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Role of organic phosphorus in sediment in a shallow eutrophic lake

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Abstract We tested the hypothesis that mineralization of molybdenum unreactive phosphorus (MUP) in pore water is the major pathway for the changes in the concentration of molybdenum-reactive P (MRP) in pore water and inorganic P in sediment particles. The concentration of inorganic P in the sediment particles increased from December to April in Lake Kasumigaura, whereas concentrations of organic P in the sediment particles and MUP in pore water decreased. These results suggest that MUP mineralization plays a key role as the source of MRP, whereas desorption of inorganic P from the sediment particles into the pore water is a minor process. One-dimensional numerical simulation of sediment particles and the pore water supported the hypothesis. Diffusive flux of MUP was small in pore water, even in near-surface layers, so mineralization was the dominant process for changing the MUP concentration in the pore water. For MRP, diffusion was the dominant process in the surface layer, whereas adsorption onto the sediment was the dominant process in deeper layers. Researchers usually ignore organic P in the sediment, but organic P in sediment particles and the pore water is a key source of inorganic P in the sediment particles and pore water; our results suggest that in Lake Kasumigaura, organic P in the sediment is an important source, even at depths more than 1 cm below the sediment surface. In contrast, the large molecular size of MUP in pore water hampers diffusion of MUP from the sediment into the overlying water.

Key Points:
- Recently, organic P in sediment particles has been recognized as a source of organic P in the pore water
- We conducted a numerical model simulation to determine which process dominates sediment P cycling
- Organic P degradation in sediment particles and mineralization in pore water more strongly affect the MUP concentration than does diffusion

Supporting Information:
- Supporting Information S1

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1. Introduction

Phosphorus (P) is one of the most important nutrients for all living organisms. High P concentrations promote primary production [*Currie and Kalff*, 1984], thereby delaying the recovery from a eutrophic state [*Søndergaard et al.*, 2005]. In shallow lakes, bottom sediment is a source of P to the water column; the release of P from the sediment accelerates eutrophication even after external P inputs have decreased [*Graneli*, 1999]. Because the release of P from sediment into the overlying water is controlled by the P concentration in the pore water, clarifying the mechanisms responsible for changes in the concentrations of inorganic and organic P in sediment particles and pore water would improve our understanding of the regulation of release of sediment P into the overlying water [*Spears et al.*, 2012, 2013].

The adsorption and desorption of inorganic P between the sediment particles and pore water have been debated mostly under hypotheses related to Fe-bound P [*Mortimer*, 1941] and polyphosphate incorporated into bacteria [*Hupfer et al.*, 1995]:

1. *Mortimer* [1941] hypothesized that P is adsorbed and desorbed between Fe-bound P (orthophosphate) and pore water through changes in the sediment redox potential. When the redox potential is low enough for reduction of Fe(III), Fe-bound P is desorbed into the pore water.
2. When the redox potential is similar to the level at which Fe(III) is reduced to Fe(II), polyphosphate-accumulating bacteria also release orthophosphate (PO_4^{3-}) into the pore water [*Hupfer et al.*, 1995].

In addition to these hypotheses about inorganic P, results with recent advances in analytical techniques, such as ^{31}P nuclear magnetic resonance analysis, have introduced into the debate the role of organic P in lake sediment [*Ahlgren et al.*, 2005; *Reitzel et al.*, 2006; *Jørgensen et al.*, 2011]. By using ^{31}P nuclear magnetic resonance analysis, researchers have found that the concentrations of organic P compounds in the sediment particles (e.g., orthophosphate monoesters and diesters) decrease with increasing depth in the sediment [*Ahlgren et al*., 2006; *Reitzel et al*., 2007; *Özkundakci et al*., 2014]. These findings suggest that organic P in the sediment particles plays a role as a source of molybdenum unreactive P (MUP, most of which is organic P) in the pore water [*Ahlgren et al*., 2006; *Reitzel et al*., 2007; *Özkundakci et al*., 2014].

Two kinds of processes could affect the MUP concentration in the pore water. One is the release of MUP in the pore water by diffusion [*Ni et al*., 2016]. Many numerical models of lake ecosystems include the release of inorganic P (molybdenum-reactive P; MRP) from the sediment into the overlying water [*Komatsu et al*., 2006; *Mandal et al*., 2015]. However, the release of MUP into the water column is ignored in most of the models. If a substantial amount of MUP is present in the pore water, the failure of these models to account for organic P in the pore water could lead them to underestimate the amount of P released from the sediment. The second process that could affect the MUP concentration in the pore water is mineralization of MUP. If MUP is labile and easily mineralized, it should be a source of MRP in pore water. Whether mineralization or diffusion is the dominant process must be clarified, especially when predicting the species of P released into the overlying water. Hence, a goal of the present study was to determine which is the dominant process affecting the MRP and MUP concentrations in pore water: mineralization of MUP, P adsorption/desorption, or diffusion.

Specifically, we hypothesized that MUP is a source of MRP in pore water, and that MRP is then adsorbed by the sediment particles. The interactions among several processes in sediment, including diffusion [*Tromp et al*., 1995; *Dale et al*., 2011, 2013], mineralization [*Sayler et al*., 1979], and adsorption/desorption [*Spears et al*., 2006], are complex. Thus, to clarify their roles, we developed a one-dimensional (1-D) numerical simulation model to analyze the flux from each process of the exchange between sediment particles and pore water. Previous studies of organic P in sediment usually measured enzymatic activities [*Feuillade and Dorioz*, 1992], but we here calculated the mass balance of inorganic and organic P for fluxes between the sediment particles and pore water.

We studied Lake Kasumigaura, Japan. In previous research, our team clarified the vertical attenuation of organic P concentrations in the sediment using ^{31}P nuclear magnetic resonance [*Shinohara et al*., 2017]. We have also observed seasonal changes in the concentration of organic P in the sediment particles, and of MRP and MUP in the pore water. The results suggest that organic P in the sediment particles supplies MUP to the pore water [*Shinohara et al*., 2017]. Given these background results, Lake Kasumigaura is a good choice for research to clarify the mass balance of organic P in the sediment and MUP.

In the current study, we conducted the following components. First, we analyzed monthly data of P in sediment to clarify how the concentrations of P species in the sediment particles (inorganic or organic P) and pore water (MRP or MUP) changed. We also analyzed the activity of phosphomonoesterase, an enzyme that hydrolyzes the phosphomonoester bond, to ascertain the potential mineralization of organic P in the sediment. Second, we analyzed the adsorption/desorption rate between the sediment particles and the pore water under oxic and anoxic conditions; this experiment was conducted to quantify these processes for inclusion in a mass-balance model. Finally, we developed a 1-D numerical model and used it to simulate physical (diffusion), chemical (adsorption/desorption), and biological (degradation and mineralization) fluxes between sediment particles and the pore water. By using numerical simulation, we were able to quantify the amounts of inorganic and organic P that are adsorbed to or desorbed from the sediment particles, as well as the diffusive flux of P in the pore water. Using such a numerical simulation model is a powerful approach to analyzing the processes responsible for P behavior in sediment [*Dale et al*., 2013]. From these results, we determined the overall mass balance for inorganic and organic P in the sediment particles and pore water, and identified the factors that most strongly affected the P dynamics.

