

Article



Effects of Lanthanum Modified Bentonite and Polyaluminium Chloride on the Environmental Variables in the Water and Sediment Phosphorus Form in Lake Yanglan, China

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Abstract: The application of lanthanum modified bentonite (Phoslock[®]) and polyaluminium chloride (PAC) is popular in the restoration of European temperate lakes; however, the effects of the application on the concentrations of phosphorus (P) in both the water and the sediments have been poorly evaluated to date. We studied the effects of the application of Phoslock[®] + PAC on the concentrations of total phosphorus (TP), particulate phosphorus (PP), soluble reactive phosphorus (SRP), total suspended solids (TSS) and chlorophyll *a* (Chl*a*) in the water, and different P forms in the sediments, in an isolated part of Lake Yanglan. The results showed that the concentrations of TP, PP, SRP, TSS and Chl*a* decreased significantly after the addition of Phoslock[®] + PAC. Moreover, the concentrations of labile-P, reductant-soluble-P and organic-P in the sediments were also significantly decreased after the Phoslock[®] + PAC application. However, the concentrations of both the stable apatite-P and residual-P in the sediments after application of Phoslock[®] + PAC were much higher than the pre-addition values, while the concentrations of metal-oxide-P did not differ significantly between the pre- and post- application conditions. Our findings imply that the combined application of Phoslock[®] and PAC can be used in the restoration of subtropical shallow lakes, to reduce the concentrations of P in the water and suppress the release of P from the sediments.

Keywords: lake restoration; lanthanum-modified bentonite; polyaluminium chloride; sediment phosphorus forms; water quality

1. Introduction

Eutrophication is the primary water quality issue for numerous aquatic ecosystems worldwide [1]. The most straightforward measure in mitigating eutrophication is the excessive reduction in external nutrient loading [2], however, lakes often show hysteresis in response to changes in nutrient loading [3]. This may be due to the persistent internal nutrient loading from the sediments to the water column, especially for phosphorus (P) [4,5]. Internal P loading derives from a pool accumulated in the sediments during the high external loading period. Considerable amounts of P in lake sediments may be bound to redox-sensitive iron compounds or fixed in relatively labile organic forms [6], which are potentially mobile and may eventually be released to the lake water [4].

Many techniques have been developed to control the internal P loading in lakes. Physical measures such as sediment dredging can directly remove the P-enriched sediments from the lake [7,8]; however, this is relatively expensive [9,10]. The application of chemicals enhances the sorption capacity of the elements in the sediments, e.g., the application of iron (Fe), alum and calcium [2,11]. The most commonly used chemicals for lake restoration



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). are solid-phase P sorbents, mainly modified clays enriched with aluminium (Al), Fe or lanthanum (La) [12–14]. The modified clays can be beneficial in driving P in the water to settle onto the lake bottom [13,15,16]. Lürling and van Oosterhout [17] showed that the most promising method in controlling in-lake P concentrations is the combination (Flock & Lock) of a flocculent (Flock) and a phosphate fixative (Lock). In this method, the flocculent strips the total P from the water column while a modified clay acts as both a sinking ballast and phosphate fixative to chemically inactivate the legacy P stored in lake beds.

Polyaluminium chloride (PAC) has strong flocculation, water-clearing properties [18] and P sorption abilities [19]. The lanthanum-modified bentonite, Phoslock[®], as a ballast and P-fixative, is effective in hampering the release of P in the sediments in European temperate lakes [20,21]. Upon interacting with free P forms, Phoslock[®] forms a highly stable mineral rhabdophane (LaPO₄·nH₂O) [22]. Phoslock[®] has a strong binding affinity to ortho-phosphate [23–25]. Some studies confirmed that the application of Phoslock[®] reduces P release from the sediments by transferring potentially mobile P (P_{mob}, NH₄Cl-P, BD-P and Org-P) into refractory fractions (e.g., apatite-bound P) [20,26–28]. However, the effects of the application of PAC + Phoslock[®] on the concentrations of P in both the water and the sediments were poorly evaluated.

We applied the combination of flocculent and lanthanum-modified bentonite to an isolated part of Lake Yanglan, China, to study the changes in concentrations and forms of P in both the water and the sediments. We predicted that (1) the concentrations of different P forms would decrease substantially in the water, while (2) the concentrations of refractory P in the sediments would increase remarkably after the combined application of PAC and Phoslock[®] to the water.

