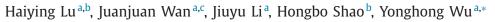
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### Periphytic biofilm: A buffer for phosphorus precipitation and release between sediments and water



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#### HIGHLIGHTS

- P migration between water, periphyton and sediment was evaluated systematically.
- Using periphyton as a buffer could affect P release and precipitation.
- Periphyton simultaneously captured P from water and sediments.
- P precipitation caused by periphyton was mainly in Ca-P and Fe/Al-P forms.

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#### ABSTRACT

The influence of periphytic biofilm on phosphorus (P) content and species between water and sediment interfaces was evaluated in a simulated experiment. Results showed that the concentration of all P species (TP, TDP, DIP, PP, and DOP) in overlying water decreased to significantly low levels ( $<0.05 \text{ mg L}^{-1}$ ) in the presence of periphytic biofilms, while the TP increased ( $>1.8 \text{ mg L}^{-1}$ ) in the control (without periphytic biofilm). Periphytic biofilm increased the water pH (maximal value at about 10) favoring co-precipitation between P and metal salt. The presence of periphytic biofilm also slowed the loss of P fractions such as Fe/Al-P and Ca-P from sediment. In addition, the P content of periphytic biofilms, mainly in forms of Fe/Al-P and Ca-P, increased by 100% after 60 d. These results suggested that periphytic biofilm was capable of entrapping P from water, attenuating P release, and storing P as a sink, thereby forming a buffer for P release and precipitation. This study not only offers some valuable insights into the role of periphytic biofilms or similar microbial aggregates in P biogeochemical processes in water-sediment interfaces, but also contributes to the management of water eutrophication from internal P loadings.

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#### 1. Introduction

Sediments play an important role in overall phosphorus (P) cycling in aquatic ecosystems, acting both as a sink and a source of P due to continuous transport of chemical species across the sediment and water interface (Jarvie et al., 2005; Jorcin and Nogueira, 2005). Many previous studies have indicated that sediment could continuously release P into the overlying water, which may result in continued eutrophication of overlying waters (Koski-Vähälä and Hartikainen, 2001; Søndergaard et al., 2003;

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http://dx.doi.org/10.1016/j.chemosphere.2015.10.129 0045-6535/© 2015 Elsevier Ltd. All rights reserved. Smith et al., 2006; Monbet et al., 2007; Wang et al., 2008; Qin, 2009; Palmer-Felgate et al., 2011). Generally, sediment P can be divided into labile P (NH<sub>4</sub>Cl–P), reductant P (BD–P), metal bound P (NaOH–P), calcium bound P (HCl–P), and residual P (Res-P) using chemical extraction methods (Rydin, 2000; Kaiserli et al., 2002; Fytianos and Kotzakioti, 2005). These P fractions in sediment however, may have different P exchangeability and bioavailability (Wang et al., 2006, 2009). It has been documented that only part of the P fractions in sediment are easily exchangeable and biologically available (such as NH<sub>4</sub>Cl–P), as most tend to adsorb on the surface or interior of various metal oxides and hydroxides (especially those of Fe, Mn, Ca and Al) (Christophoridis and Fytianos, 2006; Rzepecki, 2010; Renjith et al., 2011). Therefore,





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the evaluation of P fractions in sediment not only increases the understanding of P cycling in aquatic ecosystems, but also contributes to the management of eutrophication caused by the release of internal P loading (Kaiserli et al., 2002).

The release of P from sediments is a highly complex process and involves a number of physical processes (i.e. adsorption and desorption), chemical processes (i.e. ligand exchange and precipitation), and biological processes (i.e. release from living cells and autolysis of cells) (Christophoridis and Fytianos, 2006). Many factors can influence the release process of P between the sediment and water interface, including redox potential (Eh), pH, temperature, dissolved oxygen, salinity, and sediment resuspension (Koski-Vähälä and Hartikainen, 2001; Perkins and Underwood, 2001; Kaiserli et al., 2002; Christophoridis and Fytianos, 2006; Jin et al., 2006a, 2006b; Wang et al., 2013). Most research, however, has been based on the two phases (water and sediment), ignoring or underestimating the importance of the biota between them. For example, Wang et al. (2013) evaluated the change in P content and form in subtropical wetlands that were subjected to experimental warming, which was based on the sediment-water interface.

Periphytic biofilm, also called periphyton, is biota ubiquitously distributed between overlying water and sediments, especially on the surface of sediments and suspended particles in shallow aquatic ecosystems (Poulíčková et al., 2008; Writer et al., 2011). It is often a complex consortia of algae, bacteria and other micro-and meso-organisms (Wu et al., 2012). Many previous studies have demonstrated that periphytic biofilm plays a significant role in natural aquatic ecosystems by affecting primary production, food chains, and the migration of nutrients or contaminants in the sediment–water interface (Paerl and Pinckney, 1996; Battin et al., 2003; Writer et al., 2011; Saikia et al., 2013). In particular, periphytic biofilm is critical for P cycling between water and the sediment interface due to its high affinity for P (Scinto and Reddy, 2003; McCormick et al., 2006; Drake et al., 2012).

