 15 November, 2005.
図 2 琵琶湖におけるリン酸の鉛直分布.

Table 1 Phosphate dissolution rate from the sediment of Lake Biwa.
表 1 琵琶湖湖底堆積物からのリン酸溶出速度.

Incubation experiment			
DO mg L^{-1}	Period (h)	Dissolution rate* μmol m^{-2} day^{-1}	 mg-P m^{-2} day^{-1}
10	168	9.1 (5.1 – 13.2)	0.29 (0.16 – 0.41)
2.6	166	18.2 (3.0 – 32.8)	0.59 (0.15 – 1.02)
0	216	6.5 (4.4 – 8.5)	0.21 (0.14 – 0.26)

Field survey			
Month	Period (d)	Dissolution rate** μmol m^{-2} day^{-1}	 mg-P m^{-2} day^{-1}
April – August	98	9.8	0.30
August – November	109	8.4	0.26
April – November	207	9.2	0.29

*average (minimum – maximum).
**Dissolution rate was estimated using the DIP content in the water column below 40 m depth.

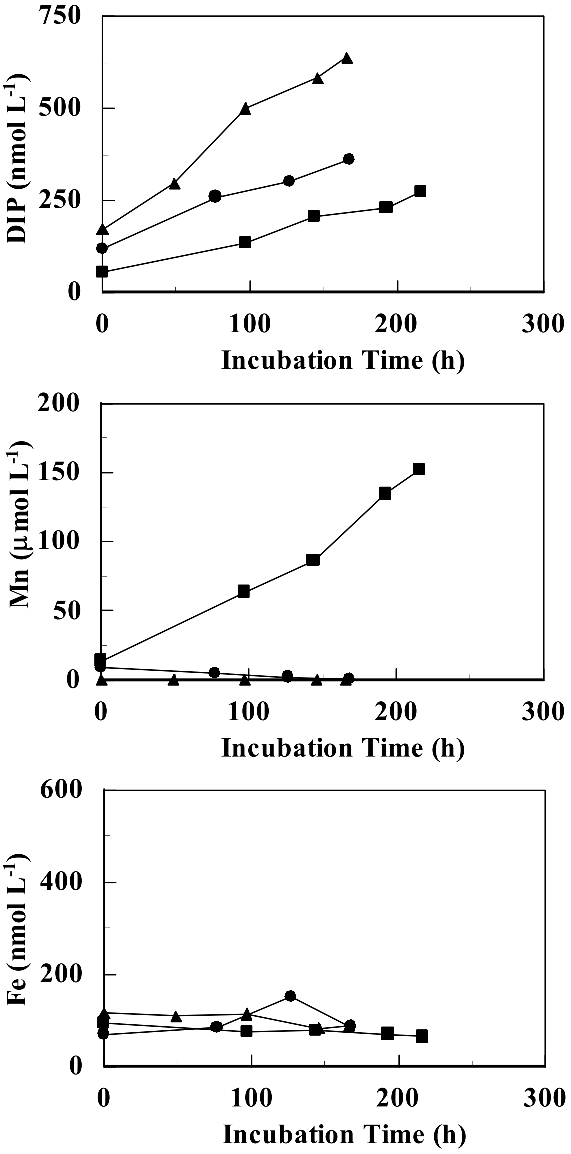

Fig. 3 Dissolution from the sediment in incubation experiments.
●: 10 mg L^{-1} DO (ORP: 480 – 550 mV); ▲: 2.6 mg L^{-1} DO (ORP: 447 – 665 mV) ; ■: 0 mg L^{-1} DO (180 – 617 mV). Water temperature: 8 ºC. pH: 6.4 – 7.7.
図 3 堆積物からのリン酸溶出実験.

its dissolution through the aerobic biodegradation of particulate organic matter on the sediment surface.