2. Materials and Methods

2.1. Study Site

Lake Yanglan (30°00′ N–30°06′ N, 114°32′–115°05′ E) is situated in Hubei Province, China (Figure 1a). It has a surface area of 369.7 ha and a mean depth of 1.7 m. Although the external nutrient loading of the lake has been reduced, the lake remains highly eutrophic, and total phosphorus (TP) concentrations can exceed 150 µg L⁻¹ [29]. It is, therefore, likely that internal P loading plays an important role in maintaining the trophic status of Lake Yanglan. A 4 ha experimental area was isolated from the lake using water-proof enclosures to conduct the restoration experiment (Figure 1b). From 31 August to 8 September 2017, 500 g m⁻² Phoslock[®] (5% La; supplied by Phoslock[®] Water Solutions Ltd., Shanghai, China) and 50 g m⁻² PAC (Al_n(OH)_mCl_{3n – m}, $\rho = 1.37$ kg L⁻¹, 8.9% Al, 21.0% Cl) was added to the water in the experimental area through a spray manifold after mixing with lake water. The amount of Phoslock[®] required to inactivate phosphorus in the system was calculated based on a 1:1 molar ratio of La/P (100 kg Phoslock[®]/1 kg P), where P was the sum of TP measured in the water column and potentially releasable P in the 0–5 cm layer of the sediment (P_{mob}, NH₄Cl-P, BD-P and Org-P) [20,30].

2.2. Sample Collection and Measurements

2.2.1. Water Samples

Water samples were taken at three sites (Figure 1b) in the experimental area before (August 16) and after (October 24) the addition of PAC and Phoslock[®]. In each sampling event, the transparency (SD) was observed using a Secchi disc. Then, the integrated water samples were pooled from different depths (0.5, 1.0 and 1.5 m) at each site using a modified Van Dorn water sampler, and a 15 L subsample for each site was brought back to the laboratory. The concentrations of TP, particulate phosphorus (PP), and soluble reactive phosphorus (SRP) in the water were analyzed according to the methods described in Wei [31]. Total suspended solids (TSS) and chlorophyll *a* (Chl*a*) in the water were analyzed using the analytical method described in Huang [32]. These methods are similar to the US standards (APHA 1998) [33]. We took 200 mL water subsamples to determine TP, PP and SRP via colorimetry after digestion with potassium persulfate (K₂S₂O₈) and sodium

hydroxide (NaOH) solution. In order to determine the TSS, 500 mL water was filtered using pre-weighted GF/C filters (Whatman, nominal pore size 1.2 μ m), which were subsequently dried at 108 °C for 24 h and weighted again. Chl*a* was measured spectrophotometrically from the matter retained on a cellulose acetate membrane (0.45 μ m, 200 mL water) after extraction with 90% (v/v) acetone for 24 h.



Figure 1. Location of Lake Yanglan (a) and the sampling sites (b) in the experimental area (sites 1–3).

2.2.2. Different Forms of Phosphorus in the Sediments

One sediment core was collected at three sampling sites (Figure 1b) using a gravity corer (core internal diameter 85 mm, length 320 mm) on August 16 (pre-application) and October 24 (post-application). The top 10 cm of each sediment core were extruded and sectioned into 2 cm slices. The sediment samples were then stored at 4 °C in the dark and transported to the laboratory for further analyses. The concentrations of labile-P (NH₄Cl-P), reductant-soluble-P (BD-P), organic-P (Org-P), metal-oxide-P (NaOH-RP), apatite-P (HCl-P), residual-P (ref-P) and TP in each layer of the sediments were measured according to Pettersson et al. [34] and Ribeiro et al. [35]. NH₄Cl-P was extracted from 1 g wet sediment by NH₄Cl solution; BD-P was extracted with BD reagent (bicarbonate-dithionite); Org-P and NaOH-RP were extracted with 0.1 M NaOH; HCl-P was extracted with 0.5 M HCl; ref-P was extracted with 1 M NaOH; TP was calculated as the sum of each form of P. The concentrations of La and Al in the sediments were extracted with HClO₄ and determined using an inductively coupled plasma optical emissions spectrometer (Thermo ICP 7000 Series) [31].

