

Phosphorus transformation under the influence of aluminum, organic carbon, and dissolved oxygen at the water-sediment interface: A simulative study

Ouchen Cai^{1*}, Yuanxiao Xiong^{1,2*}, Haijun Yang³, Jinyong Liu (✉)^{1#}, Hui Wang (✉)¹

1 State Key Joint Laboratory on Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084

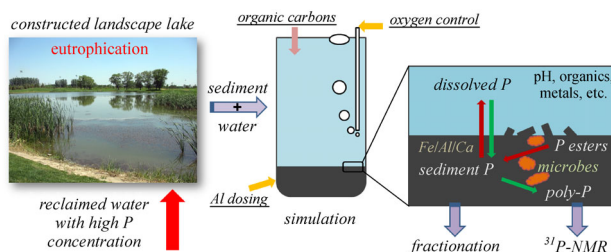
2 Beijing 101 Middle School, Beijing 100091, China

3 Department of Chemistry, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- The three simulation factors caused various changes in both water and sediment.
- Responses to simulations differed with the reported natural lakes and wetlands.
- Al has dominant effects on sediment P release control among the three factors.
- Adding sediment Al can be effective and safe under the simulated conditions.
- Polyphosphates were not generated, while added phytate was rather stable.

GRAPHIC ABSTRACT



ARTICLE INFO

Article history:

Received 8 January 2020

Revised 8 February 2020

Accepted 10 February 2020

Available online 25 March 2020

Keywords:

Phosphorus
Sediment
Simulation
Dissolved oxygen
Organic carbon
Aluminum

ABSTRACT

The effects of sediment aluminum (Al), organic carbon (OC), and dissolved oxygen (DO) on phosphorus (P) transformation, at the water-sediment interface of a eutrophic constructed lake, were investigated via a series of simulative experiments. The above three factors had various influences on dissolved P concentration, water pH, water and surface sediment appearance, and P fractions. Additions of Al had the greatest effect on suppressing P release, and the water pH remained alkaline in the water-sediment system under various OC and DO conditions. No dissolution of the added Al was detected. ³¹P-NMR characterization suggested that OC addition did not promote biological P uptake to polyphosphates under oxic conditions. The simulation result on the added phytate indicated the absence of phytate in the original lake sediment. As compared to the reported natural lakes and wetland, the water-sediment system of the constructed lake responded differently to some simulative conditions. Since Al, OC, and DO can be controlled with engineering methods, the results of this study provide insights for the practical site restorations.

© Higher Education Press and Springer-Verlag GmbH Germany, part of Springer Nature 2020

1 Introduction

Phosphorus (P) is a limiting nutrient for lake organisms and acts as a major contributor to eutrophication. As the reservoir of external P and the source of internal P, lake

sediments play vital roles in P cycling, including complex processes of chemical and biological transformation (Golterman, 2001). Simulative studies have revealed the detailed mechanism for P release or immobilization under variable conditions, such as redox potential, pH, temperature and light, (Jiang et al., 2008). Among these factors, the levels of sediment Al, OC, and DO can be directly controlled by engineering measures such as Al dosing (Jensen et al., 2015), OC control (Khoshmaesh et al., 2002; Reitzel et al., 2017) and aeration (Rosłńska et al., 2018; Yin et al., 2019).

Al dosing is an effective way to immobilize P in the

✉ Corresponding authors

E-mail: jinyong.liu101@gmail.com (J. Liu);

wanghui@tsinghua.edu.cn (H. Wang)

*These authors contributed equally to this work

#J. Liu, current address: Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA

sediment. Unlike iron (Fe)-bound P which is readily released from sediment during hypolimnion anoxia, Al-bound P is stable under both oxic and anoxic conditions if the pH is circumneutral (Huser et al., 2016). Natural lake sediments with high Al content release negligible amount of P during anoxia (Kopáček et al., 2005; Norton et al., 2008; Liu et al., 2009). Al dosing has also been applied in site restoration projects to irreversibly sequester P in the sediment (Huser et al., 2016; Zhang et al., 2019). However, this practice consumes alkalinity and thus lowers pH, which may lead to the occurrence of dissolved Al (Gensemer and Playle, 1999) and change the aquatic ecology (Reitzel et al., 2003; Steinman and Ogdahl, 2008).

Organic matter influences the surface sediment microbe activities. The uptake, storage, and release of P are of major importance in P cycling in some lakes (Jensen et al., 2015). When the microbial activity is promoted by seston, the sediment acts as a trap for P from the overlying water (Ni et al., 2019). Khoshmanesh et al. (2002) found that, under oxic conditions, dissolved orthophosphate was completely taken up by microbes in wetland sediments amended with carbon sources. However, sediment microorganisms can also quickly respond to organic matter by shifting toward anoxic conditions and decreasing the pH (Khoshmanesh et al., 1999), both of which may promote the sediment P release. Furthermore, organic matter may decrease the effectiveness of P adsorption to Al (de Vicente et al., 2008) and lead to Al hydroxide dissolution if the pH gets significantly lowered (Reitzel et al., 2013).

For over a decade, the knowledge of P at the water-sediment interface has been greatly updated with the aid of ^{31}P nuclear magnetic resonance spectroscopy (^{31}P -NMR). Orthophosphate is found to be converted by the aquatic community to a series of biogenic P compounds, such as P-monoesters, P-dieters, pyrophosphate, polyphosphates and phosphonates (Zhang et al., 2013; Read et al., 2014; Zhang et al., 2014; Zhu et al., 2018). P esters are regarded recalcitrant by being incorporated with organic matter and preserved in the sediment (Ahlgren et al., 2006; Zhu et al., 2013), while polyphosphates are considered more labile to redox-controlled decomposition (Hupfer et al., 2004). However, the current understanding of the origin and fate of these P species is still insufficient for P cycling research and eutrophication control (Ahlgren et al., 2011).

In areas with fast urban development and limited water resource, such as the metropolitan areas of China, many lakes receive reclaimed water with relatively high P concentrations as the supplement (Fang et al., 2018). Even if the reclaimed water quality is further improved, internal P cycling will still be a big concern for eutrophication. Previously, we studied a series of constructed landscape lakes (Liu et al., 2009). The lake sediments contain a high concentration of P but lack sufficient Al to suppress internal P release. It is also found that, compared with reported natural water bodies,

biogenic P compounds take very small fractions of the total sediment P. Therefore, Al dosing and aeration may be implemented to prevent sediment P release, and OC addition may also be considered to enhance P uptake by sediment microbes.

However, the effect of each engineering approach must be examined in laboratory simulation first, especially when more than one approach is to be carried out simultaneously. Taking OC addition for instance, several questions should be addressed to evaluate the practicability, such as whether the biological P conversion can be truly enhanced, whether the OC metabolism induced pH shift will affect the Al dosing, and whether there will be other issues upon OC addition. To answer these and other similar questions, a series of experiments was conducted to simulate the P transformation at the water-sediment interface of a eutrophic constructed lake. The influences of Al, OC, and DO were evaluated with overlying water P concentration and pH, as well as chemical fractionation and ^{31}P -NMR characterization of sediment P. The results provide new insights for P transformation research and lake eutrophication management.

