



Processes and their explanatory factors governing distribution of organic phosphorous pools in lake sediments



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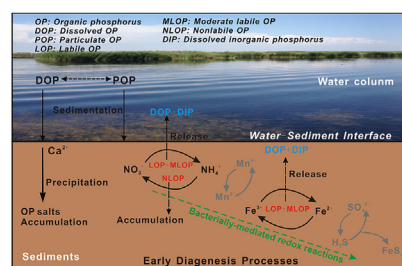
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HIGHLIGHTS

- We examine biotic and abiotic processes driving organic phosphorus fractionation.
- Organic matter composition and microorganisms play the most key roles.
- Calcium ions govern the dominant fraction by forming organic phosphate salts.
- Effects of iron and aluminum oxyhydroxides relate to their concentration levels.
- There are two fates for labile organic phosphorus pools during degradation process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 June 2015

Received in revised form

31 October 2015

Accepted 12 November 2015

Available online xxx

Handling Editor: X. Cao

Keywords:

Organic phosphorus

Fraction distribution

Driving processes and factors

Sediments

Lakes

ABSTRACT

The amount of organic phosphorus (OP) and its distribution among different pools in lake sediments depends on biotic and abiotic processes driving the OP fractionation. Key environmental factors governing these transformations processes between OP fractionations in sediments were studied on the basis of geochemical characteristics of OP pools in relation to environmental factors in the sediments. The results illustrate that the factors influencing the accumulation or depletion of different OP pools were intrinsically dependent on the composition of the deposited organic matter (OM). During the mineralization of the OM the microorganisms excrete the enzyme alkaline phosphatase, accelerating the OP hydrolysis, and thereby setting the grounds for the bacterially-mediated oxidation of OM. There are two main degradation products of the labile OP pool (LOP) and the moderately labile OP pool (MLOP): Either the OP is transformed to a dissolved organic or inorganic P form, and thereby released to water column, or OP is transformed to a non-labile OP pool and stored in the sediments. A comparative study showed that oxy-hydroxides of iron (Fe) and aluminum (Al) only played an important role in influencing OP fractionation in Lake Wuliangshuai, while the complexation reactions of OP with calcium ions and sorption to its minerals are key factors governing the OP fractionation in the two alkaline lakes. It is worth noting that a significant correlation between the Fe–P pool and the pools of LOP and MLOP

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indicates that the degradation of the rather labile OP pools are highly dependent on the iron redox reaction.

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1. Introduction

The importance of organic phosphorus (OP) as potentially bioavailable phosphorus (P) pools has been increasingly recognized (Turner et al., 2005). Recent studies on OP decomposition (Dyhrman et al., 2006; Sañudo-Wilhelmy, 2006; Stets and Cotner, 2008), fractionation (Ivanoff et al., 1998; Turner et al., 2005; Zhang et al., 2008; Zhu et al., 2013), compounds identification mainly by ^{31}P NMR (nuclear magnetic resonance spectrum) (Turner and Leytem, 2004; Ahlgren et al., 2005, 2006; Zhang et al., 2009; Xu et al., 2012) and their bioavailability (Dyhrman et al., 2006; Sañudo-Wilhelmy, 2006; Stets and Cotner, 2008) have strongly enhanced the knowledge of the role, impact and fate of OP in the environment. However, there still exists knowledge gaps' regarding the factors driving the underlying processes governing the size and distribution of OP pools in lake sediments.

The accumulation and distribution of OP in the sediment are known to be greatly influenced by physical and chemical conditions in the environment, such as the major cations composition and redox potential, and biological factors, such as microorganism activities, as well as the characteristics of the organic matter (OM). The chemical factors govern the complexation, adsorption or desorption, and precipitation or dissolution processes. OM usually form strong complex organo–mineral associations with polyvalent cations (Fe^{3+} , Al^{3+} , and Ca^{2+}). Moreover, the presence of these polyvalent cations may increase the adsorption capacity OP to the sediments by constituting a positively charged bridge between the negatively charged clay or organic sediments surfaces and the orthophosphate ions or organic anions. In additions these polyvalent ions may react with the OP to form insoluble organic phosphate salts precipitating onto the sediments surfaces (Anderson and Arlidge, 1962; De Groot and Golterman, 1993; House and Denison, 2002; Celi and Barberis, 2005).