2.3. Statistical Analyses

The concentrations of TP, PP, SRP, TSS and Chla in the water, and contents of different P forms (NH₄Cl-P, BD-P, Org-P, NaOH-RP, HCl-P, ref-P and TP), La and Al in the sediments were tested with the Student's *t*-test between the pre-application and post-application of PAC and Phoslock[®]. All statistical analyses were conducted in SPSS 18.0 software, NY, USA.

3. Results

3.1. Changes in Physico-Chemical Variables and Chla in the Water

After the application of PAC and Phoslock[®] to the experimental area of the lake, the concentrations of TP (Figure 2a), PP (Figure 2b), SRP (Figure 2c), TSS (Figure 2d) and

Chla (Figure 2e) in the water column were all significantly lower than that before the application (p < 0.05, Table 1). In comparison with the pre-application of chemicals, the concentrations of TP, PP, SRP and TSS in the water were reduced by 89%, 80%, 93% and 86%, respectively, after the application of PAC and Phoslock[®]. Water transparency (SD) increased significantly from a mean of 40 cm (before addition) to a mean of 186 cm (after addition) (Figure 2f).



Figure 2. Changes in the concentrations of total phosphorus (TP) (**a**), particulate phosphorus (PP) (**b**), soluble reactive phosphorus (SRP) (**c**), total suspended solids (TSS) (**d**) and chlorophyll *a* (Chl*a*) (**e**) in the water, and Secchi depth (SD) (**f**), in the experimental area of Lake Yanglan in pre- to post- application of PAC and Phoslock[®] periods (n = 3). * represents the significant difference (p < 0.05) between treatments using Student's *t*-test.

Table 1. Results of the Student's *t*-test for the concentrations of total phosphorus (TP), particulate phosphorus (PP), soluble reactive phosphorus (SRP), total suspended solids (TSS), chlorophyll *a* (Chl*a*) and Secchi depth (SD) of the water in the experimental area of Lake Yanglan between pre- and post- application of PAC and Phoslock[®].

| Variables | F | р | | |
|-----------|--------|---------|--|--|
| TP | 9.277 | 0.002 | | |
| PP | 2.516 | 0.003 | | |
| SRP | 13.074 | 0.001 | | |
| TSS | 1.149 | <0.0001 | | |
| Chla | 0.058 | 0.032 | | |
| SD | 16.000 | <0.0001 | | |

Significant values (p < 0.05) are shown in bold.

After the application of PAC and Phoslock[®] to the experimental area of the lake, the concentrations of NH₄Cl-P (Figure 3a), BD-P (Figure 3b), and Org-P (Figure 3c) in the 0–2 cm and 2–4 cm layers of the sediments were significantly lower than that before the application (p < 0.05, Table 2). However, the concentrations of NaOH-RP (Figure 3d) and TP (Figure 4a) showed no significant differences between the pre- and post-application. The concentrations of HCl-P (Figure 3e) in the 0–2 cm and 2–4 cm layers and ref-P (Figure 3f) in the 0–2 cm layer of the sediments increased significantly after the application of PAC and Phoslock[®] (p < 0.05, Table 2).



Figure 3. The concentrations of labile-P (NH₄Cl-P) (**a**), reductant-soluble-P (BD-P) (**b**), organic-P (Org-P) (**c**), metal-oxide-P (NaOH-RP) (**d**), apatite-P (HCl-P) (**e**) and residual-P (ref-P) (**f**) in different depths of the sediments in the treatment area of Lake Yanglan in pre- (open circle) and post- (closed circle) application of PAC and Phoslock[®] (n = 3).

