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Effect of Combined Application of Lanthanum-Based Capping Material and Biochemical Oxidant on Control of Internal Phosphorus

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Abstract: In situ capping and biochemical oxidation are two of the most commonly used methods for internal phosphorus (P) control, but there are few studies on the combined use of these two methods. In this study, two lanthanum (La)-based materials, La-modified bentonite (LMB) and the La-modified attapulgite and chitosan composite (LMA&C), were combined with calcium nitrate (CN) to investigate the effect on sediment P control. Results showed that SRP removal rates by LMB+CN and LMA&C+CN were much higher than that by LMB, LMA&C and CN alone. LMB+CN and LMA&C+CN decreased DGT-labile P flux both in overlying water and surface 65 mm sediment, while LMB and LMA&C had an effect only on overlying water and surface 10~40 mm sediment, and CN was effective only on sediments. LMB and LMA&C transformed $\text{NH}_4\text{Cl-P}$, BD-P, NaOH-SRP and NaOH-NRP in surface 20 mm sediment to HCl-P and Residual-P on day 60. CN transformed NaOH-SRP and NaOH-NRP to BD-P, resulting in the increase in $\text{NH}_4\text{Cl-P}$. LMB+CN and LMA&C+CN sequestered P in the surface 20 mm mainly as HCl-P and Residual-P, and mainly as BD-P in -20~-60 mm. Results indicate that the combination of capping by La-based material and oxidation by CN is a promising method for sediment P control.



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Keywords: internal phosphorus; lanthanum-modified bentonite; calcium nitrate; sediment–water interface

1. Introduction

Lake eutrophication has become a global environmental problem, which has great impacts on water ecological health, daily life of watershed residents and economic development [1]. Phosphorus (P) is a limiting nutrient element for algae growth and is a major factor leading to lake eutrophication and algal bloom [2]. Even though external loading has been completely controlled, the release of internal P can sustain the development of lake eutrophication for many years [3].

In situ capping and biochemical oxidation are two of the most commonly used methods for internal P control. In situ capping is to use some immobilizing agents to form a physical barrier on the sediment surface or inactivate active P to stable forms [4]. Among capping agents, lanthanum (La)-based materials are considered as very promising capping agents, especially La-modified bentonite (LMB, known commercially as Phoslock®) [5]. LMB has an La concentration of ca. 5%, and it can react with phosphate to form rhabdophane [6]. Previous studies have proved that LMB could effectively control the release of internal P from sediments at laboratory, mesocosm and whole-lake scales [1,7,8]. In situ biochemical oxidation by nitrate has long been considered as a cost-effective method for sediment remediation [9]. Nitrate is easily soluble in water, so it can easily access deep sediment, forming Fe hydroxide, which adsorbs SRP. At present, studies have proved the effectiveness of nitrate on organic pollution degradation [10,11], black and odor removal [12,13] and internal P control [14,15]. However, some studies have found that nitrate

denitrification produces gas and increases sediment porosity [16]. Studies have shown that nitrate might not be effective on P in overlying water and might even promote the sediment P release by stimulating the growth of phytoplankton [17,18]. Sun et al. [19] and Gao et al. [20] showed that the combination of LMB and calcium nitrate (CN) overcame the shortcoming of the sole use of LMB or CN, and the combined use achieved the dual effect of deep sediment P immobilization and surface sediment P blockade. Previous studies on the combined use of in situ capping and biochemical oxidation have focused on the removal effect on mobile P in water and sediments but have not investigated the transformation of P forms. The study of the transformation of P forms can further evaluate the control effect, clarify the passivation mechanism and illustrate the feasibility of in situ technology. In addition, only one successful case cannot prove the universality of La-based materials, thus it is necessary to study more combined cases of La-based materials and CN.

Chitosan is a low-cost, nontoxic, biodegradable and biocompatible polymer, and it has a high density of amino groups that give it a positive charge, which can adsorb phosphate in water [21]. Using the composite of La-based material and chitosan as a capping agent is a promising method [22]. In this study, a sediment simulation experiment was conducted to investigate the effects of the combined use of two La-based materials, LMB and the composite of La-modified attapulgite and chitosan (LMA&C), and CN on the control of internal P. Rhizon samplers, diffusive gradients in thin films (DGT) technology and P sequential extraction method were used to investigate the variations in soluble reactive P (SRP), two-dimensional DGT-labile P, and P forms. The effect of different treatments on internal P control was compared, and the mechanisms involved were explored.

2. Materials and Methods

2.1. Materials and Sample Collection

LMB with about 5% La was provided by Shanghai Fengsile Water Treatment Technology Co., Ltd. (Shanghai, China). CN ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) of analytical reagent grade was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Raw attapulgite was collected from Xuyi County in Jiangsu Province. Chitosan (85% deacetylated) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The preparation of LMA&C is similar to that of Xu et al. [22] and Zhang et al. [23]. Firstly, a certain mass of chitosan was dissolved in oxalic acid solution, then a certain mass of attapulgite was added to lanthanum nitrate solution, and finally, the two solutions were mixed. The mass ratio of La, attapulgite to chitosan was about 1:5:1. Then, the pH of the mixture was adjusted to 10 with 2 M of NaOH solution. After 24 h, the mixture was washed with pure water until neutral. After discarding the supernatant, the precipitation was put into the oven for drying at 70 °C.