2. Methods

2.1. Field Observations

We conducted field observations in Lake Kasumigaura from December 2012 to April 2013 to analyze changes in the abundance of MRP and MUP in the pore water and to measure phosphomonoesterase activity. Lake Kasumigaura is the second largest lake in Japan, with an area of 171 km^2 and a mean depth of approximately 4 m (Figure 1). The average water residence time is approximately 200 days. Total P and nitrogen (N) concentrations in the surface water are approximately 0.12 and 1.1 mg L^{-1}, respectively.

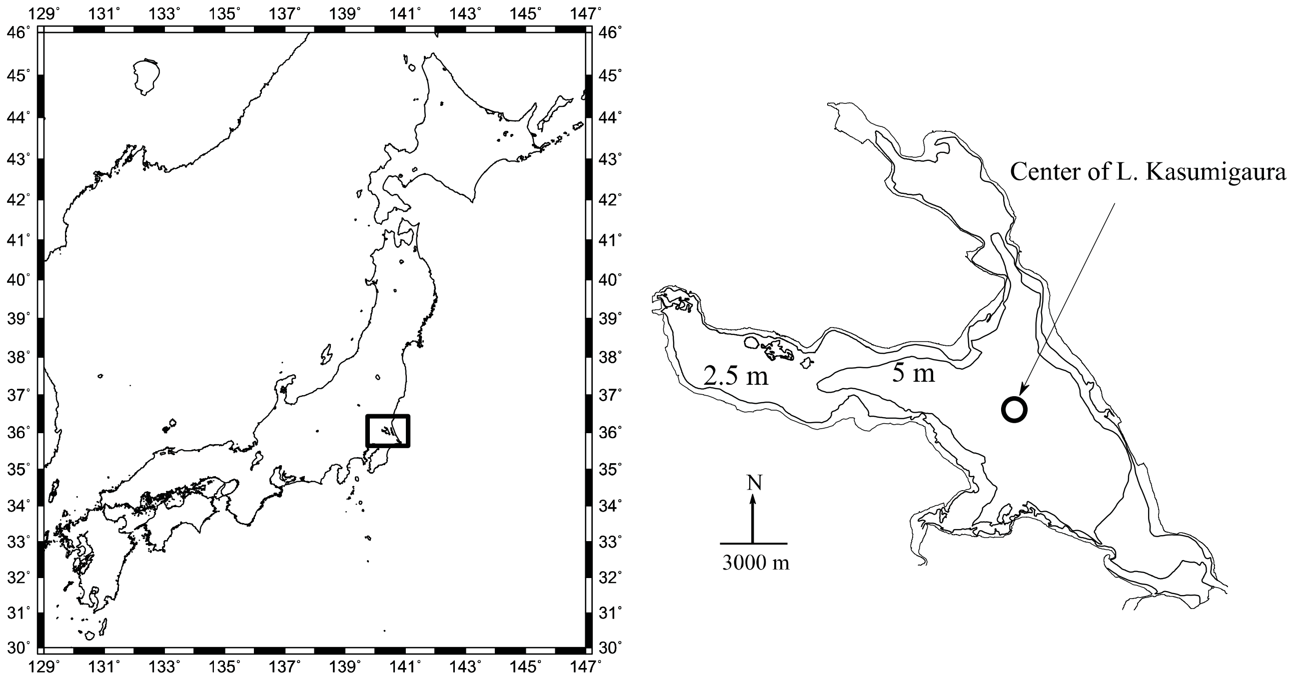

Figure 1. Map of Lake Kasumigaura. Center of Lake Kasumigaura is the sampling station for collecting sediment cores.

Sediment core samples were taken at the center of the lake, at a water depth of approximately 6 m (Figure 1), using a gravity core sampler with an acrylic pipe that was 0.5 m long ($\Phi = 11$ cm; Rigo, Tokyo, Japan). One core was taken for measurements in the field of the sediment temperature and P in the bottom water (just above the sediment surface). Immediately after the core was collected, the bottom water was gently suctioned using a syringe with a Teflon tube. The water was immediately filtered through a glass-fiber filter (GF/F; nominal pore size of 0.7 μm) and stored in the dark, packed in ice. Sediment temperature was then measured with a thermometer (TX10–01, Yokogawa, Tokyo, Japan) at intervals of approximately 2 cm from the surface.

The second core was taken to the laboratory as soon as possible (~3 h) in the dark, packed in ice. It was then stored in a refrigerator (~24 h) and sectioned as soon as possible under N_2-purged atmosphere into layers of 0–1.5, 1.5–3.0, 3.0–6.0, 6.0–9.0, 9.0–12.0, 12.0–15.0, 15.0–18.0, 18.0–21.0, 21.0–24.0, 24.0–27.0, 27.0–30.0, and 30.0–33.0 cm.

Part of the wet sediment from each layer (~5 g wet weight) was collected in a polypropylene vial for analysis of total P, inorganic P, organic P, and phosphomonoesterase activity. The remaining sediment from each layer was centrifuged at 3500 rpm for 15 min to separate the sediment particles from the pore water. The supernatant was filtered through a GF/F filter (nominal pore size: 0.7 μm) under an N_2 atmosphere and stored in a vial at −30°C until analysis.

2.2. Analysis of Phosphomonoesterase Activity

Phosphomonoesterase activity was determined using a modified version of the fluorometric method of *Freeman et al.* [1995]. In brief, 0.4 ± 0.01 g of wet sediment, 2.0 mL of distilled water, and 1.0 mL of 4-methylumbelliferyl (MUF) phosphate (3 mmol L^{-1}) were added to a tube. After 2 h of incubation at 30°C, 8 mL of ethanol (99%, v/v) was added to terminate the reaction, and the solution was then filtered through a filter (Whatman No. 5B; pore size: 2.5 μm); the filtrate was excited at 365 nm and fluorescence was measured at wavelengths of 455 nm with an RF-1500 fluorometer (Shimadzu, Kyoto, Japan). This analysis determined the amount of 4-MUF produced by phosphomonoesterase activity. The amount of 4-MUF produced by 1.0 g of the sediment per hour was adopted as the indicator of enzyme activity.

2.3. Adsorption and Desorption Experiment

To determine the rates of P adsorption and desorption between the sediment particles and the pore water, we conducted a laboratory experiment. Wet sediment was collected in March 2016 at a depth of 6–9 cm, where the highest MRP concentration was observed. We prepared 16 glass vials, with 8 under open (oxic) and 8 under closed (anoxic) conditions. After centrifugation (as described in the previous section), we placed exactly 1 g of wet sediment particles in a vial. In the closed vials, anoxic conditions were created by bubbling N_2 through Milli-Q water for more than 3 h. We then added 10 mL of Milli-Q water with initial P concentrations (C_{init}) of 0, 0.3, 0.6, and 0.9 mg L^{-1} (created by adding KH_2PO_4 with a known concentration). In the open vials, we created oxic conditions by opening the cap and incubating the vial with shaking (at 100 rpm) on a rotary shaker. To maintain anoxic conditions, we completely sealed the vials with a butyl-rubber cap over an aluminum cap to prevent oxygenation. Two replicates were prepared for each condition. We incubated the vials for 24 h at 20 ± 1°C. After the incubation, we filtered the water through a Millex membrane filter (PVDF, pore size 0.45 μm; Millipore, Darmstadt, Germany). The filtrate was then analyzed to determine the final MRP concentration (C_{final}). We fitted several curves for the relationship between the adsorbed P ($V = C_{\mathrm{init}} - C_{\mathrm{final}}$; mg L^{-1} d^{-1}) and the initial concentration (C_{init}). A linear regression of the following form gave the best results for calculating the adsorption rates:

$$V = \alpha C_{\mathrm{init}} + \beta \tag{1}$$

where α is the slope of the regression line and β is the intercept.