| Variables | 0–2 cm | | 2–4 cm | | 4–6 cm | | 6–8 cm | | 8–10 cm | |
|----------------------|--------|-------|--------|-------|--------|---------------|--------|-------|---------|-------|
| | F | р | F | р | F | р | F | р | F | р |
| NH ₄ Cl-P | 2.745 | 0.010 | 4.308 | 0.045 | 4.095 | 0.878 | 0.037 | 0.240 | 0.024 | 0.359 |
| BD-P | 0.097 | 0.032 | 0.735 | 0.008 | 6.155 | 0.282 | 2.799 | 0.765 | 0.482 | 0.126 |
| Org-P | 0.002 | 0.023 | 12.458 | 0.004 | 3.072 | 0.581 | 1.650 | 0.933 | 0.553 | 0.950 |
| NaOH-RP | 0.397 | 0.082 | 1.613 | 0.588 | 0.305 | 0.321 | 1.485 | 0.366 | 1.469 | 0.436 |
| HCl-P | 8.980 | 0.048 | 0.289 | 0.007 | 0.139 | 0.501 | 0.041 | 0.965 | 3.047 | 0.087 |
| Ref-P | 0.388 | 0.031 | 5.339 | 0.994 | 4.077 | 0.292 | 0.262 | 0.483 | 0.972 | 0.341 |
| TP | 2.133 | 0.791 | 0.749 | 0.192 | 0.509 | 0.170 | 4.079 | 0.316 | 6.682 | 0.149 |
| La | 6.301 | 0.004 | 11.215 | 0.043 | 10.097 | 0.006 | 2.508 | 0.003 | 0.692 | 0.023 |
| Al | 0.518 | 0.005 | 0.425 | 0.003 | 0.028 | \leq 0.0001 | 1.227 | 0.010 | 7.273 | 0.022 |

Table 2. Results of the Student's *t*-test for the concentrations of labile-P (NH₄Cl-P), reductant-soluble-P (BD-P), organic-P (Org-P), metal-oxide-P (NaOH-RP), apatite-P (HCl-P), residual-P (ref-P), total phosphorus (TP), Lanthanum (La) and Aluminium (Al) in the sediment in the treatment area of Lake Yanglan in pre- and post- application of PAC and Phoslock[®].

Significant values (p < 0.05) are shown in bold.

3.3. Changes in La and Al Concentrations of the Sediments

The concentrations of La and Al in all layers of the sediments (0-2, 2-4, 4-6, 6-8 and 8-10 cm layers) increased significantly after the application of PAC and Phoslock[®] (Figure 4b,c, p < 0.05, Table 2).



Figure 4. The concentrations of total phosphorus (TP) (**a**), Lanthanum (La) (**b**) and Aluminium (Al) (**c**) in different depths of the sediments in the treatment area of Lake Yanglan in the pre- (open circle) and post- (closed circle) application of PAC and Phoslock[®] (n = 3).

4. Discussion

Our results showed that the addition of PAC and Phoslock[®] to the experimental area of Lake Yanglan resulted in a significant reduction in the concentrations of TP, PP, SRP, TSS and Chl*a* in the water, and a substantial increase in water transparency (SD). Moreover, the concentrations of the potentially releasable P in the post-application sediments at the end of the experiment were much lower than at the beginning (before the addition of the chemicals). However, the application of the chemicals significantly increased the concentration of refractory P (HCl-P and Ref-P). Therefore, the combined addition of flocculent and lanthanum-modified bentonite to the water improves the water quality by both reducing the P concentrations in the water and suppressing the P release from the sediments in this subtropical shallow lake.

Phoslock[®] has P inactivation properties, where a reaction between La³⁺ and PO₄³⁻ forms a highly stable mineral rhabdophane (LaPO₄ \cdot nH₂O) that is thought to remove the P by precipitation in the water column [15,36,37]. This was confirmed by Reitzel et al. [27], who found that Phoslock[®] can reduce the P concentrations in the overlying water column by transforming SRP into highly recalcitrant P forms in the sediments. PAC also has P-binding properties which reduce the P concentrations in the water column [19]. In our study, the percentage of TP removal in the water column after the application of PAC and Phoslock[®] was 89%, higher than that in Gan et al. [38] (45%), indicating that applying a combination of PAC and Phoslock[®] was more effective than the application of Phoslock® alone. In our study, the reduction in Chla and TSS concentrations may be attributed to the strong flocculation ability of PAC [18]. Kim [39] showed that TSS is removed by PAC driving hydrolysis of the sulfate, generating insoluble Al species and aluminum hydroxide precipitates. The combined application of PAC and Phoslock[®] has been proven to effectively aggregate phytoplankton and sink them with a ballast out of the water column, improving the water transparency [17,40,41]. Thus low phytoplankton biomass was determined after the application of PAC and Phoslock[®] in our study.

