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Immobilization and Release Behavior of Phosphorus on Phoslock-Inactivated Sediment under Conditions Simulating the Photic Zone in Eutrophic Shallow Lakes

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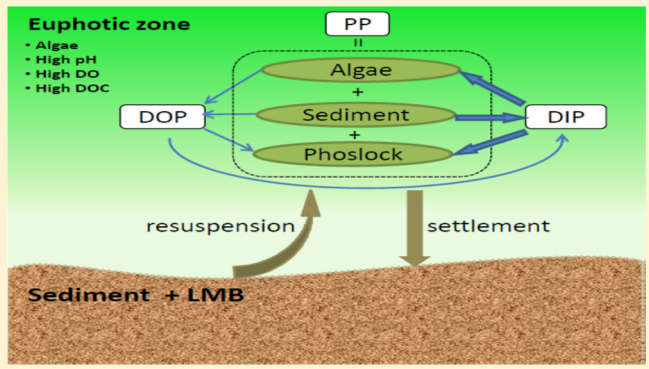
Supporting Information

ABSTRACT: Phosphorus-inactivating agents (PIAs) have increasingly been applied and extensively investigated to control internal phosphorus loading in lakes. However, little is known about the behavior of PIA-amended sediment in terms of phosphorus immobilization and release when the sediment is resuspended in the photic layer, whose environment differs from the lake bed. Lanthanum-modified bentonite (LMB) is a popular PIA product. In this study, the 33 day core incubation experiment under dark conditions showed that capping sediment with LMB efficiently decreased the concentration of total phosphorus, total dissolved phosphorus, and dissolved inorganic phosphorus (DIP) by 90, 87, and 99%, respectively. Resuspension into overlying water under light conditions at high pH, high dissolved organic carbon, and in the presence of algae significantly impedes the performance of LMB. However, the adoption of a higher LMB dose improved the performance, including a reduction in the phosphorus level and control of algal growth. The dynamics of the phosphorus migration when the LMB-inactivated sediment was resuspended into the photic zone mainly involves the release of DIP from the sediment and the uptake of DIP by algae and LMB. In conclusion, a higher dose is needed in the PIA (particularly Phoslock) application in shallow productive lakes where sediment resuspension occurs frequently.



1. INTRODUCTION

Although a number of nutrients are required for algal growth, phosphorus is widely recognized as the nutrient that regulates the production of algae in standing freshwater bodies such as lakes, ponds, and reservoirs.[1,2] Therefore, reducing the phosphorus level in surface waters is an important measure toward controlling algae overgrowth and the management of eutrophication. For this purpose, the external phosphorus supply and internal phosphorus loading release from sediment must be controlled.[3,4]

Phoslock, a lanthanum-modified bentonite (LMB) clay, was developed by the Commonwealth Scientific and Industrial Research Organization of Australia in the 1990s for lake restoration to control internal phosphorus loading.[5−7] Phoslock can strongly bind orthophosphate anions to form the mineral rhabdophane ($LaPO_4{\cdot}nH_2O$).[6] This mineral is very stable and resistant to weathering over geological time because phosphorus bound by La is retained under anaerobic conditions in the sediment (La is not sensitive to oxidation−reduction reactions and thus maintains stability under anaerobic conditions)[8,9] and over a pH range between 5.0 and 9.7.[8,10] Aging of rhabdophane may lead to the formation of monazite ($LaPO_4$), which is even more stable than rhabdophane.[11−13]

LMB has been applied to ∼200 water bodies across a wide geographic distribution.[10] Several field experiments have confirmed the effectiveness of LMB in binding phosphorus released from sediment. For instance, LMB application in Laguna Niguel Lake in California greatly decreased the total phosphorus (TP) and soluble reactive phosphorus by >80 and >95%, respectively, in the water column and reduced the cyanobacteria density from 33 300 to 1200 cells/mL on average.[14] Similarly, Spears et al.[15] analyzed the data obtained from 18 lakes over 2 years following the application of LMB and found that the concentrations of TP, soluble reactive phosphorus, and chlorophyll *a* decreased significantly (>62%), while the Secchi disk depth and the coverage of macrophytes increased significantly.

LMB can scavenge dissolved phosphorus from the water column during the settling process. Once settled onto the surface of the sediment bed, a layer composed of LMB at the sediment/water interface is formed, which can intercept the phosphorus diffused from the sediment to the overlying

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water.[16] However, physical disruptions or bioturbation can disturb the capping layer, and as a result, the LMB material can be buried vertically[17] or translocated horizontally.[18] This activity is particularly important in shallow lakes, which experience episodic resuspension of sediment driven by hydrodynamic processes that include wind-induced waves and current-induced turbulence.[19−21] Meis[22] found that, at 4 months post-application in the shallow eutrophic lake of Loch Flemington in the U.K., the sediment La concentration was significantly higher in the top 10 cm of the sediment compared to that observed under preapplication conditions, indicating that LMB can be mixed into the sediment 10 cm below the water/sediment interface.