Generally, the high affinity of periphytic biofilm to P is due to its assimilation (Guzzon et al., 2008), adsorption (Scinto and Reddy, 2003; Lu et al., 2014a, 2014b), co-precipitation (Dodds, 2003; Hill and Fanta, 2008), and interception or entrapment (Adey et al., 1993) of P from water. Consequently, periphytic biofilm can act as a potential sink of P in water (McCormick et al., 2006). Some previous studies have found that P migration between water and sediment interfaces were controlled more by periphytic biofilm than diffusion (Woodruff et al., 1999b; Gainswin et al., 2006; Pietro et al., 2006). It has also been recently suggested that the presence of periphytic biofilm in the water-sediment interface could not only decrease the P content in overlying water, but also reduce the release of sediment P to overlying waters (Wu et al., 2010; Zhang et al., 2013). The changes of P concentrations and fractions between a sediment-periphytic biofilm-overlying water system however, have not been systematically investigated. Therefore, how P migrates in this 'three-phase' system and whether the presence of periphytic biofilm can alter P migration and transformation are still not clear.

The objectives of the study were to (1) systematically evaluate the change of P concentration and species between overlying water and sediments in the presence of periphytic biofilms; (2) assess the role of periphytic biofilms in P migration between overlying water and sediments; and (3) clarify P content and forms in periphytic biofilms. This study will help us to clarify the role of periphytic biofilm in P migration between overlying water and sediments. It will also provide valuable information for better understanding of P cycling in wetlands that contain periphytic biofilms or similar microbial assemblages.

#### 2. Material and methods

#### 2.1. Cultivation of periphytic biofilm

Periphytic biofilms were incubated in a glass tank (50 cm length, 20 cm width, and 60 cm height). The water ( $\sim$ 50 L) used for the periphytic biofilm gathering was collected from Xuanwu Lake in Nanjing, Jiangsu province of China. Industrial soft carriers (diameter 12 cm and length 55 cm, Jineng Environmental Protection Company of YiXing, China) were immersed into the water for microorganism gathering. The modified BG-11 medium (5 L, composing of 0.1 g NaCO<sub>3</sub>, 0.75 g NaNO<sub>3</sub>, 0.2 g K<sub>2</sub>HPO<sub>4</sub>, 0.375 g MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.18 g CaCl<sub>2</sub>·2H<sub>2</sub>O, 14.3 mg H<sub>3</sub>BO<sub>4</sub>, 9.05 mg MnCl<sub>2</sub>·4H<sub>2</sub>O, 1.1 mg ZnSO<sub>4</sub>, 1.95 mg Na<sub>2</sub>MoO<sub>4</sub>, 0.395 mg CuSO<sub>4</sub>·5H<sub>2</sub>O, 24.7 mg Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 30 mg citric acid and ammonium ferric citrate) was added periodically (weekly) to sustain periphytic biofilm growth. To reduce the influence of environmental conditions on periphyton growth, the tank was kept in a greenhouse with air temperature maintained between 25 and 35 °C. By day 60 many native micro-organisms had grown on the carriers and formed dense and stable periphytic biofilm (green in color). The periphytic biofilms were collected and used in the following experiments.

#### 2.2. Experimental design

The sediments used in the experiments were collected from the shallow area of Xuanwu Lake. After air-drying, the large rocks and wood pieces in the sediment were carefully picked out. Then, simulation of the water-sediment interface was conducted in 5.0 L capacity beakers. Firstly, 1.0 kg of dry sediment (TP:  $12.29 \pm 0.75 \text{ mg kg}^{-1}$ , Labile-P:  $1.02 \pm 0.07 \text{ mg kg}^{-1}$ , Fe/Al-P:  $3.67 \pm 0.36 \text{ mg kg}^{-1}$ , Ca-P:  $6.34 \pm 0.24 \text{ mg kg}^{-1}$ ) was added to the beaker. Secondly, 3.0 L water (20 mg  $L^{-1}$  NaCO<sub>3</sub>, 150 mg  $L^{-1}$ NaNO<sub>3</sub>, 10 mg L<sup>-1</sup> K<sub>2</sub>HPO<sub>4</sub>, 75 mg L<sup>-1</sup> MgSO<sub>4</sub>·7H<sub>2</sub>O, 36 mg L<sup>-1</sup> CaCl<sub>2</sub>·2H<sub>2</sub>O, pH: 7.8) was slowly poured into the beaker along the inside wall to avoid the re-suspension of sediments. Finally, the beaker was kept static for 24 h to settle any suspended sediments. To avoid the evaporative loss of water, distilled water was added periodically (every 7 days), keeping the water level in the beakers constant. The periphytic biofilms together with their carrier substrates were carefully taken out of the tank, divided into similar sized aliquots, and placed into the beakers at the sediment-over water interface. Each beaker received one periphyton aliquot, each 5 cm, about 20 g periphyton (wet weight). In the control, carrier substrates with no periphytic biofilms were added. Additionally, the control was covered with black cardboard to avoid periphytic biofilm formation at the water-sediment interface. A total of six beakers were prepared, three treatment and three controls. To avoid the influence of environmental conditions on the experiment, the beakers were kept in a greenhouse with air temperature between 25 and 30 °C.

#### 2.3. Samples and analyses

About 10 ml water and 5 g sediment (wet weight) were sampled each time. The water was sampled by a 20 mL injector, the sediment was sampled by a modified injector (10 mL). The modified injector was slowly inserted under the periphyton layer and sucked out sediments (the periphyton had spread all over the sediment surface after one month of the experiment). The experiment started on September 10, 2013, with water and sediments sampled at 0 d, 7 d, 15 d, 30 d, and 60 d. Total P (TP), total dissolved P (TDP), and dissolved inorganic P (DIP) in water were determined by a Flow injection analyzer (SEAL AA3, German).

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