We found that the changes from releasable P fractions to residual forms in the top layers of sediments were in line with the previous studies, where only Phoslock[®] was applied [27,30,38,42]. The NH₄Cl-P can be easily released and then used by phytoplankton [35,42,43]. The BD-P is sensitive to redox changes and can be released under anoxia or low redox conditions [44,45]; thus, it is considered as a bioavailable P pool [46]. The release-sensitive P species (e.g., NH₄Cl-P, BD-P and Org-P) lead to the release of P under appropriate conditions [4,47]. A study by Wang et al. [48] showed that the BD-P was the main source of P released from the sediments, and the main source of P for the overlying water. Thus, the reduction of release-sensitive NH₄Cl-P, BD-P and Org-P content in our study indicated that the combined application of flocculent and lanthanum-modified bentonite can reduce the P release from the sediments in Lake Yanglan.

The study by Meis et al. [20] showed that, due to the application of Phoslock[®], the HCl-P fraction increased, and thus the P-binding capacity increased in the sediments. The increase in the mass of more refractory fractions (HCl-P and Ref-P) likely reduces the magnitude of P cycling between the sediments and the water-column [20,27], resulting in a reduction in sediment P release. Our study showed a similar result, i.e., significantly more HCl-P and Ref-P was observed in the top 2 cm of the sediments after the application of PAC and Phoslock[®]. In our study, the non-significant change in TP concentration indicated that the P_{mob} fraction was transformed into refractory P-fractions, including HCl-P and Ref-P, in the top 2 cm of sediments after the application of PAC and Phoslock[®].

A significant increase in sediment La and Al content was observed after application in the upper 10 cm of sediments in our study. Sediment P-binding capacity was, therefore, higher in post-application sediments due to an increase in La and Al-P-binding sites. This was similar to the finding by Bishop et al. [30] and van Oosterhout et al. [49] that sediment-associated La did increase above background in Laguna Niguel Lake (742 mg kg⁻¹ DW post-treatment vs. 27 mg kg⁻¹ pre-treatment) and Lake Rauwbraken (Berkel-Enschot, The Netherlands) (7–6702 mg kg⁻¹ DW post-treatment vs. 0.5–7.0 mg kg⁻¹ pre-treatment)

in the upper 20 cm of sediments. The phosphate-binding capacity of La is not affected by anoxic events and is effective over a much wider pH range and variable lake factors than Fe and Al salts [23,36,50]. Therefore, the application of La produces more efficient P sorption than Al alone [51]. Thus, the application of PAC and lanthanum-modified bentonite increased the P-binding in the sediments by La and Al.

Our results show that the combined application of PAC and Phoslock[®] can significantly improve water quality by precipitating P in the water column and binding P in the sediments by changing mobile P into refractory forms. Bishop and Richardson [28] found that Phoslock[®] significantly decreased the water column's total P levels and shifted mobile sediment P fractions (i.e., labile, reductant-soluble, organic) to the residual fraction after 2 years of the Phoslock[®] application. Araújo et al. [52] evaluated the effect of PAC in turbidity and total phosphorus, and found that PAC reduced total P concentrations and turbidity. However, there are no long-term published studies in subtropical regions. Further studies are needed to monitor the long-term changes in both water column and sediment P in order to evaluate the effectiveness of the combined application of PAC and Phoslock[®] in restoring ecological status of subtropical eutrophic lakes.

