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Title: Assessing the impacts of phosphorus inactive clay on phosphorus release control and phytoplankton community structure in eutrophic lakes

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Keywords: Phosphorus; phosphorus inactive clay (PIC); Phoslock®; water-sediment interface; eutrophication; phytoplankton community

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Abstract: Addressing the challenge that phosphorus is the key factor and cause for eutrophication, we evaluated the phosphorus release control performance of a new phosphorus inactive clay (PIC) and compared with Phoslock®. Meanwhile, the impacts of PIC and Phoslock® on phytoplankton abundance and community structure in eutrophic water were also discussed. With the dosage of 40 mg/L, PIC effectively removed 97.7% of total phosphorus (TP) and 98.3% of soluble reactive phosphorus (SRP) in eutrophic waters. In sediments, Fe/Al-phosphorus and organic phosphorus remained stable whereas Ca-phosphorus had a significant increase of 13.1%. The results indicated that PIC may form the active overlay at water-sediment interface and decrease the bioavailability of phosphorus. The phytoplankton abundance was significantly reduced by PIC and decreased from (1.0-2.4)×107 cells/L to (1.3-4.3)×106 cells/L after 15 d simultaneous experiment. The phytoplankton community structure was also altered, where Cyanobacteria and Bacillariophyceae were the most inhibited and less dominant due to their sensitivity to phosphorus. After PIC treatment, the residual lanthanum concentration in water was 1.44-3.79 μg/L, and the residual aluminium concentration was low as 101.26-103.72 μg/L, which was much less than the recommended concentration of 200 μg/L. This study suggests that PIC is an appropriate material for phosphorus inactivation and algal bloom control, meaning its huge potential application in eutrophication restoration and management.

*Cover Letter

To:
Editor of Environmental Pollution

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29th February 2016

Dear Editor

I would like to submit this manuscript, entitled "*Assessing the impacts of phosphorus inactivation clay on phosphorus release control and phytoplankton community structure in eutrophic lakes*", for the consideration in *Environmental Pollution*.

This work developed a new phosphorus inactivation clay, achieving: 1) long-term phosphorus immobilization for 15 days; 2) over 97.7% and 98.3% removal efficiency for total and soluble active phosphorus; 3) strong inhibition phytoplankton abundance from (1.0-2.4)×10^7 cells/L to (1.3-4.3)×10^6 cells/L; 4) low La^{3+} (<3.79 µg/L) and Al^{3+} (<104.09 µg/L) residue for drinking water safety. This work provides more evidence to show the feasibility of phosphorus inactivation clay in phosphorus immobilization and phytoplankton inhibition for further application in eutrophic lake restoration.

This work has been presented on *The 3rd National Symposium of Sediment Environment & Pollution Control* (Nanjing, China).

Conflict of Interest

No conflict of interest exits in the submission of this manuscript, and the manuscript has approved by all authors for publication. The authors would like to declare that the work described is original research that has not been published previously, and is not under consideration for publication elsewhere, in whole or in part. It has not been submitted to *Environmental Pollution* before.

The Graphic Abstract was drawn by the authors themselves without any citation from the internet.

Thanks for your consideration. If you have any questions, please feel free to contact with me.

Yours sincerely

Dr Dayi Zhang

Reviewers' comments:
Thanks for the efforts and kinds suggestions of the reviewers. We have carefully revised the whole manuscript according to the comments. The sentences with yellow background colour represent the revision to specific comment and the sentences with blue background colour refer to the general major revision in the main text. Some other minor revision has also been made to improve the quality of the manuscript.

Reviewer #2: This study ENVPOL-D-16-00534R1 "Assessing the impacts of phosphorus inactive clay on phosphorus release control and phytoplankton community structure in eutrophic lakes" investigated a phosphorus inactivation phenomenon of PIC treatment for eutrophication control; they also studied the impacts of PIC on the abundance and structure of phytoplankton community. The study found an efficiency mechanism of phosphorus inactivation, which blocks phosphorus into the water-sediment interface in 15 days. It is an interesting study. The experimental design was in general good and targeted the study's major objective. In my opinion, the authors' interpretation of the results was clearly presented. However, some details should be revised, especially in citied references. Some sentences should be language polished to avoid confusion.

Minor comments & suggestion
Abstract
1. 97.7% of total phosphorus (TP) and 98.3% of soluble reactive phosphorus (SRP) in eutrophic water.
   Response: Thank you for the comments and we have revised the sentence in accordance with the suggestion.
2. The results indicated that PIC may form the active overlay at water-sediment interface and decrease the bioavailability of phosphorus.
   Response: Thank you for the comments and we have revised the sentence in accordance with the suggestion.
3. In sediments
   Response: Thank you for the comments and we have revised the sentence in accordance with the suggestion.
4. After PIC treatment, the residual lanthanum and aluminium concentrations in water were low as XXX, which were much less than the recommended concentrations of XX.
   Response: Thank you for the comments and we have revised the sentence in accordance with the suggestion. However, there is no guideline for La in WHO standard and therefore we only reference the 200 ug/L recommended concentration of Al. The revised sentence is:
   "After PIC treatment, the residual lanthanum concentration in water was 1.44-3.79 μg/L, and the residual aluminium concentration was low as 101.26-103.72 μg/L, which was much less than the recommended concentration of 200 μg/L."
5. This study suggested that XXX, meaning its huge potential application in XXX.
   Response: Thank you for the comments and we have revised the sentence in accordance with the suggestion.

Main text
6. Change the p-value as p, no need to indicate word "value".
   Response: Thank you for the comments and we have corrected all the places in the manuscript.
7. Line 48 and plays an essential role in aquatic ecosystem.
   Response: Thank you for the comments and we have revised the sentence.
8. Line 65, its good performance of phosphorus release control in several lakes
   Response: Thank you for the comments and we have revised the sentence.
9. Line 71, considering the importance of lake ecological stability, it is XX
   Response: Thank you for the comments and we have revised the sentence.

10. Line 75-82, To identify the practicability of PIC treatment and clarify the potential impacts of PIC on aquatic ecosystem, the present study compared the efficiency of phosphorus release control and structure changes of phytoplankton community after PIC treatment with after phoslock treatment in a 15-day experiment.
    Response: Thank you for the comments and we have revised the sentence.
11. Remove we hypothesis and the conclusion help XXX. These sentences were empty and normally forecast in the end or conclusion, not in introduction part.
    Response: Thank you for the comments. The hypothesis and conclusion were suggested by another reviewer and we added this part the in revised version. As suggested by this reviewer, we have revised the sentence and move this part into conclusion.
12. Line 94, Sediment samples about 5.0 kg were collected at the same sites XX.
    Response: Thank you for the comments and we have revised the sentence as suggested.
13. Line 119 Ck can't direct use with no any explanation, is that meaning the control group.
    Response: Thank you for the comments and it does mean the control group. We have revised the sentence as "The control group with neither PIC nor Phoslock® amendment was named as CK treatment for comparison with Phoslock® or PIC treatments".
14. Line 147 the phosphorus of each fraction was determined according XX.
    Response: Thank you for the comments and we have revised the sentence as suggested.
15. Please shorted the part of Results, indicate the main results, concise description.
    Response: Thank you for the comments and we have revised the whole results as suggested, marked with blue background colour.
16. Line 184, give the details of EDS analysis in Figure or Table or supplementary data. "The EDS element analysis indicated a high proportion of aluminium in bentonite as the active element for phosphorus immobilization", this sentence is a summary or description, not the real results, the EDS analysis may be an important direct evidence of active overlay. I think this part should be revised and show much more details and results.
    Response: Thank you for the comments and we have added the data of EDS analysis in the supplementary material. The key results are demonstrated and discussed in the main text to show evidence of active overlay by aluminium. We do not include very detailed analysis since the PIC synthesis part has been submitted to other journals and we try to avoid multiple submission.
17. Line 225-234 the present of active overlay is just the implication, change "could" may form CC and affect the sediment phosphorus profiles.
    Response: Thank you for the comments and we have revised the sentence as suggested.
18. Shorted the results of line 235-242.
    Response: Thank you for the comments and we have shorten the paragraph as suggested.
19. Line 278 they those was confused. Please change the express of sentences.
    Response: Thank you for the comments and we have revised the sentence for clearer expression, as "The residual lanthanum concentrations after PIC treatment were much lower (<20%) than those after Phoslock® treatment ($p<0.01$)".

Discussion

20. Line 285-287 the Redfield ratio means the N:P stoichiometry in plankton tends to the N:P mole composition of seawater, especially a remarkably similar ratio of dissolved nitrate to phosphate, not the TN/TP ratio. It is no necessary to cite the Redfield ratio because of no ratio results showed in details. Focused on the main point, not various.
    Response: Thank you for the comments and we have deleted the sentence for a clearer description as: "The ratios of TN to TP in Shanzi Reservoir and Xingyu Lake ranged from 35 to 145 (mole:mole), indicating that phosphorus concentration is relatively lower and behaves as the key nutrient factor causing the eutrophication in both waters."
21. Please not repeat much results in this part.

Response: Thank you for the comments and we have deleted most of the repeated results in this part, marked with blue background colour.

22. Line 330-339. Shorted the words, do not repeated the common results in Discussion.
    Response: Thank you for the comments and we have revised the whole paragraph for clearer statement.
23. Line 349 cited the Figure 5.
    Response: Thank you for the comments and the figure is appropriately cited.
24. Line 353 not the first time report, Bacillariophyceae also decrease. Change the sentences.
    Response: Thank you for the comments. We have deleted "for the first time". Meanwhile, in this sentence, we would like to address the specific surpression of harmful algae, not repeating the results from the previous sentence. Thus according to the comments, we have revised the sentence as "Since the majority of harmful algae belongs to the phylum Cyanobacteria (Johnk et al., 2008; Landsberg, 2002; Paerl et al., 2001), our results suggested that PIC can particularly supress some harmful algae more than other algal species, with the unexpected strong performance in reducing algal bloom and preventing their recurring.".
25. The cell size of Cyanobacteria is normally smaller than Bacillariophyceae, they also can tolerate the low phosphorus, especially some marine cyanobacteria was removed by PACl-modified clay. I think the time of this experiment on phytoplankton community change was limited, maybe long term (>1 or 2 month) could support your conclusion.
    Yu ZM, Zou JZ, Ma XN (1995) Application of clays to removal of red tide organisms III. The coagulation of kaolin on red tide organisms. Chinese Journal of Oceanology and Limnology 13: 62-70.
    Response: Thank you for the comments and we have cited the reference appropriately. We do agree with reviewer's kind suggestion that the experiment should last for longer time. However, the present study is only small scale lab test and not suitable for investigation over 15 days, because of limited water volume and artificial conditions far-away from the field. Some mesocosm experiment is undergoing to reveal the long-term (over 3 months) effects of PIC on phytoplankton community change and we hope to add some additional insight in this area in our future papers.
26. Line 414 were "verified".
    Response: Thank you for the comments and we have corrected the sentence according to the comments.
27. Line 432 mesocosm experiment.
    Response: Thank you for the comments and we have corrected the sentence according to the comments.

Conclusion

28. Line 442 "the PIC dosage was positively correlated with the residual TP and SRP" was confused. That means PIC applied more, the residual nutrient more.
    Response: Thank you for the comments and it is our mistakes. The sentence has been corrected as "The PIC dosage was positively correlated with the removal of TP and SRP".
29. Change the express of line 442-444
    Summary the main points
    1.
    2.
    3.
    I think author needs rewrite the conclusion part.
    Response: Thank you for the comments and we have revised the conclusion thoroughly according to the comments.

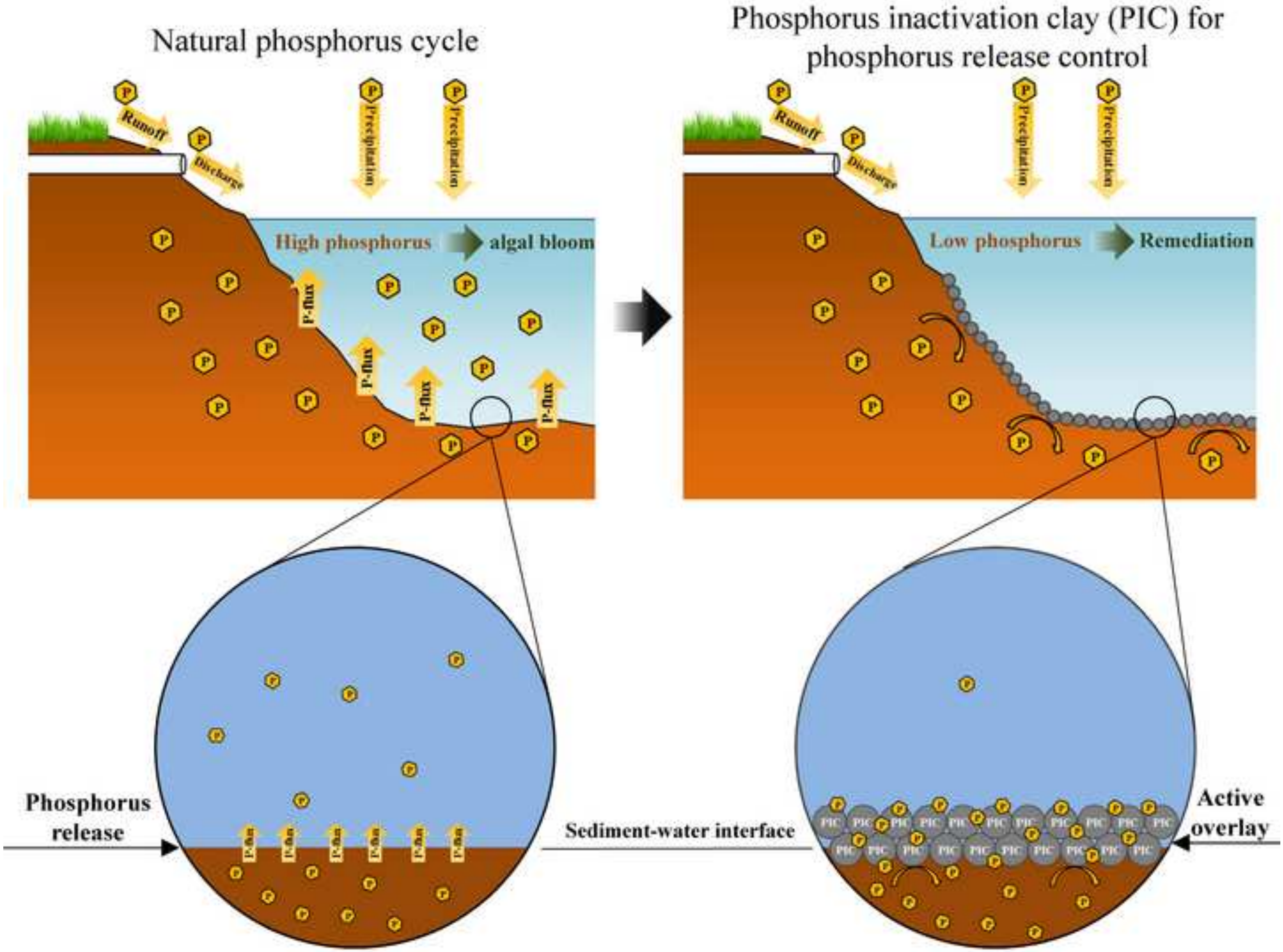
30. Table 2 indicate the SDP, there was no records of explanation in this submission.
    Response: Thank you for the comments. It is our typos and it should be TDP. We have corrected the word.