Even when LMB has been buried in the surface sediment, its effectiveness toward the mitigation of internal phosphorus loading has not necessarily been lost, but instead, a new stage starts because LMB can still function as a phosphorus sink to capture phosphorus from pore water. Because phosphorus bound by LMB is stable, the sediment phosphorus in the releasable fractions may eventually become inactivated, contributing to the control of phosphorus release from the sediment.[23]

However, in addition to the damage to the evenly distributed capping layer, the disturbance can also cause the sediment and LMB to be resuspended into the photic layer of the overlying water, where enough light is present for photosynthesis to take place so that sunlight and carbon dioxide gas are converted into organic carbon (in phytoplankton) and oxygen gas. Due to the photosynthesis activity of algae, the environment in the photic layer differs from the lake bed; that is, the former has a generally high pH (it can exceed pH 10 during major phytoplankton blooms in poorly buffered systems),[3,23,24] high dissolved organic carbon (DOC),[25] high dissolved oxygen (DO), and algae present. Although phosphorus-inactivating agents (PIAs), including LMB, are increasingly being applied and extensively investigated to control internal phosphorus loading in lakes, little is known about how PIA-amended sediment behaves in terms of phosphorus immobilization and release when it is resuspended into the photic layer. Such knowledge is of utmost importance when considering the use of PIAs to control the internal phosphorus loading in large shallow eutrophic lakes where much sediment resuspension occurs frequently in the photic zone. Although a high DO concentration is not expected to influence the immobilization or release of LMB because of the insensitivity of La to oxidation−reduction conditions, high pH and a high DOC concentration may greatly influence the performance of LMB. In addition, the uptake/release of phosphorus by algae may further complicate the behavior of phosphorus in the photic zone in eutrophic shallow lakes.

The goal of this study was to investigate the dynamics of phosphorus migration and the efficacy of LMB to reduce the phosphorus level in overlying water by conducting experiments in which the sediment and LMB-amended sediment were repeatedly resuspended in water with algae and light radiation that mimic conditions of the photic zone. LMB is an important tool in phosphorus-management programs, and the results are thus useful in the planning for PIA (particularly Phoslock) application in shallow productive lakes.

2. MATERIALS AND METHODS

In this study, intact sediment core experiments were first performed to evaluate the efficacy of LMB for controlling internal phosphorus loading when the LMB was placed at the sediment/water interface without resuspension. Then, the phosphorus immobilization/release in the water overlying the sediment and the LMB-amended sediment were examined with resuspension. The results under dark conditions without algae and under light conditions with algae were compared to understand the influence of photic zone conditions (including high pH, high DO, high DOC, and the presence of algae) on phosphorus immobilization/release by LMB. The zero equilibrium phosphorus concentration (EPC_0) was measured to better understand the flux of phosphorus between water and sediment as influenced by LMB. Finally, the effect of pH in the presence of DOC was investigated to gain further insights into the behavior of phosphorus in the photic zone of eutrophic shallow lakes.

2.1. Materials. The LMB sample used in this study was provided by Shanghai Phoslock Water Solutions Ltd. On 5 May 2018, intact sediment cores (~20 cm) were extracted in clear acrylic tubes (7 cm in internal diameter and 60 cm in length) from a eutrophic pond located at 31°1′21″N, 121°25′30″E in Shanghai, China. The pond is a shallow water body with a total surface area of approximately 0.5 ha and an average depth of approximately 1.45 m. Further details on this pond have been reported by Fan et al.[26] Triplicate control and triplicate LMB treatment cores (six in total) were extracted. After extraction of the cores, the bottom of the cores was immediately sealed with screw caps, placed vertically in a plastic lattice frame, and transported back to the laboratory within 4 h of collection. A 100 L water sample was collected at the site and was passed through a 500-mesh sieve to remove zooplankton before laboratory incubation and pond water analysis. This stock pond water contained TP concentrations of 233 μg/L, total dissolved phosphorus (TDP) of 159 μg/L, and dissolved inorganic phosphorus (DIP) of 104 μg/L.

In addition to the cores, surface sediment (upper 5 cm) was also obtained for later laboratory uses, such as the measurement of the zero equilibrium phosphorus concentration (EPC_0), and to examine the effects of resuspension on phosphorus migration. For this purpose, sediment cores from five different locations and taken at a depth >10 cm were sampled with a clear acrylic tube 7 cm in internal diameter and 60 cm in length. The cores were extruded to a plate, and the top 5 cm was then retained. The sediment was thoroughly mixed, freeze-dried, and finally ground to pass through an 80-mesh (0.178 mm pore size) sieve. The TP concentration of the sediment was 1116 μg/g.

The colonial cyanobacterium *Microcystis aeruginosa*, a species that can form harmful algal blooms in many eutrophic freshwater environments in China, was used in this study. The original cyanobacteria sample was obtained from the culture collection of the Institute of Hydrobiology, Chinese Academy of Sciences. In our laboratory, the alga was continuously cultured in BG-11 medium in continuous light of 2000 lx at 25 °C, where it was maintained at log-phase growth.