2 Materials and methods

2.1 Site description

The studied sediment and water were collected from one of the constructed lakes in a golf course located in north-eastern Beijing (Liu et al., 2009). The surface area of the lake is 1.5 ha, and the mean depth is 1.5 m. By the sampling time in summer, the lake had been using the reclaimed water containing 0.7 to 3.0 mg P/L as a supplement for three years. The surrounding landscape lawns, fed with manure and chemical P fertilizers, also contributed significant P pollution to the lake. The total P content in the calcareous sediment (molar ratio of $\text{Ca}/(\text{Al} + \text{Fe}) = 1.0$) was 1490 mg/kg. The P level in the lake water stayed above 0.15 mg P/L throughout the year; however, no algae bloom has ever happened, possibly due to the allelopathy of the exuberant macrophytes (Gross, 2003) near the bank (calamus) and in the water (reed). The lake water remained alkaline (pH 7.4 to 8.5), although the supplement water was slightly acidic (pH 6.5 to 7.0).

2.2 Material collection and reactors setup

The lake water was collected in PET bottles, and surface sediments (0 to 2.5 cm depth) were collected by a Tamura grab sampler from five distant spots on the lake bottom. Water and sediment samples were respectively stored at -20°C and -80°C until use.

In a 5 L beaker, 1.5 kg of wet sediment and 3 L of lake water were combined into a slurry and homogenized with

magnetic stirring and pumped aeration for 8 h. The solid phase was collected after centrifugation at 5000 r/min for 10 min. Each of the nine 2.5 L brown glass bottle reactors was loaded with 100 g of the processed sediment and 200 mL of lake water. For each reactor, sodium phytate (65 mg, Sigma-Aldrich P8810) and 2-phosphorylpropionic acid (7.5 mg, Alfa-Aesar) were dissolved in 10 mL of lake water, and the solution was slowly introduced into the mixture under fast stirring. The purpose of the phytate introduction is to examine whether sediment microbes can degrade this P-monoester at a significant rate under the simulated conditions (Suzumura and Kamatani, 1995). Phosphonates were detected in some natural lake sediments and considered to be both chemically and biologically stable (Ahlgren et al., 2006), probably due to the stability of the P–C bond. Hence, the 2-phosphorylpropionic acid, a typical phosphonate compound, was added as a reference to evaluate the chemical extraction for ^{31}P -NMR analysis. The mixture was further stirred and aerated for 12 h, and the suspension was left to settle, resulting in a flat water-sediment interface. Sediment in one of the nine reactors was collected and stored at 80°C until being analyzed as the “initial” sediment. For the rest eight reactors, another 2 L of lake water was slowly introduced into each reactor. The reactors were configured with different Al, OC and DO levels (Table 1). The Al treatment was achieved by slowly adding a solution (10 mL) of 320 mg of poly aluminum chloride (PAC) into the overlying water under vigorous stirring. The molar ratio between the added Al and sediment mobile P (Reitzel et al., 2003) was approximately 4, the same ratio used in the reported site restoration project (Reitzel et al., 2005). After floc formation, the water-floc-sediment mixtures were stirred for 12 h under aeration and then left to settle for 6 h. The Al hydroxide was thus dispersed into the sediment, with no floc visible on the sediment top. The OC addition was realized by adding a solution (10 mL) of sodium acetate (377 mg) and glucose (276 mg) into each designated reactor. Each carbon source contributed 50 mg C/L. The carbon source types and concentrations were chosen based on Khoshmanesh et al. (1999) and Hupfer et al. (2004). DO was controlled by continuously bubbling air or nitrogen to maintain >4.5 mg/L in oxic reactors and <1 mg/L in anoxic reactors. All reactors were placed away from sunlight and incubated at room temperature (22°C to 24°C) for 30 days.

Table 1 Configurations of DO, OC and sediment (Al) for the eight reactors

Reactor	A	B	C	D	E	F	G	H
DO ^{a)}	–	–	–	–	+	+	+	+
OC ^{b)}	+	–	+	–	+	–	+	–
Al ^{b)}	+	+	–	–	+	+	–	–

2.3 Water and sediment analysis

During the simulation period, DO and temperature of the overlying water were monitored daily with a Rex JPB-607 DO meter. pH was measured in situ with a Mettler Toledo SG2 pH-meter. At each sampling time, 10 mL of the overlying water was taken by a syringe and replaced by 10 mL of deionized water to maintain the constant overlying water volume. After 0.45- μm membrane (cellulose acetate) filtration, orthophosphate was measured by molybdate colorimetry (S.E.P.A. China, 2002). Dissolved metal concentrations were measured by Thermo IRIS Intrepid inductively coupled plasma-atomic emission spectroscopy (ICP-AES). At the end of the simulation, the overlying water in each reactor was carefully removed by the siphon and pipette to avoid sediment resuspension. Surface sediments (5 mm thick) were collected, immediately frozen at -80°C and lyophilized.

For fractionation analysis, 0.4 g of the lyophilized sediment sample was fractionated twice with each of the following extractants: 1 M NH_4Cl at 25°C for 1 h, 0.11 M $\text{NaHCO}_3\text{-Na}_2\text{S}_2\text{O}_4$ (BD) at 40°C for 30 min, 1 M NaOH at 25°C for 16 h, and 0.5 N HCl at 25°C for 24 h (Lake et al., 2007; Liu et al., 2009). All fractions were centrifuged at 8000 r/min for 5 min, and the supernatants were filtered through 0.45- μm membrane filters. Extracted P concentration was quantified by molybdate colorimetry after $\text{K}_2\text{S}_2\text{O}_8$ digestion (S.E.P.A. China, 2002).

For ^{31}P -NMR analysis, 2.0 g of the lyophilized sediment sample was pre-extracted with 20 mL of 0.067 M Na_2EDTA at 25°C for 1 h with the purpose of (1) reducing the NMR spectrum interference by reducing paramagnetic metals and (2) removing ions catalyzing the polyphosphate fragmentation (Hupfer et al., 2004). After centrifugation at 10,000 r/min for 5 min and supernatant decantation, a 20 mL of solution containing 0.25 M NaOH and 0.05 M Na_2EDTA was used to extract the sediment at 25°C for 16 h (Cade-Menun and Preston, 1996). After centrifugation at 15000 r/min for 10 min, the supernatants were filtered through 0.45- μm membrane filters and neutralized by 0.5 M HCl to reduce biogenic P degradation during the followed lyophilization (Cade-Menun et al., 2006; Reitzel et al., 2006).

For the preparation of a ^{31}P -NMR sample, 200 mg of the lyophilized residual powder was dissolved in 0.6 mL of D_2O and 0.1 mL of 10 M NaOH. An additional 25 mg of $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ was also added, with the purpose of reducing line broadening by chelating free paramagnetic ions (Turner and Newman, 2005) and prevent the fragmentation of polyphosphates (Hupfer et al., 2004), if any. The ^{31}P -NMR spectra were recorded at ambient temperature (22°C–25°C) on a JEOL ECA 600 spectrometer operating at 242.95 MHz for ^{31}P , using a 5.2 μs pulse (45°), a delay time of 2.0 s, an acquisition time of 0.54 s, and broadband proton decoupling. Between 9500 and

29100 scans were acquired depending on P concentration. Data were processed using 1-Hz line broadening. Chemical shifts were indirectly referenced to external 85% H_3PO_4 (at $\delta = 0.0$), and the assignment of peaks was done by comparison with literature.