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References

- Smith, V.H.; Schindler, D.W. Eutrophication science: Where do we go from here? *Trends Ecol. Evol.* 2009, 24, 201–207. [CrossRef] [PubMed]
- Cooke, G.D.; Welch, E.B.; Peterson, S.A.; Nichols, S.A. Restoration and Management of Lakes and Reservoirs, 3rd ed.; CRC Press: Boca Raton, FL, USA; Taylor & Francis Group: Boca Raton, FL, USA, 2005.
- Jeppesen, E.; Kristensen, P.; Mortensen, E.; Søndergaard, M.; Lauridsen, T. Recovery resilience following a reduction in external phosphorus loading of shallow eutrophic Danish lakes: Duration, regulating factors and methods for overcoming resilience. *Mem. Ist. Ital. Idrobiol.* 1991, 48, 127–148.
- Søndergaard, M.; Jensen, J.P.; Jeppesen, E. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* 2003, 506–509, 135–145. [CrossRef]
- Jeppesen, E.; Søndergaard, M.; Jensen, J.P.; Havens, K.E.; Anneville, O.; Carvalho, L.; Coveney, M.F.; Deneke, R.; Dokulil, M.T.; Foy, B.; et al. Lake responses to reduced nutrient loading an analysis of contemporary long-term data from 35 case studies. *Freshw. Biol.* 2005, *50*, 1747–1771. [CrossRef]
- Søndergaard, M.; Jensen, J.P.; Jeppesen, E. Retention and internal loading of phosphorus in shallow, eutrophic lakes. *Sci. World J.* 2001, 1, 427–442. [CrossRef]
- 7. Peterson, S.A. Lake restoration by dredging. *Water Resour. Bull.* **1982**, *18*, 423–435. [CrossRef]
- 8. Hupfer, M.; Hilt, S. Lake restoration. In *Ecological Engineering*; Jørgensen, S.E., Fath, B., Eds.; Elsevier: Oxford, UK, 2008; pp. 2080–2093.
- 9. Welch, E.B.; Cooke, G.D. Internal phosphorus loading in shallow lakes: Importance and control. *Lake Reserv. Manag.* 2005, 21, 209–217. [CrossRef]
- Fan, C.; Zhong, J.; Zhang, L.; Liu, C.; Shen, Q. Research progress and prospect of environmental dredging decision-making of lake sediment. J. Lake Sci. 2020, 32, 1254–1277. [CrossRef]