2.4. Chemical Analysis

We determined the MRP concentration in pore water using the molybdenum blue method of *Murphy and Riley* [1962] by using an autoanalyzer (QuAAtro, BLTec, Tokyo, Japan). To analyze total dissolved P, the pore water was first digested with persulfate solution [*APHA*, 1995] and then analyzed by the molybdenum blue method. MUP was calculated as the difference between total dissolved P and MRP. The minimum detection limit for MRP was 1.9 μg L^{-1}.

Before analyzing inorganic and organic P in the sediment, we dried the collected sediment from each depth at 105°C to constant weight. To measure the concentrations of inorganic and organic P in the sediment, we used the methods of *O'Halloran and Cade-Menun* [1993]. In brief, P was extracted from sediment in 25 mL H_2SO_4 (0.5 mol L^{-1}) before combustion (inorganic P) and after combustion (total P). The extraction was conducted for approximately 16 h, and the solution was then centrifuged (2500 rpm for 10 min). The supernatant was then filtered through a GF/F filter. Total and inorganic P in the solutions were analyzed by the molybdenum blue method as above. The organic P concentration in the sediment particles was quantified as the difference between the total and inorganic P concentrations in the sediment particles.

2.5. Model Description and Theory

We developed a 1-D diffusion model for pore water and the sediment particles based on previously developed methods [*Krom and Berner*, 1981; *Amirbahman et al*., 2013]:

$$\varphi \partial_t C_p = \partial_z \left(\varphi D_{\mathrm{p}} \partial_z C_p \right) + \varphi \sum R_{\mathrm{p}} \quad \text{(pore water)} \tag{2}$$

$$(1-\varphi) \partial_t C_{\mathrm{s}} = \partial_z ((1-\varphi) D_{\mathrm{s}} \partial_z C_{\mathrm{s}}) + (1-\varphi) \sum R_{\mathrm{s}} \quad \text{(sediment)} \tag{3}$$

where φ is porosity (dimensionless, observed value supporting information Figure S1), ∂_t and ∂_z represent the partial differentials with respect to time and depth, respectively, in the sediment, C_p is the concentration of MRP (C_{MRP}; mg L^{-1}) or MUP (C_{MUP}; mg L^{-1}), C_s is the inorganic (C_{IPsed}; mg g^{-1} dw) or organic P concentration in the sediment particles (C_{OPsed}; mg g^{-1} dw), D_p is the tortuosity-corrected molecular diffusion coefficient for pore water (cm^2 s^{-1}) [*Boudreau*, 1996], D_s is the diffusion coefficient for bioturbation (cm^2 s^{-1}), z is the sediment depth (cm), and R_{p} and R_{s} are terms in the mass-balance model for the pore water and the sediment, respectively. Porosity data was obtained in October 2012 by precisely analyzing the water content per unit volume of the sediment (supporting information Figure S1). The diffusion coefficient for a variety of molecular sizes and the sediment temperature were calculated from the Stokes-Einstein relation [*Wang et al*., 2003; *Lewandowski and Hupfer*, 2005]. Details are provided as supporting information SI1.1 and supporting information Figure S1. We assumed that high-molecular-size organic P (e.g., DNA, RNA, and phospholipids) was present (i.e., molecular size = 35,000 Da) [*Kawasaki et al*., 2011].

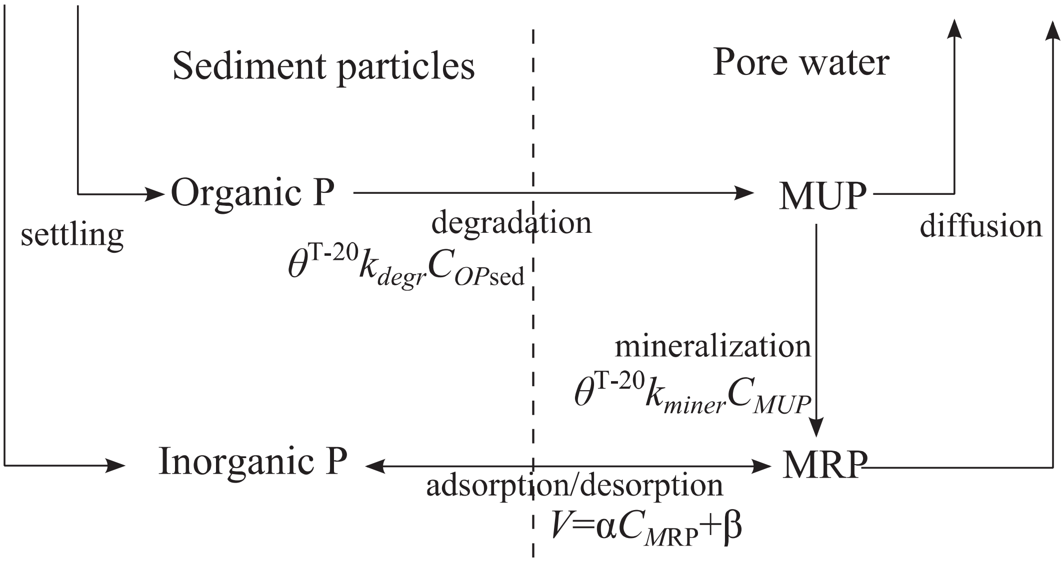

Figure 2. Schematic diagram of the model developed in the current study.

The flux (J; mg cm^{-2} s^{-1}) of P between two adjacent sediment layers and the rate of release from the sediment into the overlying water was calculated by using Fick's first law, as follows [*Tammeorg et al.*, 2015]:

$$J=-D_p\partial_z C_p \tag{4}$$

2.6. Model of P Transport Between Sediment and Pore Water

We calculated the mass balance of P (the terms R_p and R_s in equations (2) and (3), respectively) using the numerical simulation model described in Figure 2, with the parameter values shown in Table 1. R_p represents the rate of change of concentration of MRP (R_{MRP}) and MUP (R_{MUP}) and R_s represents the rate of change of concentration of IP$_{sed}$ (R_{IPsed}) and OP$_{sed}$ (R_{OPsed}). We considered four compartments in the simulation: inorganic P in the sediment particles, organic P in the sediment particles, MRP in pore water, and MUP in pore water. The mass-balance model was developed as follows:

$$\sum R_{MRP}=\text{ mineralization}-\text{adsorption} \tag{5}$$

$$\sum R_{MUP}=\text{degradation}-\text{ mineralization} \tag{6}$$

$$\sum R_{IPsed}=\text{adsorption}/\text{desorption} \tag{7}$$

Table 1. Parameters of the Mass-Balance Model[a]