3 Results

3.1 P concentration change in the overlying water

As shown in Fig. 1, at day 0 the orthophosphate concentrations in the overlying water of all reactors were around 1 mg/L. However, during the 30 days of simulation, different Al, OC, and DO conditions led to greatly varied P concentrations and P uptake/release features. Sediment Al content had a dominant influence. Four sediments dosed with PAC (A, B, E, and F) removed most ortho-P from overlying water within one day, and the P levels remained below 0.2 mg/L regardless of differing DO and OC concentrations. In contrast, all the four sediments without Al addition (C, D, G, and H) released P into the overlying water; the ortho-P concentrations stayed above 1 mg/L.

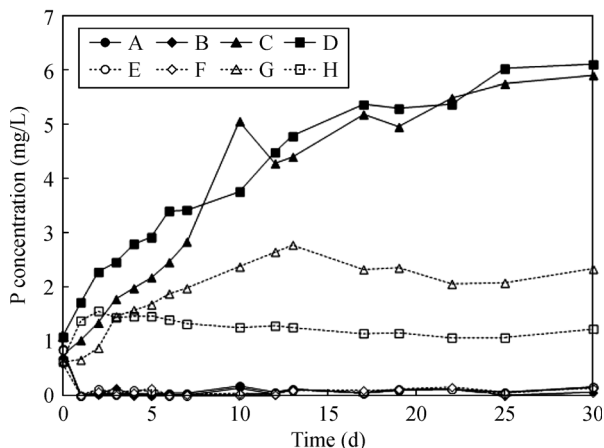


Fig. 1 Orthophosphate concentration changes in the overlying water of the eight reactors during the simulation period. Reactors A, B, C, D: oxic; E, F, G, H: anoxic. Reactors A, C, E, G: organic carbon added; Reactors A, B, E, F: Al added.

For the sediments without Al addition, the influence of DO is pronounced. Under anoxic conditions (C and D) the sediments kept releasing P due to the dissolution of Fe and Mn matrices (see below) and reached 6 mg/L at the end of the simulation. Under oxic conditions (G and H) the sediments released much less P than C and D. After a P releasing period, the P concentrations in G and H started to slightly decrease at day 13 and day 3, respectively.

The apparent influence of organic carbons is only observed in oxic G and H, both of which were not amended with Al. Although DO levels in oxic reactors were

constantly over 4.5 mg/L, the addition of 100 mg/L OC in reactor G resulted in a longer P releasing period than in reactor H. The P release under oxic conditions could be attributed to microbial activities (Jiang et al., 2008). This is different from the discovery by (Khoshmanesh et al., 1999) that glucose and acetate addition led to a fast and full P removal by wetland sediment microbes from the overlying water.

3.2 pH change of the overlying water

Figure 2(a) shows the overlying water pH during the simulation period for all reactors. Starting from the initial value of 7.6, the pH change in each reactor varied due to the different Al, OC, and DO conditions. In general, pH in anoxic reactors (A, B, C, and D) were lower than in oxic reactors (E, F, G, and H). This is in accordance with the previous report on wetland sediment simulation (Khoshmanesh et al., 1999). However, the opposite effect was observed in the simulative study on Taihu Lake sediment (Wang et al., 2008).

For the demonstration of the influences of Al and OC, the pH curve pairs (the other two parameters being the same) are separately plotted in Figs. 2(b) and 2(c), respectively. In general, the reactor with Al-dosed sediment had a slightly lower pH than the counterpart (Fig. 2 (b)). For the pairs B/D, E/G, and F/H, sharp pH increases were observed during the first several days, probably due to the release of sediment alkaline substances into the water taken from the lake surface. However, this increase was not shown in reactors A and C, where 100 mg/L organic carbon was added under anoxic condition. From the comparison pairs A/B and C/D (Fig. 2(c)), the OC addition lowered pH during the first half of the simulation period. However, under oxic conditions, the reactors with amended OC showed higher pH, as seen in the pairs E/F and G/H. Nevertheless, although the highest overlying water pH reached near 9, dissolved Al was not detected by ICP-AES (detection limit 10 $\mu\text{g/L}$) in all overlying water samples.

3.3 Water and sediment appearance

Figure S1 shows the overlying water collected from each reactor at the end of the 30-day simulation. In contrast to the oxic reactors (E, F, G, and H) with colorless and transparent overlying waters, waters from anoxic reactors showed different colors and turbidity. Especially for A and C amended with organic carbons, the water turned pink and red-brown, respectively. For the other two without OC addition, the overlying water was colorless in B and light yellow in D. However, after the 0.45- μm filtration, all samples became colorless and transparent. After the samples were left to stand for 10 days at 4°C, colored precipitates formed, and the water became clear. Thus, the colored material should be most probably biogenic

Table 2 P recovery with sediment extractions

Sediment	Total P (NaOH-EDTA) (mg P/kg)	Phosphonate (NaOH-EDTA) (mg P/kg)	NH ₄ Cl-P + BD-P + NaOH-P (Fractionation) (mg P/kg)	P _{NaOH-EDTA} / P _{NH₄Cl+BD+NaOH} ratio
Initial	620	25.4	976	63.5%
A	793	50.8	1054	75.2%
B	676	66.9	844	80.0%
C	495	6.4	655	75.6%
D	608	38.3	814	74.7%
E	743	17.1	1122	66.2%
F	863	34.5	1269	68.0%
G	600	4.8	1079	55.6%
H	618	6.8	1196	51.7%