2.2. Core Incubation Experiments. Cores were maintained in the dark at room temperature. A 1.05 L volume of the water sample was added to each tube, with care being taken not to disturb the sediment surface. The cores were then allowed to settle for a period of 24 h and LMB was then added to the cores of the LMB treatments using an LMB/releasable phosphorus mass ratio of 200:1, based on the releasable phosphorus content in the upper 5 cm of the sediment [loosely bound phosphorus (labile-P), reductant-soluble phosphorus

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(BD-P), metal-oxide adsorbed phosphorus (NaOH-P), and organic-bound phosphorus (Org-P)] quantified by sequential phosphorus extraction, as described in a previous article.[26] The LMB was added as a suspension to assure that it would be homogeneously distributed onto the sediment surface. After being allowed to stand for 48 h so that the LMB could settle, 100 mL of blue green algae medium (BG-11 medium) was added to maintain the same initial conditions as those used in our subsequent resuspension experiments in which BG-11 and algae were used. Thus, a water column depth of 30 cm was generated.

After being allowed to stand for another 24 h, the samples were used in 33 day incubation experiments. On days 0, 4, 8, 12, 16, 20, 26, and 32, the DO and pH of the overlying water were determined on site in the cores 15 cm below the water/air interface using a DO meter (model INESA JPB-607A, detection limit 0.3 mg/L) and a pH meter (Hach Sension+), respectively. A 60 mL water sample was collected 8 cm above the water/sediment interface using a syringe to analyze the TP, TDP, and DIP using the molybdenum blue colorimetric method.[27] The water sample was digested with potassium persulfate solution prior to the TP analysis. For measurement of the TDP, the water sample was filtered through a 0.45 μm cellulose acetate membrane filter and then digested with potassium persulfate solution. DIP analysis was directly carried out using the filtrate. After sampling, 60 mL of fresh pond water was added to the tubes to maintain a constant volume of overlying water. Because the sampling of overlying water and the replacement with stock pond water during the period of the incubation were performed, cumulative data corrections to the concentration of all P parameters were done using eq 1

$$C_{ic} = C_i + \frac{\sum_{i=2}^{n} (C_{i-1} - C_s)V_i}{V} \quad (1)$$

where C_{ic} is the corrected phosphorus concentration at the sampling time i; C_i and C_{i-1} are the determined phosphorus concentrations (mg/L) of overlying water at sampling time i and $i-1$, respectively; C_s is the phosphorus concentration in stock pond water; V_i is the volume of stock pond water replaced after each sampling to render a constant total volume of overlying water; n is the total sampling time; and V is the total volume of overlying water. C_{ic} is the same as C_i when $i = 1$ because the first sampling (on day 0) was done before the supplementation with fresh pond water.

2.3. Zero Equilibrium Phosphorus Concentration. The EPC_0 is the critical phosphorus concentration at which neither adsorption (flux from water to solid) nor release (flux from sediment to water) occurred.[28,29] The adsorption isotherm of phosphate at low initial phosphorus concentrations (<300 μg/L) was measured to obtain EPC_0. Forty milliliters of KH_2PO_4 solutions at different concentrations ranging from 0 to 300 μg P/L were placed into 50 mL centrifuge tubes. After the addition of 1 g of freeze-dried sediment with or without LMB amendment (the LMB/releasable phosphorus mass ratio was 200:1 or 400:1, denoted as LMB and LMB × 2, respectively), the tubes were shaken at 25 °C for 48 h. Preliminary tests confirmed that this adsorption time was sufficient to attain equilibrium under oxic conditions (final DO ~4 mg/L). The suspension was then centrifuged, and the phosphorus concentration in the supernatant was determined. The amount of adsorbed phosphorus was calculated from the difference between the phosphorus concentration before and after the adsorption process.

2.4. Resuspension Experiment. To evaluate the efficiency of LMB to reduce the phosphorus level in water when the sediment was repeatedly disturbed in the photic zone, a resuspension experiment was set up with the following six treatments: (1) sediment only, (2) sediment + algae, (3) sediment + LMB, (4) sediment + LMB + algae, (5) sediment + LMB × 2, and (6) sediment + LMB × 2 + algae. The experiments were conducted in triplicate at room temperature in beakers 9.5 cm in internal diameter and 20 cm in height using 1.05 L of pond water (corresponding to the volume of the 30 cm water column used in the core incubation experiments) and 11.3 g of sediment (corresponding to the amount of 0.3 cm surface sediment used in the core incubation experiments). This mimics the resuspension of 0.3 cm of surface sediment in the overlying water. For (3) and (4), the LMB/releasable phosphorus mass ratio was 200:1, based on the releasable phosphorus content in the sediment. However, an additional triplicate LMB treatment using an LMB/releasable phosphorus mass ratio of 400:1 was carried out for (5) and (6) to test whether the phosphorus release and growth of algae could be controlled using a higher LMB dose (as much as 2-fold). For treatments (2), (4), and (6), 100 mL of cultured *M. aeruginosa* (the concentration of chlorophyll *a* was 468 μg/L) in BG-11 medium was added (the initial chlorophyll *a* concentration was 48 μg/L), whereas for treatments (1), (3), and (5), 100 mL of BG-11 medium without algae was added to maintain the same solute concentration in the water sample. In addition, treatments (1), (3), and (5) were kept under dark conditions, whereas for treatments (2), (4), and (6), a lamp was used for each beaker to generate continuous light of ca. 500 lx at the water/air interface (the temperature under the lamps was only slightly (0.6 °C on average) higher than that under the dark). After the samples had been allowed to stand for 72 h, the 33 day resuspension experiments were conducted. On days 0, 4, 8, 12, 16, 20, 26, and 32, the DO and pH were measured on site at 10 cm below the water/air interface. Then, 60 mL of water was withdrawn for the determination of TP, TDP, DIP chlorophyll *a*, and DOC concentrations of the overlying water. After supplementation with 60 mL of fresh pond water, the sediment with or without LMB was resuspended. Phosphorus concentrations were corrected according to eq 1. Chlorophyll *a* was measured according to standard methodology,[27] whereas the DOC was measured using a CHNOS elemental analyzer (model Vario ELIII) after the water had been filtered through a 0.45 μm membrane filter. The resuspension was performed to produce a fully mixed state using a stirrer operated at 300 rpm for 15 min, with the blade of the stirrer positioned 8 cm above the sediment/water interface.