31. Table 3 inactive clay dosage, the end concentration or added concentration?
    Response: Thank you for the comments and it is the added PIC concentration. We have corrected the content as suggested.
32. Table 4 The residual lanthanum and aluminium concentrations (<mu>g/L) of water in Shanzi Reservoir and Xingyu Lake after different treatments.
    Response: Thank you for the comments and we have corrected the table title as recommended.
33. Keep the same size of font in results. And please indicate the abbreviation (especially CK and PIC) in the end of the table and add the unit and different treatments title in table.
    Response: Thank you for the comments and the table has been corrected according to the comments.
34. The explained detials of graphs should indicate in figure caption or sub-caption, not in graphs. For distinguishing between Shanzi Reservoir and Xingyu Lake could highlight in Figures. Figure 1 TP (A and C represent with PIC, E and G represent with Phoslock) and SRP (B and D represent with PIC, F and H represent with Phoslock) in caption indication, not in graphs.
    Response: Thank you for the comments and we have revised the graph and figure captions.
35. Figure 2 remove the explanation in graph, indicate in the figure title "Shanzi Reservior (PIC in A, Phoslock in B) and Xinyu Lake (PIC in C, Phoslock in D)", delete this kind of express "phosphorus fraction in sediment", the author indicated in figure caption, not need in graphs.
    Response: Thank you for the comments and we have corrected both graph and figure caption.
36. Figure 3 the same title change as Figure 2, do not use TDP and SRP in top form.
    Response: Thank you for the comments and we have revised the graph and figure captions.
37. Figure 4 the same change of indication in title as Figure 2.
    Response: Thank you for the comments and we have revised the graph and figure captions.
38. Figure 5 the empty cycle was in bigger size than other symbols. Highlight the PIC data to the front, in this figure, readers cannot see, also add details of explanation in figure caption or sub-caption.
    Response: Thank you for the comments and we have carefully revised the caption for Figure 5 and the symbols.

References

39. Special symbol of some authors name, e.g. Lürling and van Oosterhout, 2010, 2012, and 2013, López-Sánchez. Swartzen-Allen, S. L. No need indicate the journal location of Chemical Reviews. Please carefully re-check the whole manuscript and cited references. There are still some details needs to revise before publication. Shorted the main text excluding reference in 8000 words.
    Response: Thank you for the comments and we have checked/corrected all the mistakes in the reference. The word count for the main text is shortened to 5158 words (excluding reference), plus 4 tables and 5 figures (counting for 300 words each).
40. Please make sure all format conform the requirements of EP.
    Response: Thank you for the comments and we have further corrected some mistakes to meet the format requirement of EP.

Graphical Abstract



Highlights

- Phosphorus inactivation clay for effective phosphorus immobilization
- Over 97.7% and 98.3% removal efficiency for total and soluble active phosphorus
- Strongly inhibit phytoplankton from $(1.0\text{-}2.4)\times10^7$ cells/L to $(1.3\text{-}4.3)\times10^6$ cells/L
- Significantly alter phytoplankton community structure
- Low La (<3.79 μg/L) and Al (<104.09 μg/L) residue for drinking water safety

Assessing the impacts of phosphorus inactive clay on phosphorus release control and phytoplankton community structure in eutrophic lakes

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Abstract

Addressing the challenge that phosphorus is the key factor and cause for eutrophication, we evaluated the phosphorus release control performance of a new phosphorus inactive clay (PIC) and compared with Phoslock®. Meanwhile, the impacts of PIC and Phoslock® on phytoplankton abundance and community structure in eutrophic water were also discussed. With the dosage of 40 mg/L, PIC effectively removed 97.7% of total phosphorus (TP) and 98.3% of soluble reactive phosphorus (SRP) in eutrophic waters. In sediments, Fe/Al-phosphorus and organic phosphorus remained stable whereas Ca-phosphorus had a significant increase of 13.1%. The results indicated that PIC may form the active overlay at water-sediment interface and decrease the bioavailability of phosphorus. The phytoplankton abundance was significantly reduced by PIC and decreased from (1.0-2.4)×10^7 cells/L to (1.3-4.3)×10^6 cells/L after 15 d simultaneous experiment. The phytoplankton community structure was also altered, where Cyanobacteria and Bacillariophyceae were the most inhibited and less dominant due to their sensitivity to phosphorus. After PIC treatment, the residual lanthanum concentration in water was 1.44-3.79 μg/L, and the residual aluminium concentration was low as 101.26-103.72 μg/L, which was much less than the recommended concentration of 200 μg/L. This study suggests that PIC is an appropriate material for phosphorus inactivation and algal bloom control, meaning its huge potential application in eutrophication restoration and management.

Keywords: Phosphorus; phosphorus inactive clay (PIC); Phoslock®; water-sediment interface; eutrophication; phytoplankton community

Capsule abstract

Phosphorus inactive clay effectively immobilizes phosphorus in eutrophic waters, forms active overlay for 15-day phosphorus release control, and inhibits algal bloom.

1. Introduction

Water eutrophication is a worldwide problem in water quality control, and algal bloom is one of the most serious challenges in drinking water safety (Brookes and Carey, 2011). In most aquatic ecosystems resilience to eutrophication, phosphorus is identified as the key restrict nutrient (Schindler et al., 2008). Sediment is the sink of organic matters in the geochemical environment and plays an essential role in aquatic ecosystem. It is not only the habitat for benthic and aqueous organisms, but also the place where a variety of nutrients migrates and transforms (Gulati and van Donk, 2002). Furthermore, sediment has been regarded as the main endogenous source of phosphorus in most of the eutrophication cases, consequently resulting in the failure of algal bloom control when the exogenous nutrients are cut off (Søndergaard et al., 2007; Spears et al., 2012). Even worse, the recruitment of benthic species enhances the phosphorus release and cause phosphorus accumulation in aqueous phase, consequently aggravating algal bloom (Barbiero and Welch, 1992; Xie et al., 2003). It is necessary to develop effective treatments, with high efficiency, low cost and minimal ecological risks, for endogenous phosphorus release control and water restoration (Hickey and Gibbs, 2009).

Recently, Phoslock® becomes a popular phosphorus inactive material (Robb et al., 2003; Spears et al., 2013a), which stabilizes the aqueous active phosphorus by forming the $LaPO_4$ chelate precipitate ($La^{3+}+PO_4^{3-}\rightarrow LaPO_4\downarrow$, Ksp = $10^{-24.7}$-$10^{-25.7}$). The settlement of chelate precipitate further forms the "active overlay" at water-sediment interface, contributing to long-term phosphorus release control (Gibbs et al., 2011). As the most investigated and applied phosphorus inactive materials (Lürling and Faassen, 2012; Meis et al., 2012; Moos et al., 2014; van Oosterhout and Lürling, 2013), Phoslock® has attracted much attention in its good performance of phosphorus release control in several lakes (Reitzel et al., 2013; Spears et al., 2013b) or the potential ecological risks after Phoslock® amendment (Lürling and Tolman, 2010; Wagenhoff et al., 2012). Though researches have discussed the change of phytoplankton abundance in Phoslock® treatments (Lürling and van Oosterhout, 2013; Waajen et al., 2016), there is still limited study addressing the dynamics and response of phytoplankton community during phosphorus release control process (Lang et al., 2016). Considering the importance of lake ecological stability, it is particularly necessary to assess the phytoplankton community after water quality restoration practices.

In this research, we assessed the phosphorus release control for 15 days by a novel phosphorus inactive clay (PIC) in two types of eutrophic water, deep reservoir (Shanzi Reservoir) as drinking water source and shallow landscape water (Xingyu Lake). To identify the practicability of PIC treatment and clarify its impacts on aquatic ecosystem, the present study compared the efficiency of phosphorus release control and structure changes of phytoplankton community after PIC treatment with those after Phoslock® treatment.

2. Materials and Methods

2.1 Sites and sample collection

The eutrophic water samples were collected by plexiglass sampler in October 2014 and January 2015 in Xingyu Lake (N26°1'40", E119°12'23") and Shanzi reservoir (N26°22'33", E119°18'53"), respectively. These two waters suffered from serious eutrophication in early spring and late summer (Su et al., 2016), and the present study focused on the phosphorus release control during winter season to reduce the risks of spring algal bloom. At each sampling point, about 50.0 L of water samples were collected. The 1,000 mL water sample was added with Lugol's iodine solution as antiseptic and disinfectant immediately for phytoplankton community analysis. The rest of water samples were directly stored at 4°C within 1 day for further chemical analysis and phosphorus inactivation experiment. Sediment samples about 5.0 kg were collected at the same sites by Petersen grab (437 330, Bottom Sampler acc. to Van Veen, 20×30×60 cm), immediately transferred into plastic bags and stored at -20°C for chemical analysis or 4°C for phosphorus inactivation experiment.

2.2 PIC and phosphorus adsorption isotherm

In the present study, PIC was an aluminium-modified bentonite clay synthesized as previously described (Hao et al., 2014). The bentonite clay behaved as the carrier for the reactive aluminium for phosphorus immobilization. The Phoslock® was purchased from Sichuan Phoslock Environmental Water Treatment Company. To test the phosphorus adsorption isotherm, the 0.2 g PIC was air-dried and directly added into 50 mL deionized water, supplemented with phosphorus concentration of 0, 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 mg/L. After constant stirring at 26 ℃ at 240 rpm for series of time (0, 6, 9, 15, 30, 60, 240, 420, 720 and 1440 min), the suspension was centrifuged at 4,000 rpm for 10 min and the supernatant was further analyzed for residual phosphorus concentration.

2.3 Phosphorus inactivation and release control experiment

The phosphorus inactivation and release control treatments were set up in column test (2.5 L plastic barrel). For each treatment, the 2,000 mL water samples were gently overlaid on 200.0 g sediments. The cultivation condition was 12h:12h light-dark-cycle (photon flux density was 65 μmoles/m^2·s) and 15°C. Intermittent aeration was conducted within the whole light period (12 hours each day) to simulate the *in-situ* physical disturbance at water-sediment interface in winter season. From previous research on the optimal amendment of Phoslock® and the phosphorus adsorption capacity of PIC, the ratio of Phoslock® or PIC to SRP was suggested as 100:1 to achieve the best phosphorus immobilization performance (Reitzel et al., 2013). From the chemical analysis of phosphorus in the water samples, the optimal Phoslock® or PIC dosage was around 30 mg/L. Therefore, the dosage of Phoslock® or PIC was set as 10, 20, 30 and 40 mg/L, and they were amended gently into the column after air dried. The control group with neither PIC nor Phoslock® amendment was named as *CK* treatment for comparison with Phoslock® or PIC treatments. The water samples were collected on 1, 3, 5, 7, 9, 12 and 15 days. All the treatments were carried out in triplicates.

2.4 Chemical analysis

A JSM7500F (JOEL, Japan) scanning electron microscope (SEM) was used to study the morphology of PIC by and the energy-dispersive X-ray spectroscopy (EDS) was obtained TEAM™ EDS system (EDAX, USA). In 15-day phosphorus release control experiment, the values of pH and dissolved oxygen (DO) in water samples were measured by a pH meter (pH B-8, CSDIHO, China) and portable DO meter (JPB-607, INESA, China), respectively. Total nitrogen (TN) was determined by alkaline potassium persulfate digestion UV spectrophotometric method (Zhang et al., 2010). The soluble reactive phosphorus (SRP) in water sample was directly measured by molybdenum blue UV spectrophotometric method (Murphy and Riley, 1962). The extraction of phosphorus species in sediment samples followed the Standards Measurements and Testing (SMT) method (Ruban et al., 2001) as a widely applied routine method for studying phosphorus fractions in sediments (Pardo et al., 2004). Briefly, the sediment was grounded to 100 mesh after air-dried. The 0.20 g of sediment powder was added into 20 mL 1.0 mol/L NaOH and shaken for 16 hours. After centrifugation at 4,000 rpm for 20 min, the 10 mL supernatant was added with 4 mL 3.5 mol/L HCl and stabilized for 16 h as Fe/Al-phosphorus (Fe/Al-P) fraction. The pellets were further resuspended in 20 mL 1.0 mol/L HCl and kept shaking for 16 h as Ca-phosphorus (Ca-P) fraction. For inorganic phosphorus (IP) and organic phosphorus (OP) fraction, the 0.20 g sediment was added with 20 mL 1.0 mol/L HCl and the IP fraction was within the supernatant after 16 h by stabilization. After gently washed by deionized water, the pellets were burned in muffle furnace at 450°C for 3 h and dissolved in 20 mL 1.0 mol/L HCl. The OP fraction was in the supernatant after 16 h shaking and centrifugation. The total dissolved phosphorus (TDP) and SRP in interstitial water of sediments was extracted in the supernatant by centrifuging the sediment at 4,000 rpm for 5 min. For TP fraction in sediments, the 0.20 g sediment was burned directly in muffle furnace at 450°C for 3 h, dissolved in 20 mL 3.5 mol/L HCl and finally stabilized for 16 h. For TP in water and TDP in supernatant, the water sample was digested by potassium persulfate. The phosphorus of each fraction was determined according to the ammonium molybdate spectrophotometric method (ISO, 2004), using a UV-Vis spectrophotometer with 700 nm wave length (UV-1100, MAPADA, China).

Lanthanum and aluminium measurement followed the inductively coupled plasma mass spectrometry (ICP-MS) method (Kajiya et al., 2004). After centrifugation at 10,000 rpm for 10 min, the supernatant passed through 20 μm filter and was injected into ICP-MS X-Series II (Thermo Scientific, USA). Argon was the cooling, assistant and carrier gas, with the flow rate of 13.0 L/min, 0.8 L/min and 0.82 L/min, respectively. In this study, the determination was carried out in the X Series Default mode (three points per peak) with 10 ms detention time and 3 s total sampling time.