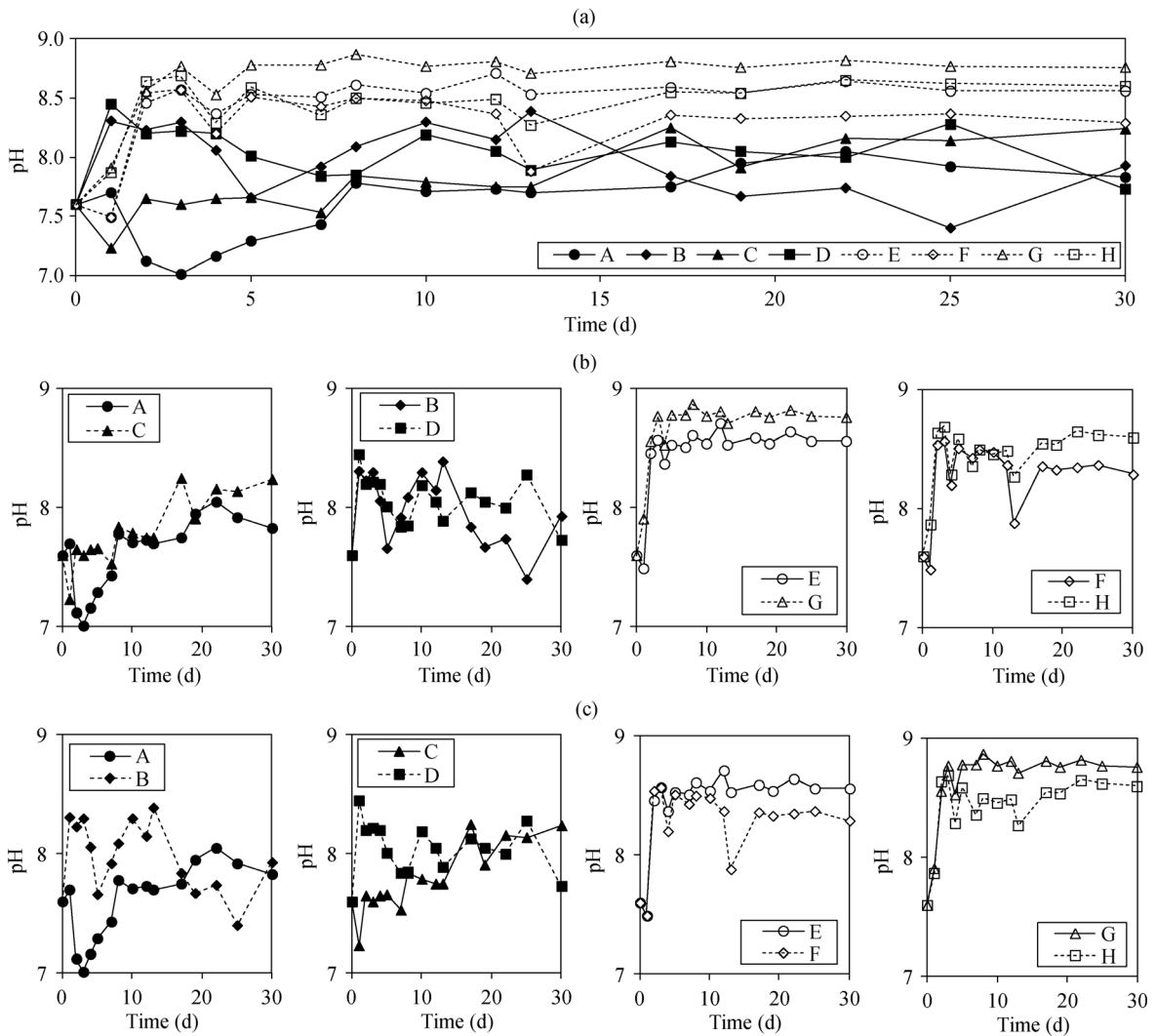


Fig. 2 (a) Overlying water pH changes of the eight reactors during the simulation period. (b) Comparison of the effects of added Al. Dotted lines indicate the reactors not amended with Al. (c) Comparison of the effects of organic carbon. Dotted lines indicate the reactors not amended with OC. Reactors A, B, C, D: oxitic; E, F, G, H: anoxic. Reactors A, C, E, G: organic carbon added; Reactors A, B, E, F: Al added.

macromolecules. The color difference among A, B, C, and D is visibly apparent such that the concentration could be readily estimated as $C > A > D > B$, and correlated to microbial activities that converted small molecular organic carbons into humus (Liu et al., 2016). As suggested by comparisons A/B and C/D, OC addition promoted color and turbidity formation. On the other hand, the effect of Al addition is also obvious; comparisons A/C and B/D indicate that Al addition could reduce the color (Egemos et al., 2010) with the same OC conditions. Abundant sediment Al could absorb humics from the overlying water, and it might also suppress the anoxic release of sediment humics initially bound to Fe hydroxides.

In the beginning, the sediment interfaces with the overlying water in all reactors were dark gray and flat (Fig. S2). After 30 days of simulation, surface sediment in the four oxic reactors (E to H) turned yellow for 3 to 5 mm of thickness. Due to the hydrological disturbance by air bubbling, these sediment surfaces looked flat and rich in pores. Sediment surface in the four anoxic reactors (A to D) remained dark gray. Under anoxic conditions, gas bubbles intermittently emitted from the sediment and created fissures and cracks on the surface. Similar to the trend of the overlying watercolor, OC-amended reactors A and C had more ruptured sediment surfaces than those of sets B and D. Sediment Al also had an influence on the degree of rupture to sediment surfaces; Al-added sediments A and B had smoother surfaces than those of C and D, respectively. Since gas emission could cause sediment surface resuspension and liberate labile P in the porewater to the overlying water (Zhang et al., 2019), abundant sediment Al may have beneficial effects for reducing disruption-induced P release.

3.4 Sediment P fractionation

Sediment P fractions at the surface sediment are shown in

Fig. 3. The fraction $\text{NH}_4\text{Cl-P}$ represents the loosely bound P, including pore water P, CaCO_3 associated P and decaying bacteria cells leached P (Liu et al., 2009). After the 30-day simulation, sediments in anoxic reactors A, B, C, and D had a decreased amount of $\text{NH}_4\text{Cl-P}$ compared to the initial sediment. This may be explained by gas emission disruption, as well as P transformation into other fractions. In contrast, this P fraction in oxic reactors G and H (without Al addition) increased to more than twice of the value in the initial sediment.

The fraction BD-P represents the redox-sensitive P forms mainly bound to Fe hydroxide and Mn compounds (Liu et al., 2009). Under anoxic conditions (A, B, C, and D), this fraction decreased due to the dissolution of Fe and Mn matrices under low redox condition. Under oxic conditions, the sediments in OC amended reactors (E and G) remained the BD-P level as in the initial sediment, while the other two without OC addition (F and H) had BD-P increased for about 160 mg/kg.

The fraction NaOH-P mainly includes P bound to Al hydroxides and organic materials (Liu et al., 2009). Sediments amended with Al had significantly increased NaOH-P under both anoxic (A and B) and oxic (E and F) conditions. As observed from Fig. 1 and Fig. 5, although the sediment BD-P of A and B decreased, the overlying water P did not increase. Under either anoxic or oxic condition, the sediment tended to release P into the water, whereas adequate Al was able to effectively capture the mobile P. It is worth noting that, increased NaOH-P in the oxic sediments (E and F) might be attributed to the P release from the lower anoxic layer that remained dark color.

The HCl-P fraction is assumed to consist mainly of apatite P and considered to be relatively stable, contributing to a permanent P burial in the sediments (Liu et al., 2009). The amounts of this P fraction in all sediments were similar, indicating that the Al, OC, and DO factors did not

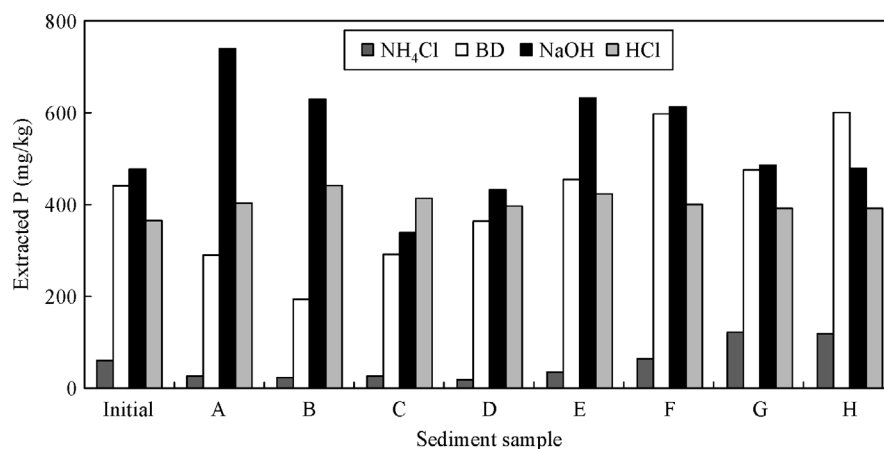


Fig. 3 P fractionation of sediment samples. Reactors A, B, C, D: oxic; E, F, G, H: anoxic. Reactors A, C, E, G: organic carbon added; Reactors A, B, E, F: Al added.