2.5. Effect of pH. The effect of pH on the binding of phosphate was evaluated in 50 mL centrifuge tubes. To ensure the accurate addition of a small amount of LMB, a stock suspension was first prepared by continuous mixing of 2.48 g of LMB with 1 L of deionized water. Subsamples of 1 mL were taken from this suspension and transferred to centrifuge tubes containing 40 mL of phosphate solution (with a concentration of 620 μg/L) containing humic acid (a widely used model DOC compound, which was supplied by Aldrich Chemical in the form of sodium salt, and had been extracted from waters draining an open-pit mine in Oberhessen, Germany) and 0.01 M NaCl (used as the background electrolyte). This dose

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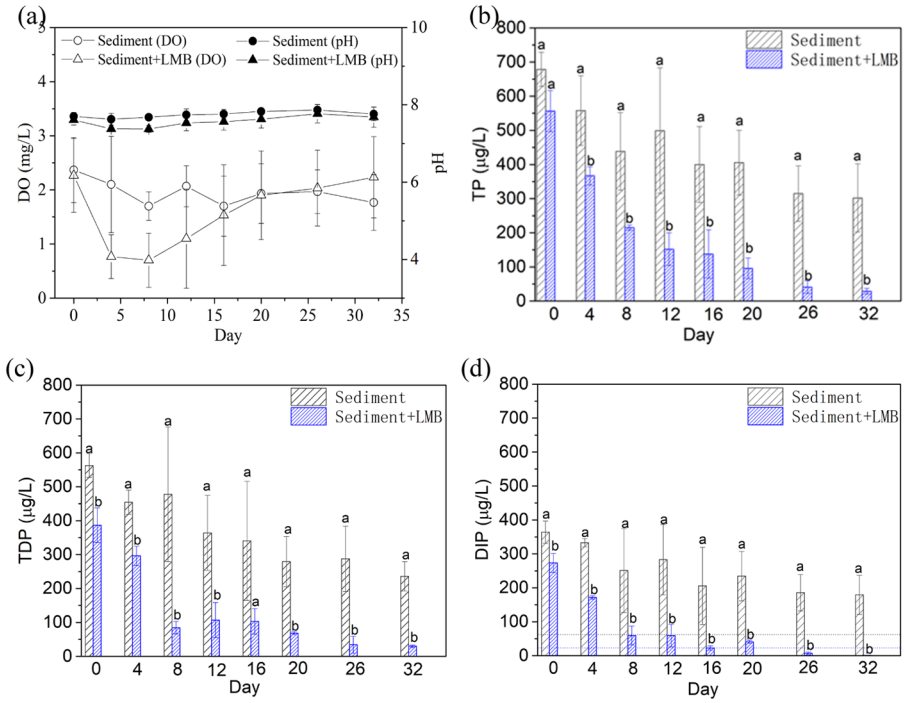

Figure 1. Variations of pH and DO (a), TP (b), TDP (c), and DIP (d) concentrations in the water column overlying sediment and LMB-amended sediment in the core incubation experiment. Error bars represent the standard error of the mean (n = 3). Means with different letters indicate a significant difference (Student−Newman−Keuls multiple range tests, $p < 0.05$). The black and blue dotted lines represent the EPC_0 for sediment and sediment-LMB × 2, respectively.

Table 1. Changes in the Concentrations of TP, TDP, and DIP and the Concentrations of Different P Species before and after the Core Incubation Experiment (Unit: μg/L Except Where Otherwise Specified)[b]

	sediment			sediment + LMB		
P species	day 0	day 32	decreased by (%)	day 0	day 32	decreased by (%)
TP	679 ± 50	302 ± 100	56	557 ± 60	29 ± 8	95
TDP	562 ± 35	235 ± 43	58	387 ± 51	30 ± 3	92
DIP	364 ± 33	179 ± 57	51	273 ± 28	1 ± 1	100
DOP[a]	198	56	72	114	29	75
PP[a]	117	67	43	170	−1	100

[a]Calculated from the difference between the TDP and DIP for DOP and the difference between the TP and TDP for particulate phosphorus (PP), respectively. Therefore, the standard deviation was not given. [b]The plus and minus signs indicate the standard deviation.