Water and sediment samples were collected from the Nanfei River estuary, the main inlet river of Lake Chaohu in China. On 26 December 2018, lake water was collected from the sampling site using a Perspex container. DO and pH of the water of the sampling site were 2.70 mg/L and 7.10, respectively. SRP and $\text{NH}_4^+\text{-N}$ of the water were 0.71 and 6.57 mg/L, respectively. Several intact sediment cores were collected using a perspex core sampler with an internal diameter of 11 cm or 8.4 cm. The bottom of the column was sealed with a rubber plug. The height of the overlying water was about 12 cm. Sediment cores were kept upright and transported to the laboratory within 4 h after collection.

2.2. Experimental Core Microcosm Setup

Column sediments were divided into the control, LMB, LMA&C, LMB+CN and LMA&C+CN groups. Rhizon samplers were installed on the columns with an internal diameter of 11 cm at depths of −5, −25, −50 and −80 mm (the minus denotes the position below the sediment–water interface (SWI)). Lake water was siphoned into the columns to supplement the overlying water loss. Then, all columns were incubated at 25 °C in a water bath before treatment. Then, in the LMB group, LMB was added to the water with a dosage of 0.21 g/cm²; in the LMA&C group, LMA&C was added to the water with a dosage of

0.07 g/cm²; in the CN group, CN solution prepared using lake water was injected into the sediment at a depth of −50 mm with a dosage of 30 g N/cm²; in the LMB+CN group, CN solution was firstly injected into the sediment at a depth of −50 mm with a dosage of 30 g N/cm², and then LMB was added to the water with a dosage of 0.21 g/cm²; in the LMA&C+CN group, CN solution was firstly injected into the sediment at a depth of −50 mm with a dosage of 30 g N/cm², and then LMA&C was added to the water with a dosage of 0.07 g/cm². All columns were incubated at 25 °C in a water bath for 60 days.

The pore waters were collected through Rhizon samplers before and after being treated for 8, 30 and 60 days for the analysis of SRP. After being treated for 8, 30 and 60 days, column sediments with an internal diameter of 8.4 cm were sliced into 2 cm intervals to a depth of 10 cm, and then the layered sediment samples were homogenized and freeze-dried for the fractional P extraction. On day 8, the AgI DGT was inserted into one of the columns for the imaging of DGT-labile sulfide flux. On day 60, the Zr-oxide DGT was inserted into one of the columns for the imaging of DGT-labile P flux. The DGT devices were removed after 24 h and then washed with deionized water.

2.3. DO Measurements by Planar Optode

The DO planar optode was prepared according to Li et al. [24]. Briefly, dissolve 10 mg of Platinum(II)5, 10, 15, 20-tetrakis-(2, 3, 4, 5, 6-pentafluorophenyl) porphyrin (PtTFPP), 20 mg of reference fluorophore coumarin C545 (C545T) and 500 mg of polystyrene in 10 mL of toluene. Then, coat the above solution evenly onto the surface of a transparent polyethylene terephthalate (PET) film. Next, coat a thin layer of DC3140 silicone rubber on the surface of the PET film. The silicone layer was further cured for 24 h in a hood.

The DO planar optode (length × width, 2 cm × 7 cm) was attached to the inner side of a rectangular plexiglass box (length × width × height, 10 cm × 10 cm × 25 cm). Some of the column sediments were sectioned at 2 cm intervals, homogenized, and re-placed into the box. All the boxes were incubated at 25 °C in a water bath before treatment. Then, the sediments were treated by different agents according to the method mentioned above. DO images were obtained by a charge-coupled device camera before and after being treated for 8, 30 and 60 days. DO profiles before treatment (0 day) in each group were used as a control.

2.4. Chemical Analysis

SRP was determined by the molybdenum blue method [25]. A sequential extraction method was used to extract different P forms according to Rydin et al. [26]. 1 M of NH₄Cl, 0.11 M of Na₂S₂O₄/NaHCO₃, 0.1 M of NaOH and 0.5 M of HCl were respectively used to extract NH₄Cl-P, BD-P, NaOH-P and HCl-P. NaOH-SRP and NaOH-TP were measured respectively after the filtration and digestion of NaOH solution, and NaOH-NRP was calculated as NaOH-TP minus NaOH-SRP. TP was extracted by 3.5 M of HCl for 16 h before being burned for 3 h at 450 °C. Residual P was calculated by subtracting the extractable P species from TP.