OP pools in the sediments are also intrinsically linked with the composition and physiochemical characteristics of the originally deposited OM (Oluyedun et al., 1991). The driving factors governing the rate of accumulation and degradation of OM and OP bear therefore naturally close resemblance. The importance of enzymes, such as phosphatases, nucleases and phytase, in the breakdown of OP compounds has been well documented, while the abiotic pathways for the degradation of OP compounds have received substantially less attentions (Turner et al., 2005). Since 2000, more attentions has been given on the significance of OP degradation on water column P (Søndergaard et al., 1996; Rydin, 2000; Kaiserli et al., 2002; Spears et al., 2007) and the adsorption of OP compounds onto pure reactive Fe oxides (Celi and Barberis, 2005; Ruttenberg and Sulak, 2011). A dynamic mechanism may be involved in the stabilization of OP in sediments during the early diagenetic process, such as the dynamic transformation between OP pools driven by the abiotic process, the relations of OM fractions with OP fractionations, effects of abiotic factors or process in regulating the size and distribution of OP pools in lake sediments (e.g. Fe and Al oxyhydroxides, calcium ions and its minerals, ammonification and nitrification). However, little is known about these mechanism, especially relevant studies in aquatic systems are limited (Rietra et al., 2001; Turner et al., 2005; Huang and Zhang, 2010; Xu et al., 2013). Accordingly, the objects of this study

therefore were to (1) investigate the characteristics of OP fractionations in sediments, (2) interpret the geochemical information derived from the correlations between OP pools and the OM composition and physiochemical characteristics, (3) highlight the role of complexation and precipitation reactions with polyvalent cations in stabilizing OP pools in lakes sediments, (4) assess the factors that govern the distribution of OP pools in aquatic environment. This article aims to provide a better understanding of the geochemical processes governing the distribution of OP pools in lake sediments.

2. Materials and methods

2.1. Study area

Lake Wuliangsu Hai (WLSH) ($40^{\circ}46' - 41^{\circ}08' \text{N}$, $108^{\circ}41' - 108^{\circ}58' \text{E}$) located in the Inner Mongolia plateau at 1019 m a.s.l. Even though it is the largest lake (333 km^2) in the Yellow River basin, China, it is rather shallow with a mean depth of only 0.7 m. The climate of the watershed is dry with only 200 mm average annual precipitation along with a mean annual air temperature of 6.5°C , fuelling a potential evaporation of 2200 mm/yr. The major source of water to the lake is from farmland drainage of the Hetao Irrigation District, flowing into the lake through the Main Canal, the Eighth Canal and the Ninth Canal (Fig. 1). Due to heavy nutrients loads from the Hetao agricultural region, it has turned into a macrophyte-dominated aqueous system where *Phragmites communis* Trin and *Potamogeton pectinatus* L. are the two dominant species among only eleven species of macrophyte recorded in the lake. More than half of the lake is covered by emergent vegetation, mainly *Phragmites communis* Trin (Fig. 1). This heavy growth of macrophytes leads annually to a 9–13 mm thick layer of fresh plant litter in the lake bottom, which rests on a sediment layer consisting primarily of organic matter (Lü et al., 2008).

2.2. Sediment sampling

Sediments from Lake Wuliangsu Hai were sampled in August 2011. The surface sediments (0–10 cm) were collected using a KC collector mod B (Swedaq), while sediment cores were sampled applying a SA Beaker collector (Eijkelpamp). Three sediment cores named WLSH7 (44 cm), WLSH9 (44 cm), and WLSH11 (100 cm) (Fig. 1) were sectioned into 2-cm slices immediately after collection and stored in sealed polyethylene bags. Samples were transported to the laboratory in iceboxes ($<4^{\circ} \text{C}$). At the laboratory the sediments were freeze-dried, ground gently in a mortar and sieved through a standard 100-mesh sieve prior to analysis. Simultaneously, overlying water samples were collected for all sampling sites for determination of dissolved OP (DOP). These water samples were filtered through 0.45 mm polycarbonate filters, acidified to pH 1.0 with hydrochloric acid, and stored refrigerated in glass bottles. In addition, physiochemical data of sediments and overlying water that were sampled in a similar manner from Lake Hulun (HLH) are included in this study. See description detailed in [Supplementary Material \(SM\) Text S1.1 and Fig. S1](#).

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