



Distribution of organic phosphorus species in sediment profiles of shallow lakes and its effect on photo-release of phosphate during sediment resuspension

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ABSTRACT

In this work, the distribution of organic phosphorus (P_o) species in sediment profiles of five shallow lakes was analyzed and its effect on the photo-release of dissolved phosphate (P_i) was investigated during sediment resuspension under simulated sunlight irradiation. The results show that P_o was highly enriched in the surface sediment and gradually decreased as sediment depths increased: 33.10 ± 2.55 – 96.71 ± 7.60 mg/kg, 33.55 ± 2.34 – 142.86 ± 5.73 mg/kg, 57.50 ± 3.46 – 149.68 ± 7.67 mg/kg, 55.18 ± 4.67 – 168.73 ± 8.31 mg/kg, 98.75 ± 7.56 – 275.74 ± 10.70 mg/kg for Lake Hou, Lake Tuan, Lake Tangling, Lake Guozheng and Lake Miao, respectively. The photo-release amount of dissolved P_i in the resuspension composed of surface sediments was also higher than that of deep sediment during sediment resuspension under the simulated sunlight irradiation for 9 h. The potential reasons for these results are: (1) difference in morphology and composition of sediments at different depths: the mean particle size of sediment decreased first and then increased as sediment depths increased; (2) difference in composition of P_o species with depths in the sediment profiles: more photolytic P_o species existed in surface sediments confirmed by sequential extraction and ³¹P NMR analysis; and (3) more $\cdot OH$ production in the resuspension composed of surface sediment under simulated sunlight irradiation, which directly influence the photo-release of dissolved P_i from photodegradation of organic phosphorus. All of these results indicate that the distribution of organic phosphorus species in the sediment profiles plays an important role in P cycle and its photodegradation during sediment resuspension may be one of the potential pathways for phosphate supplement in shallow lakes.

1. Introduction

Water eutrophication leads to overgrowth of phytoplankton and formation of blooms that endanger the health of water bodies (Molen et al., 1998; Brooks et al., 2016). Phosphorus (P) is a key factor in water eutrophication (Hudson et al., 2000). Excessive P input, both from external loading and internal cycling, is one of the major causes for water eutrophication (Søndergaard et al., 2003). While reduction and mitigation of external phosphorus input can be achieved via effective controls, the release of internal phosphorus from sediments has become a big challenge and major contributor for the lake eutrophication

processes (Søndergaard et al., 2007; Spears et al., 2012; Ma et al., 2019). Internal phosphorus can enter water column under certain biogeochemical conditions such as wind-driven undercurrent bioturbation, or biological activity (O'Brien et al., 1981; Froelich et al., 1988; Filippelli and Delaney, 1996). When dissolved phosphate (P_i) is taken up and assimilated by primary producers in water, the transformation of internal organic phosphorus (P_o) to P_i in sediments becomes an important supplementary way for providing phosphorus for phytoplankton growth (Feng et al., 2018). However, the pathway and influencing factors of this transformation process has not been completely understood due to the complex compositions of phosphorus species in

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eutrophic shallow lakes and limited analytical techniques.

The degradation of organic phosphorus in lakes releases dissolved P_i through biomineralization and chemical decomposition processes (Froelich et al., 1982; Gachter and Meyer, 1993; Gardolinski et al., 2004; Jensen et al., 2006; Li et al., 2011; Kim et al., 2015). Previous research studies have focused mostly on the biomineralization of organic phosphorus (Zhou et al., 2002; Wang and Pant, 2010; Ni et al., 2016; Soliman et al., 2017; Bastamia et al., 2018). In comparison, few studies have focused on the photochemical transformation of P_o into P_i , especially in shallow waters such as lakes and coastal aquatic environments (Huo et al., 2011). Francko and Heath (1982) found that dissolved P_i was released when humic-Fe- P_i complexes were irradiated by UV. The mechanism for the release of phosphate was attributed to the humic-based reduction of Fe(III) to Fe(II) due to the consistent reaction rate of Fe(III) photoreduction and phosphate release. Studies on the lability of phosphorus in humic acid found that orthophosphate was released in the enzymatic hydrolysis and UV irradiation treatment. Enzymatic hydrolysis released hydrolyzable P_o , and UV irradiation released orthophosphate by breaking down phosphate-humic acid complexes (He et al., 2006, 2009, 2011). Southwell et al. (2010) irradiated the suspension composed of autoclaved finer sediments ($< 30 \mu\text{m}$) and filtered seawater and found that more dissolved P_i was released under sunlight irradiation than that of dark condition. A follow-up study showed that the release of dissolved P_i is strongly affected by the composition of organic matter in the sediment (Southwell et al., 2011). Results from our previous work showed that the photo-release of dissolved P_i from resuspended sediment exposed to simulated sunlight irradiation (Li et al., 2017). Reactive oxygen species, generated from naturally present photosensitizers in water, such as NO_3^- , Fe^{3+} , DOM, accelerated the degradation of organic phosphorus and released phosphate under simulated sunlight irradiation, which is highly sensitive to the species of organic phosphorus (Liu et al., 2017; Jiang et al., 2016). However, little is known about the effect of the distribution of organic phosphorus species in sediment profiles on the release of dissolved P_i by sunlight irradiation during sediment resuspension.