AgI binding gels retrieved from the AgI-DGTs were scanned directly by a scanner (CanoScan 5600F, Canon, Beijing, China). Zr-oxide binding gels retrieved from the Zr-oxide DGTs were placed into 300 mL of molybdenum reagent at 35 °C for 45 min for coloration and then were placed into 4 °C deionized water to terminate the color reaction. The colored Zr-oxide gels were then scanned by a scanner (CanoScan 5600F, Beijing, China).

2.5. Data Analysis

The scanned images of AgI and colored Zr-oxide binding gels were converted to grayscale intensity by ImageJ software (ImageJ 1.52v), and then the cumulative quantity (*M*) was obtained by a calibration curve [27,28]. The flux was calculated by Equation (1).

$$F_{\text{DGT}} = M/(At) \quad (1)$$

where *A* represents the exposed area of the binding gel, and *t* represents the deployment time of the DGT probes in sediments.

The DO concentration can be calculated by the modified Stern–Volmer equation [29]:

$$R/R_0 = \alpha + (1 - \alpha)/(1 + K_{SV}C) \quad (2)$$

where R and R_0 is the fluorescence intensity ratio (Red/Green) in the present and absence of O_2 , respectively, C is the DO concentration, K_{SV} is the Stern–Volmer quenching constant, α is the non-quenchable fraction of the fluorescence signal.

3. Results and Discussion

3.1. Variations in DO at the Sediment–Water Interface

Variations in the DO at the SWI before and after treatment are shown in Figure 1. According to experience, the oxic–anoxic interface (OAI) coincided with SWI. After being treated for 8 and 60 days by LMB and LMA&C, a completely anoxic layer of 2~5 mm thickness was observed on the original SWI. The capping of finely ground and compacted capping particles might have prevented DO from entering sediment [30,31]. The DO concentration at −20~−30 mm of the sediment increased slightly on day 8 and day 60. This indicated that the DO concentration in surface sediments could be slightly increased by La-based materials. This might be due to improvements in water quality caused by the capping of La-based materials. After being treated for 8 and 60 days by CN, LMB+CN and LMA&C+CN, the OAI rose by 6~11 mm. Previous studies indicated that gas production by denitrification could increase sediment porosity [16]. We inferred that the increase in sediment porosity led to the elevation of the OAI.

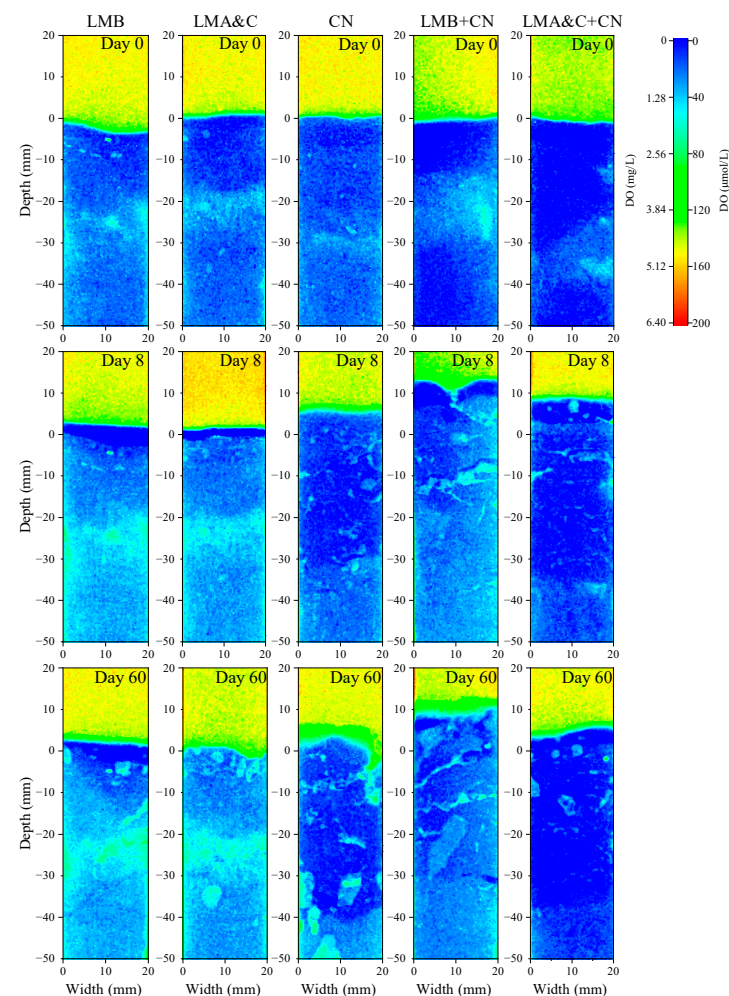


Figure 1. Variations in the DO at the sediment–water interface before and after treatment.