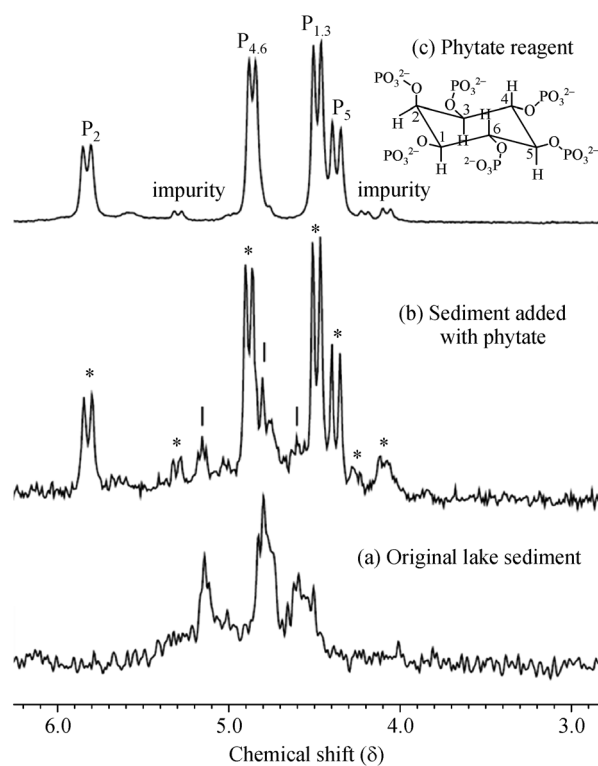


Fig. 4 ^{31}P -NMR spectra for the NaOH-EDTA extract of (a) original lake sediment, (b) “initial” sediment sample added with phytate, and (c) excess phytate spiked in sediment extract. In (b), * indicates the signal of added phytate reagent; | indicates the signal of other P-monoesters detected in the original lake sediment.

have significant short-term influence, although some previous studies proposed that the organism process might play some role in HCl-P transformation (Wang et al., 2008).

3.5 Biogenic P transformation

NaOH-EDTA extraction covered 495 to 863 mg P/kg from the sediments in reactors A-H and the initial sediment sample (Table 2). The P species diversity detected by ^{31}P -NMR was uniform for all the nine samples, although the intensity and relative integration area of each peak among spectra varied. However, extracted phosphonate (as the reference standard) ranged from 4.8 to 66.9 mg P/kg. Especially, the extracted amount in A, B, D, and F significantly exceeded the amount extracted from the “initial” sediment. Thus it is likely that mineral and biological processes under variable simulation conditions led to differences in P extractability. The NaOH-EDTA extracted P may not be directly used for comparison on the quantitative change of each biogenic P species. Detailed reasoning is presented in the Discussion.

The comparison of the P-monoester regions between the original lake sediment (before amending with phytate and phosphonate) and the phytate-amended sediment (Fig. 4) clearly suggested that the original sediment did not contain phytate in an amount above the NMR detection limit. Both the P-monoester compounds in the original sediment and added phytate could be simultaneously seen in the NaOH-EDTA extract of the phytate-amended sediment. Figure 5 shows the comparison of P species in the original lake sediment and in the representative sediment from reactor E after 30 days of simulation. The species presented in the original sediment (e.g. DNA and pyrophosphate), as well as the added phytate and phosphonate, were still abundant after simulation. This also applies to all other post-simulation sediments (spectra not shown), indicating these biogenic P species could not be significantly degraded under the various combination of Al, OC, and DO conditions for a month. No new P species was generated

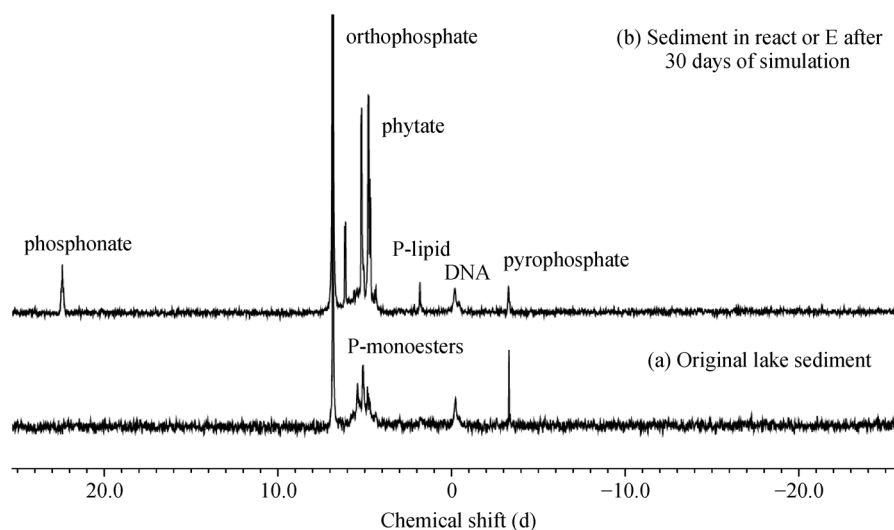


Fig. 5 ^{31}P -NMR spectra for the NaOH-EDTA extracts of (a) original lake sediment and (b) sediment from reactor E after simulation. The peaks of orthophosphate are not fully displayed.

during the simulation, either. Unlike Khoshmanesh et al. (2002) where the ^{31}P -NMR detected polyphosphate amount was comparable to orthophosphate and P-monooesters in NaOH-EDTA extracts, no such signal (chemical shift near 20 ppm) was detected in any sediment samples in our study. Reactor E was amended with a similar amount of organic carbons as used in Khoshmanesh et al. (2002) and aerated, but no microbial activity toward polyphosphate conversion was indicated from ^{31}P -NMR characterization.

4 Discussion

4.1 Influences of Al, OC, and DO

Among a series of factors that could influence P transformation and water quality, Al, OC, and DO can be controlled by engineering approaches to affect the two P immobilization strategies—mineral fixation and biological conversion. The three factors can affect each other via the change of pH. For example, DO levels affect microbial activities and lead to varied water pH; microbial degradation of OC consumes DO and change pH; altered pH may cause Al hydroxide dissolution. However, in this study, due to the good buffering capacity of the sediment, even the water in reactors A and C (added with 100 mg/L OC under anoxic conditions) remained alkaline. Thus, the Al dissolution as Al^{3+} would not be possible. Besides, although the highest pH (8.8) in oxic reactor E may potentially dissolve Al hydroxide as $\text{Al}(\text{OH})_4^-$ (Reitzel et al., 2013), Al was not detected in the overlying water of all reactors, possibly due to the complex chemistry at the water-sediment interface that prevented the release of soluble Al species.

Despite that OC addition as high as 100 mg C/L promoted microbial growth that increased color and turbidity, P levels were constantly low in the overlying water of the reactors with Al addition. Fractionation results suggest that abundant Al would scavenge $\text{NH}_4\text{Cl-P}$ or BD-P, which could otherwise enter the overlying water upon disturbance or anoxia, respectively. Under various conditions of OC and DO, as well as the subsequently altered pH, sediments supplemented with Al effectively suppressed P release into the overlying water, and did not leach detectable amount of Al. Therefore, sediment Al is the more decisive factor for P control than DO and OC. The actual OC levels in the studied lake systems are much lower than 100 mg/L. The site application of Al at the studied dosage may be effective for P control and safe for the aquatic ecosystem.