corresponds to an LMB/P mass ratio of 100:1. The concentration of humic acid was 20 mg/L, which represents a DOC concentration of ∼10 mg C/L in water equilibrated with sediment or LMB-amended sediment without algae (the experiments of Section 2.4). The suspensions were adjusted to attain the desired pH ranging from approximately 5.5 to approximately 10.5 by the addition of 0.1 M HCl and NaOH. After being shaken for 48 h at 25 °C at 180 rpm in the thermostatic chamber (model TS-2102C), the suspensions were filtered and the phosphate concentration of the filtrates was determined. The amount of phosphate adsorbed was calculated based on the difference in the P concentration before and after the adsorption. The pH of the equilibrium solution was also measured using a Hach Sension+ pH meter. Blank tests, which did not contain LMB, were also carried out. Experiments were performed in triplicate.

2.6. Statistical Analysis. Data were analyzed using one-way analysis of variance, followed by means testing between treated groups and the control and/or between different treated groups using the Student−Newman−Keuls multiple range tests. Homogeneity of variance was tested using Bartlett's test. Statistical analysis was performed using the Statistical Analysis System (SAS 8.2; SAS Institute, Cary, NC). All significance levels mentioned in the text are $p < 0.05$.

3. RESULTS

3.1. Core Incubation Studies without Resuspension. The pH of the water in the untreated cores and cores treated with the modified clay remained at a relatively constant value, fluctuating between 7.4 and 7.8 throughout the 33 day incubation period (Figure 1a). The DO concentration of the water column was low, but oxic conditions were maintained, and the DO was not depleted (ranging from 0.8 to 2.5 mg/L). No substantial difference was observed in the DO concentration between the untreated and LMB-treated cores (Figure 1a).

The phosphorus concentration in water showed a gradual decrease over the course of the experiment for both the untreated and treated cores (Figure 1b−d). The reduction in the concentration of TP, TDP, and DIP in the water overlying the LMB-capped sediment reached 95, 92, and 100%,

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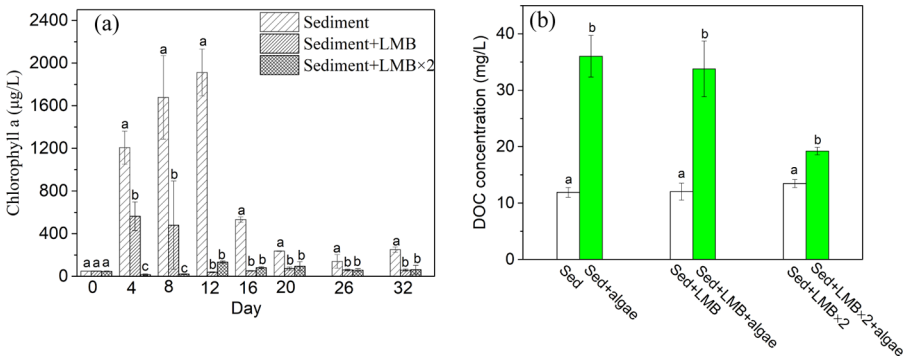

Figure 2. Variation in the chlorophyll *a* concentration in water overlying sediments untreated or treated with LMB at different doses during the 33 day resuspension experiment (a); comparison of DOC concentration in water overlying sediment untreated or treated with LMB at different doses with or without algae during the 33 day resuspension experiment (b). Sed denotes sediment. Data are presented as the mean value and standard deviation of triplicate experiments. Means with different letters indicate a significant difference (Student−Newman−Keuls multiple range tests, $p < 0.05$).

respectively, after the incubation period. At day 32, the concentrations of TP, TDP, and DIP were as low as 29 ± 8, 30 ± 3, and 1 ± 1 μg/L, respectively (Table 1).

Capping with LMB significantly reduced the phosphorus concentration in the overlying water at each sampling time ($p < 0.05$). Nevertheless, the reduction was increased with the incubation time. At day 32, the concentrations of TP, TDP, and DIP were reduced by 90, 87, and 99%, respectively, in the presence of LMB.

3.2. Zero Equilibrium Phosphorus Concentration. The EPC_0 of the original and LMB-amended sediments was measured using the adsorption behavior of phosphate at a low initial concentration (<300 μg/L) (Figure S1). The EPC_0 was calculated as the initial phosphorus concentration at which the adsorption capacity = 0 on the linear portion of the adsorption curve (relationship between the amount of adsorbed phosphate and the initial phosphate concentration). Linear regression analysis indicated that the data were well fitted to the adsorption curve (R^2 exceeded 0.999 for both the original and LMB-inactivated sediments). The EPC_0 was estimated as 62, 33, and 23 μg/L for the original sediment, sediment-LMB, and sediment-LMB × 2, respectively. Thus, for the upper oxic zone of the sediment, the addition of LMB lowered the EPC_0 value and thus reduced the risk of phosphorus release from the sediment, changing the sediment from a phosphorus source to a phosphorus sink.