3.2. Variations in DGT-Labile Sulfide Flux in the Sediment–Water Profile

Variations in the DGT-labile sulfide flux after being treated for 8 days are shown in Figure 2. The sulfur forms involved in DGT-labile sulfide are mainly dissolved sulfur, including S^{2-} , HS^- and H_2S [32]. LMB decreased DGT-labile sulfide flux in the overlying water and surface 15 mm sediments, and LMA&C decreased the flux in the overlying water. The removal of DGT-labile sulfide from overlying water and surface sediments might be caused by the sedimentation of LMB and LMA&C. CN decreased DGT-labile sulfide flux in the overlying water and surface 100 mm sediment to nearly 0. As an electron acceptor, nitrate drives autotrophic and heterotrophic denitrifiers to oxidize reduced sulfide into SO_4^{2-} in sediments [12,13,16]. LMB+CN and LMA&C+CN also decreased DGT-labile sulfide in the overlying water and surface sediment, but the removal rates were lower than that of the CN group. However, the oxidation of CN with the sediments was incomplete on the 8th day, and the location of CN injection and DGT placement might have caused the uneven distribution of sulfur and incomplete removal. Previous studies had shown that, after complete oxidation, the removal rate of DGT-labile sulfide flux by LMB+CN was equivalent to that of CN alone [33].

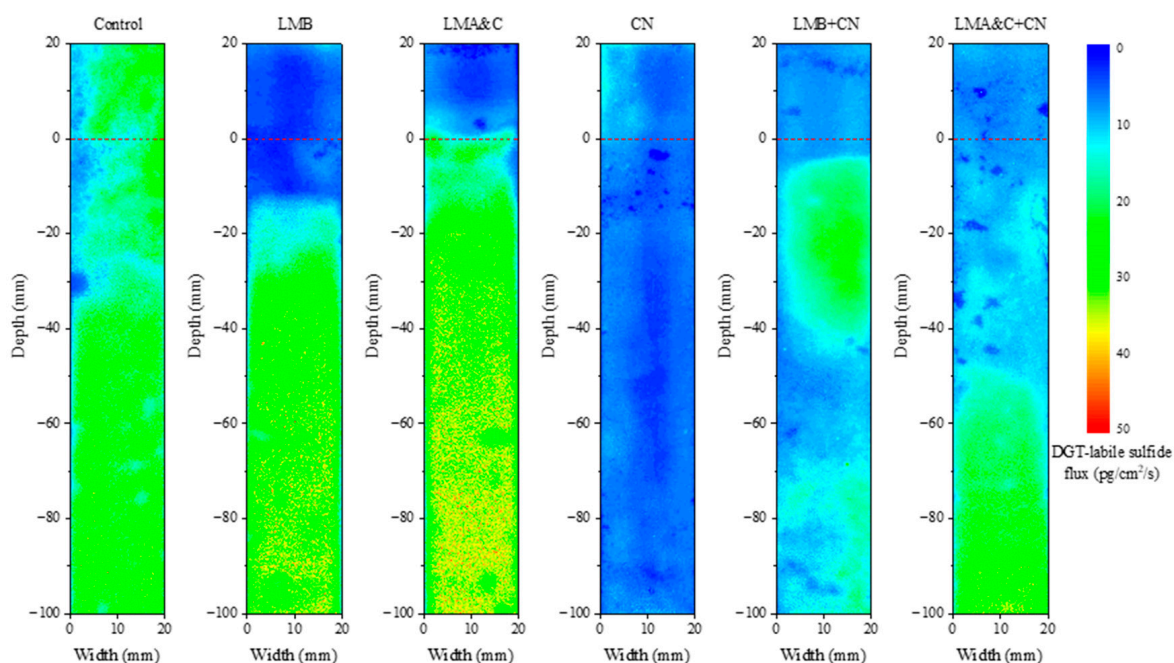


Figure 2. Variations in the DGT-labile sulfide flux in the sediment–water profile after being treated for 8 days.

3.3. Variations in SRP Concentration in Pore Water

The variations in SRP concentrations with time in different groups are shown in Figure 3. In the control group, vertically, SRP increased first and then decreased. LMB and LMA&C decreased the SRP concentration to <0.05 mg/L at a sediment depth of -5 mm with removal rates of 68–100%, but the vertical distribution of SRP was still like that of the control. CN, LMB+CN and LMA&C+CN all decreased SRP concentrations to <0.13 mg/L at depths of -5 , -25 , -50 and -80 mm on days 10 and 30 with removal rates of 21–100% and changed the vertical distribution of SRP. On day 60, SRP at -25 , -50 and -80 mm in the CN and LMB+CN groups, and -80 mm in the LMA&C+CN group, rebounded to some extent. The SRP removal rates at -25 , -50 and -80 mm in LMB+CN and LMA&C+CN groups were much higher than that of LMB and LMA&C alone at -25 , -50 and -80 mm, and higher than that of CN alone at -5 and -80 mm.