		Values					
Parameter (Unit)	Variables	Parameter 1 (Minimum)	Parameter 2	Default	Parameter 3	Parameter 4 (Maximum)	
Mineralization rate (days^{-1})	k_{miner}	0.22	0.86	**1.50**	1.65	1.80	Phosphomonoesterase activities
Degradation rate (days^{-1})	k_{degr}	1.37×10^{-7}	2.00×10^{-3}	$\mathbf{4.00 \times 10^{-3}}$	5.56×10^{-3}	7.12×10^{-3}	*Tromp et al.* [1995]
Adsorption (mg L^{-1} d^{-1})	V			$\boldsymbol{\alpha x+\beta}$			Equation. (10b)
Molecular size (Da)	Mw	2000	3000	**35,000**	100,000	150,000	*Kawasaki et al.* [2011]
Temperature function	θ			**1.04**			
Diffusion coefficient for bioturbation (cm^2 s^{-1})	D_s			$\mathbf{3.17 \times 10^{-7}}$			*Park and Jaffé* [1996]

[a] Bold values are the default values for the scenarios. The columns of the parameters 1–4 refer to the values for the sensitivity analysis. The values for the sensitivity analysis increase from the left (Parameter 1: minimum) to the right column (Parameter 4: maximum).

$$\sum R_{\mathrm{OPsed}} = -\mathrm{degradation} \tag{8}$$

where $\sum R_{\mathrm{MRP}}$ is the sum of the rate of change of concentration of MRP in pore water (mg L^{-1}), $\sum R_{\mathrm{MUP}}$ is the sum of the rate of change of concentration of MUP in pore water (mg L^{-1}), $\sum R_{\mathrm{IPsed}}$ is the sum of the rate of change of concentration of inorganic P in the sediment (mg g^{-1} dw), and $\sum R_{\mathrm{OPsed}}$ is the sum of the rate of change of concentration of organic P in the sediment (mg g^{-1} dw). The detailed equations for each process are shown in the supporting information SI1.2.

The parameters we used were based on results both from previous studies and this study. Note that we estimated the rates of mineralization driven by phosphomonoesterase activity by dividing the amount of MUF added to the sediment in the experiment.

2.7. Boundary Conditions

For the boundary conditions at the deepest end (bottom) of the core for all P species, we used the Neumann boundary condition ($\partial C/\partial z=0$). For surface boundary conditions of inorganic and organic P in the sediment particles, we calculated the inorganic and organic P concentrations considering settling matters. We assumed that the concentrations of settling inorganic and organic P from the water column were similar to those of the surface sediment. We estimated the amount of P settled to the sediment by means of a sediment trap experiment, which is described in detail in the supporting information SI1.3 and supporting information Figure S3. For the surface boundary condition of MRP and MUP, we used the measured P concentrations just above the bottom, interpolated over time to input the daily values (see supporting information Figure S4).

2.8. Mass-Balance Calculations and Scenarios

P concentrations in the pore water were simulated from 12 December 2012 to 11 April 2013 (120 days). We set the length of the sediment core to 31.5 cm and the thickness of each layer to 0.25 cm for the vertical resolution. The time step (Δt) was 1800 s and solved by using an implicit scheme. We regarded the first month (December) as the spin-up period and analyzed the remaining data from January to April for the mass-balance calculations. Initial P concentrations (MRP, MUP, inorganic, and organic P in sediment particles) were set by the data obtained from field observations.

We defined three scenarios for this analysis. Scenario 1 omits the exchange of P (i.e., no R term in equations (2) and (3)) to analyze whether simple diffusion could explain the changes in P concentrations in the pore water. Scenario 2 is the orthophosphate exchange model (equation (1)) obtained from the P adsorption/desorption experiments based on the assumption of anoxic conditions for the adsorption equation. Scenario 3 includes both inorganic and organic P as well as their adsorption and degradation. In Scenario 3, we also used anoxic conditions for the adsorption/desorption of orthophosphate. We conducted a sensitivity analysis (section 2.9) using Scenario 3, with the parameters shown in Table 1.

2.9. Sensitivity Analysis

To identify the most influential parameter on the results of model calculation, we conducted a sensitivity analysis. We analyzed the sensitivities of the model to the rate of organic P degradation in the sediment, the rate of MUP mineralization, the molecular size of MUP, temperature, adsorption rates, the settling rate, resuspension rate, and porosity. The sensitivity (%) was calculated as

$$\mathrm{Sensitivity} = \frac{1}{n}\sum \frac{z_{2i}}{z_{1i}} \times 100, \tag{9}$$

where z_{1i} is the calculated default value of the parameter (Table 1) and z_{2i} is the calculated value when the parameter was adjusted by ±10% and ±30% from the default value. The final concentration in April 2013 was used for the sensitivity analysis.

2.10. Statistical Analysis

To analyze the difference in the simulated concentration of each P form from the field and simulation values, we used paired t tests to detect significant differences, with significance at $p < 0.05$. We also used one-way analysis of variance (ANOVA) to detect significant differences with significance at $p < 0.05$.

3. Results

3.1. P Concentrations in Sediment and Pore Water

Concentrations of inorganic and organic P in the sediment particles changed both vertically and over time (Figure 3). Both differed significantly between December and April (paired t test: inorganic P, $t_{11} = 3.61$, $p < 0.01$; organic P, $t_{11} = 9.32$, $p < 0.01$). The difference in inorganic P concentrations between December and April (ΔP mg g^{-1} dw month^{-1}) was significantly negatively correlated with the difference in organic P concentrations between December and April (Pearson's $r = -0.86$, $p < 0.01$, $n = 13$; supporting information Figure S2). Furthermore, ΔP of inorganic and organic P in the sediment particles between December and April exhibited no significant difference (ANOVA; $F_{1,22} = 0.71$, $p = 0.41$).

The MRP and MUP concentrations in pore water also changed both vertically and over time (Figure 3). MRP concentrations differed significantly between December (0.18 mg L^{-1}) and April (0.32 mg L^{-1} (paired t test: $t_{11} = 4.05$, $p < 0.01$)). In contrast, MUP concentrations in December (0.14 mg L^{-1}) and April (0.11 mg L^{-1}) did not differ significantly (paired t test: $t_{11} = 1.47$, $p = 0.09$). The observed rate of MRP release from the sediment into the overlying water, calculated using equation (4), ranged from 0.10 to 0.22 mg m^{-2} d^{-1} during December and April.

The values of phosphomonoesterase activity ranged from 0.32 to 5.54 μmol g^{-1} dw h^{-1} (Figure 3). The activity decreased rapidly with depth in the top 7 cm of the sediment, then decreased more gradually thereafter, but did not differ significantly between December and April (mean in December, 1.42 μmol g^{-1} dw h^{-1}; mean in April, 1.29 μmol g^{-1} dw h^{-1}; paired t test: $t_{11} = 1.06$, $p = 0.16$).

3.2. Rates of P Adsorption and Desorption

The concentration of P increased linearly with the initial concentration under both oxic and anoxic conditions (Figure 4); the linear regressions were both strong and significant under both conditions: $r = 0.99$ at $p < 0.01$. The regression equations used to represent the adsorption/desorption rate were as follows:

$$\begin{cases} V = 0.78C_{init} - 0.044 \ (10a: \ \text{oxic}) \\ V = 0.70C_{init} - 0.082 \ (10b: \ anoxic) \end{cases}$$

The x-intercepts of the oxic and anoxic lines were 0.056 and 0.117 mg L^{-1}, respectively; consequently, P could be adsorbed if MRP concentrations were higher than these intercept values.