3.3. Resuspension Studies. The growth of algae was controlled by the presence of LMB (Figure 2a). On average, the chlorophyll *a* concentration was 750, 171, and 64 μg/L for sediment, sediment-LMB, and sediment-LMB × 2, respectively, during the course of the experiment. Algal blooms developed rapidly in the water overlying the sediment or sediment-LMB. The peak chlorophyll *a* concentration was 1912, 393, and 133 μg/L for sediment, sediment-LMB, and sediment-LMB × 2, respectively.

Even without algae present, the water samples contained 12−14 mg/L of DOC, which did not vary with the addition of the LMB (Figure 2b). The pond water originally had this DOC concentration. Proliferation of algae considerably increased the DOC content, which was much higher in the sediment or sediment-LMB samples than in the sediment-LMB × 2 sample, which corresponds to the difference in chlorophyll *a*.

Under dark conditions, the pH of water overlying the sediment with or without the modified clay during the whole course of the resuspension experiment was relatively constant, fluctuating between 7.7 and 8.0 (Figure S2). The presence of algae under light conditions generally increased the pH, but the pH varied largely at different sampling times depending on the growth state of the algae. For instance, in water overlying sediment or sediment-LMB, the pH exceeded 9.0 during the initial stage when the outbreak of algae with high chlorophyll *a* concentration was recorded (Figure S2). On average, the pH followed the order: sediment (8.9) > sediment-LMB (8.7) > sediment-LMB × 2 (8.4), which was in agreement with the growth state of the algae (Figure 2).

The variation in DO followed the same pattern as the pH (Figure S2). A significant correlation between DO and pH was confirmed, with R^2 values of 0.953, 0.825, and 0.897 for sediment, sediment-LMB, and sediment-LMB × 2, respectively ($p < 0.05$). Thus, the growth of algae also determined the DO level, with a high chlorophyll *a* concentration that corresponded to the high pH and high DO due to the photosynthesis of algae.

Under dark conditions without algae, the presence of LMB greatly decreased the levels of TP, TDP, and DIP in the water during the resuspension experiments (Figure 3 and Table 2). On average, the concentrations of TP, TDP, and DIP were reduced by 90, 91, and 97%, respectively, in the presence of LMB. Although the difference in the concentration of each phosphorus species between the two LMB treatments was small, increasing the dose twofold reduced the phosphorus concentrations further, resulting in a decrease of 93, 97, and 100% for TP, TDP, and DIP, respectively.

Under light conditions with algae, the concentrations of TP, TDP, and DIP followed the same order: sediment ≫ sediment-LMB> sediment-LMB × 2 (Table 2, Figures 3 and S3). However, the presence of algae under light conditions significantly decreased the binding efficiency of LMB to phosphorus. On average, the concentrations of TP, TDP, and DIP were reduced by 66, 60, and 74%, respectively, in the presence of LMB and by 70, 80, and 100% with LMB × 2.

However, the presence of algae significantly increases the TP concentration in pond water overlying either sediment or sediments amended with LMB (Figure S3). In fact, most TP exists as particulate phosphorus (PP) in the presence of algae. This shows the accumulation of phosphorus as PP because of the assimilation and storage of phosphorus by the algae. In contrast, in the presence of algae, the concentrations of TDP

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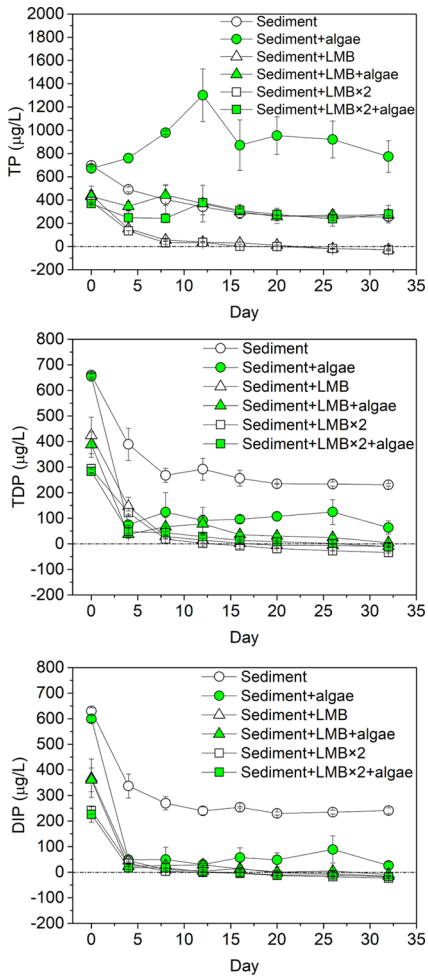

Figure 3. Changes in TP (upper), TDP (middle), and DIP (lower) concentrations in pond water overlying sediment and LMB-amended sediment in the 33 day resuspension experiment. Presented data are mean value and standard deviation of triplicate experiments. The slightly negative data of the phosphorus concentrations at longer incubation time, calculated using eq 1, were due to the higher phosphorus concentration in the stock pond water than that in the water overlying the cores.

and DIP in the water overlying the sediment decrease significantly (Figure S3). The decrease in TDP can be largely explained by the reduction in the DIP concentration. The TDP and DIP for water overlying the LMB-treated sediments were low, but a slight and overall significant increase in TDP in the presence of algae was observed (Figure S3).