- 11. Søndergaard, M.; Wolter, K.D.; Ripl, W. Chemical treatment of water and sediments with special reference to lakes. In *Handbook of Restoration Ecology*; Perrow, M., Davy, T., Eds.; Cambridge University Press: Cambridge, UK, 2002; Volume 10.
- 12. Yuan, X.Z.; Pan, G.; Chen, H.; Tian, B.H. Phosphorus fixation in lake sediments using LaCl3-modified clays. *Ecol. Eng.* 2009, *35*, 1599–1602. [CrossRef]
- Gibbs, M.M.; Hickey, C.W.; Özkundakci, D. Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: Sediment incubations. *Hydrobiologia* 2011, 658, 253–275. [CrossRef]
- 14. Zamparas, M.; Gianni, A.; Stathi, P.; Deligiannakis, Y.; Zacharias, I. Removal of phosphate from natural waters using innovative modified bentonites. *Appl. Clay Sci.* 2012, 62, 101–106. [CrossRef]
- 15. Spears, B.M.; Meis, S.; Anderson, A.; Kellou, M. Comparison of phosphorus (P) removal properties of materials proposed for the control of sediment p release in UK lakes. *Sci. Total Environ.* **2013**, *442*, 103–110. [CrossRef]
- 16. Epe, T.S.; Finsterle, K.; Yasseri, S. Nine years of phosphorus management with lanthanum modified bentonite (Phoslock) in a eutrophic, shallow swimming lake in Germany. *Lake Reserv. Manag.* **2017**, *33*, 119–129. [CrossRef]
- 17. Lürling, M.; van Oosterhout, F. Controlling eutrophication by combined bloom precipitation and sediment phosphorus inactivation. *Water Res.* 2013, 47, 6527–6537. [CrossRef]
- 18. Delgado, S.; Diaz, F.; Garcia, D.; Otero, N. Behaviour of inorganic coagulants in secondary effluents from a conventional wastewater treatment plant. *Filtr. Sep.* **2003**, *40*, 42–46. [CrossRef]
- Łopata, M.; Gawrońska, H. Phosphorus immobilization in Lake Głęboczek following treatment with polyaluminum chloride. Oceanol. Hydrobiol. Stud. 2008, 37, 99–100. [CrossRef]
- 20. Meis, S.; Spears, B.M.; Maberly, S.C.; Perkins, R.G. Assessing the mode of action of Phoslock in the control of phosphorus release from the bed sediments in a shallow lake (Loch Flemington, UK). *Water Res.* **2013**, *47*, 4460–4473. [CrossRef]
- Copetti, D.; Finsterle, K.; Marziali, L.; Stefani, F.; Tartari, G.; Douglas, G.; Reitzel, K.; Spears, B.M.; Winfield, I.J.; Crosa, G.; et al. Eutrophication management in surface waters using lanthanum modified bentonite: A review. *Water Res.* 2016, 97, 162–174. [CrossRef] [PubMed]
- Douglas, G.D.; Adeney, J.A.; Zappia, L.R. Sediment Remediation Project:1998/9 Laboratory Trial Report CSIRO Land and Water; Report No. 6/00; CSIRO: Clayton South, Australia, 2000.
- Douglas, G.B.; Robb, M.S.; Coad, D.N.; Ford, P.W. A review of solid phase adsorbents for the removal of phosphorus from natural and waste waters. In *Phosphorus in Environmental Technology e Removal, Recovery, Applications*; Valsami-Jones, E., Ed.; IWA Publishing: London, UK, 2004; Volume 13, pp. 291–320.
- 24. Haghseresht, F. A Revolution in Phosphorous Removal. Phoslock Water Solutions Ltd. In, 21. 2005. Available online: http://www.phoslock.com.au (accessed on 12 December 2015).
- 25. Haghseresht, F.; Wang, S.; Do, D.D. A novel lanthanum-modified bentonite, Phoslock, for phosphate removal from wastewaters. *Appl. Clay Sci.* **2009**, *46*, 369–375. [CrossRef]
- 26. Jin, X.; Wang, S.; Pang, Y.; Wu, F. Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake. *China Environ. Pollut.* **2006**, *139*, 288–295. [CrossRef]
- 27. Reitzel, K.; Lotter, S.; Dubke, M.; Egemose, S.; Jensen, H.S.; Andersen, F.Ø. Effects of Phoslock treatment and chironomids on the exchange of nutrients between sediment and water. *Hydrobiologia* **2013**, 703, 189–202. [CrossRef]
- 28. Bishop, W.M.; Richardson, R.J. Influence of Phoslock on legacy phosphorus, nutrient ratios, and algal assemblage composition in hypereutrophic water resources. *Environ. Sci. Pollut. Res.* **2018**, *25*, 4544–4557. [CrossRef] [PubMed]
- 29. Gan, L. Effects of Lanthanum Modified Bentonite on the Overlying Water Phosphorus and the Sediment Phosphorus Forms Concentrations in Eutrophic Shallow Lakes. Master's Thesis, Jinan University, Tripoli, Lebanon, 30 June 2015.
- Bishop, W.M.; McNabb, T.; Cormican, I.; Willis, B.E.; Hyde, S. Operational evaluation of Phoslock phosphorus locking technology in Laguna Niguel Lake, California. *Water Air Soil Pollut*. 2014, 225, 1–11. [CrossRef]
- 31. Wei, F. Water and Wastewater Monitoring and Analysis Method Guide: Middle Volume; China Environmental Science Press: Beijing, China, 1997.
- 32. Huang, X. Survey, observation and analysis of lake ecology. In *Standard Methods for Observation and Analysis in Chinese Ecosystem Research Network*; Standards Press of China: Beijing, China, 1999; p. 247. (In Chinese)
- 33. APHA. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.
- 34. Pettersson, K.; Boström, B.; Jacobsen, O. Phosphorus in sediments—Speciation and analysis. *Hydrobiologia* **1988**, 170, 91–101. [CrossRef]
- 35. Ribeiro, D.C.; Martins, G.; Nogueira, R.; Cruz, J.V.; Brito, A.G. Phosphorus fractionation in volcanic lake sediments (Azores– Portugal). *Chemosphere* **2008**, *70*, 1256–1263. [CrossRef]
- 36. Ross, G.; Haghseresht, F.; Cloete, T.M. The effect of pH and anoxia on the performance of Phoslock, a phosphorus binding clay. *Harmful Algae* **2008**, *7*, 545–550. [CrossRef]
- Dithmer, L.; Lipton, A.S.; Reitzel, K.; Warner, T.E.; Lundberg, D.; Nielsen, U.G. Characterization of phosphate sequestration by a Lanthanum modified bentonite clay: A solid-state NMR, EXAFS, and PXRD study. *Environ. Sci. Technol.* 2015, 49, 4559–4566. [CrossRef] [PubMed]
- 38. Gan, L.; Zhong, P.; Su, L.; Liu, Z. Effects of Lanthanum modified bentonite on the water phosphorus concentration and sediment phosphorus form in a shallow eutrophic lake. *J. Lake Sci.* **2019**, *31*, 1219–1228. [CrossRef]