2.5 Biological analysis

The phytoplankton community structure and abundance in all the water samples was determined with a binocular biological microscope (Motic, BM-1000, Guangzhou) (Casamayor et al., 2000). The 20 mL water samples with Lugol's iodine fixation were centrifuged at 10,000 rpm for 10 min and concentrated to the final volume of 100 μL by deionized water. The identification and counting of phytoplankton species was conducted in the 0.1 mL counting chamber (20 mm × 20 mm) with three individual replicates. All the measurement was carried out at 4°C in dark, and the phytoplankton abundance was calculated with the unit of cells per liter (cells/L) by Equation (1).

$$N = \left(\frac{A}{A_0} \times \frac{1}{V}\right) \times n \times 1000 \quad (1)$$

Here, N is phytoplankton abundance per microlitre water sample (cells/mL). A and V refer to the area (mm^2) and volume (0.1 mL) of counting chamber, respectively. A_0 represents the counting area (mm^2), and n is the number of phytoplanktons within the counting area (cells).

2.6 Data analysis

SPSS 17.0 was used for all statistical analysis. Between different treatments, the statistical significance of differences in phosphorus concentration and phytoplankton abundance was calculated by two-way ANOVA (Table 2). All the data were checked for normality (Shapiroe Wilk) and heteroscedasticity (Equal Variance test). The correlation between PIC/Phoslock® dosage and phosphorus immobilization performance was analysed by the Pearson correlation coefficient by bivariate tool in SPSS. The phytoplankton community structure with/without PIC or Phoslock® treatment was clustered by principal components analysis (PCA). The significant level for all the statistical analysis was $p<0.05$.

3. Results

3.1 Phosphorus adsorption by PIC

The morphology of PIC before and after phosphorus fixation was illustrated in Figure S1. The original PIC showed the round shape with an average diameter of 3 μm. After phosphorus adsorption, the particle size increased to 5 μm attributing to the nested PO_4^{3-} molecules in the crystal structure. From the EDS analysis results (Figure S1C and Table S1), the aluminium had a high atom proportion of 9.82% in PIC, significantly higher than that in raw bentonite (Li et al., 2016). Accordingly, the ratio of Na_2CO_3 to Al_2O_3 was estimated as 2.5:1 in PIC, and the results confirmed the successful bentonite-modification with aluminium as the active element for phosphorus immobilization. Phosphorus adsorption on PIC followed the Langmuir adsorption isotherm, indicating the monolayer adsorption mechanisms (Figure S2). The maximum phosphorus adsorption capacity (Q_{max}) was 9.93 mg/g and the Langmuir constant (K_L) associated with adsorption energy was 25.3 L/mg.

3.2 Phosphorus removal in water phase

Nutrient conditions in Shanzi Reservoir and Xingyu Lake were listed in Table 1. The TN and TP in Shanzi Reservoir varied in seasons, ranging from 0.15 to 1.14 mg/L and 20 to 80 μg/L, respectively. Xingyu Lake had a significant higher TN and TP due to more nutrients input and smaller water volume as landscape water. The addition of PIC or Phoslock® slightly decreased the water pH value (Figure S3), gradually declining from 7.40 to 6.82-6.93 in waters from Shanzi Reservoir and from 7.50 to 7.23-7.31 in waters from Xingyu Lake, respectively. They were both significantly lower than that in the *CK* treatment ($p=0.03$). The values of DO in all the treatments showed the same declining trend ($p=0.01$, Figure S4).

The 15-day phosphorus release control performance of PIC and Phoslock® was illustrated in Figure 1 and Table 3. Except *CK* and 10 mg/L PIC/Phosock® treatments, a significantly dramatic decline of TP was observed within 1 day ($p<0.001$). Afterwards, the residual phosphorus remained stable with tiny fluctuation (p=0.150, Table 2). The TP removal efficiency was positively correlated with PIC dosage (p=0.002), and the Pearson coefficient is 0.918 for Shanzi Reservoir (p<0.001) and 0.945 for Xingyu Lake (p<0.001), respectively. When the PIC dosage was above 20 mg/L, the residual TP was less than 20 μg/L. Compared to the maximum phosphorus adsorption capacity (Table 3), there was a negative correlation between the dosage and phosphorus adsorption efficiency of PIC (Pearson coefficient is -0.892 in Shanzi Reservoir, p=0.003; Pearson coefficient is -0.828 in Xingyu Lake, p=0.011). Compared to Phoslock® (Figure 1E and 1G), PIC had a better TP removal efficiency (p=0.001).

Similarly, a significant removal of SRP was observed for all the PIC and Phoslock® treatments (p<0.001). The SRP concentrations were lower than 10 μg/L from Day 1 to Day 15 in PIC (Fig. 1B and 1D) and Phoslock® (Fig. 1F and 1H) treatments. The SRP removal efficiencies were positively correlated with PIC dosage (Pearson coefficient 0.898 in Shanzi Reservoir, p<0.001; Pearson coefficient 0.590 in Xingyu Lake, p=0.001). The performance of SRP reduction after Phoslock® treatment was similar to that after PIC treatment (p=0.721, Table 2).

3.3 Impacts of PIC on sediment and interstitial water phosphorus profiles

The amendment of PIC and Phoslock® can form the "active overlay" and may affect the sediment phosphorus profiles. Our results indicated that Ca-P and IP had a significant increase after PIC treatment (Figure 2), from 95.34 μg/g to 127.05 μg/g (p<0.001) and 360.54 μg/g to 413.99 μg/g (p=0.004), respectively. The PIC dosage was positively correlated with the concentrations of Ca-P (Pearson coefficient 0.910, p<0.001) and IP (Pearson coefficient 0.845, p<0.001). For SRP and Fe/Al-P in sediments, there was no significant difference (p>0.05, Table 2 and Figure 2) before and after PIC or Phoslock® addition. Meanwhile, all the phosphorus fractions in sediments showed no remarkable difference between PIC and Phoslock® treatments (Table 2), indicating the similar mechanisms and performance of these two phosphorus inactive materials.

From phosphorus concentrations in interstitial water of the sediments from Shanzi Reservoir and Xingyu Lake (Figure 3), both TDP and SRP had a slightly increasing trend in either PIC or Phoslock® treatments. The TDP and SRP concentration in Shanzi Reservoir was 240-320 μg/L and 60-90 μg/L, respectively, and they were 330-400 μg/L and 30-50 μg/L in Xingyu Lake. Nevertheless, there was no significant difference between each dosage or between PIC and Phoslock® treatments from two-way ANOVAs (Table 2).

3.4 Phytoplankton community structure change

Both Shanzi Reservoir and Xingyu Lake were eutrophic waters with high phytoplankton abundance (*Original* in Figure 4). The dominant phytoplankton was Bacillariophyceae (7.76×10^6 cells/L), accounting for 85.80% of the total population in water from Shanzi Reservoir, followed by Chlorophyta (1.04×10^6 cells/L, 11.48%), Cryptophyta (1.70×10^5 cells/L, 1.88%), Euglenophyta (5.66×10^4 cells/L, 0.63%) and Cyanobacteria (1.89×10^4 cells/L, 0.21%). In Xingyu Lake, the total phytoplankton abundance was 2.03×10^7 cells/L, and the community was consisted of Chlorophyta (8.17×10^6 cells/L, 40.34%), Bacillariophyceae (4.19×10^6 cells/L, 20.69%), Cyanobacteria (4.10×10^6 cells/L, 20.25%) and Euglenophyta (3.69×10^6 cells/L, 18.25%) at phylum level.

PIC and Phoslock® amendment affected the phytoplankton abundance and community structure (Figure 4). In *CK* treatment, the total phytoplankton abundance increased to 9.63×10^6 cells/L and 2.38×10^7 cells/L in Shanzi Reservoir and Xingyu Lake, 6.5% and 17.4% higher than original waters (p=0.02). In PIC treatments, the total phytoplankton abundance decreased to $(0.014\text{-}0.626)\times10^6$ cell/L in Shanzi Reservoir (Figure 4A) and $(0.002\text{-}0.429)\times10^7$ cell/L in Xingyu Lake (Figure 4C). The phytoplankton inhibition rates ranged from 93.6%-99.9% and 82.0%-99.9% respectively, slightly higher than those of Phoslock® treatments (Figure 4B and 4D). The phytoplankton abundance was negatively correlated with PIC dosage (Pearson correlation coefficient -0.815 for Shanzi Reservoir and -0.852 for Xingyu Lake, $p<0.05$).

There was a significant difference in phytoplankton community structure after PIC or Phoslock® treatments from PCA plot (Figure 5). The locations of phytoplankton community of both Shanzi Reservoir and Xingyu Lake in *CK* treatment were close to those of original waters. With the increasing PIC/Phoslock® dosage, the phytoplankton community groups of both waters co-clustered, with longer distance to the *Original* and *CK* groups. The most obvious change (Figure 4) was the significant increase of Euglenophyta and Cryptophyta. Accordingly, Bacillariophyceae and Cyanobacteria were the main declining phylum.

3.5 La/Al residues after PIC treatment

To further evaluate the potential ecological risks of PIC, the residual lanthanum and aluminium were measured and listed in Table 4. Since lanthanum was not the formula in PIC, there was no significant difference in lanthanum concentrations before and after PIC amendment ($p>0.05$). The residual lanthanum concentrations after PIC treatment were much lower (<20%) than those after Phoslock® treatment ($p<0.01$). The residual aluminium after PIC treatment was 101.26

μg/L and 103.72 μg/L for waters from Shanzi Reservoir and Xingyu Lake respectively, similar to those in Phoslock® treatment (p>0.05). Considering the levels of residual lanthanum and aluminium, PIC had relatively lower ecological risks than Phoslock®.

4. Discussion

4.1 Dynamic change of phosphorus profiles in water and sediment

The ratios of TN to TP in Shanzi Reservoir and Xingyu Lake range from 35 to 145 (mole:mole), indicating that phosphorus concentration is relatively lower and behaves as the key nutrient factor causing the eutrophication in both waters. Furthermore, the endogenous release from sediments is also viewed as a key pathway of phosphorus nutrients for aquatic ecosystem. The present study therefore investigated the 15-day phosphorus release process at the water-sediment interface, considering the impacts of phosphorus inactive materials (PIC and Phoslock®) on phosphorus immobilization and phytoplankton community.

In all the treatments, the high phosphorus removal efficiency and stability after 15-day experiment demonstrated that the functional sites on PIC surface can effectively immobilize phosphorus, particularly the soluble and active fraction. PIC had a similar maximum phosphorus adsorption capacity to previously reported Phoslock® (9.5-10.5 mg/g) (Haghseresht et al., 2009). Its high Langmuir constant also indicated the strong binding strength between phosphorus molecules and PIC (Lin et al., 2015). From the negative correlation between PIC/Phoslock® dosage and phosphorus adsorption efficiency, we suggested abundant active sites on PIC and Phoslock®, which contributed to further phosphorus immobilization and prevented phosphorus release from sediment for at least 15 days. Similar to Phoslock®, PIC remained phosphorus inactivation capacity and behaved as the "active overlay" at the water-sediment interface after the settlement.

The slight decrease of pH value during PIC treatment might be attributed to the acidity of bentonite clay, which was the main ingredient of PIC (Liu et al., 2015; Penner and Lagaly, 2001), or the hydrolysis and exchange of element (Swartzen and Matijevi, 1974). The pH value shows significant impacts on the phosphorus immobilization efficiency of phosphorus inactive materials, particularly when the bentonite clay is used (Haghseresht et al., 2009; Reitzel et al., 2005). In the present study, the declining pH values further improved the stability of phosphorus precipitate. The results fitted well with previous research that the phosphorus inactivation performance is dependent on the physical and chemical features of the targeted water samples (Huser, 2012).

Previous research has revealed that sediment OP is positively correlated with the dosage of Phoslock® (Meis et al., 2013). Nevertheless, the OP concentration in sediment did not change with PIC addition in our study. It was reported that more phosphorus is released from sediment under anaerobic conditions (Geng et al., 2007; Hupfer and Lewandowski, 2008; Song et al., 2011). The increasing sediment OP is attributed to the settling phytoplankton and/or debris from decomposing macrophytes (Meis et al., 2013). The high DO concentration (Figure S4) in our work indicated the aerobic condition throughout the experiment. Thus, though the original phytoplankton abundance was of high level, the aerobic condition did not promote the transformation and release of phosphorus in sediment, causing less OP variation in sediments. Meanwhile, the aquatic SRP/TP ratio decreased after PIC treatment, similar to the previous results of Phoslock® (Reitzel et al., 2013). It indicated that PIC primarily reacts with the active fraction of phosphorus (SRP), and its phosphorus immobilization is dependent on the natural phosphorus cycling at the water-sediment interface.

The water-sediment interface plays a key role in phosphorus transportation and exchange. In all the PIC and Phoslock® treatments, the concentrations of TDP and SRP in interstitial water of sediments (Figure 3) were much higher than aqueous TP and SRP. From Yin's study, SRP fluxes are determined by the phosphorus gradient across sediment-water interface (Yin and Kong, 2015). A strong SRP flux is therefore expected after PIC/Phoslock® treatment, but our results showed the stable TP and SRP in waters throughout the 15-day experiment. It hinted limited phosphorus release from sediments, suggesting the formation of "active overlay" at the sediment surface by PIC or Phoslock® and effective phosphorus release control.

4.2 *Mechanisms of phytoplankton community change*

Algal bloom is the direct evidence of water eutrophication (Anderson et al., 2002; Smith, 2003), when the exceeding growth of various algae caused serious challenges in drinking water safety, particularly the toxigenic algae like *Microcystis aeruginosa*, *Aphanizomenon flos-aquae* and *Anabaena flosaguas* (Codd et al., 2005; Collins, 1978). By immobilizing phosphorus as the key nutrient in aquatic phase and blocking its release from the sediment, Phoslock® effectively reduces the nutrient level and maintained the oligotrophic condition (Schindler et al., 2008). Accordingly, our results showed that PIC had similar performance of significantly reducing phytoplankton abundance by immobilizing phosphorus and minimizing the active phosphorus (Figure 5). More interestingly, Bacillariophyceae and Cyanobacteria were identified as the key declining phytoplankton phylum in both eutrophic waters. Since the majority of harmful algae belongs to the phylum Cyanobacteria (Johnk et al., 2008; Landsberg, 2002; Paerl et al., 2001), our results suggested that PIC particularly supressed some harmful algae more than other algal species, with the unexpected strong performance in reducing algal bloom and preventing their recurring. It is hypothesized that Euglenophyta and Cryptophyta are not sensitive to inorganic phosphorus and can tolerate low phosphorus environment after phosphorus inactive clay treatment (Burgi et al., 2003; Chisholm and Stross, 1976). On the contrast, the phosphorus-sensitive Bacillariophyceae and Cyanobacteria are significantly affected by low phosphorus pressure (Lagus et al., 2004; Levine and Schindler, 1999; Lippemeier et al., 2001). Lang et al. reported the decreasing cyanobacteria after Phoslock® treatment in shallow water Loch Flemington, which is explained by the less competitive advantage of cyanobacteria under reduced phosphorus conditions (Lang et al., 2016). Similar results are also found in shallow reservoir in California (Bishop et al., 2014) and marine cyanobacteria removal by polyaluminium chloride modified clay (Yu et al., 1995). The close distance of phytoplankton community after PIC and Phoslock® treatment (Figure 5) indicated the similar community structure trends affected by the two phosphorus inactive materials, showing their feasibility in preventing algal bloom formation. However, the cell size of Cyanobacteria is normally smaller than Bacillariophyceae, indicating their stronger tolerance to low phosphorus. A larger scale of mesocosm experiment is therefore suggested to address the long-term effects of PIC on phytoplankton community dynamics, particularly harmful cyanobacterial abundance under low phosphorus conditions.