3.4. Effect of pH on the Phosphorus Uptake by LMB.

At neutral pH, the adsorption capacity of phosphate by LMB was high (Figure 4). The phosphorus-binding ability of LMB decreased in solutions with the increase in the pH. For instance, at pH ∼ 9, the adsorption capacity was reduced by 31% when compared with the value at pH of ∼6.

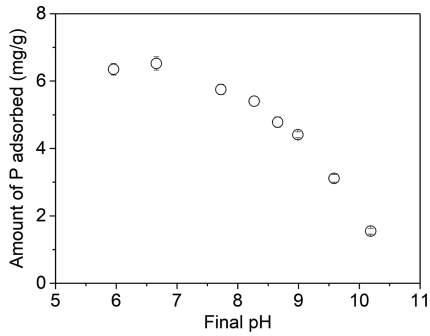

Figure 4. Effect of pH on the adsorption of P from water by LMB.

4. DISCUSSION

An examination of the dynamic variations in TP, TDP, and DIP allows the behavior of the different phosphorus species in water to be investigated. In addition to the directly measured DIP, the PP (the difference between TP and TDP) and dissolved organic phosphorus (DOP, the difference between TDP and DIP) can also be estimated. The concentrations of these different phosphorus species at day 0 and day 32 in the core studies conducted under dark conditions are listed in Table 1. The initial DIP concentrations at day 0 in the cores with or without LMB were much higher than their corresponding EPC_0. Therefore, the gradual decline in the DIP concentration over the course of the experiment was not surprising because adsorption (flux from water to solid) will take place when the phosphorus concentration exceeds the EPC_0.[29−32] At day 32, the DIP concentration in water overlying the sediment was still much higher than the EPC_0, whereas it reached a concentration well below the EPC_0 for the cores with LMB-capped sediment (Figure 1d). The former can be interpreted as resulting from the static conditions that were retained during the core incubation period, whereas the EPC_0 was measured under fully mixed conditions. Hence, the DIP in water in the cores has to diffuse downward into the sediment below the sediment/water interface for phosphorus adsorption, which takes time compared with the conditions used to measure the EPC_0. However, in the case of the cores with the LMB-capped sediment, this low DIP concentration can be

Table 2. Average P Concentrations of TP, TDP, and DIP during the Course of the 33 day Resuspension Experiment (Excluding Day 0) (Unit: μg/L)[b]

treatment	TP	TDP	DIP	DOP[a]	PP[a]
sediment	329 ± 38	272 ± 25	258 ± 16	14	57
sediment + alga	937 ± 136	97 ± 35	50 ± 27	47	840
sediment + LMB	34 ± 8	24 ± 11	7 ± 7	17	10
sediment + LMB + alga	322 ± 71	39 ± 15	13 ± 8	26	283
sediment + LMB × 2	22 ± 3	8 ± 6	(−3) ± 2	11	14
sediment + LMB × 2 + alga	281 ± 50	19 ± 9	(−1) ± 6	20	262

[a]Calculated from the difference between TDP and DIP for DOP and the difference between TP and TDP for PP, respectively. Therefore, the standard deviation was not given. [b]The plus and minus signs indicate the standard deviation.

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attributed to LMB forming a capping layer, and thus, the DIP can directly interact with "pure" LMB, which differs from the conditions used for the EPC_0 measurements, where phosphorus interacts with a mixture of sediment and LMB.

In addition to DIP, both the PP and DOP also decrease significantly after the core incubation period for both untreated and LMB-treated sediment. The reduction in PP can be attributed to the settlement of fine particles under static conditions without resuspension, while the decrease in DOP may be ascribed to the adsorption by inorganic solid particles (sediment and LMB) and its decomposition by bacteria. It appears that the existence of LMB promotes the settling of fine particles, leading to a much greater reduction in the PP content.

Importantly, capping with LMB without disturbance and in the absence of algae in the core studies greatly reduced the phosphorus level in the water. The mechanism of how LMB controls the internal phosphorus loading involves the removal of dissolved phosphorus from the water column by LMB and the interception of phosphorus during the diffusion of phosphorus from the sediment to overlying water due to the formation of a reactive LMB barrier at the sediment/water interface after settling.[16,23,33] Whether the LMB capping promotes anoxia and release of more DIP/DOP is important. Therefore, static LMB cappings must be able to deal with this situation. The effectiveness to trap released phosphorus depends on the phosphorus-uptake capacity and the magnitude of phosphorus flux. Calculations indicate that the capacity of LMB for phosphorus capture was reduced slightly (<1%) even when the phosphorus in the water column was completely stripped by LMB. Thus, the potential of LMB to intercept phosphorus was high. In addition, a low DIP level in the overlying water will increase the concentration gradient between the water column and the sediment, which will induce a greater diffusion flux. Therefore, the interception effect would be significant after day 26 when the DIP in water overlying the LMB-amended sediment was low (<3 μg/L); consequently, the diffusion of phosphorus from the sediment toward the overlying water would be high.