Phosphate dissolution from the sediment surface

In order to elucidate the mechanism of DIP increase in the bottom water of Lake Biwa, incubation experiments were Fig. carried out using the experimental setup shown in Fig. 1. Water temperature and pH in the experimental setup were maintained at 8 °C and around 7.0 (6.4 – 7.7), respectively, which are equivalent to the values usually observed in the bottom water of the lake throughout the year (Sugiyama et al., 2005; Lake Biwa Environmental Research Institute, 2014). DO concentrations were maintained at 10 mg L^{-1} as the value in the well aerated bottom water, 2.6 mg L^{-1} as usually observed in the bottom water at the end of the stagnation period (Lake Biwa Environmental Research Institute, 2014), and 0 mg L^{-1} as oxygen-depleted bottom water. Figure 3 shows the results of the incubation experiments. DIP concentration increased with incubation time under all the experimental conditions tested, and the phosphate dissolution rate from the sediment was calculated. As shown in Table 1, the estimated values using the initial and final concentrations in the incubation experiments (Fig. 3) agreed well with those obtained from the field survey of Lake Biwa (Fig. 2). Both dissolved manganese and iron concentrations were almost constant in the experiments with O_2 bubbling (DO: 10 and 2.6 mg L^{-1}) in contrast to phosphate. These results suggest that the DIP increase at these concentration levels of DO is caused by aerobic biodegradation of particulate organic matter on the sediment surface. It is, therefore, inferred that the same mechanism works at the bottom of Lake Biwa and forms vertical distribution profiles of DIP, as seen in Fig. 2.

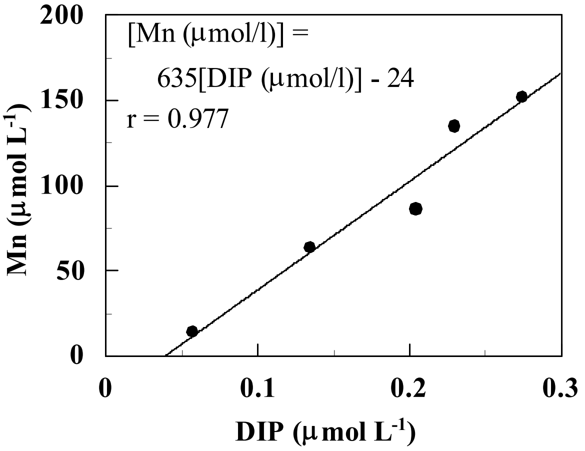

Fig. 4 Correlation between dissolved inorganic phosphate and manganese concentrations in the incubation experiment at 0 mg L^{-1} DO and 8 ºC water temperature.
The line in the figure was obtained by the linear least-squares method with all the data sets.
図 4 溶出実験（溶存酸素濃度 : 0 mg L^{-1}，水温 : 8 °C）における溶存態無機リン酸濃度とマンガン濃度の相関.

Dissolved manganese concentration increased

Table 2 Redox sequence progressed in natural water.
表 2 自然水中での酸化還元順列.

Oxygen reduction:
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \rightarrow 106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$

Nitrate reduction:
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ HNO_3 \rightarrow 106\ CO_2 + 69\ NH_3 + H_3PO_4 + 53\ H_2O$

Manganese (IV) reduction:
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\ MnO_2 \rightarrow 212\ Mn^{2+} + 106\ CO_3^{2-} + 212\ OH^- + 16\ NH_3 + H_3PO_4$

Iron (III) reduction:
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\ Fe_2O_3 + 212\ H_2O \rightarrow$
$424\ Fe^{2+} + 106\ CO_3^{2-} + 636\ OH^- + 16\ NH_3 + H_3PO_4$

Sulfate reduction:
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \rightarrow 53\ H_2S + 106\ HCO_3^- + 16\ NH_3 + H_3PO_4$

Organic matter is assumed to have an elemental composition corresponding to the Redfield ratio (Redfield et al., 1963).