3.3. 1-D Diffusion Coupling in the P Exchange Model

Among the three modeled scenarios, Scenario 1 did not satisfactorily explain the observed changes in the concentrations of inorganic and organic P in the sediment particles from December to April (Figures 5a–5d); therefore, simple diffusion greatly underestimated the MRP concentrations in the pore

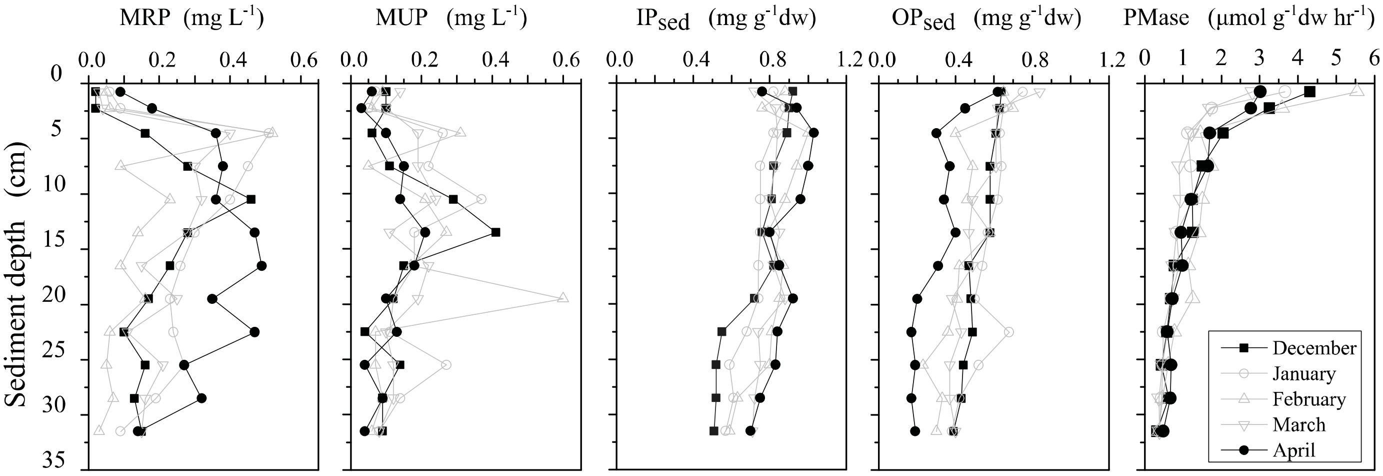

Figure 3. Results of field observation of inorganic P in sediment particles (IP_{sed}), organic P in sediment particles (OP_{sed}), molybdenum-reactive P in pore water (MRP), molybdenum unreactive P in pore water (MUP), and phosphomonoesterase activity (PMase) in sediment.

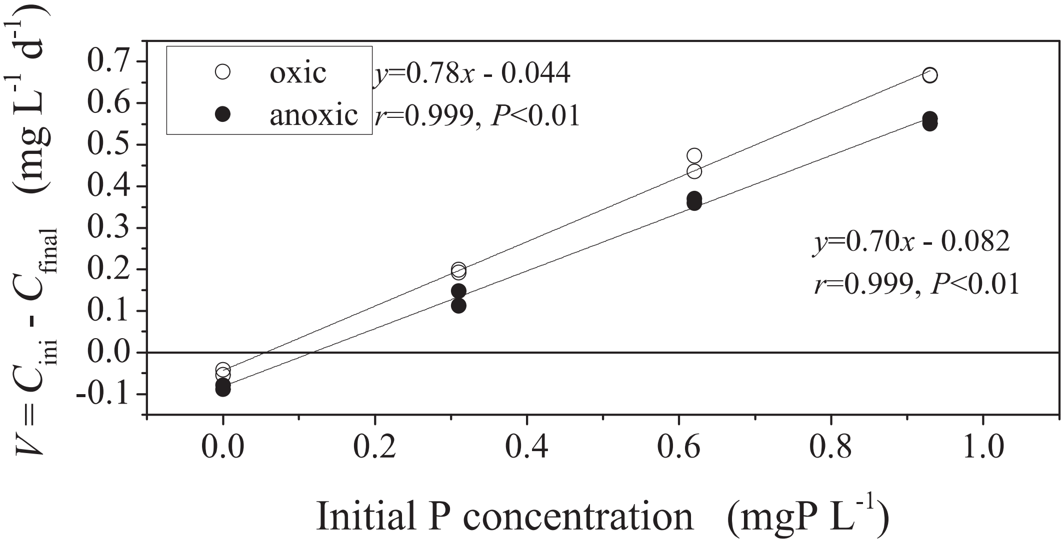

Figure 4. Results of laboratory incubations with Lake Kasumigaura sediment. The positive values mean adsorption whereas the negative values mean desorption.