In our resuspension studies conducted under dark conditions without algae, the change in the phosphorus concentration in the water was similar to the behavior observed in the core incubation studies. However, under light conditions with algae, the solution physicochemical conditions were substantially different and characterized by high pH and high DO and DOC concentrations compared with those values observed under dark conditions without algae (Figures 1a, S2, and 2). The high pH and high DO conditions are attributed to the photosynthesis by the algae, whereas algae-derived dissolved organic matter arises extracellularly via metabolic excretion and intracellularly via the autolysis of cells or death from an external factor (e.g., virus attack) in aquatic and artificial ecosystems.[25] The nature of algae-derived dissolved organic matter is very complex, but its major fractions include carbohydrates and proteins[25,34] and humic substances.[35,36]

Under alkaline conditions, the adsorption of phosphorus by LMB was hindered (Figure 4). At the same time, phosphorus bound to metal oxides such as iron and aluminum oxides can be released from the sediment into water under alkaline conditions.[24,37] In addition, a significant negative effect of dissolved organic carbon (DOC) on the sequestration of phosphorus by LMB also has been previously reported.[15,38,39] Therefore, one would expect a much higher DIP concentration under light conditions in view of the pH and DOC concentration. Nevertheless, our results show that the DIP concentration was much lower under light conditions for sediment when compared to that observed under dark conditions (Table 2). For LMB-amended sediments, the DIP concentration was very low under both light and dark conditions (Table 2). The reason the DIP concentration remained low in pond water under light conditions, in spite of the high pH and high DOC concentration, was likely because of the rapid algal uptake. In fact, with the bloom of cyanobacteria, the DIP concentration decreased sharply from day 0 to day 4 in the water overlying the sediment (Figure 3). In water overlying the LMB-amended sediment, the uptake by both algae and LMB resulted in an even greater reduction in the DIP concentration (Figure 3). Therefore, because of the depletion of DIP, algae did not grow well over a long period for sediment or sediment-LMB or during the whole incubation period for sediment-LMB × 2 (Figure 3). As the DIP concentrations were maintained below the EPC_0 of the sediments due to the rapid phosphorus uptake by algae, the release of phosphorus may have been promoted.[29] Therefore, the combination of uptake by algae and LMB under resuspension and light conditions acts as a mechanism for pumping phosphorus out of the sediment.[40] Similarly, many studies have reported an increase in the TP concentration following natural or experimental sediment resuspension events in lakes, but have shown no or only weak evidence for an increase in the DIP concentration.[41−44] They also explained the increase in TP by the increase in the suspended solids and the lack of change in the DIP concentration by the rapid uptake of phosphorus by bacteria and algae, especially in phosphorus-limited systems. In addition, because heterotrophic bacteria can take up phosphorus and because the pond water had so much organic matter, the role of these bacteria in the dark experiments would be important.

The dynamics of phosphorus migration when LMB-amended sediment was resuspended in the photic zone is shown schematically in Figure S4. To analyze the phosphorus flux, the average concentrations of PP, DOP, and DIP were estimated for the resuspension experiment (Table 2). The presence of algae resulted in a significant decrease in the DIP concentration, but a slight increase in DOP, suggesting that a large DIP flux had occurred from water to algae, and a small DOP flux, from the algae to water. Furthermore, the presence of the LMB causes a significant decrease in the DIP concentration, but the change in the DOP was small, implying that a large DIP flux and very small DOP flux occurred from the water to the LMB. An additional incubation experiment (data not shown) indicated that the DIP concentration in water overlying sediment without LMB and algae, but with the pH adjusted to ~9.5, was as high as 420 μg/L, whereas the DOP level was as low as 50 μg/L. This suggests that a substantial net DIP flux and a negligible DOP flux occurred from the sediment to the water. Consequently, the dynamics of the phosphorus migration when the LMB-inactivated sediment was resuspended into the photic zone mainly involves the release of DIP from the sediment and the uptake of DIP by algae and LMB (Figure S4).

Under light conditions in the presence of algae, the PP concentration was high when compared with those observed under dark conditions without algae. After each resuspension event, the beakers were left to stand for at least four days to

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allow the settling of the solids. It is possible that there was still a small amount of suspended fine particles in the water. However, as resuspension events were induced under both light and dark conditions, the difference in the PP concentration between them can be attributed to the phosphorus in the algae. Therefore, the algae act as a phosphorus sink in the water column in the short term. However, it should be pointed out that in the long term, the phosphorus stored in the algae also functions as a source of DIP in water because the algae settled into sediment will become a part of the organic phosphorus fraction, which is releasable.[14,18,45] On the other hand, the phosphorus fixed by LMB occurs mostly as HCl-P, which is stable under common lake conditions.[14,29,46,47] Therefore, LMB can control the bloom of algae by reducing the phosphorus level in water and by fixing phosphorus in a stable form. However, the results of this study indicate that a higher dose of LMB may be required to simultaneously control the growth of algae in addition to sustaining a low phosphorus concentration level in shallow lakes where resuspension events are common.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b04093.

Relationship between the initial P concentration and the amount of P adsorbed on the original and LMB-amended sediments, the variations of pH and DO in water overlying sediment in the light condition with suspension, the statistical comparison between light vs dark in the resuspension experiments, and the dynamics of phosphorus migration when LMB-amended sediment was resuspended into the photic zone (Figures S1−S4) (PDF)

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Notes

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