4.3 Ecological risk assessment

The additives of phosphorus inactivate materials may cause the increase of metal ions in aquatic environment, which possibly leads to their accumulation in the food chain and finally show risks to human health. Lanthanum is the reactive component of Phoslock® with such potential risks. The LD_{50} of $LaCl_3$ is 4200 mg La per kilogram body weight for rats (Cochran et al., 1950). A median threshold effects of $LaCl_3$ for Daphnia and Scenedesmus are reported as 160 mg La/L after 4 hours and 0.15 mg La/L for after 4 days, respectively (Bringmann and Kuhn, 1959). High level $LaCl_3$ exposure (>1 mg/L) can cause the death of fish within 24 hours (Peterson et al., 1974). Compared to Phoslock®, PIC did not use lanthanum as the ingredient in the present work. The residual lanthanum after PIC treatment was similar to the aquatic background in both eutrophic waters and much lower than that after Phoslock® treatment, showing relatively less ecological and health impacts.

Meanwhile, aluminium also has significant acute toxicity (Srinivasan et al., 1999). Particularly in acidic waters (pH 4.2 to 5.6), 0.1-0.2 mg/L aluminium can cause the reduction of survival and growth of larvae and postlarvae (Baker and Schofield, 1982). As for the risks on human health, the possibility of an association between aluminium and neuropathological diseases including presenile dementia, dialysis encephalopathy and Alzheimer's disease is frequently hypothesized. The kidney dialysis patients suffer dementia when their dialysis fluid contains an aluminium concentration of 0.08 mg/L (Davison et al., 1982). The presence of aluminium in drinking water has given rise to discussions on possible health effects, because of its suspected connection with Alzheimer's diseases or dialysis encephelopathy (Jekel and Heinzmann, 1989). Higher rate of Alzheimer’s disease is observed when the aluminium concentration exceeds 0.11 mg/L (Martyn et al., 1989), and similar results are found in the cases of animal neuropathological disorders (Kopeloff et al., 1942). World Health Organization (WHO) thus suggests the health-based value of 0.9 mg Al/L for drinking water, with detailed restriction of 0.1-0.2 mg Al/L for water after coagulation treatment (WHO, 2004). In the present work, the residual concentration of Al in water was about 0.1 mg/L after PIC and Phoslock® treatment. Though not exceeding the WHO recommended values, it still might be a potential source of aluminium release to water. Previous research revealed that the majority of residual lanthanum and aluminium is within the top 10 cm of sediments (Meis et al., 2013; Reitzel et al., 2005), and their ecological and health risks are then at low level as an engineering approach for phosphorus release control. We therefore suggested that the health risk of applying PIC or Phoslock® is limited, but it needs careful monitoring and assessment in practical application in reservoir or other drinking water sources.

4.4 Perspectives

Phosphorus is the key factor causing eutrophication and important for water quality. There are many attentions on its immobilization or release control from sediments. The application of various phosphorus inactive materials, including Phoslock®, has therefore attracted increasing attentions from both academia and industries around the world. Phoslock® is proved to immobilize phosphorus by creating phosphorus precipitate, form “active overlay” on the top of the sediment to block phosphorus releasing into the aquatic phase, and effectively trap the aquatic soluble phosphorus from other pathways (Meis et al., 2013). The present study addressed the phosphorus release control of PIC in eutrophic waters and compared its performance with widely accepted and applied Phoslock®. Their similar phosphorus immobilization behavior and impacts on the phytoplankton abundance and community were verified.

Applying Phoslock®, PIC or other phosphorus inactive materials is a strategic water restoration approach for eutrophic water quality management. Treatments in summer or autumn can immobilize all the SRP from aquatic phase. It may minimize the available phosphorus, reduce phytoplankton abundance and achieve short-term water quality improvement. As for the treatments in winter or spring, the phosphorus inactive materials can form the “active overlay” at the water-sediment interface and effectively block the phosphorus release from sediment. This strategy focuses on locking phosphorus within the sediment and contributes to long-term water quality recovery. Combined with other water restoration methods, like coagulation or oxidation, their performance can be even enhanced (Lürling and Faassen, 2012). Most of the previous research on phosphorus inactive materials has highlighted the performance of phosphorus fixation or immobilization (Lürling and Tolman, 2010; Spears et al., 2013a; Wagenhoff et al., 2012). Recently, their impacts on phytoplankton abundance and community structure are getting more attentions to be considered in eutrophic water restoration actions (Lürling and van Oosterhout, 2013; Lang et al., 2016; Waajen et al., 2016). Although our study aims to answer these questions, the laboratory-scale experiment cannot simulate the field reality where the phosphorus cycle and phytoplankton community are affected by numerous environmental factors (Paerl and Otten, 2013). The latest research has focused on the large-sized mesocosm experiment on long-term impacts of phosphorus inactive materials on phytoplankton abundance and community (Lang et al., 2016), and more work is suggested to address this question to evaluate the engineering parameters and the ecological consequence on the aquatic system for long-term phosphorus release control, especially in drinking water reservoirs.

5. Conclusion

The present study demonstrated the phosphorus inactivation by a new PIC in natural eutrophic waters from Shanzi Reservoir and Xingyu Lake. After 15 days experiment, PIC achieved effective phosphorus reduction, blocked phosphorus release from sediments, and significantly altered the phytoplankton community structure. The main results included:

1. The initial PIC dosage was negatively correlated with the aqueous residual TP and SRP, and the highest TP and SRP removal efficiency achieved 97.7% and 98.3%, respectively.
2. The phytoplankton abundance was significantly decreased with the increasing PIC dosage and the lowest residual phytoplankton abundance was less than 0.01% of

original eutrophic waters, attributing to the oligotrophic condition of phosphorus reduction.

3. Of all the phytoplanktons, the abundance of phylum Bacillariophyceae and Cyanobacteria was most reduced due to their higher sensitivity to phosphorus.
4. The residual lanthanum and aluminium concentrations after PIC treatment were at low levels and had minimal ecological or health risks.

The present work helps our deeper understanding on the performance of applying PIC to improve eutrophic water quality and its potential impacts on aquatic ecosystem. Our study shows that PIC is feasible for phosphorus release control and can be a practical tool in water quality restoration.

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Figure caption

Figure 1. The 15-day control performance of phosphorus release with PIC and Phoslock® treatments. (A) and (C) represent TP in PIC treatments; (E) and (G) represent TP in Phoslock® treatments. (B) and (D) represent SRP in PIC treatments; (F) and (H) represent SRP in Phoslock® treatments.

Figure 2. Phosphorus profiles in surface sediments with PIC and Phoslock® treatments. (A) for PIC and (B) for Phoslock® treatment in Shanzi Reservoir. (C) for PIC and (D) for Phoslock® treatment in Xingyu Lake. The subgraphs represent phosphorus fraction in each treatment, respectively.

Figure 3. TDP and SRP concentrations in interstitial water of sediments with PIC and Phoslock® treatments. (A) for PIC and (B) for Phoslock® treatment in Shanzi Reservoir. (C) for PIC and (D) for Phoslock® treatment in Xingyu Lake.

Figure 4. Abundance and structure changes of phytoplankton communities with PIC and Phoslock® treatments. (A) for PIC and (B) for Phoslock® treatment in Shanzi Reservoir. (C) for PIC and (D) for Phoslock® treatment in Xingyu Lake.

Figure 5. PCA analysis of phytoplankton community structure with PIC and Phoslock® treatments. The categories of phytoplankton community in either PIC (green) or Phoslock® (red) treatments co-cluster, with long distance to the *Original* (white) and *CK* (grey) groups in both Shanzi Reservoir (circle) and Xingyu Lake (triangle).

Table

Table 1. Nutrient conditions in Shanzi Reservoir and Xingyu Lake.

Water samples	Season	TN (mg/L)	TP (μg/L)	TN/TP	pH	DO (mg/L)
Shanzi Reservoir	Autumn	0.15-1.03	20-80	35-57	7.50-7.65	8.50-8.70
	Winter	1.28-1.14	20-60	64-72	7.48-7.62	8.78-8.86
Xingyu Lake	Autumn	3.51-4.34	110-160	49-87	7.40-7.55	8.82-8.95
	Winter	2.72-11.72	120-240	50-145	7.39-7.53	10.11-10.32

Table 2. F- and p-values of two-way ANOVAs on different phosphorus fractions in waters and sediments from Shanzi Reservoir and Xingyu Lake with/without PIC or Phoslock® treatments (Details of two-way ANOVAs for each phosphorus fraction in Table S2-S10).

Source	**Water**		**Sediment**					**Interstitial water**	
	TP	**SRP**	**TP**	**Fe/Al-P**	**Ca-P**	**IP**	**OP**	**TDP**	**SRP**
PIC/Phoslock	F=11.7 *p*=0.001	F=0.13 *p*=0.721	F=0.33 *p*=0.579	F=0.01 *p*=0.940	F=1.21 *p*=0.298	F=1.81 *p*=0.208	F=0.01 *p*=0.957	F=3.20 *p*=0.099	F=3.72 *p*=0.078
Dosage	F=1026.1 *p*=0.002	F=811.5 *p*<0.001	F=3.31 *p*=0.057	F=0.40 *p*=0.804	F=12.31 *p*=0.001	F=7.68 *p*=0.004	F=0.04 *p*=0.997	F=0.25 *p*=0.903	F=0.03 *p*=0.998
Time	F=1.64 *p*=0.150	F=1.25 *p*=0.291	NT	NT	NT	NT	NT	NT	NT

NT = not tested.

Table 3. Phosphorus removal efficiency at water-sediment interface of Shanzi Reservoir and Xingyu Lake.

Site	The added PIC concentration (mg/L)	Adsorption amount (mg/g)	Adsorption efficiency	TP removal efficiency	SRP removal efficiency
Shanzi Reservoir	10	8.98-10.00	90.4%-100.7%	60.0%-64.2%	73.9%-87.4%
	20	9.39-10.10	94.5%-101.7%	61.3%-64.6%	88.4%-98.4%
	30	7.82-8.23	78.8%-82.9%	94.0%-97.2%	87.8%-100.0%
	40	6.02-6.43	60.6%-64.7%	96.4%-98.9%	100.0%-100.0%
Xingyu Lake	10	9.18-11.20	92.5%-111.0%	29.9%-33.5%	68.5%-98.3%
	20	9.59-10.51	96.6%-105.8%	64.5%-67.2%	83.3%-100.0%
	30	8.91-9.46	89.7%-95.2%	94.0%-96.9%	80.9%-100.0%
	40	6.84-7.40	68.8%-74.5%	97.6%-99.0%	89.3%-100.0%

Table 4. The residual lanthanum and aluminium concentrations in Shanzi Reservoir and Xingyu Lake after different treatments.

	Treatment	**Lanthanum (μg/L)**	**Aluminium (μg/L)**
Shanzi Reservoir	Original water	1.25±0.21	59.15±9.11
	CK	1.32±0.17	68.79±11.97
	Phoslock®	26.04±0.27	99.38±20.88
	PIC	1.44±0.18	101.26±15.14
Xingyu Lake	Original water	3.21±0.22	62.90±12.98
	CK	3.53±0.39	70.11±16.79
	Phoslock®	23.12±1.01	104.09±19.01
	PIC	3.79±0.51	103.72±15.86

CK: Treatment without Phoslock® or PIC amendment.

PIC: Phosphorus inactive clay treatment.

Assessing the impacts of phosphorus inactive clay on phosphorus release control and phytoplankton community structure in eutrophic lakes

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Abstract

Addressing the challenge that phosphorus is the key factor and cause for eutrophication, we evaluated the phosphorus release control performance of a new phosphorus inactive clay (PIC) and compared with Phoslock®. Meanwhile, the impacts of PIC and Phoslock® on phytoplankton abundance and community structure in eutrophic water were also discussed. With the dosage of 40 mg/L, PIC effectively removed 97.7% of total phosphorus (TP) and 98.3% of soluble reactive phosphorus (SRP) in eutrophic waters. In sediments, Fe/Al-phosphorus and organic phosphorus remained stable whereas Ca-phosphorus had a significant increase of 13.1%. The results indicated that PIC may form the active overlay at water-sediment interface and decrease the bioavailability of phosphorus. The phytoplankton abundance was significantly reduced by PIC and decreased from (1.0-2.4)×10^7 cells/L to (1.3-4.3)×10^6 cells/L after 15 d simultaneous experiment. The phytoplankton community structure was also altered, where Cyanobacteria and Bacillariophyceae were the most inhibited and less dominant due to their sensitivity to phosphorus. After PIC treatment, the residual lanthanum concentration in water was 1.44-3.79 μg/L, and the residual aluminium concentration was low as 101.26-103.72 μg/L, which was much less than the recommended concentration of 200 μg/L. This study suggests that PIC is an appropriate material for phosphorus inactivation and algal bloom control, meaning its huge potential application in eutrophication restoration and management.

Keywords: Phosphorus; phosphorus inactive clay (PIC); Phoslock®; water-sediment interface; eutrophication; phytoplankton community

Capsule abstract

Phosphorus inactive clay effectively immobilizes phosphorus in eutrophic waters, forms active overlay for 15-day phosphorus release control, and inhibits algal bloom.