substantially at 0 mg L^{-1} DO and reached 130 – 168 μmol L^{-1} (7.2 – 9.2 mg L^{-1}) after 216 h incubation. However, the dissolved iron concentration did not increase under the same condition. Dissolved inorganic phosphate and manganese concentrations correlated well with each other in this experiment, with a correlation coefficient of 0.977, as shown in Fig. 4. A Mn/P ratio of 635 mol mol^{-1} was obtained from the slope of the linear regression line in the figure. Organic matter with an elemental composition of the Redfield ratio (C:N:P = 106:16:1 (mol:mol:mol); Redfield et al., 1963) is degraded bio-geochemically in natural waters following the redox sequence and reactions listed in Table 2 (Stumm and Morgan, 1995; Masuzawa, 2005). Therefore, if DIP increases through microbially mediated oxidation reactions of particulate organic matter by the reduction of manganese (IV) oxide, and if its organic matter has the elemental composition of the Redfield ratio, the DIP and dissolved manganese concentrations will increase with the Mn/P ratio of 212 mol mol^{-1}. Of course, manganese ions are also present in the particulate organic matter composed of phyo- and zoo-plankton (Martin and Knauer, 1973; Masuzawa et al., 1988; Ho et al., 2003). However, these manganese ions hardly affect the Mn/P ratio, because Redfield type elemental composition of plankton organic tissue is C:N:P:Mn = 106:16:1:0.0004 (Bruland et al., 1991) and manganese concentration in the tissue is very low compared to that of phosphorus. Figure 4 shows a good linear relationship between dissolved inorganic phosphate and manganese concentrations, but the Mn/P ratio of the linear regression line, 635 mol mol^{-1}, was much higher than the one expected from the Redfield ratio. This difference might be attributed to the differing values of C/P ratio in the particulate organic matter on the sediment surface from the Redfield ratio. We measured the elemental composition of the sediment collected in Lake Biwa in May, 2005. The organic C/N and organic C/P ratios (mol mol^{-1}) ranged from 9.2 to 11.0 (C/N) and from 895 to 2090 (C/P), respectively. These C/P ratios are very different from the Redfield ratio. Kimura (2000) and Yoshimizu et al. (2002) also reported the same tendency about the elemental composition of the settling particles near the bottom of Lake Biwa. Their C/P ratios were 289 (Kimura, 2000) and 241 (Yoshimizu et al., 2002). If the C:N:P ratio of the particulate organic matter is a:b:1, the microbially mediated oxidation reaction of the matter by the reduction of manganese (IV) oxide is described by the following equation.

$$(CH_2O)_a(NH_3)_b(H_3PO_4) + 2a\ MnO_2 \rightarrow 2a\ Mn^{2+} + a\ CO_3^{2-} + 2a\ OH^- + b\ NH_3 + H_3PO_4$$

Therefore, dissolved inorganic phosphate and manganese concentrations increase with the Mn/P ratio of 2a mol mol^{-1}. It is probable that the DIP increase in the incubation experiment at 0 mg L^{-1} DO was caused by the reduction of manganese (IV) oxide. However, as the particulate organic matter on the sediment surface has a much higher C/P ratio

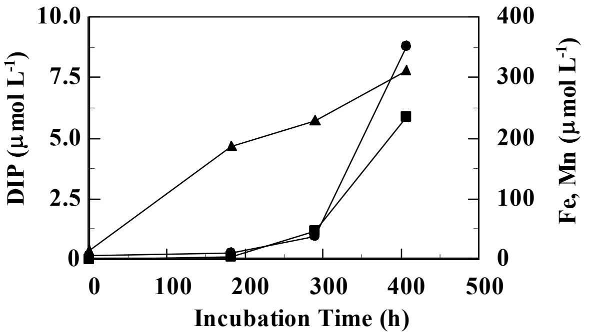

Fig. 5 Dissolution from the sediment in the incubation experiment at 0 mg L^{-1} DO and 25 ºC water temperature.
●: DIP; ▲: Mn; ■: Fe. pH: 6.8 – 7.1. ORP: -240 – 150 mV
図5 堆積物からのリン酸溶出実験（溶存酸素濃度：0 mg L^{-1}，水温：25 °C）.

