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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 $(1.0\text{--}2.4) \times 10^7$ cells/L to $(1.3\text{--}4.3) \times 10^6$ 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 $\mu\text{g/L}$, and the residual aluminium concentration was low as 101.26–103.72 $\mu\text{g/L}$, which was much less than the recommended concentration of 200 $\mu\text{g/L}$. 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.

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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 ($\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4 \downarrow$, $K_{sp} = 10^{-24.7} \text{--} 10^{-25.7}$). 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 (Lüring and Faassen, 2012;

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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 1000 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 °C at 240 rpm for series of time (0, 6, 9, 15, 30, 60, 240, 420, 720 and 1440 min), the suspension was centrifuged at 4000 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 2000 mL water samples were gently overlaid on 200.0 g

sediments. The cultivation condition was 12 h:12 h light-dark-cycle (photon flux density was 65 $\mu\text{mol}/\text{m}^2 \text{ s}$) and 15 °C. Intermittent aeration was conducted within the whole light period (12 h 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 and the energy-dispersive X-ray spectroscopy (EDS) was obtained by 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 sediments 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 h. After centrifugation at 4000 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 4000 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 10000 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

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