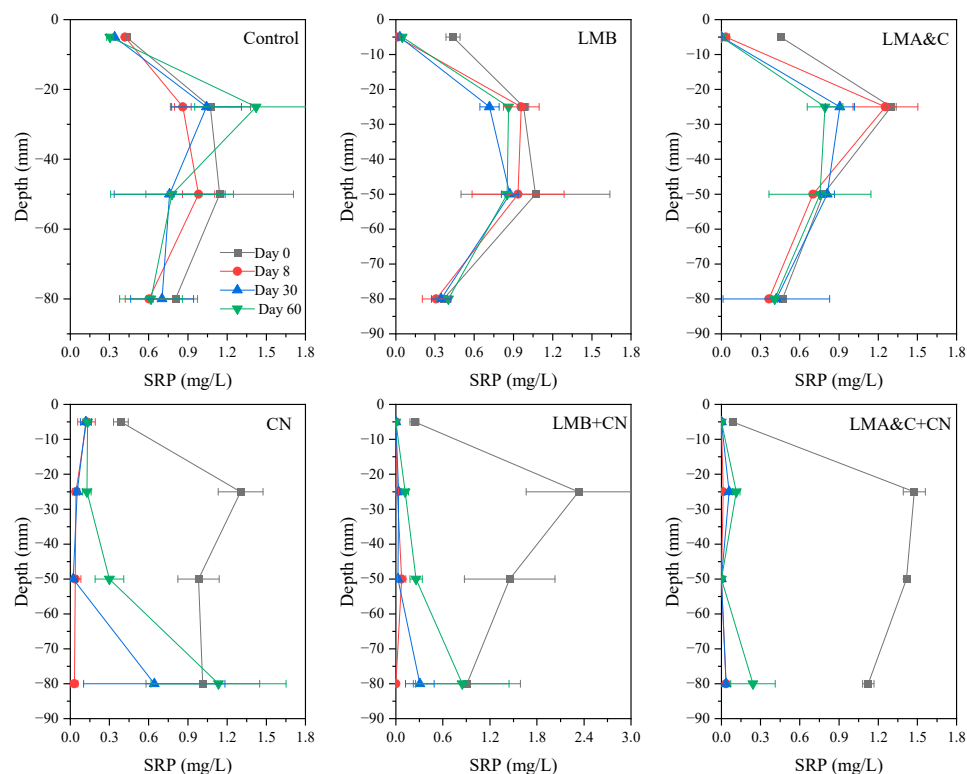


Figure 3. Variations in SRP concentrations with time in different groups.

LMB and LMA&C adsorb SRP in the process of falling after adding to the water [30]. Lanthanum ion (La^{3+}) in La-based materials captures and immobilizes phosphate at a ratio of 1:1 to form an insoluble La phosphate phase [34]. The amount of LMB and LMA&C added to water was excessive for SRP in water, and thus after falling onto the sediment, LMB and LMA&C continued to adsorb SRP near the SWI. La-based materials would enter the deeper sediment under the disturbance of benthic fauna in the in situ intact column sediment [35], resulting in a decrease of SRP in deep pore water.

CN can oxidize reduced Fe (including soluble Fe, labile Fe, amorphous FeS mineral and pyrite) into Fe hydroxide, which has many adsorption sites [13]. The phosphate is then adsorbed by the Fe hydroxide [14,15]. Since CN was injected at -50 mm and dissolved CN easily diffused into the upper and lower sediments, SRP at depths of -25 , -50 , and -80 in the CN, LMB+CN and LMA&C+CN groups was all decreased. However, probably due to solid-phase replenishment and diffusion of SRP in deeper sediment, SRP rebounded after 60 days.

3.4. Variations in DGT-Labile P Flux in the Sediment-Water Profile

Variations in DGT-labile P flux after being treated for 60 days are shown in Figure 4. The P flux measured by the DGT method involves SRP and some sediment weakly bound P which can supplement pore water SRP. LMB and LMA&C decreased DGT-labile P flux in the overlying water and surface 5–20 mm sediment to nearly 0. The controlled depth of LMB was 40 mm and was much deeper than that of LMA&C. We speculated that the possible reasons were the different dosages and the different effects of the two La-based materials on the life activities of the benthic fauna. Previous studies have shown significant differences in the control depth of mobile P between sediments with and without benthic fauna [30,36].