It is also worth mentioning that, in this study, the DO influence is opposite to what was observed in Wang et al. (2008), where anoxic conditions led to elevated pH due to photosynthesis and denitrification. The pH increase under oxic conditions upon OC addition was also inconsistent

with the report (Abril and Frankignoulle, 2001) where CO_2 production and nitrification under oxic conditions consumed alkalinity. These interesting disparities indicate different mineral constituent and microbial activity of the studied water-sediment interface with those of reported aquatic systems. This shows the necessity of simulation studies before any practical remediation procedure is to be carried out.

4.2 Implications for Al addition

The Al dosage in this study was 4 times the molar ratio of sediment mobile P, which was defined as $(\text{NH}_4\text{Cl-P}) + (\text{BD-P}) + (\text{NaOH-nrP})$ (Reitzel et al., 2003). The practical PAC application to Lake Sønderby with this Al/P ratio maintained a low water P level for at least two years (Reitzel et al., 2005). For the sediments dosed with Al in this study, the resulted molar ratios of $(\text{NaOH-Al}):(\text{BD-Fe}) = 2:1$ and $(\text{NaOH-Al}):[(\text{NH}_4\text{Cl-P}) + (\text{BD-P})] = 14:1$ did not respectively meet the proposed threshold of 3:1 and 25:1, which were summarized from statistics of natural lake sediment that suppressed anoxic P release (Kopáček et al., 2005). However, the Al dosage used here was sufficient to suppress P release, even though a high level of dissolved organics also competed for the adsorption sites on Al hydroxides (de Vicente et al., 2008), as indicated by the overlying watercolor comparison. Furthermore, Al addition reduced the gas emission rupture of the sediment surface.

It is also noteworthy that, in this study, Al floc was dispersed in the sediment to simulate natural lake sediments that are rich in Al (Kopáček et al., 2005), rather than precipitated as a floc layer over the sediment. First, the floc layer coverage can be readily removed by hydrological disturbance, such as anoxic gas emission and aeration from the top. Second, the floc layer directly exposes large surfaces of amorphous Al hydroxide to the water phase, such that elevated (or lowered) pH may induce considerable Al dissolution. In natural catchment lake ecosystems, Al in the acidic flows forms colloidal hydroxides by the carbonate buffering system and bio-generated alkalinity in the lake and consequently stabilized P in the sediment (Kopáček et al., 2005). Accordingly, for P immobilization and color reduction (Egemose et al., 2010) of water bodies with controlled water sources (e.g., the studied golf course landscape lakes), Al addition may be implemented in a continuous low dosage (Malecki-Brown et al., 2010) in the water supply, rather than in a one-time large-scale Al dosing on the lake surface. The latter may cause a sudden alkalinity drop and aquatic community disturbance (Steinman and Ogdahl, 2008).

4.3 Presence and conversion of biogenic P

With ^{31}P -NMR spectroscopy, Hupfer et al. (2004) detected a major portion of the non-reactive P as polyphosphates in

NaOH-EDTA extracts of lake sediments. The ^{31}P -NMR study also showed that acetate addition under oxic conditions stimulated orthophosphate uptake and conversion into polyphosphates by sediment microbes (Khoshmanesh et al., 2002; Zhang et al., 2016). However, in this study, no polyphosphate was detected, despite that NMR sample preparation was modified with additional procedures to minimize the polyphosphate degradation. On the one hand, therefore, polyphosphates were not an abundant component, if any, of the sediment P pool in the investigated constructed landscape lakes. On the other hand, OC addition under oxic conditions had little benefit for P immobilization but instead led to a series of adverse effects such as water quality deterioration, sediment surface disruption, and even P release. This disparity over original presence and stimulated the formation of polyphosphates in the sediment demonstrates the difference among water systems- natural lakes (Hupfer et al., 2004; Ahlgren et al., 2011; Read et al., 2014), wetland (Khoshmanesh et al., 2002) and constructed lakes (Liu et al., 2009).

Similarly, the result of this study clears the doubts on the presence and conversion of phytate in constructed lake sediment. In some early reports on lake sediments, the crowded and broadened peaks in the P-monoester region were assigned as phytate, which was traditionally considered as the most abundant P-monoester in soil and sediment (Ahlgren et al., 2006; Reitzel et al., 2006; Zhang et al., 2009). However, spiking experiments showed the absence of phytate in some soil (Smernik and Warwick, 2007) and sediment (Liu et al., 2009) samples. In the simulative experiment of Suzumura and Kamatani (1995) on marine sediment, amended phytate almost completely decomposed within 40 days under anoxic conditions. They proposed the mechanism to be the enzymatic hydrolysis after phytate was dissolved from Fe complexes under anoxia. However, since NaOH-EDTA mainly liberated P that was bound to Al and organic matrices, it is not surprising that phytate could ward off enzymatic attacks through immobilization with Al hydroxides, which are inert to redox conditions. Based on the fact that phytate signals were absent in original sediment samples, and the added phytate was rather stable under a variety of conditions, we propose that the phytate amount in the original lake sediment was negligible. Among biogenic P compounds in the environment, phytate has some distinctive properties, such as exceptional chemical stability and strong binding capacity with metals (Turner et al., 2002). Hence, sediment restoration strategies based on phytate conservation should be used only if the presence of phytate is verified.

Although quantifications of biogenic P species in soil and lake sediment samples have been done in numerous previous studies, ^{31}P -NMR spectroscopic analysis on alkaline (e.g. NaOH, NaOH-EDTA, etc.) extracts may

not be suitable for quantifying the dynamic conversion of biogenic P. First, to obtain an adequate amount of P but a limited amount of extraction chemicals (in large excess of P and causing solubility and viscosity issues) in the ^{31}P -NMR sample, the extractant/sediment ratio is relatively low (Liu et al., 2009; Ahlgren et al., 2011; Qu et al., 2019) compared to the fractionation extraction, where multiple rinses with high extractant/sediment ratios (Liu et al., 2009) were used to ensure a sufficient extraction of P for quantitative analysis. In this study, fractionated $\text{NH}_4\text{Cl-P}$, BD-P , and NaOH-P showed dynamic changes during the simulation, but NaOH-EDTA extraction only recovered 52%–80% of $(\text{NH}_4\text{Cl-P}) + (\text{BD-P}) + (\text{NaOH-P})$. Bai et al. (2009) also noticed that organic P extracted for ^{31}P -NMR analysis was only a small fraction of the total sediment P. Second, the different recovery ratios of the phosphonate reference (Table 2) suggest that P species could enter other mineral bound forms, which are relatively resistant to NaOH-EDTA extraction. We found in earlier tests (data not shown) that NaOH-EDTA extraction could not effectively liberate Fe or Mn-bound P in the sediment samples. Therefore, the NaOH-EDTA extracted P may not fully represent the biogenic P profile in the sediment. Recent studies on methodologies also revealed that the amount of extracted P and fractions of each biogenic P species were greatly affected by extraction chemicals (Ding et al., 2010b), extraction procedure (Ahlgren et al., 2007; Ding et al., 2010a) and even sample pretreatment (Cheesman et al., 2007). The spiking analysis showed that some major monoester-P compounds were possibly generated from diester-P (e.g., phospholipids) hydrolysis during the alkaline extraction (Doolette et al., 2009). In addition, for an accurate quantification for each biogenic P species, it is necessary to allow full P nucleus relaxation times (McDowell and Cade-Menun, 2006) and obtain sufficient signal to noise ratios (Cade-Menun et al., 2006), which however the majority of previous studies did not fulfill because substantially long instrument time might be needed. Therefore, we propose that ^{31}P -NMR can be used for qualitative analysis to identify the presence of certain characteristic biogenic P species, such as phytate and polyphosphates. However, the dynamic P transformation in the sediments may not be appropriately quantified, due to the potential misinterpretation by so many factors mentioned above.