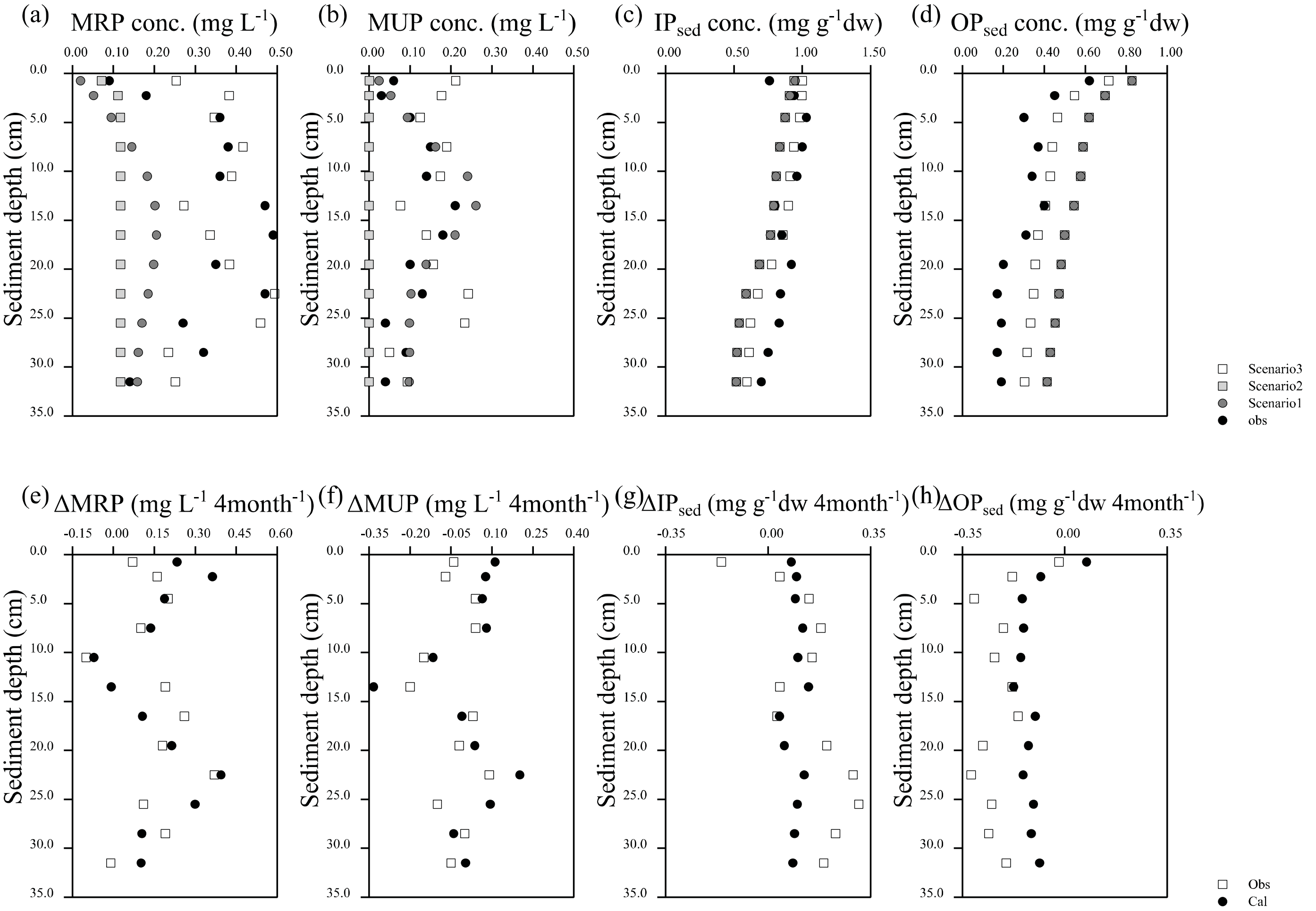

Figure 5. Profiles of calculated and observed P species in Lake Kasumigaura sediment. (a–d) The results of 10 April 2013. (e–h) The differences between the concentrations between December 2012 and April 2013.

water. In Scenario 2, which includes the adsorption/desorption rate in equation (10b), MRP concentrations were underestimated; the observed adsorption rates were substantially higher. Furthermore, MUP concentrations were near zero because there was no supply by degradation of organic P in sediment particles. In Scenario 3, including both degradation and adsorption, the simulated P concentrations in both the sediment and the pore water were similar to the observed P values (Figure 5). We observed the significant difference in the MRP concentrations (paired *t* test: $t_{11} = 4.26$, $p < 0.01$), inorganic P in the sediment particles ($t_{11} = 11.7$, $p < 0.01$), and organic P in the sediment particles ($t_{11} = 5.86$, $p < 0.01$) between December and April, but MUP concentrations did not differ significantly ($t_{11} = 0.36$, $p = 0.17$) between December and April in Scenario 3.

Because Scenario 3 reflects the observed changes of the P concentrations of both sediment particles and pore water, we used Scenario 3 and the observed results in our subsequent calculations to analyze the differences in the concentrations of MRP, MUP, inorganic P, and organic P between December and April (Figures 5e–5h). Although improvement of the simulation is still needed, in particular for MRP and MUP concentrations (Figure 5), the mass balance of the current model was reliable as demonstrated by the slight difference in ΔP between observed and simulated values during the 4 months.

3.4. Mass Balance for P Flows Between Sediment and Pore Water

The major pathway for P in the sediment differed between the top 1 cm and the deeper layers (Figures 6 and 7). We observed high diffusion of MRP in the surface sediment, at approximately 1.1×10^{-4} mg cm^{-2} d^{-1}, but the flux decreased rapidly with increasing depth (Figure 6). The rates of organic P degradation in the sediment and of mineralization of MUP to MRP had the same magnitude below 1.0 cm (3.8×10^{-5} and 3.7×10^{-5} mg cm^{-2} d^{-1}, respectively), but MRP diffusion was the dominant process in the top 1.0 cm (Figure 7). In contrast, at greater depths adsorption as inorganic P and mineralization were the dominant processes and they were the same magnitude. The diffusive flux of MUP was much lower than the fluxes driven by the other processes at both depths.

3.5. Sensitivity Analysis

Among the variables, the MUP concentration was sensitive to many of the parameters (Table 2), in particular, the rate of organic P degradation in the sediment particles and the rate of MUP mineralization. The MRP concentration was also sensitive to porosity, the rate of organic P degradation, and the adsorption equation, as the oxic adsorption (equation (10a)) decreased the MRP concentration in the pore water. In the sediment, inorganic and organic P concentrations were sensitive to the rate of organic P degradation but not to the

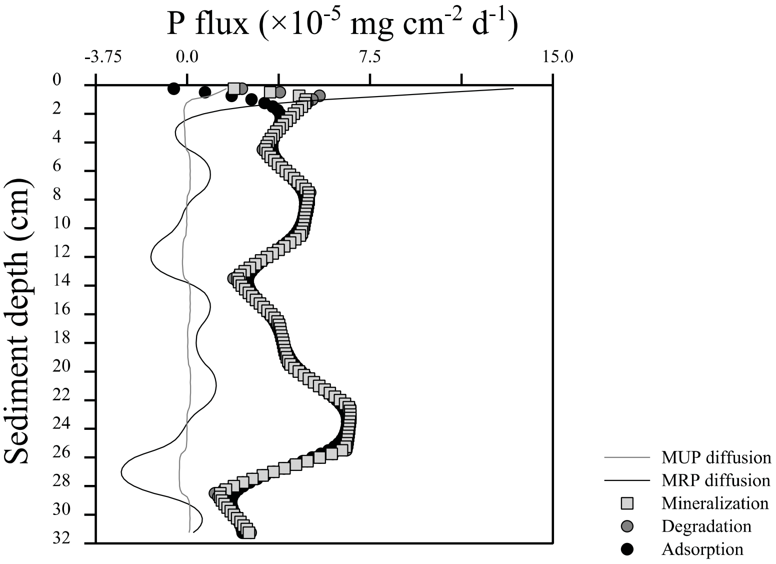

Figure 6. The averaged flux in Lake Kasumigaura sediment due to each process in the model: MRP adsorption, organic P degradation, MUP mineralization, MRP diffusion, and MUP diffusion.