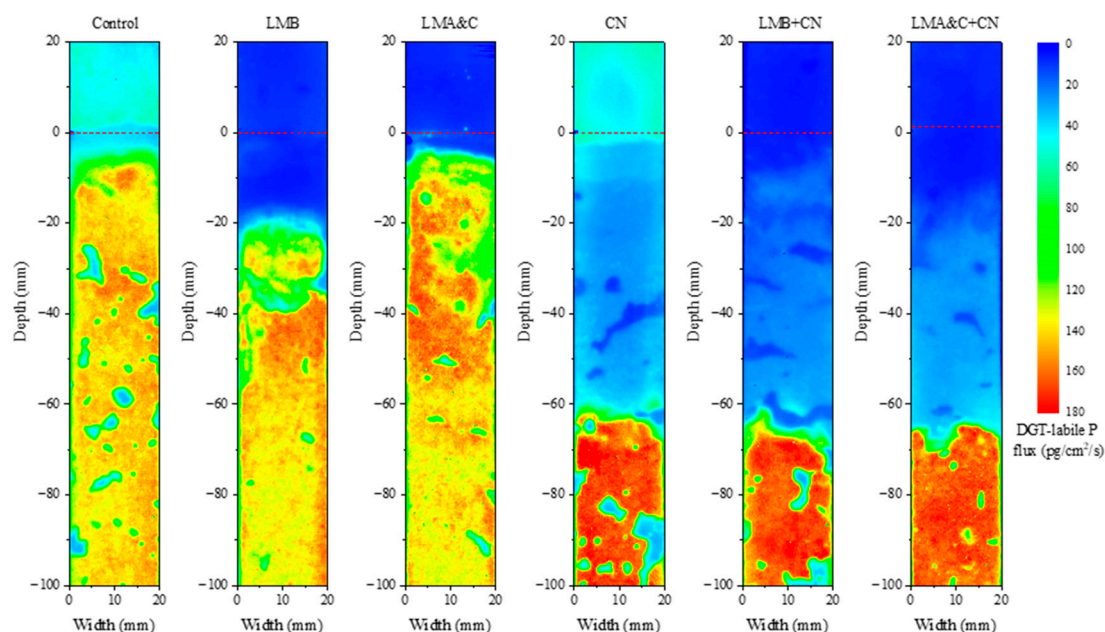


Figure 4. Variations in DGT-labile P flux in the sediment–water profile after being treated for 60 days.

CN significantly decreased DGT-labile P flux in surface 65 mm sediment into $\sim 40 \text{ pg/cm}^2/\text{s}$ but had no effect on P in the overlying water. It was consistent with the results of previous studies in which mobile P in overlying water was not significantly decreased by CN or even increased [17,19]. Due to the increased sediment porosity, substance exchange at the SWI might be intensified, leading to the unexpected internal P release from sediment. The controlled depth by CN in our study was much less than previously reported [37], and this might be due to insufficient CN dose in our study.

DGT-labile P flux in the surface 65 mm sediment was significantly decreased by LMB+CN and LMA&C+CN, the controlled depth was much higher than that of LMB and LMA&C alone. And, unlike CN alone, DGT-labile P flux in the overlying water was decreased to 0 in the LMB+CN and LMA&C+CN groups. But there was a phenomenon worth noting: In the CN, LMB+CN and LMA&C+CN groups, DGT-labile P flux below -65 mm all increased to $180 \text{ pg/cm}^2/\text{s}$, which was much higher than $140 \text{ pg/cm}^2/\text{s}$ in the control. Further research is needed to determine the cause of SRP rise in uncontrolled deep sediments.

3.5. Variations in P Fractionation in Sediment

Variations in P fractionation in sediment are shown in Figure 5. $\text{NH}_4\text{Cl-P}$ represents the loosely sorbed P. BD-P represents the redox-sensitive P forms, mainly bound to Fe hydroxides and Mn compounds [38,39]. $\text{NH}_4\text{Cl-P}$ and BD-P in surface 20 mm sediment were decreased both by LMB and LMA&C on days 8, 30 and 60, but BD-P in depths of $-20 \sim -100 \text{ mm}$ was slightly increased. NaOH-SRP represents P bound to metal oxides mainly of Al and Fe. NaOH-NRP represents P in microorganisms including poly-P, organic P in detritus and P bound in humic compounds [38,39]. NaOH-SRP and NaOH-NRP in $-20 \sim -60 \text{ mm}$ were increased by LMB and LMA&C on days 8 and 30, but in surface 20 mm sediment, they increased on days 8 and 30 and then decreased on day 60. The capping of La-modified materials may create a new type of microenvironment across SWI and hence favor the growth of different bacteria in the surface sediment [3,40]. Thus, we suspect that the decrease in NaOH-NRP may be related to the changes of microbial activity. HCl-P represents P forms sensitive to low pH, assumed to consist mainly of apatite P and P bound to carbonates [38,39]. HCl-P in surface 40 mm sediment increased with time in the LMB and LMA&C groups, and the increase in the surface 20 mm was much greater than that in the $-20 \sim -40 \text{ mm}$ sediment. Residual-P in surface 20 mm was increased by LMB and LMA&C

on day 60. Residual-P is refractory P [38,39]. Results indicated that LMB and LMA&C transformed more mobile P forms into stable P forms. And those results were consistent with the results of Yin et al. [3]. According to Dithmer et al. [41], most of the sequestered P by LMB was as rhabdophane ($\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, $n \leq 3$) and 26% was as loosely bound redox-sensitive P species on the surface of rhabdophane. Chitosan in LMA&C has a high density of amino groups that give it a positive charge, which attracts negatively charged anions [21]. In addition, the bentonite in LMB and attapulgite in LMA&C all have Al components, which likely remove P through the formation of Al-P. Thus, in our study, the temporary increase in BD-P and NaOH-SRP in the surface 20 mm sediment was observed. Due to the enough La in the surface layer, the temporarily formed BD-P and NaOH-SRP were eventually transformed into Ca-bound P and refractory P. The biodegradability of chitosan is likely to cause the re-release of part of the adsorbed P. However, SRP rebound was not observed in the LMA&C group during the experimental period. This might also be attributed to enough La in the composite, which binds the re-released P into a more stable form.