1. Introduction

Water eutrophication is a worldwide problem in water quality control, and algal bloom is one of the most serious challenges in drinking water safety (Brookes and Carey, 2011). In most aquatic ecosystems resilience to eutrophication, phosphorus is identified as the key restrict nutrient (Schindler et al., 2008). Sediment is the sink of organic matters in the geochemical environment and plays an essential role in aquatic ecosystem. It is not only the habitat for benthic and aqueous organisms, but also the place where a variety of nutrients migrates and transforms (Gulati and van Donk, 2002). Furthermore, sediment has been regarded as the main endogenous source of phosphorus in most of the eutrophication cases, consequently resulting in the failure of algal bloom control when the exogenous nutrients are cut off (Søndergaard et al., 2007; Spears et al., 2012). Even worse, the recruitment of benthic species enhances the phosphorus release and cause phosphorus accumulation in aqueous phase, consequently aggravating algal bloom (Barbiero and Welch, 1992; Xie et al., 2003). It is necessary to develop effective treatments, with high efficiency, low cost and minimal ecological risks, for endogenous phosphorus release control and water restoration (Hickey and Gibbs, 2009).

Recently, Phoslock® becomes a popular phosphorus inactive material (Robb et al., 2003; Spears et al., 2013a), which stabilizes the aqueous active phosphorus by forming the $LaPO_4$ chelate precipitate ($La^{3+}+PO_4^{3-}\rightarrow LaPO_4\downarrow$, Ksp = $10^{-24.7}$-$10^{-25.7}$). The settlement of chelate precipitate further forms the “active overlay” at water-sediment interface, contributing to long-term phosphorus release control (Gibbs et al., 2011). As the most investigated and applied phosphorus inactive materials (Lürling and Faassen, 2012; Meis et al., 2012; Moos et al., 2014; van Oosterhout and Lürling, 2013), Phoslock® has attracted much attention in its good performance of phosphorus release control in several lakes (Reitzel et al., 2013; Spears et al., 2013b) or the potential ecological risks after Phoslock® amendment (Lürling and Tolman, 2010; Wagenhoff et al., 2012). Though researches have discussed the change of phytoplankton abundance in Phoslock® treatments (Lürling and van Oosterhout, 2013; Waajen et al., 2016), there is still limited study addressing the dynamics and response of phytoplankton community during phosphorus release control process (Lang et al., 2016). Considering the importance of lake ecological stability, it is particularly necessary to assess the phytoplankton community after water quality restoration practices.

In this research, we assessed the phosphorus release control for 15 days by a novel phosphorus inactive clay (PIC) in two types of eutrophic water, deep reservoir (Shanzi Reservoir) as drinking water source and shallow landscape water (Xingyu Lake). To identify the practicability of PIC treatment and clarify its impacts on aquatic ecosystem, the present study compared the efficiency of phosphorus release control and structure changes of phytoplankton community after PIC treatment with those after Phoslock® treatment.

2. Materials and Methods

2.1 Sites and sample collection

The eutrophic water samples were collected by plexiglass sampler in October 2014 and January 2015 in Xingyu Lake (N26°1'40", E119°12'23") and Shanzi reservoir (N26°22'33", E119°18'53"), respectively. These two waters suffered from serious eutrophication in early spring and late summer (Su et al., 2016), and the present study focused on the phosphorus release control during winter season to reduce the risks of spring algal bloom. At each sampling point, about 50.0 L of water samples were collected. The 1,000 mL water sample was added with Lugol's iodine solution as antiseptic and disinfectant immediately for phytoplankton community analysis. The rest of water samples were directly stored at 4°C within 1 day for further chemical analysis and phosphorus inactivation experiment. Sediment samples about 5.0 kg were collected at the same sites by Petersen grab (437 330, Bottom Sampler acc. to Van Veen, 20×30×60 cm), immediately transferred into plastic bags and stored at -20°C for chemical analysis or 4°C for phosphorus inactivation experiment.

2.2 PIC and phosphorus adsorption isotherm

In the present study, PIC was an aluminium-modified bentonite clay synthesized as previously described (Hao et al., 2014). The bentonite clay behaved as the carrier for the reactive aluminium for phosphorus immobilization. The Phoslock® was purchased from Sichuan Phoslock Environmental Water Treatment Company. To test the phosphorus adsorption isotherm, the 0.2 g PIC was air-dried and directly added into 50 mL deionized water, supplemented with phosphorus concentration of 0, 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 mg/L. After constant stirring at 26 ℃ at 240 rpm for series of time (0, 6, 9, 15, 30, 60, 240, 420, 720 and 1440 min), the suspension was centrifuged at 4,000 rpm for 10 min and the supernatant was further analyzed for residual phosphorus concentration.

2.3 Phosphorus inactivation and release control experiment

The phosphorus inactivation and release control treatments were set up in column test (2.5 L plastic barrel). For each treatment, the 2,000 mL water samples were gently overlaid on 200.0 g sediments. The cultivation condition was 12h:12h light-dark-cycle (photon flux density was 65 μmoles/m^2·s) and 15°C. Intermittent aeration was conducted within the whole light period (12 hours each day) to simulate the *in-situ* physical disturbance at water-sediment interface in winter season. From previous research on the optimal amendment of Phoslock® and the phosphorus adsorption capacity of PIC, the ratio of Phoslock® or PIC to SRP was suggested as 100:1 to achieve the best phosphorus immobilization performance (Reitzel et al., 2013). From the chemical analysis of phosphorus in the water samples, the optimal Phoslock® or PIC dosage was around 30 mg/L. Therefore, the dosage of Phoslock® or PIC was set as 10, 20, 30 and 40 mg/L, and they were amended gently into the column after air dried. The control group with neither PIC nor Phoslock® amendment was named as *CK* treatment for comparison with Phoslock® or PIC treatments. The water samples were collected on 1, 3, 5, 7, 9, 12 and 15 days. All the treatments were carried out in triplicates.

2.4 Chemical analysis

A JSM7500F (JOEL, Japan) scanning electron microscope (SEM) was used to study the morphology of PIC by and the energy-dispersive X-ray spectroscopy (EDS) was obtained TEAM™ EDS system (EDAX, USA). In 15-day phosphorus release control experiment, the values of pH and dissolved oxygen (DO) in water samples were measured by a pH meter (pH B-8, CSDIHO, China) and portable DO meter (JPB-607, INESA, China), respectively. Total nitrogen (TN) was determined by alkaline potassium persulfate digestion UV spectrophotometric method (Zhang et al., 2010). The soluble reactive phosphorus (SRP) in water sample was directly measured by molybdenum blue UV spectrophotometric method (Murphy and Riley, 1962). The extraction of phosphorus species in sediment samples followed the Standards Measurements and Testing (SMT) method (Ruban et al., 2001) as a widely applied routine method for studying phosphorus fractions in sediments (Pardo et al., 2004). Briefly, the sediment was grounded to 100 mesh after air-dried. The 0.20 g of sediment powder was added into 20 mL 1.0 mol/L NaOH and shaken for 16 hours. After centrifugation at 4,000 rpm for 20 min, the 10 mL supernatant was added with 4 mL 3.5 mol/L HCl and stabilized for 16 h as Fe/Al-phosphorus (Fe/Al-P) fraction. The pellets were further resuspended in 20 mL 1.0 mol/L HCl and kept shaking for 16 h as Ca-phosphorus (Ca-P) fraction. For inorganic phosphorus (IP) and organic phosphorus (OP) fraction, the 0.20 g sediment was added with 20 mL 1.0 mol/L HCl and the IP fraction was within the supernatant after 16 h by stabilization. After gently washed by deionized water, the pellets were burned in muffle furnace at 450°C for 3 h and dissolved in 20 mL 1.0 mol/L HCl. The OP fraction was in the supernatant after 16 h shaking and centrifugation. The total dissolved phosphorus (TDP) and SRP in interstitial water of sediments was extracted in the supernatant by centrifuging the sediment at 4,000 rpm for 5 min. For TP fraction in sediments, the 0.20 g sediment was burned directly in muffle furnace at 450°C for 3 h, dissolved in 20 mL 3.5 mol/L HCl and finally stabilized for 16 h. For TP in water and TDP in supernatant, the water sample was digested by potassium persulfate. The phosphorus of each fraction was determined according to the ammonium molybdate spectrophotometric method (ISO, 2004), using a UV-Vis spectrophotometer with 700 nm wave length (UV-1100, MAPADA, China).

Lanthanum and aluminium measurement followed the inductively coupled plasma mass spectrometry (ICP-MS) method (Kajiya et al., 2004). After centrifugation at 10,000 rpm for 10 min, the supernatant passed through 20 μm filter and was injected into ICP-MS X-Series II (Thermo Scientific, USA). Argon was the cooling, assistant and carrier gas, with the flow rate of 13.0 L/min, 0.8 L/min and 0.82 L/min, respectively. In this study, the determination was carried out in the X Series Default mode (three points per peak) with 10 ms detention time and 3 s total sampling time.

2.5 Biological analysis

The phytoplankton community structure and abundance in all the water samples was determined with a binocular biological microscope (Motic, BM-1000, Guangzhou) (Casamayor et al., 2000). The 20 mL water samples with Lugol's iodine fixation were centrifuged at 10,000 rpm for 10 min and concentrated to the final volume of 100 μL by deionized water. The identification and counting of phytoplankton species was conducted in the 0.1 mL counting chamber (20 mm × 20 mm) with three individual replicates. All the measurement was carried out at 4°C in dark, and the phytoplankton abundance was calculated with the unit of cells per liter (cells/L) by Equation (1).

$$N = \left(\frac{A}{A_0} \times \frac{1}{V}\right) \times n \times 1000 \quad (1)$$

Here, N is phytoplankton abundance per microlitre water sample (cells/mL). A and V refer to the area (mm^2) and volume (0.1 mL) of counting chamber, respectively. A_0 represents the counting area (mm^2), and n is the number of phytoplanktons within the counting area (cells).

2.6 Data analysis

SPSS 17.0 was used for all statistical analysis. Between different treatments, the statistical significance of differences in phosphorus concentration and phytoplankton abundance was calculated by two-way ANOVA (Table 2). All the data were checked for normality (Shapiroe Wilk) and heteroscedasticity (Equal Variance test). The correlation between PIC/Phoslock® dosage and phosphorus immobilization performance was analysed by the Pearson correlation coefficient by bivariate tool in SPSS. The phytoplankton community structure with/without PIC or Phoslock® treatment was clustered by principal components analysis (PCA). The significant level for all the statistical analysis was $p<0.05$.

3. Results

3.1 Phosphorus adsorption by PIC

The morphology of PIC before and after phosphorus fixation was illustrated in Figure S1. The original PIC showed the round shape with an average diameter of 3 μm. After phosphorus adsorption, the particle size increased to 5 μm attributing to the nested PO_4^{3-} molecules in the crystal structure. From the EDS analysis results (Figure S1C and Table S1), the aluminium had a high atom proportion of 9.82% in PIC, significantly higher than that in raw bentonite (Li et al., 2016). Accordingly, the ratio of Na_2CO_3 to Al_2O_3 was estimated as 2.5:1 in PIC, and the results confirmed the successful bentonite-modification with aluminium as the active element for phosphorus immobilization. Phosphorus adsorption on PIC followed the Langmuir adsorption isotherm, indicating the monolayer adsorption mechanisms (Figure S2). The maximum phosphorus adsorption capacity (Q_{max}) was 9.93 mg/g and the Langmuir constant (K_L) associated with adsorption energy was 25.3 L/mg.

3.2 Phosphorus removal in water phase

Nutrient conditions in Shanzi Reservoir and Xingyu Lake were listed in Table 1. The TN and TP in Shanzi Reservoir varied in seasons, ranging from 0.15 to 1.14 mg/L and 20 to 80 μg/L, respectively. Xingyu Lake had a significant higher TN and TP due to more nutrients input and smaller water volume as landscape water. The addition of PIC or Phoslock® slightly decreased the water pH value (Figure S3), gradually declining from 7.40 to 6.82-6.93 in waters from Shanzi Reservoir and from 7.50 to 7.23-7.31 in waters from Xingyu Lake, respectively. They were both significantly lower than that in the *CK* treatment (p=0.03). The values of DO in all the treatments showed the same declining trend (p=0.01, Figure S4).

The 15-day phosphorus release control performance of PIC and Phoslock® was illustrated in Figure 1 and Table 3. Except *CK* and 10 mg/L PIC/Phosock® treatments, a significantly dramatic decline of TP was observed within 1 day ($p<0.001$). Afterwards, the residual phosphorus remained stable with tiny fluctuation (p=0.150, Table 2). The TP removal efficiency was positively correlated with PIC dosage (p=0.002), and the Pearson coefficient is 0.918 for Shanzi Reservoir (p<0.001) and 0.945 for Xingyu Lake (p<0.001), respectively. When the PIC dosage was above 20 mg/L, the residual TP was less than 20 μg/L. Compared to the maximum phosphorus adsorption capacity (Table 3), there was a negative correlation between the dosage and phosphorus adsorption efficiency of PIC (Pearson coefficient is -0.892 in Shanzi Reservoir, p=0.003; Pearson coefficient is -0.828 in Xingyu Lake, p=0.011). Compared to Phoslock® (Figure 1E and 1G), PIC had a better TP removal efficiency (p=0.001).

Similarly, a significant removal of SRP was observed for all the PIC and Phoslock® treatments (p<0.001). The SRP concentrations were lower than 10 μg/L from Day 1 to Day 15 in PIC (Fig. 1B and 1D) and Phoslock® (Fig. 1F and 1H) treatments. The SRP removal efficiencies were positively correlated with PIC dosage (Pearson coefficient 0.898 in Shanzi Reservoir, p<0.001; Pearson coefficient 0.590 in Xingyu Lake, p=0.001). The performance of SRP reduction after Phoslock® treatment was similar to that after PIC treatment (p=0.721, Table 2).

3.3 Impacts of PIC on sediment and interstitial water phosphorus profiles

The amendment of PIC and Phoslock® can form the "active overlay" and may affect the sediment phosphorus profiles. Our results indicated that Ca-P and IP had a significant increase after PIC treatment (Figure 2), from 95.34 μg/g to 127.05 μg/g (p<0.001) and 360.54 μg/g to 413.99 μg/g (p=0.004), respectively. The PIC dosage was positively correlated with the concentrations of Ca-P (Pearson coefficient 0.910, p<0.001) and IP (Pearson coefficient 0.845, p<0.001). For SRP and Fe/Al-P in sediments, there was no significant difference (p>0.05, Table 2 and Figure 2) before and after PIC or Phoslock® addition. Meanwhile, all the phosphorus fractions in sediments showed no remarkable difference between PIC and Phoslock® treatments (Table 2), indicating the similar mechanisms and performance of these two phosphorus inactive materials.

From phosphorus concentrations in interstitial water of the sediments from Shanzi Reservoir and Xingyu Lake (Figure 3), both TDP and SRP had a slightly increasing trend in either PIC or Phoslock® treatments. The TDP and SRP concentration in Shanzi Reservoir was 240-320 μg/L and 60-90 μg/L, respectively, and they were 330-400 μg/L and 30-50 μg/L in Xingyu Lake. Nevertheless, there was no significant difference between each dosage or between PIC and Phoslock® treatments from two-way ANOVAs (Table 2).