5 Conclusions

Al, OC, and DO had various influences on the P transformation at the sediment-water interface. Al showed dominant effects on P immobilization from overlying water and sequestration in the sediment. Elevated Al content in the sediment also reduced the color and turbidity of the overlying water, as well as the anoxic gas emission

from the sediment. OC addition in the water did not cause apparent biological P immobilization; instead, it increased P release from Al-deficient sediments, caused water quality deterioration, and promoted anoxic gas emission. Aeration can improve the water quality and prevent BD-P decrease, but using aeration alone could not effectively prevent sediment P release. The pH changes under all simulations did not cause Al dissolution into overlying water. Adding sediment Al would be effective and safe for P control if the external P pollution is cut off. Due to the limitations of current ^{31}P -NMR analysis methods, dynamic changes of biogenic P species could not be quantified to identify the influences of the three simulative factors. However, qualitative conclusions can be made on the absence of polyphosphates and persistence of the spiked phytate in the sediments under all simulation conditions. Therefore, OC addition and aeration could not promote the biological conversion of P into sediment polyphosphates as occurred in other aquatic systems. As a relatively stable monoester P compound, phytate probably not contributed to a significant fraction of P in the original lake sediment. These simulative studies provide useful information on P transformation in constructed lake systems. Corresponding engineering approaches, especially the Al addition strategy, warrant further detailed investigations in both laboratory- and field-scale studies.

Acknowledgements This study was supported by the National Key Research Project on Water Environment Pollution Control in China (Nos. 2012ZX07301 and 2017ZX07202002).

Electronic Supplementary Material Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s11783-020-1227-z> and is accessible for authorized users.

References

- Abril G, Frankignoulle M (2001). Nitrogen-alkalinity interactions in the highly polluted Scheldt basin (Belgium). *Water Research*, 35(3): 844–850
- Ahlgren J, de Brabandere H, Reitzel K, Rydin E, Gogoll A, Waldebäck M (2007). Sediment phosphorus extractants for phosphorus-31 nuclear magnetic resonance analysis: A quantitative evaluation. *Journal of Environmental Quality*, 36(3): 892–898
- Ahlgren J, Reitzel K, Danielsson R, Gogoll A, Rydin E (2006). Biogenic phosphorus in oligotrophic mountain lake sediments: Differences in composition measured with NMR spectroscopy. *Water Research*, 40(20): 3705–3712
- Ahlgren J, Reitzel K, De Brabandere H, Gogoll A, Rydin E (2011). Release of organic P forms from lake sediments. *Water Research*, 45(2): 565–572
- Bai X, Ding S, Fan C, Liu T, Shi D, Zhang L (2009). Organic phosphorus species in surface sediments of a large, shallow, eutrophic lake, Lake Taihu, China. *Environmental Pollution*, 157(8–9): 2507–2513
- Cade-Menun B J, Navaratnam J A, Walbridge M R (2006). Characterizing dissolved and particulate phosphorus in water with ^{31}P nuclear magnetic resonance spectroscopy. *Environmental Science & Technology*, 40(24): 7874–7880
- Cade-Menun B J, Preston C M (1996). A comparison of soil extraction procedures for ^{31}P NMR spectroscopy. *Soil Science*, 161(11): 770–785
- de Vicente I, Jensen H S, Andersen F Ø (2008). Factors affecting phosphate adsorption to aluminum in lake water: Implications for lake restoration. *Science of the Total Environment*, 389(1): 29–36
- Ding S, Bai X, Fan C, Zhang L (2010a). Caution needed in pretreatment of sediments for refining phosphorus-31 nuclear magnetic resonance analysis: Results from a comprehensive assessment of pretreatment with ethylenediaminetetraacetic acid. *Journal of Environmental Quality*, 39(5): 1668–1678
- Ding S, Xu D, Li B, Fan C, Zhang C (2010b). Improvement of ^{31}P -NMR spectral resolution by 8-hydroxyquinoline precipitation of paramagnetic Fe and Mn in environmental samples. *Environmental Science & Technology*, 44(7): 2555–2561
- Doolette A L, Smernik R J, Dougherty W J (2009). Spiking improved solution phosphorus-31 nuclear magnetic resonance identification of soil phosphorus compounds. *Soil Science Society of America Journal*, 73(3): 919–927
- Egemose S, Reitzel K, Andersen F Ø, Flindt M R (2010). Chemical lake restoration products: Sediment stability and phosphorus dynamics. *Environmental Science & Technology*, 44(3): 985–991
- Fang T, Wang H, Cui Q, Rogers M, Dong P (2018). Diversity of potential antibiotic-resistant bacterial pathogens and the effect of suspended particles on the spread of antibiotic resistance in urban recreational water. *Water Research*, 145: 541–551
- Gensemer R W, Playle R C (1999). The bioavailability and toxicity of aluminum in aquatic environments. *Critical Reviews in Environmental Science and Technology*, 29(4): 315–450
- Golterman H L (2001). Phosphate release from anoxic sediments or ‘What did Mortimer really write?’. *Hydrobiologia*, 450(1–3): 99–106
- Gross E M (2003). Allelopathy of aquatic autotrophs. *Critical Reviews in Plant Sciences*, 22(3–4): 313–339
- Hupfer M, Rube B, Schmieder P (2004). Origin and diagenesis of polyphosphate in lake sediments: A ^{31}P -NMR study. *Limnology and Oceanography*, 49(1): 1–10
- Huser B J, Egemose S, Harper H, Hupfer M, Jensen H, Pilgrim K M, Reitzel K, Rydin E, Futter M (2016). Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Research*, 97: 122–132
- Jensen H S, Reitzel K, Egemose S (2015). Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia*, 751(1): 189–199
- Jiang X, Jin X, Yao Y, Li L, Wu F (2008). Effects of biological activity, light, temperature and oxygen on phosphorus release processes at the sediment and water interface of Taihu Lake, China. *Water Research*, 42(8–9): 2251–2259
- Khoshmanesh A, Hart B T, Duncan A, Beckett R (1999). Biotic uptake and release of phosphorus by a wetland sediment. *Environmental Technology*, 20(1): 85–91