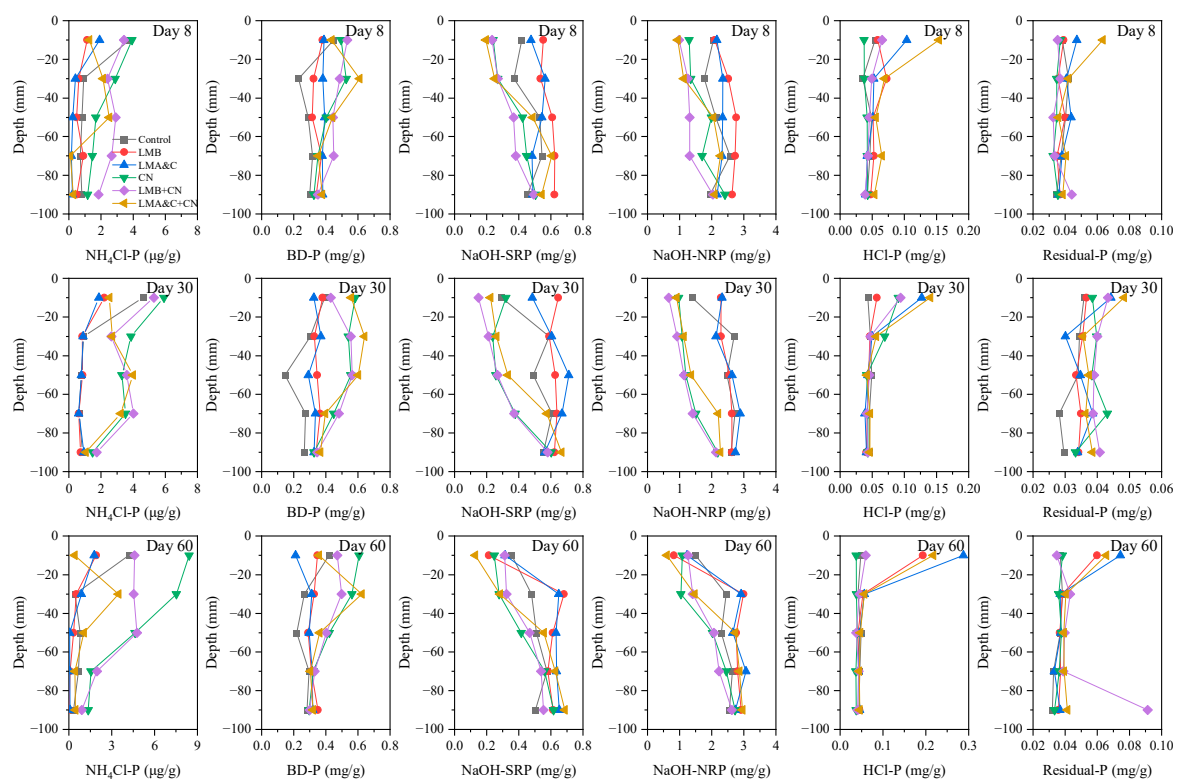


Figure 5. Variations in phosphorus fractionation in sediment after being treated for 8, 30 and 60 days.

CN increased $\text{NH}_4\text{Cl-P}$ and BD-P in surface 80 mm sediment on days 8, 30 and 60. NaOH-SRP and NaOH-NRP in surface 80 mm were decreased by CN on days 8 and 30, but they recovered in depths of $-40 \sim -80$ mm on day 60. Nitrate denitrification oxidized the reduced substances in the sediment, such as Fe(II), sulfide and organic matter [13], likely leading to P release originally adsorbed on them. After Fe was oxidized to Fe hydroxide, the original released P was re-adsorbed as BD-P. However, CN treatment resulted in the increase in $\text{NH}_4\text{Cl-P}$, which was unfavorable for the control of internal P. The increase in $\text{NH}_4\text{Cl-P}$ was also observed in previous studies [17,42].