3.4 Phytoplankton community structure change

Both Shanzi Reservoir and Xingyu Lake were eutrophic waters with high phytoplankton abundance (*Original* in Figure 4). The dominant phytoplankton was Bacillariophyceae (7.76×10^6 cells/L), accounting for 85.80% of the total population in water from Shanzi Reservoir, followed by Chlorophyta (1.04×10^6 cells/L, 11.48%), Cryptophyta (1.70×10^5 cells/L, 1.88%), Euglenophyta (5.66×10^4 cells/L, 0.63%) and Cyanobacteria (1.89×10^4 cells/L, 0.21%). In Xingyu Lake, the total phytoplankton abundance was 2.03×10^7 cells/L, and the community was consisted of Chlorophyta (8.17×10^6 cells/L, 40.34%), Bacillariophyceae (4.19×10^6 cells/L, 20.69%), Cyanobacteria (4.10×10^6 cells/L, 20.25%) and Euglenophyta (3.69×10^6 cells/L, 18.25%) at phylum level.

PIC and Phoslock® amendment affected the phytoplankton abundance and community structure (Figure 4). In *CK* treatment, the total phytoplankton abundance increased to 9.63×10^6 cells/L and 2.38×10^7 cells/L in Shanzi Reservoir and Xingyu Lake, 6.5% and 17.4% higher than original waters (p=0.02). In PIC treatments, the total phytoplankton abundance decreased to $(0.014\text{-}0.626)\times10^6$ cell/L in Shanzi Reservoir (Figure 4A) and $(0.002\text{-}0.429)\times10^7$ cell/L in Xingyu Lake (Figure 4C). The phytoplankton inhibition rates ranged from 93.6%-99.9% and 82.0%-99.9% respectively, slightly higher than those of Phoslock® treatments (Figure 4B and 4D). The phytoplankton abundance was negatively correlated with PIC dosage (Pearson correlation coefficient -0.815 for Shanzi Reservoir and -0.852 for Xingyu Lake, $p<0.05$).

There was a significant difference in phytoplankton community structure after PIC or Phoslock® treatments from PCA plot (Figure 5). The locations of phytoplankton community of both Shanzi Reservoir and Xingyu Lake in *CK* treatment were close to those of original waters. With the increasing PIC/Phoslock® dosage, the phytoplankton community groups of both waters co-clustered, with longer distance to the *Original* and *CK* groups. The most obvious change (Figure 4) was the significant increase of Euglenophyta and Cryptophyta. Accordingly, Bacillariophyceae and Cyanobacteria were the main declining phylum.

3.5 La/Al residues after PIC treatment

To further evaluate the potential ecological risks of PIC, the residual lanthanum and aluminium were measured and listed in Table 4. Since lanthanum was not the formula in PIC, there was no significant difference in lanthanum concentrations before and after PIC amendment ($p>0.05$). The residual lanthanum concentrations after PIC treatment were much lower (<20%) than those after Phoslock® treatment ($p<0.01$). The residual aluminium after PIC treatment was 101.26

μg/L and 103.72 μg/L for waters from Shanzi Reservoir and Xingyu Lake respectively, similar to those in Phoslock® treatment (p>0.05). Considering the levels of residual lanthanum and aluminium, PIC had relatively lower ecological risks than Phoslock®.

4. Discussion

4.1 Dynamic change of phosphorus profiles in water and sediment

The ratios of TN to TP in Shanzi Reservoir and Xingyu Lake range from 35 to 145 (mole:mole), indicating that phosphorus concentration is relatively lower and behaves as the key nutrient factor causing the eutrophication in both waters. Furthermore, the endogenous release from sediments is also viewed as a key pathway of phosphorus nutrients for aquatic ecosystem. The present study therefore investigated the 15-day phosphorus release process at the water-sediment interface, considering the impacts of phosphorus inactive materials (PIC and Phoslock®) on phosphorus immobilization and phytoplankton community.

In all the treatments, the high phosphorus removal efficiency and stability after 15-day experiment demonstrated that the functional sites on PIC surface can effectively immobilize phosphorus, particularly the soluble and active fraction. PIC had a similar maximum phosphorus adsorption capacity to previously reported Phoslock® (9.5-10.5 mg/g) (Haghseresht et al., 2009). Its high Langmuir constant also indicated the strong binding strength between phosphorus molecules and PIC (Lin et al., 2015). From the negative correlation between PIC/Phoslock® dosage and phosphorus adsorption efficiency, we suggested abundant active sites on PIC and Phoslock®, which contributed to further phosphorus immobilization and prevented phosphorus release from sediment for at least 15 days. Similar to Phoslock®, PIC remained phosphorus inactivation capacity and behaved as the "active overlay" at the water-sediment interface after the settlement.

The slight decrease of pH value during PIC treatment might be attributed to the acidity of bentonite clay, which was the main ingredient of PIC (Liu et al., 2015; Penner and Lagaly, 2001), or the hydrolysis and exchange of element (Swartzen and Matijevi, 1974). The pH value shows significant impacts on the phosphorus immobilization efficiency of phosphorus inactive materials, particularly when the bentonite clay is used (Haghseresht et al., 2009; Reitzel et al., 2005). In the present study, the declining pH values further improved the stability of phosphorus precipitate. The results fitted well with previous research that the phosphorus inactivation performance is dependent on the physical and chemical features of the targeted water samples (Huser, 2012).

Previous research has revealed that sediment OP is positively correlated with the dosage of Phoslock® (Meis et al., 2013). Nevertheless, the OP concentration in sediment did not change with PIC addition in our study. It was reported that more phosphorus is released from sediment under anaerobic conditions (Geng et al., 2007; Hupfer and Lewandowski, 2008; Song et al., 2011). The increasing sediment OP is attributed to the settling phytoplankton and/or debris from decomposing macrophytes (Meis et al., 2013). The high DO concentration (Figure S4) in our work indicated the aerobic condition throughout the experiment. Thus, though the original phytoplankton abundance was of high level, the aerobic condition did not promote the transformation and release of phosphorus in sediment, causing less OP variation in sediments. Meanwhile, the aquatic SRP/TP ratio decreased after PIC treatment, similar to the previous results of Phoslock® (Reitzel et al., 2013). It indicated that PIC primarily reacts with the active fraction of phosphorus (SRP), and its phosphorus immobilization is dependent on the natural phosphorus cycling at the water-sediment interface.

The water-sediment interface plays a key role in phosphorus transportation and exchange. In all the PIC and Phoslock® treatments, the concentrations of TDP and SRP in interstitial water of sediments (Figure 3) were much higher than aqueous TP and SRP. From Yin's study, SRP fluxes are determined by the phosphorus gradient across sediment-water interface (Yin and Kong, 2015). A strong SRP flux is therefore expected after PIC/Phoslock® treatment, but our results showed the stable TP and SRP in waters throughout the 15-day experiment. It hinted limited phosphorus release from sediments, suggesting the formation of "active overlay" at the sediment surface by PIC or Phoslock® and effective phosphorus release control.

4.2 Mechanisms of phytoplankton community change

Algal bloom is the direct evidence of water eutrophication (Anderson et al., 2002; Smith, 2003), when the exceeding growth of various algae caused serious challenges in drinking water safety, particularly the toxigenic algae like *Microcystis aeruginosa*, *Aphanizomenon flos-aquae* and *Anabaena flosaguas* (Codd et al., 2005; Collins, 1978). By immobilizing phosphorus as the key nutrient in aquatic phase and blocking its release from the sediment, Phoslock® effectively reduces the nutrient level and maintained the oligotrophic condition (Schindler et al., 2008). Accordingly, our results showed that PIC had similar performance of significantly reducing phytoplankton abundance by immobilizing phosphorus and minimizing the active phosphorus (Figure 5). More interestingly, Bacillariophyceae and Cyanobacteria were identified as the key declining phytoplankton phylum in both eutrophic waters. Since the majority of harmful algae belongs to the phylum Cyanobacteria (Johnk et al., 2008; Landsberg, 2002; Paerl et al., 2001), our results suggested that PIC particularly supressed some harmful algae more than other algal species, with the unexpected strong performance in reducing algal bloom and preventing their recurring. It is hypothesized that Euglenophyta and Cryptophyta are not sensitive to inorganic phosphorus and can tolerate low phosphorus environment after phosphorus inactive clay treatment (Burgi et al., 2003; Chisholm and Stross, 1976). On the contrast, the phosphorus-sensitive Bacillariophyceae and Cyanobacteria are significantly affected by low phosphorus pressure (Lagus et al., 2004; Levine and Schindler, 1999; Lippemeier et al., 2001). Lang et al. reported the decreasing cyanobacteria after Phoslock® treatment in shallow water Loch Flemington, which is explained by the less competitive advantage of cyanobacteria under reduced phosphorus conditions (Lang et al., 2016). Similar results are also found in shallow reservoir in California (Bishop et al., 2014) and marine cyanobacteria removal by polyaluminium chloride modified clay (Yu et al., 1995). The close distance of phytoplankton community after PIC and Phoslock® treatment (Figure 5) indicated the similar community structure trends affected by the two phosphorus inactive materials, showing their feasibility in preventing algal bloom formation. However, the cell size of Cyanobacteria is normally smaller than Bacillariophyceae, indicating their stronger tolerance to low phosphorus. A larger scale of mesocosm experiment is therefore suggested to address the long-term effects of PIC on phytoplankton community dynamics, particularly harmful cyanobacterial abundance under low phosphorus conditions.

4.3 Ecological risk assessment

The additives of phosphorus inactivate materials may cause the increase of metal ions in aquatic environment, which possibly leads to their accumulation in the food chain and finally show risks to human health. Lanthanum is the reactive component of Phoslock® with such potential risks. The LD_{50} of $LaCl_3$ is 4200 mg La per kilogram body weight for rats (Cochran et al., 1950). A median threshold effects of $LaCl_3$ for Daphnia and Scenedesmus are reported as 160 mg La/L after 4 hours and 0.15 mg La/L for after 4 days, respectively (Bringmann and Kuhn, 1959). High level $LaCl_3$ exposure (>1 mg/L) can cause the death of fish within 24 hours (Peterson et al., 1974). Compared to Phoslock®, PIC did not use lanthanum as the ingredient in the present work. The residual lanthanum after PIC treatment was similar to the aquatic background in both eutrophic waters and much lower than that after Phoslock® treatment, showing relatively less ecological and health impacts.

Meanwhile, aluminium also has significant acute toxicity (Srinivasan et al., 1999). Particularly in acidic waters (pH 4.2 to 5.6), 0.1-0.2 mg/L aluminium can cause the reduction of survival and growth of larvae and postlarvae (Baker and Schofield, 1982). As for the risks on human health, the possibility of an association between aluminium and neuropathological diseases including presenile dementia, dialysis encephalopathy and Alzheimer's disease is frequently hypothesized. The kidney dialysis patients suffer dementia when their dialysis fluid contains an aluminium concentration of 0.08 mg/L (Davison et al., 1982). The presence of aluminium in drinking water has given rise to discussions on possible health effects, because of its suspected connection with Alzheimer's diseases or dialysis encephelopathy (Jekel and Heinzmann, 1989). Higher rate of Alzheimer's disease is observed when the aluminium concentration exceeds 0.11 mg/L (Martyn et al., 1989), and similar results are found in the cases of animal neuropathological disorders (Kopeloff et al., 1942). World Health Organization (WHO) thus suggests the health-based value of 0.9 mg Al/L for drinking water, with detailed restriction of 0.1-0.2 mg Al/L for water after coagulation treatment (WHO, 2004). In the present work, the residual concentration of Al in water was about 0.1 mg/L after PIC and Phoslock® treatment. Though not exceeding the WHO recommended values, it still might be a potential source of aluminium release to water. Previous research revealed that the majority of residual lanthanum and aluminium is within the top 10 cm of sediments (Meis et al., 2013; Reitzel et al., 2005), and their ecological and health risks are then at low level as an engineering approach for phosphorus release control. We therefore suggested that the health risk of applying PIC or Phoslock® is limited, but it needs careful monitoring and assessment in practical application in reservoir or other drinking water sources.

4.4 Perspectives

Phosphorus is the key factor causing eutrophication and important for water quality. There are many attentions on its immobilization or release control from sediments. The application of various phosphorus inactive materials, including Phoslock®, has therefore attracted increasing attentions from both academia and industries around the world. Phoslock® is proved to immobilize phosphorus by creating phosphorus precipitate, form “active overlay” on the top of the sediment to block phosphorus releasing into the aquatic phase, and effectively trap the aquatic soluble phosphorus from other pathways (Meis et al., 2013). The present study addressed the phosphorus release control of PIC in eutrophic waters and compared its performance with widely accepted and applied Phoslock®. Their similar phosphorus immobilization behavior and impacts on the phytoplankton abundance and community were verified.

Applying Phoslock®, PIC or other phosphorus inactive materials is a strategic water restoration approach for eutrophic water quality management. Treatments in summer or autumn can immobilize all the SRP from aquatic phase. It may minimize the available phosphorus, reduce phytoplankton abundance and achieve short-term water quality improvement. As for the treatments in winter or spring, the phosphorus inactive materials can form the “active overlay” at the water-sediment interface and effectively block the phosphorus release from sediment. This strategy focuses on locking phosphorus within the sediment and contributes to long-term water quality recovery. Combined with other water restoration methods, like coagulation or oxidation, their performance can be even enhanced (Lürling and Faassen, 2012). Most of the previous research on phosphorus inactive materials has highlighted the performance of phosphorus fixation or immobilization (Lürling and Tolman, 2010; Spears et al., 2013a; Wagenhoff et al., 2012). Recently, their impacts on phytoplankton abundance and community structure are getting more attentions to be considered in eutrophic water restoration actions (Lürling and van Oosterhout, 2013; Lang et al., 2016; Waajen et al., 2016). Although our study aims to answer these questions, the laboratory-scale experiment cannot simulate the field reality where the phosphorus cycle and phytoplankton community are affected by numerous environmental factors (Paerl and Otten, 2013). The latest research has focused on the large-sized mesocosm experiment on long-term impacts of phosphorus inactive materials on phytoplankton abundance and community (Lang et al., 2016), and more work is suggested to address this question to evaluate the engineering parameters and the ecological consequence on the aquatic system for long-term phosphorus release control, especially in drinking water reservoirs.