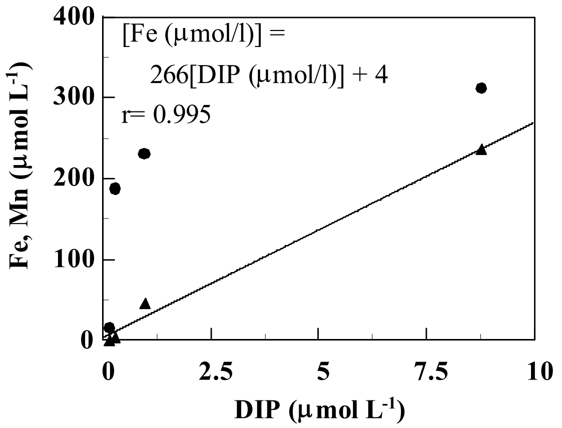

Fig. 6 Correlation between dissolved concentrations of inorganic phosphate and manganese or inorganic phosphate and iron in the incubation experiment at 0 mg L^{-1} DO and 8 ºC water temperature.
●: Mn vs. DIP; ▲: Fe vs. DIP.
The line in the figure was obtained by the linear least-squares method with all the data sets of phosphate and iron.
図6 溶出実験（溶存酸素濃度：0 mg L^{-1}，水温：25 °C）における溶存態無機リン酸濃度とマンガン・鉄濃度の相関.

than the Redfield ratio, phosphate and manganese ions dissolved into the lake water with a very high Mn/P ratio as shown in Fig. 4.

The dissolved iron concentration did not increase at all even in the incubation experiment at 0 mg L^{-1} DO, as mentioned earlier (Fig. 3). In other experiments, the dissolved iron concentration was monitored at 0 mg L^{-1} DO for 452 h (about 19 days, water temperature: 8.0 °C, pH: 6.6 – 7.0), but no increase was detected. These results suggest that the reduction of iron (III) oxide does not occur for a long period after the depletion of DO in the bottom water of Lake Biwa under the current conditions, because manganese oxides are abundantly present in the bottom sediment (Nakashima, 1982; Takamatsu et al., 1985) and delay the reduction of iron (III) oxides.

Effect of water temperature on the phosphate dissolution

Incubation at room temperature (25ºC) accelerated phosphate and iron dissolution from the sediment (Fig. 5). Dissolved iron concentrations abruptly increased after 200 h incubation at 0 mg L^{-1} DO, although as mentioned previously, this type of increase was not observed during the experiment at 8 ºC, even after incubation for 452 h. These results suggest that water temperature affects the microbially mediated reduction of iron (III) oxide significantly.

DIP also increased abruptly along with iron. Thus, in this experiment, DIP did not correlate well with manganese but instead with iron, as shown in Fig. 6. However, the Fe/P ratio obtained from the slope of the linear regression line was 266 mol mol^{-1}, which was smaller than that expected from the Redfield ratio (424 mol mol^{-1}, Table 1) in contrast to the Mn/P ratio shown in Fig. 4. The phosphate dissolution rate was also very high in this incubation experiment and ranged 193 – 317 μmol m^{-2} day^{-1} (6.0 – 9.8 mg-P m^{-2} day^{-1}). These results suggest that the main reaction leading to the DIP increase changed from manganese (IV) to iron (III) reduction in the incubation experiment at 25 ºC and that the phosphate was supplied not only by the degradation of particulate organic matter but also by the reductive dissolution of ferric phosphate and phosphate-adsorbed iron (III) oxide. Therefore, if global warming raises the bottom water temperature in the future, the microbially mediated reduction of iron (III) oxides would quickly proceed even in the deep bottom water of Lake Biwa.

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