LMB+CN and LMA&C+CN increased $\text{NH}_4\text{Cl-P}$ and BD-P in depths of $-20 \sim -60$ mm on days 8, 30 and 60. But unlike CN, LMB+CN and LMA&C+CN had no obvious effect on $\text{NH}_4\text{Cl-P}$ in surface 20 mm. NaOH-SRP and NaOH-NRP were decreased by LMB+CN and LMA&C+CN in surface 80 mm on days 8 and 30, but they recovered in depths of $-40 \sim -80$ mm on day 60. HCl-P in surface 40 mm sediment increased with time in

the LMB+CN and LMA&C+CN groups, and the increase in the surface 20 mm was much greater than that in the −20~−40 mm sediment. Residual-P in surface 20 mm was increased by LMA&C+CN on day 60. After the combination of La-based materials and CN, NH_4Cl -P increase in the surface 20 mm was inhibited compared to CN alone. The sequestered P by LMB+CN and LMA&C+CN is mainly as HC-P and Residual-P in the surface 20 mm and as Fe-hydroxide-bound P in −20~−60 mm.

3.6. Implication for the Combined Application in the Control of Internal P

Both two combined methods in our study were effective for SRP and DGT-labile P removal in at least 60 mm of sediment. The passivated P in the deeper sediment (−20~−60 mm) is mainly as Fe-hydroxide-bound P. The “transition layer” (−20~−60 mm) rich in Fe hydroxide can continuously adsorb SRP diffused from deeper sediments (below −60 mm). The “transition layer” can also prevent internal P release in case of slight sediment re-suspension. As a potential bioavailable P, Fe-hydroxide-adsorbed P is likely to desorb under the disturbance of benthos, cyanobacteria and aquatic plants, so it still has a certain risk of inducing algal blooms. However, when combined with La-based materials, the capping layer can mitigate this risk to a certain extent. A capping layer with a certain thickness forms not only a physical barrier on surface sediment but a chemically active passivation layer, which can continuously convert the exposed SRP into Ca-bound P and Residual-P. Ca-bound P is a relatively stable fraction of sedimentary P and contributes to a permanent burial of P in sediments [38]. Residual-P is refractory P, which is more stable than Ca-bound P. To some extent, sediment P was prevented from entering the overlying water by the capping layer. The combined application of in situ capping and biochemical oxidation will also be helpful for reducing the economic cost because the cost per unit area of CN is much less than the cost per unit area of La composites. The results of our study provide a possibility for the combined application of in situ capping and biochemical oxidation in the control of internal P.

However, how to overcome nitrate escape from sediment to the water body is still a challenging job. Nitrate escape to water not only leads to the loss of effective electron acceptor but also increases the nitrogen load of the water. Yang et al. [16] developed controlled-release nitrate pellets and applied them at different sediment depths and found that application of the pellets at depth decreased the nitrate release and the secondary risks. This gave us implications for the combined use of capping and biochemical oxidation. In the future, it is possible to try to develop a composite pellet of capping and oxidizing agents and apply it to a certain depth of sediment. In addition, the composition of the capping agent should also be optimized to achieve a win-win effect of economic and environmental effects. Biological adsorbents or industrial and agricultural wastes, such as chitosan and slag, can be appropriately added, and the adsorption properties should first be improved by heat treatment, acid-base treatment and other methods. In any case, the cost of La composite is a key issue in the management of lake eutrophication, and it still needs continuous and unremitting efforts.

4. Conclusions

- (1) LMB and LMA&C decreased the SRP concentration to <0.05 mg/L at depths of −5 mm after 8, 30 and 60 days. CN, LMB+CN and LMA&C+CN decreased SRP concentrations to <0.13 mg/L at depths of −5, −25, −50 and −80 mm on days 10 and 30, but on day 60, SRP at −80 mm rebounded to some extent. The SRP removal rates of the two combined groups were much higher than that of LMB and LMA&C alone at −25, −50 and −80 mm, and higher than that of CN alone at −5 and −80 mm.
- (2) LMB decreased DGT-labile P flux in the overlying water and 40 mm surface sediment, and LMA&C decreased DGT-labile P flux in overlying water and 10 mm surface sediment. CN decreased DGT-labile P flux in surface 65 mm sediment but had no obvious effect on DGT-labile P in the overlying water. LMB+CN and LMA&C+CN decreased DGT-labile P flux in overlying water and surface 65 mm sediment. The

- control effect on DGT-labile P by the two combined groups was much better than that of LMB, LMA&C and CN alone.
- (3) NH_4Cl -P, BD-P, NaOH-SRP and NaOH-NRP in the surface 20 mm were transformed into HCl-P and Residual-P by LMB and LMA&C on day 60. The NaOH-NRP removal might be attributed to the improved microenvironment in the SWI, which was favorable for microbial growth. CN transformed NaOH-SRP and NaOH-NRP to BD-P through the formation of Fe hydroxide and resulted in the increase in NH_4Cl -P. In the LMB+CN and LMA&C+CN groups, the sequestered P in the surface 20 mm was mainly passivated to HC-P and Residual-P, and in $-20\sim-60$ mm was passivated to Fe-hydroxide-bound P.
 - (4) Both the two combined methods in our study were effective for SRP and DGT-labile P removal in at least 60 mm of sediment. The “transition layer” ($-20\sim-60$ mm) rich in Fe hydroxide and the capping layer (surface 20 mm) rich in La effectively prevented the release of internal P.

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