5. Conclusion

The present study demonstrated the phosphorus inactivation by a new PIC in natural eutrophic waters from Shanzi Reservoir and Xingyu Lake. After 15 days experiment, PIC achieved effective phosphorus reduction, blocked phosphorus release from sediments, and significantly altered the phytoplankton community structure. The main results included:

1. The initial PIC dosage was negatively correlated with the aqueous residual TP and SRP, and the highest TP and SRP removal efficiency achieved 97.7% and 98.3%, respectively.
2. The phytoplankton abundance was significantly decreased with the increasing PIC dosage and the lowest residual phytoplankton abundance was less than 0.01% of

original eutrophic waters, attributing to the oligotrophic condition of phosphorus reduction.

3. Of all the phytoplanktons, the abundance of phylum Bacillariophyceae and Cyanobacteria was most reduced due to their higher sensitivity to phosphorus.
4. The residual lanthanum and aluminium concentrations after PIC treatment were at low levels and had minimal ecological or health risks.

The present work helps our deeper understanding on the performance of applying PIC to improve eutrophic water quality and its potential impacts on aquatic ecosystem. Our study shows that PIC is feasible for phosphorus release control and can be a practical tool in water quality restoration.

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Figure caption

Figure 1. The 15-day control performance of phosphorus release with PIC and Phoslock® treatments. (A) and (C) represent TP in PIC treatments; (E) and (G) represent TP in Phoslock® treatments. (B) and (D) represent SRP in PIC treatments; (F) and (H) represent SRP in Phoslock® treatments.

Figure 2. Phosphorus profiles in surface sediments with PIC and Phoslock® treatments. (A) for PIC and (B) for Phoslock® treatment in Shanzi Reservoir. (C) for PIC and (D) for Phoslock® treatment in Xingyu Lake. The subgraphs represent phosphorus fractions in each treatment, respectively.

Figure 3. TDP and SRP concentrations in interstitial water of sediments with PIC and Phoslock® treatments. (A) for PIC and (B) for Phoslock® treatment in Shanzi Reservoir. (C) for PIC and (D) for Phoslock® treatment in Xingyu Lake.

Figure 4. Abundance and structure changes of phytoplankton communities with PIC and Phoslock® treatments. (A) for PIC and (B) for Phoslock® treatment in Shanzi Reservoir. (C) for PIC and (D) for Phoslock® treatment in Xingyu Lake.

Figure 5. PCA analysis of phytoplankton community structure with PIC and Phoslock® treatments. The categories of phytoplankton community in either PIC (green) or Phoslock® (red) treatments co-cluster, with long distance to the *Original* (white) and *CK* (grey) groups in both Shanzi Reservoir (circle) and Xingyu Lake (triangle).

Table

Table 1. Nutrient conditions in Shanzi Reservoir and Xingyu Lake.

Water samples	Season	TN (mg/L)	TP (μg/L)	TN/TP	pH	DO (mg/L)
Shanzi Reservoir	Autumn	0.15-1.03	20-80	35-57	7.50-7.65	8.50-8.70
	Winter	1.28-1.14	20-60	64-72	7.48-7.62	8.78-8.86
Xingyu Lake	Autumn	3.51-4.34	110-160	49-87	7.40-7.55	8.82-8.95
	Winter	2.72-11.72	120-240	50-145	7.39-7.53	10.11-10.32

Table 2. F- and p-values of two-way ANOVAs on different phosphorus fractions in waters and sediments from Shanzi Reservoir and Xingyu Lake with/without PIC or Phoslock® treatments (Details of two-way ANOVAs for each phosphorus fraction in Table S2-S10).

Source	**Water**		**Sediment**					**Interstitial water**	
	TP	**SRP**	**TP**	**Fe/Al-P**	**Ca-P**	**IP**	**OP**	**TDP**	**SRP**
PIC/Phoslock	F=11.7 *p*=0.001	F=0.13 *p*=0.721	F=0.33 *p*=0.579	F=0.01 *p*=0.940	F=1.21 *p*=0.298	F=1.81 *p*=0.208	F=0.01 *p*=0.957	F=3.20 *p*=0.099	F=3.72 *p*=0.078
Dosage	F=1026.1 *p*=0.002	F=811.5 *p*<0.001	F=3.31 *p*=0.057	F=0.40 *p*=0.804	F=12.31 *p*=0.001	F=7.68 *p*=0.004	F=0.04 *p*=0.997	F=0.25 *p*=0.903	F=0.03 *p*=0.998
Time	F=1.64 *p*=0.150	F=1.25 *p*=0.291	NT	NT	NT	NT	NT	NT	NT

NT = not tested.

Table 3. Phosphorus removal efficiency at water-sediment interface of Shanzi Reservoir and Xingyu Lake.

Site	The added PIC concentration (mg/L)	Adsorption amount (mg/g)	Adsorption efficiency	TP removal efficiency	SRP removal efficiency
Shanzi Reservoir	10	8.98-10.00	90.4%-100.7%	60.0%-64.2%	73.9%-87.4%
	20	9.39-10.10	94.5%-101.7%	61.3%-64.6%	88.4%-98.4%
	30	7.82-8.23	78.8%-82.9%	94.0%-97.2%	87.8%-100.0%
	40	6.02-6.43	60.6%-64.7%	96.4%-98.9%	100.0%-100.0%
Xingyu Lake	10	9.18-11.20	92.5%-111.0%	29.9%-33.5%	68.5%-98.3%
	20	9.59-10.51	96.6%-105.8%	64.5%-67.2%	83.3%-100.0%
	30	8.91-9.46	89.7%-95.2%	94.0%-96.9%	80.9%-100.0%
	40	6.84-7.40	68.8%-74.5%	97.6%-99.0%	89.3%-100.0%

Table 4. The residual lanthanum and aluminium concentrations in Shanzi Reservoir and Xingyu Lake after different treatments.

	Treatment	Lanthanum (μg/L)	Aluminium (μg/L)
Shanzi Reservoir	Original water	1.25±0.21	59.15±9.11
	CK	1.32±0.17	68.79±11.97
	Phoslock®	26.04±0.27	99.38±20.88
	PIC	1.44±0.18	101.26±15.14
Xingyu Lake	Original water	3.21±0.22	62.90±12.98
	CK	3.53±0.39	70.11±16.79
	Phoslock®	23.12±1.01	104.09±19.01
	PIC	3.79±0.51	103.72±15.86

CK: Treatment without Phoslock® or PIC amendment.

PIC: Phosphorus inactive clay treatment.

Figure
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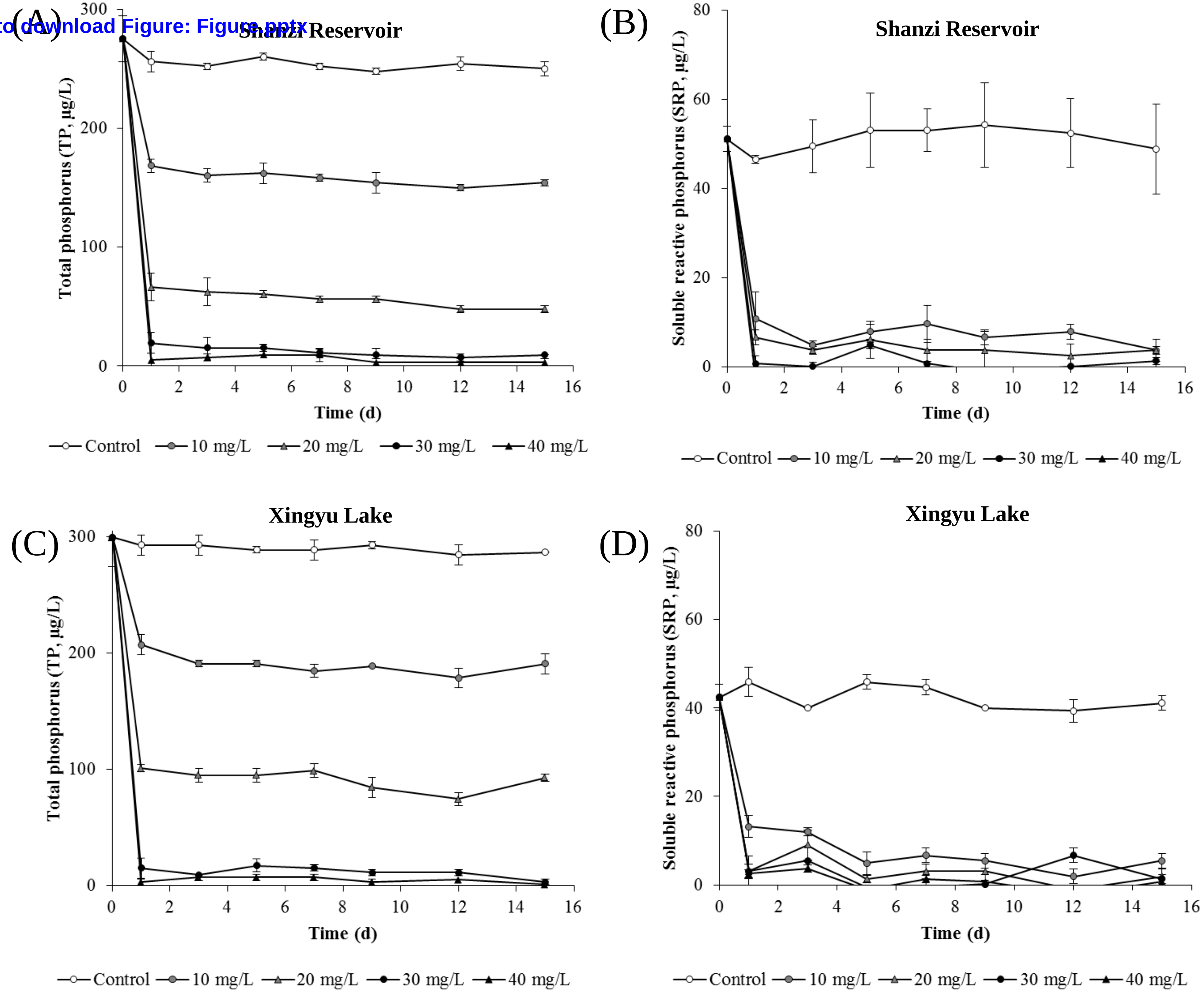


Figure 1

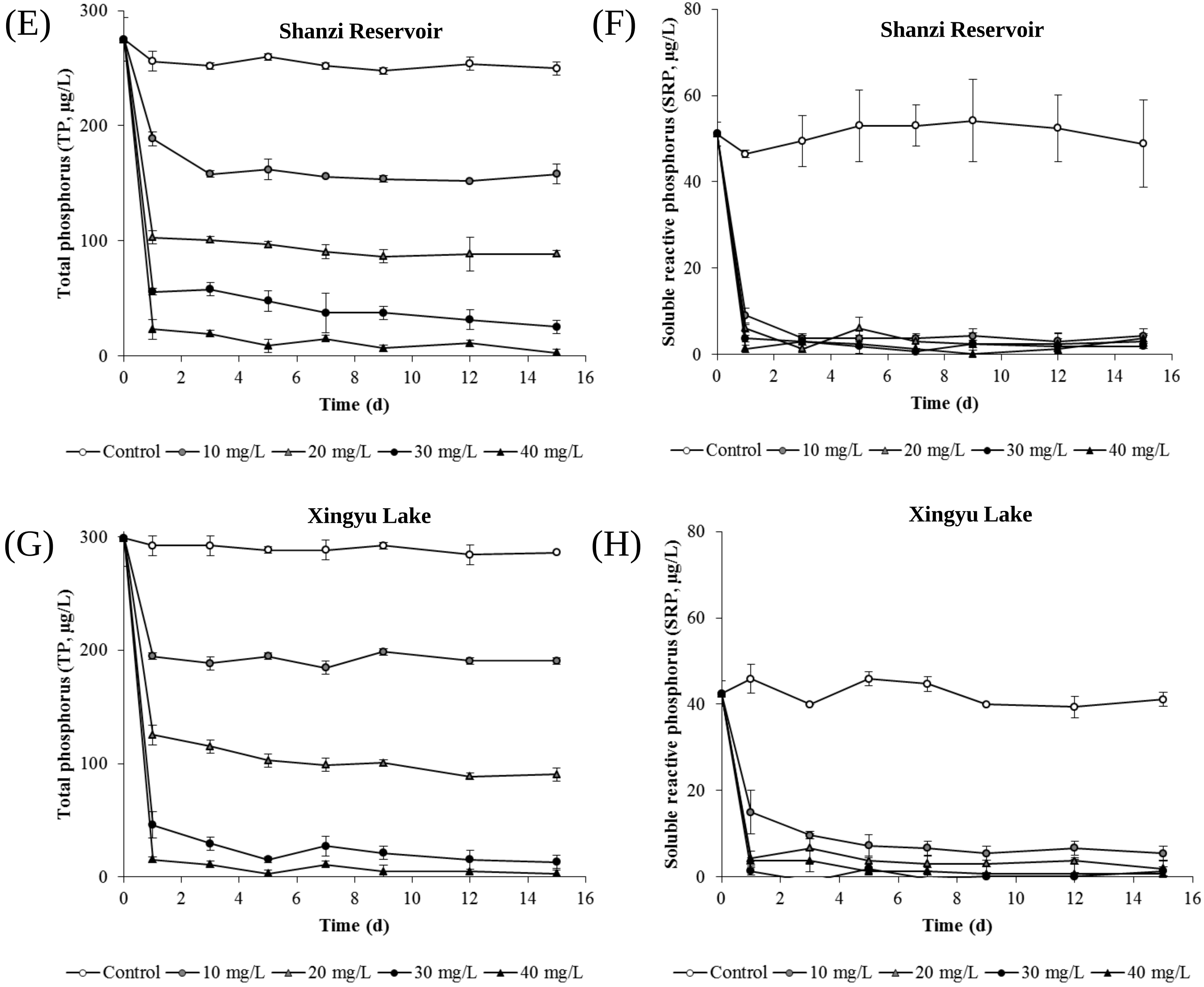
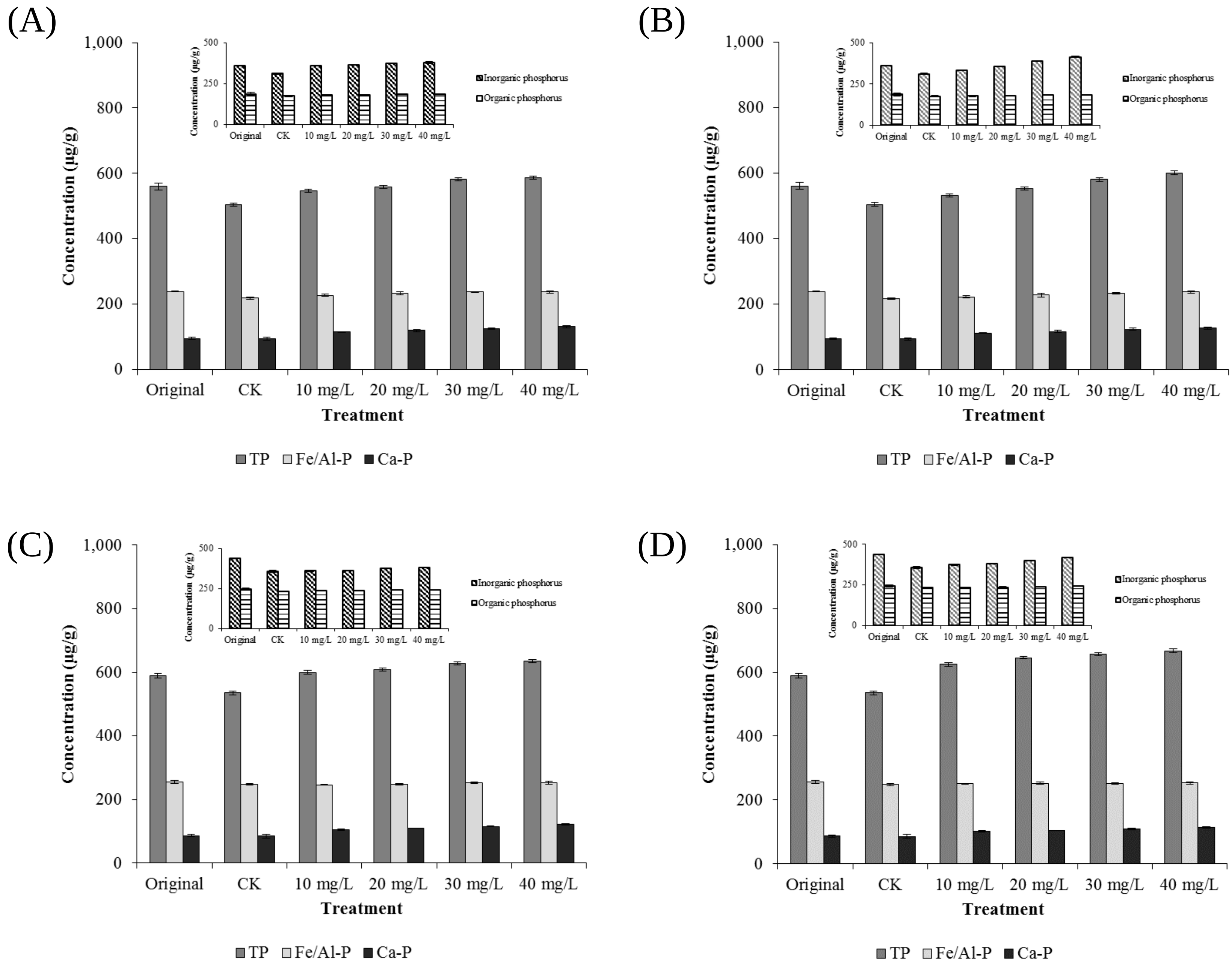