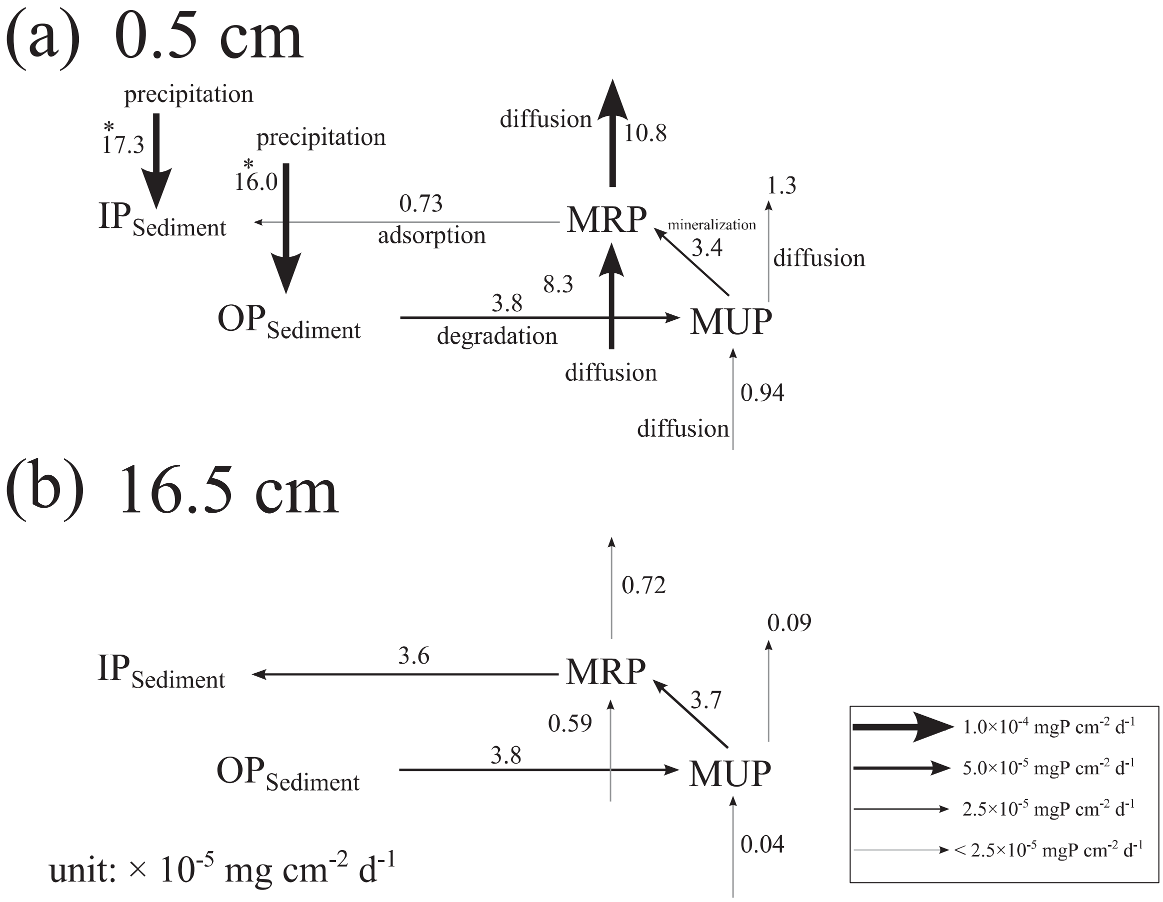

Figure 7. Results of the numerical mass-balance calculations (values $\times 10^{-5}$ mg cm^{-2} d^{-1}) for inorganic P in sediment particles (IP_{sed}), organic P in sediment particles (OP_{sed}), molybdenum-reactive P in pore water (MRP), and molybdenum unreactive P in pore water (MUP) at the sediment depths of (a) 0.5 cm and (b) 16.5 cm. The line widths represent the flux of P between compartments. The settling flux (*) was the average flux into the top 1 cm of sediment.

other parameters. Changes in the porosity also strongly affected the MRP and MUP concentrations in the pore water.

4. Discussion

4.1. Potential Mineralization of P in the Sediment of Lake Kasumigaura

The P flux from sediment into the overlying water usually accounts for a large proportion of P in the water column [*Perkins and Underwood*, 2001; *Søndergaard et al.*, 2003; *Spears et al.*, 2007]. In the case of Lake Kasumigaura, the P flux from the lake-bottom sediment accounts for 28.8% of the total P input into the water column [*Ministry of Land Infrastructure Transport and Tourism in Japan*, 2008]. The most striking aspect of the current study is that the MUP supply and its mineralization were major pathways that supplied MRP from the winter to the spring. Given the similar rates of change of inorganic and organic P in the sediment during these 4 months (supporting information Figure S2), degradation of organic P and adsorption of inorganic P were comparable during the observation period.

Phosphomonoesterase activity in the sediment of Lake Kasumigaura (from 0.32 to 5.54 μmol g^{-1} dw h^{-1}) was comparable to or greater than that in other lakes, such as 5.82 µmol g^{-1} dw h^{-1} in Lake Taihu [*Zhang et al.*, 2007] and 0.041–0.813 μmol g^{-1} dw h^{-1} in Lake Kinneret [*Hadas and Pinkas*, 1997]. Our result reflects the rapid hydrolysis of organic P (orthophosphate monoesters) into orthophosphate ions in pore water [*Feuillade and Dorioz*, 1992]. The high phosphomonoesterase activity in Lake Kasumigaura is reasonable because of the large proportion of labile organic P in the surface sediment [*Shinohara et al.*, 2012].

Table 2. Results of Sensitivity Analysis[a]

	Variable (Unit)	Simulated Values	MRP	MUP	IP_{sed}	OP_{sed}
Molecular size	*MW* (Da)	2,000	99.8	99.9	100.0	100.0
		5,000	99.9	99.9	100.0	100.0
		100,000	100.0	100.0	100.0	100.0
		150,000	100.1	100.1	100.0	100.0
Porosity	φ	0.95	**128.9**	145.8	99.3	99.5
		0.98	111.1	117.7	99.6	99.7
Adsorption	*V* (mg L^{-1} d^{-1})	Oxic	75.8	100.0	100.1	100.0
Settling rate	Settling (g m^{-2} d^{-1})	−30%	99.7	99.6	99.7	99.6
		−10%	99.9	99.9	99.9	99.9
		10%	100.1	100.1	100.1	100.1
		30%	100.3	100.4	100.3	100.4
Temperature	*t* (°C)	−1.00°C	98.2	101.1	99.6	101.1
		−0.50°C	99.1	100.6	99.8	100.6
		0.50°C	100.9	99.4	100.2	99.4
		1.00°C	101.8	98.9	100.4	98.9
Degradation	k_{degr} (days^{-1})	1.37×10^{-7}	**34.0**	**0.80**	**88.5**	**133.9**
		0.002	72.1	58.2	94.7	115.7
		0.006	116.1	123.9	103.7	89.3
		0.007	128.0	141.6	**106.9**	**79.8**
Mineralization	k_{min} (days^{-1})	0.22	100.3	**684.7**	99.5	100.0
		0.86	100.0	174.0	99.9	100.0
		1.80	100.0	83.5	100.0	100.0
		1.65	100.0	91.0	100.0	100.0
Resuspension rate	α	0.24	102.7	103.9	102.4	104.1
		0.40	101.9	102.8	101.7	102.9
		0.60	100.9	101.4	100.9	101.5
		0.72	100.4	100.6	100.3	100.6

[a] Bold values mark the most sensitive factor for each P species in the model. The simulated values of porosity, settling rate, and temperature are the difference from the default values.

Desorption of MRP from the sediment into the pore water is limited because the MRP concentration (Figure 3, 0.02–0.52 mg L^{-1}) was usually within the range of adsorption (Figure 4: >0.056 mg L^{-1} under oxic conditions, >0.117 mg L^{-1} under anoxic conditions). These results and the associated changes in the concentrations of P in the sediment and the pore water support our hypothesis that MUP in the pore water could be the source of MRP, and that the MRP produced from MUP could then be adsorbed onto the sediment.

4.2. Mass Balance of P Between the Sediment and Pore Water

The numerical results of the scenario analyses are consistent with our hypothesis. Simple diffusion (Scenario 1) did not satisfactorily describe the significant increases and decreases of the inorganic and organic P concentrations in the sediment from December to April. Scenario 1 was therefore inconsistent with the field observations. The adsorption rate equation (equation (10b)) in the simulation model indicates that MRP was adsorbed onto the sediment particles, but the model underestimated the observed values (Scenario 2). In contrast, the results for the model in which MRP is constantly supplied from MUP in the pore water (Scenario 3) best matched the observed values.

Because the diffusive flux of MUP is much smaller than the fluxes that result from degradation and mineralization (Figure 6), this result supports our hypothesis that mineralization is the dominant process for MUP, rather than diffusion. We attribute this low diffusive flux to the large molecular size of MUP, which may be high (35,000 Da) owing to the large contents of DNA, RNA, and phospholipids in the organic P; as a result, the large MUP molecules would not easily diffuse out of the pore water (e.g., $D_p = 7.80 \times 10^{-7}$ cm^2 s^{-1}; calculated by the Stokes-Einstein's relation (see supporting information SI 1.1)). Organic matter with a high molecular size is labile [*Amon and Benner*, 1994], and this makes MUP the dominant source of MRP in the pore water.