- Khoshmanesh A, Hart B T, Duncan A, Beckett R (2002). Luxury uptake of phosphorus by sediment bacteria. *Water Research*, 36(3): 774–778
- Kopáček J, Borovec J, Hejzlar J, Ulrich K, Norton S A, Amirbahman A (2005). Aluminum control of phosphorus sorption by lake sediments. *Environmental Science & Technology*, 39(22): 8784–8789
- Lake B A, Coolidge K M, Norton S A, Amirbahman A (2007). Factors contributing to the internal loading of phosphorus from anoxic sediments in six Maine, USA, lakes. *Science of the Total Environment*, 373(2–3): 534–541
- Liu J, Wang H, Yang H, Ma Y, Cai O (2009). Detection of phosphorus species in sediments of artificial landscape lakes in China by fractionation and phosphorus-31 nuclear magnetic resonance spectroscopy. *Environmental Pollution*, 157(1): 49–56
- Liu S, Zhu Y, Meng W, He Z, Feng W, Zhang C, Giesy J P (2016). Characteristics and degradation of carbon and phosphorus from aquatic macrophytes in lakes: Insights from solid-state ^{13}C NMR and solution ^{31}P NMR spectroscopy. *Science of the Total Environment*, 543(Pt A): 746–756
- Malecki-Brown L M, White J R, Brix H (2010). Alum application to improve water quality in a municipal wastewater treatment wetland: Effects on macrophyte growth and nutrient uptake. *Chemosphere*, 79(2): 186–192
- McDowell R W, Cade-Menun B J, (2006). An examination of spin-lattice relaxation times for analysis of soil and manure extracts by liquid state phosphorus-31 nuclear magnetic resonance spectroscopy. *Journal of Environmental Quality*, 35(1): 293–302
- Ni Z, Wang S, Zhang B T, Wang Y, Li H (2019). Response of sediment organic phosphorus composition to lake trophic status in China. *Science of the Total Environment*, 652: 495–504
- Norton S A, Coolidge K, Amirbahman A, Bouchard R, Kopáček J, Reinhardt R (2008). Speciation of Al, Fe, and P in recent sediment from three lakes in Maine, USA. *Science of the Total Environment*, 404(2–3): 276–283
- Qu Y, Wang C, Guo J, Huang J, Fang F, Xiao Y, Ouyang W, Lu L (2019). Characteristics of organic phosphorus fractions in soil from water-level fluctuation zone by solution ^{31}P -nuclear magnetic resonance and enzymatic hydrolysis. *Environmental Pollution*, 255 (Pt 2):113209
- Read E K, Ivancic M, Hanson P, Cade-Menun B J, McMahon K D (2014). Phosphorus speciation in a eutrophic lake by ^{31}P NMR spectroscopy. *Water Research*, 62: 229–240 doi:10.1016/j.watres.2014.06.005
- Reitzel K, Ahlgren J, Gogoll A, Jensen H S, Rydin E (2006). Characterization of phosphorus in sequential extracts from lake sediments using ^{31}P nuclear magnetic resonance spectroscopy. *Canadian Journal of Fisheries and Aquatic Sciences*, 63(8): 1686–1699
- Reitzel K, Balslev K A, Jensen H S (2017). The influence of lake water alkalinity and humic substances on particle dispersion and lanthanum desorption from a lanthanum modified bentonite. *Water Research*, 125: 191–200
- Reitzel K, Hansen J, Andersen F Ø, Hansen K S, Jensen H S (2005). Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environmental Science & Technology*, 39(11): 4134–4140
- Reitzel K, Hansen J, Jensen H S, Andersen F v, Hansen K S (2003). Testing aluminum addition as a tool for lake restoration in shallow, eutrophic Lake Sønderby, Denmark. *Hydrobiologia*, 506(1–3): 781–787
- Reitzel K, Jensen H S, Egemose S (2013). pH dependent dissolution of sediment aluminum in six Danish lakes treated with aluminum. *Water Research*, 47(3): 1409–1420
- Rosińska J, Kozak A, Dondajewska R, Kowalczywska-Madura K, Gołdyn R (2018). Water quality response to sustainable restoration measures: Case study of urban Swarzędzkie Lake. *Ecological Indicators*, 84: 437–449
- S.E.P.A. China (2002). Monitor and Analysis Method of Water and Wastewater. 4th ed. Beijing: Chinese Environment Science Press, 243–248 (in Chinese)
- Smernik R J, Dougherty W J (2007). Identification of phytate in phosphorus-31 nuclear magnetic resonance spectra: The need for spiking. *Soil Science Society of America Journal*, 71(3): 1045–1050
- Steinman A D, Ogdahl M (2008). Ecological effects after an alum treatment in Spring Lake, Michigan. *Journal of Environmental Quality*, 37(1): 22–29
- Suzumura M, Kamatani A (1995). Mineralization of inositol hexaphosphate in aerobic and anaerobic marine sediments: Implications for the phosphorus cycle. *Geochimica et Cosmochimica Acta*, 59(5): 1021–1026
- Turner B L, Papházy M J, Haygarth P M, McKelvie I D (2002). Inositol phosphates in the environment. *Philosophical Transactions of Royal Society B*, 357(1420): 449–469
- Turner B L, Newman S (2005). Phosphorus cycling in wetland soils: the importance of phosphate diesters. *Journal of Environmental Quality*, 34(5): 1921–1929
- Wang S, Jin X, Bu Q, Hao L, Wu F (2008). Effects of dissolved oxygen supply level on phosphorus release from lake sediments. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 316(1-3): 245–252
- Yin H, Wang J, Zhang R, Tang W (2019). Performance of physical and chemical methods in the co-reduction of internal phosphorus and nitrogen loading from the sediment of a black odorous river. *Science of the Total Environment*, 663: 68–77
- Zhang R, Wang L, Wu F, Song B (2013). Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and ^{31}P NMR. *Journal of Environmental Sciences (China)*, 25(6): 1124–1130
- Zhang R, Wu F, He Z, Zheng J, Song B, Jin L (2009). Phosphorus composition in sediments from seven different trophic lakes, China: A phosphorus-31 NMR study. *Journal of Environmental Quality*, 38(1): 353–359
- Zhang S, Yi Q, Buyang S, Cui H, Zhang S (2019). Enrichment of bioavailable phosphorus in fine particles when sediment resuspension hinders the ecological restoration of shallow eutrophic lakes. *Science of the Total Environment*, 710:135672 doi:10.1016/j.scitotenv.2019.135672
- Zhang W, Jin X, Ding Y, Zhu X, Rong N, Li J, Shan B (2016). Composition of phosphorus in wetland soils determined by SMT and solution ^{31}P -NMR analyses. *Environmental Science and Pollution Research International*, 23(9): 9046–9053

- Zhang W, Tang W, Zhang H, Bi J, Jin X, Li J, Shan B (2014). Characterization of biogenic phosphorus in sediments from the multi-polluted Haihe River, China, using phosphorus fractionation and ^{31}P -NMR. *Ecological Engineering*, 71: 520–526
- Zhu Y, Feng W, Liu S, He Z, Zhao X, Liu Y, Guo J, Giesy J P, Wu F (2018). Bioavailability and preservation of organic phosphorus in lake sediments: Insights from enzymatic hydrolysis and ^{31}P nuclear magnetic resonance. *Chemosphere*, 211: 50–61
- Zhu Y, Wu F, He Z, Guo J, Qu X, Xie F, Giesy J P, Liao H, Guo F (2013). Characterization of organic phosphorus in lake sediments by sequential fractionation and enzymatic hydrolysis. *Environmental Science & Technology*, 47(14): 7679–7687