- 39. Kim, S.C. Application of response surface method as an experimental design to optimize coagulation–flocculation process for pre-treating paper wastewater. J. Ind. Eng. Chem. 2016, 38, 93–102. [CrossRef]
- Noyma, N.P.; de Magalhães, L.; Furtado, L.L.; Mucci, M.; van Oosterhout, F.; Huszar, V.L.; Marinho, M.M.; Lürling, M. Controlling cyanobacterial blooms through effective flocculation and sedimentation with combined use of flocculants and phosphorus adsorbing natural soil and modified clay. *Water Res.* 2016, 97, 26–38. [CrossRef] [PubMed]
- 41. Waajen, G.; van Oosterhout, F.; Douglas, G.; Lürling, M. Management of eutrophication in Lake De Kuil (The Netherlands) using combined flocculant–Lanthanum modified bentonite treatment. *Water Res.* **2016**, *97*, 83–95. [CrossRef] [PubMed]
- Meis, S.; Spears, B.M.; Maberly, S.C.; O'Malley, M.B.; Perkins, R.G. Sediment amendment with Phoslock in Clatto Reservoir (Dundee, UK): Investigating changes in sediment elemental composition and phosphorus fractionation. *J. Environ. Manag.* 2012, 93, 185–193. [CrossRef] [PubMed]
- 43. Jing, L.; Liu, X.; Bai, S.; Wu, C.; Ao, H.; Liu, J. Effects of sediment dredging on internal phosphorus: A comparative field study focused on iron and phosphorus forms in sediments. *Ecol. Eng.* **2015**, *82*, 267–271. [CrossRef]
- 44. Boström, B.; Andersen, J.M.; Fleischer, S.; Jansson, M. Exchange of phosphorus across the sediment-water interface. In *Phosphorus in Freshwater Ecosystems. Developments in Hydrobiology*; Persson, G., Jansson, M., Eds.; Springer: Dordrecht, The Netherlands, 1988; Volume 48, pp. 229–244. [CrossRef]
- 45. Rydin, E. Potentially mobile phosphorus in Lake Erken sediment. Water Res. 2000, 34, 2037–2042. [CrossRef]
- 46. Li, D.; Huang, Y. Sedimentary phosphorus fractions and bioavailability as influenced by repeated sediment resuspension. *Ecol. Eng.* **2010**, *36*, 958–962. [CrossRef]
- 47. Boström, B. Potential mobility of phosphorus in different types of lake sediment. *Int. Rev. Gesamten. Hydrobiol.* **1984**, *69*, 457–474. [CrossRef]
- 48. Wang, S.; Jin, X.; Zhao, H.; Wu, F. Phosphorus fractions and its release in the sediments from the shallow lakes in the middle and lower reaches of Yangtze River area in China. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, 273, 109–116. [CrossRef]
- 49. Van Oosterhout, F.; Waajen, G.; Yasseri, S.; Marinho, M.M.; Noyma, N.P.; Mucci, M.; Douglas, G.; Lürling, M. Lanthanum in water, sediment, macrophytes and chironomid larvae following application of Lanthanum modified bentonite to lake Rauwbraken (The Netherlands). *Sci. Total Environ.* **2020**, *706*, 135188. [CrossRef]
- 50. Huser, B.J.; Egemose, S.; Harper, H.; Hupfer, M.; Jensen, H.; Pilgrim, K.M.; Reitzel, K.; Rydin, E.; Futter, M. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Res.* **2016**, *97*, 122–132. [CrossRef] [PubMed]
- 51. Yang, C.; Yang, P.; Yin, H. In situ control of internal nutrient loading and fluxes in the confluence area of an eutrophic lake with combined P inactivation agents and modified zeolite. *Sci. Total Environ.* **2021**, 775, 145745. [CrossRef] [PubMed]
- 52. Araújo, F.; dos Santos, R.H.; Becker, V.; Attayde, J.L. The use of polyaluminium chloride as a restoration measure to improve water quality in tropical shallow lakes. *Acta Limnol. Bras.* **2018**, *30*, e109. [CrossRef]