The simulation results based on Scenario 3 show that the major MRP pathway differs between the top 1 cm of the sediment and deeper layers (Figure 7). In the surface layer, the MRP mineralized from MUP diffuses into the water column; in contrast, most mineralized P in deeper layers is adsorbed onto the sediment particles. Information about how the sediment layers affect the release of P from the sediment into the overlying water is limited, but the results of our mass-balance model are consistent with those of *Kamiya et al.*

[2017], who showed that only the top 2 cm of the sediment affects the release of P from the sediment into the overlying water.

4.3. Sensitivity and Uncertainty

Among the parameters of the mass-balance model, we found that the rate of MUP mineralization and the rate of organic P degradation in the sediment particles strongly affect the MUP concentration (Table 2). In contrast, the rate of organic P degradation in the sediment and adsorption under oxic conditions strongly affect the MRP concentrations in the pore water: increased degradation and decreased adsorption will increase the MRP concentration. Our analysis suggests that the degraded MUP is rapidly hydrolyzed, thereby supplying MRP to the pore water. The adsorption of MRP could be regulated by both oxic and anoxic conditions. Overall, degradation of the organic P in the sediment should most strongly affect the concentrations of the various forms of P (MRP, MUP, and inorganic and organic P).

Porosity strongly affected both MRP and MUP in the pore water (Table 2). The vertical changes in porosity are slight (see supporting information Figure S1), but even a simulated 5% change in porosity increased MUP in the pore water by approximately 46% from the default value (Table 2). We did not monitor changes in the sediment porosity over time, but previous research suggests that porosity is changed by the macrobenthos [*Wheatcroft*, 2006]. Information about changes in the macrobenthos density in Lake Kasumigaura is limited, but the population of one macrobenthos taxon, the *Chironomidae* spp., is substantial [*Iwakuma*, 1992]. The model's ability to predict MRP and MUP tended to be worst at depths of 20–25 cm in the sediment (supporting information Figure S5), and this may result from insufficient data for changes in the sediment porosity over time. Thus, in future research, an additional equation should be developed to predict the porosity changes due to a range of factors, including the population of macrobenthos and compaction under the weight of the sediment.

One drawback of the model that we developed is how it handles the concentrations of MRP and MUP in the surface layer of the sediment. The model overestimated the rate of MRP release from the sediment into the water column: observed values ranged from 0.10 to 0.22 mg m^{-2} d^{-1}; simulated values averaged 1.34 mg m^{-2} d^{-1}. The MUP mass balance in the surface layer was also inconsistent with the observations. The simulated MUP concentration in the surface layer increased slightly from December to April, whereas the concentration decreased in the field observations. Thus, we cannot quantitatively evaluate the release of P from the sediment into the overlying water with the present model, although the observed rate is within the range reported in a previous study (MRP release rates ranging from 0 to 10 mg m^{-2} d^{-1}) [*Ishii et al.*, 2010]. This overestimate of the release rate from the sediment to the overlying water can be explained by three factors that we did not account for. First, changes in the concentrations of MRP and MUP are affected by enzymatic activity and the P compound composition [*Shinohara et al.*, 2012], but our model did not account for microbial effects, and particularly for the response of these organisms to oxic and anoxic conditions. The P compound composition of the settling matter is unclear, and could affect the rate of organic P degradation at the sediment surface (Figure 6). Second, we could not include spatiotemporal changes in some factors that affect P exchange between the sediment and the pore water, such as the ionic strength, the nitrate concentration, the mineral element composition (e.g., Fe, Al, Ca, and Mn), and the dissolved oxygen concentration [*Jensen and Andersen*, 1992]. *Penn et al.* [2000] found that a thin oxygenated layer at the top of the sediment greatly hampers the release of MRP from the sediment into the overlying water, but the depth of such layers in Lake Kasumigaura is not known. Further experiments with control of the dissolved oxygen concentration are needed to improve our model's ability to account for oxygenation conditions. The importance of redox conditions cannot be ignored, and in future research, it will be necessary to obtain more data on their effect on P mobility so that this effect can be incorporated in an improved model. Third, release of P from the sediment into the overlying water is affected by the thickness of the boundary layer, which is determined by the current velocity [*Nakamura and Inoue*, 1996; *Inoue and Nakamura*, 2012].

4.4. Environmental Implications

We used several approaches to clarify the origins of MRP in the pore water, and found that MUP was a key source. Once produced, MRP could be adsorbed onto the sediment particles in deep sediment (at depths >1.0 cm below the sediment surface). Because phytoplankton blooms (cyanobacteria) sometimes occur in the spring in Lake Kasumigaura, it seems likely that the release of P from the sediment could promote the blooms by contributing P, which is a limiting nutrient for their growth. The transformation of organic P in the winter is likely to be a key process in Lake Kasumigaura [*Shinohara et al*., 2017].

The importance of organic P in the sediment that we observed is also likely to be observed in other lakes where organic P in the sediment and pore water accounts for a large proportion of the P stock. Our finding is not unique; *Kamiya et al*. [2001] reported that organic P (MUP) could also be released from the bottom sediment in Lake Shinji (Shimane Prefecture, Japan), a brackish lake. Microbial mineralization of P is also a dominant process for orthophosphate production in the pore water of ocean sediment [*Goldhammer et al*., 2011]. Further investigation is warranted to clarify the role of organic P during the summer, when the redox potential decreases just below the sediment surface. In future research, it will also be necessary to study the redox potential in and above the sediment and how it changes seasonally so that these effects can be included in our model.

The major finding in the current study is that MUP concentrations are affected more by mineralization of MUP in the pore water than by diffusion. In the current study, we used a MUP to MRP mineralization rate (1.5 days^{-1}) higher than those used in other studies (e.g., 0.006 day^{-1}) [*Boers and Van Hese*, 1988]. However, our model provides that, given the mass balance between organic P in the sediment particles and MUP, use of this higher MUP to MRP mineralization rate in our model is consistent with the observed mass balance between organic P and MUP in sediment.

Further improvement of our model is still needed to simulate P concentrations in sediment. To improve the model, the flux from orthophosphate diesters to orthophosphate must be quantified because of the large amounts of orthophosphate diesters in the sediment in Lake Kasumigaura [*Shinohara et al*., 2012, 2017]. For the rapid hydrolysis of phosphomonoesters, orthophosphate monoesters can be supplied from orthophosphate diesters. Furthermore, the enzymatic activities should be changed by various factors, such as temperature, dissolved oxygen, and the concentrations of orthophosphate diesters and monoesters [*Ding and Sun*, 2005].

In summary, we evaluated the role of organic P in sediment particles and pore water by using field observations, incubations, and model simulations. Organic P in sediment particles is a potentially important source of MUP and MRP in the pore water in Lake Kasumigaura, even below 1 cm in the sediment. Because the molecular size of the MUP in the pore water is large, the release of MUP from the sediment into the overlying water is slow. Instead, MUP supplied from organic P in the sediment becomes a source of MRP in the pore water. Further investigation is required to estimate the amount of MRP released from the top 1 cm of the sediment into the overlying water so that this process can be incorporated into our model, because diffusion is likely to be a dominant process within this layer.

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