(E)
Shanzi Reservoir
Total phosphorus (TP, μg/L)
Time (d)
Control
10 mg/L
20 mg/L
30 mg/L
40 mg/L
(F)
Shanzi Reservoir
Soluble reactive phosphorus (SRP, μg/L)
Time (d)
Control
10 mg/L
20 mg/L
30 mg/L
40 mg/L
(G)
Xingyu Lake
Total phosphorus (TP, μg/L)
Time (d)
Control
10 mg/L
20 mg/L
30 mg/L
40 mg/L
(H)
Xingyu Lake
Soluble reactive phosphorus (SRP, μg/L)
Time (d)
Control
10 mg/L
20 mg/L
30 mg/L
40 mg/L

Figure 1



(A)
(B)
(C)
(D)
Concentration (μg/g)
Treatment
Original
CK
10 mg/L
20 mg/L
30 mg/L
40 mg/L
TP
Fe/Al-P
Ca-P
Inorganic phosphorus
Organic phosphorus

Figure 2

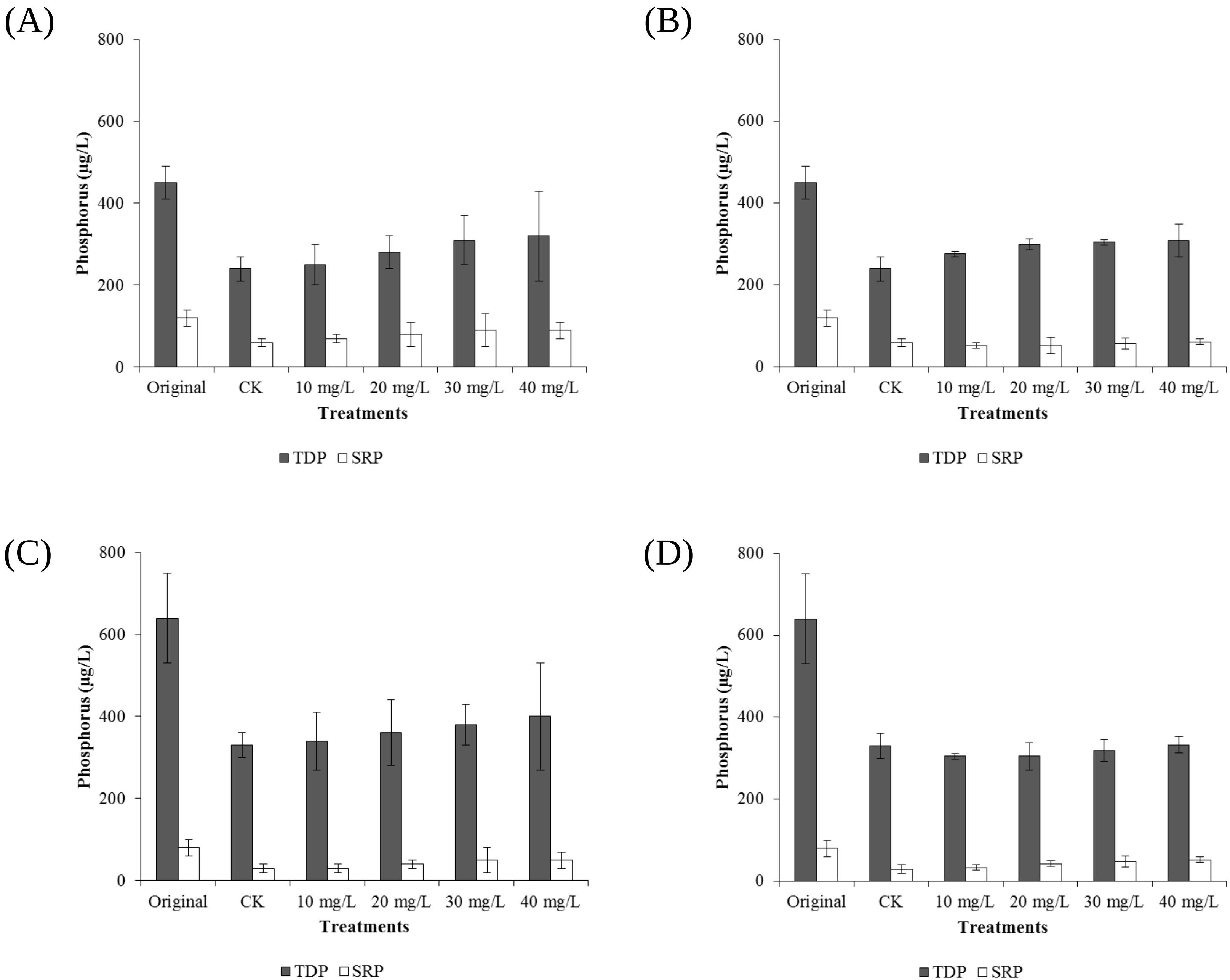
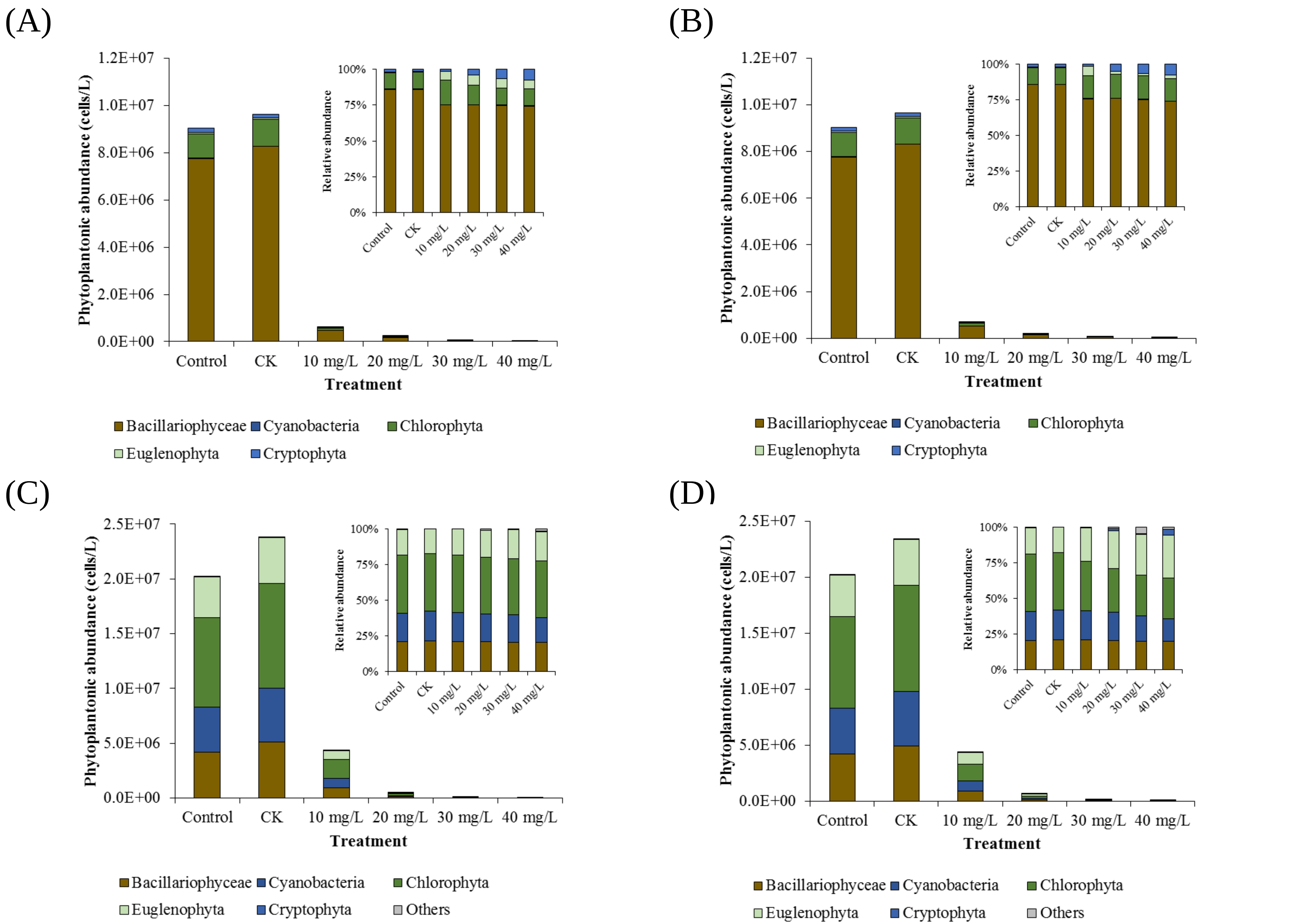
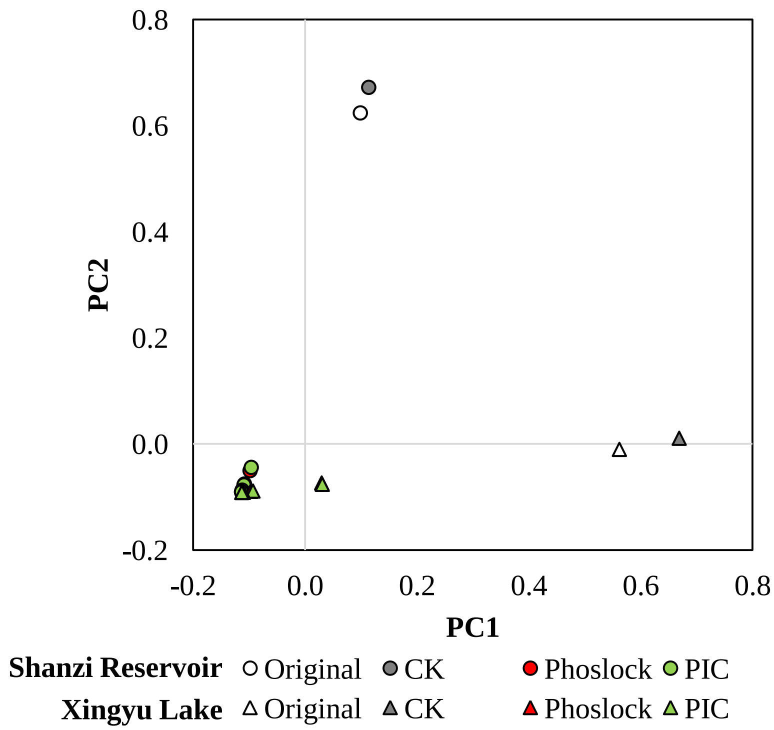

(A)
Phosphorus (μg/L)
800
600
400
200
0
Original
CK
10 mg/L
20 mg/L
30 mg/L
40 mg/L
Treatments
TDP
SRP
(B)
Phosphorus (μg/L)
800
600
400
200
0
Original
CK
10 mg/L
20 mg/L
30 mg/L
40 mg/L
Treatments
TDP
SRP
(C)
Phosphorus (μg/L)
800
600
400
200
0
Original
CK
10 mg/L
20 mg/L
30 mg/L
40 mg/L
Treatments
TDP
SRP
(D)
Phosphorus (μg/L)
800
600
400
200
0
Original
CK
10 mg/L
20 mg/L
30 mg/L
40 mg/L
Treatments
TDP
SRP

Figure 3



(A)
(B)
(C)
(D)
Phytoplantonic abundance (cells/L)
Relative abundance
Treatment
Control
CK
10 mg/L
20 mg/L
30 mg/L
40 mg/L
Bacillariophyceae
Cyanobacteria
Chlorophyta
Euglenophyta
Cryptophyta
Others

Figure 4



0.8
0.6
0.4
0.2
0.0
-0.2
PC2
-0.2
0.0
0.2
0.4
0.6
0.8
PC1
Shanzi Reservoir
Original
CK
Phoslock
PIC
Xingyu Lake
Original
CK
Phoslock
PIC

Figure 5

Supplementary Material

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