In this work, the effects of the distribution of organic phosphorus species in the sediment profiles on the release of dissolved P_i during sediment resuspension under simulated sunlight irradiation was studied. The objectives of this study were to (1) determine the distribution of organic phosphorus species in sediment profiles of shallow lakes, and (2) investigate its effect on the photo-release of dissolved P_i during sediment resuspension under simulated sunlight irradiation. The results contribute to the understanding of the impacts of internal phosphorus cycle on the lake eutrophication.

2. Materials and methods

2.1. Study area and samples collection

Lake Dong is a typical large shallow lake located in Wuhan, China. Due to the human activities and geographic location (Liu et al., 2006), Lake Dong was divided into five sub-lakes including Lake Hou, Lake Tuan, Lake Tangling, Lake Guozheng, and Lake Miao. The five lakes showed different ecological conditions, and the submerged plants in the Lake Hou grew well, while algal blooms have occurred many times in Lake Miao. The characteristics of the five sub-lakes are summarized in Table 1.

Twenty different sediment and water samples were collected from five shallow lakes in August 2016 using sediment core sample type Beeker (BWT2-04.23.SA, Waterland International Co., Ltd., Holland). The distribution of sample sites is shown in Fig. 1. The sediment samples from the same sub-lake and same depth were mixed to obtain uniform sample. The sediment samples were lyophilized at -80°C and autoclaved at 120°C for 30 min to inactivate microorganisms before used. The lake water was filtered by $0.2 \mu\text{m}$ membrane and stored at 4°C to be used.

Table 1

Properties of the five shallow lakes.

Lake	Water area km^2	Mean depth m	DO mg/L	pH	NTU	Chla $\mu\text{g/L}$	TP (water) mg/L
Lake Hou	4.92	3.25	9.43	8.16	6.38	7.98	0.04
Lake Tuan	4.48	3.52	9.19	8.10	7.56	7.20	0.03
Lake Tangling	5.67	2.38	8.25	8.23	16.71	15.76	0.06
Lake Guozheng	12.71	3.55	8.74	8.28	19.48	17.22	0.07
Lake Miao	1.61	2.98	12.98	8.67	12.27	57.64	0.13

2.2. Experimental and analytical procedures

2.2.1. Photolysis experiment setup

To prepare a simulated suspension, 2 g autoclaved sediment sample was added into 250 mL filtered lake water in a graduated cylinder, which was then stirred at 200 rpm for 30 min. After stirring, the sample was settled down for 5 min, and then the top 10 cm water was sampled and added into a quartz reaction tube for photolysis experiments. The photolysis was performed in a Phchem III rotating photo-reactor (Newport Corporation, China, Fig. S1). A 500W xenon lamp in the center of the photo-reactor was used to provide simulated sunlight (emission spectrum shown in Fig. S2). A quartz cold trap and ventilation device was used to maintain the reactor's internal temperature at $35 \pm 2^\circ\text{C}$. The average light intensity of the outer wall of the quartz tube is $65 \pm 5 \text{ mW cm}^{-2}$, monitored by a radiometer (M520, Newport Corporation, Beijing, China). The light energy was simulated at a similar energy level to that of the lake surface in summer. The dark treatment was conducted under the same experimental conditions except that the reaction tube was wrapped with tin foil to prevent light irradiation. Subsamples (10 mL each) were collected at predetermined time intervals and filtered through a $0.45 \mu\text{m}$ microfilter before analysis.

2.2.2. P_o fractions in resuspended sediment

P_o fractions in sediment were determined as Lü et al. (2015) reported, which was based on the modified sequential extraction procedure of Ivanoff et al. (1998). The sediment P_o was fractionated into labile organic phosphorus (LOP), moderately labile organic phosphorus (MLOP) and non-labile organic phosphorus (NLOP). The details of this method are as follows: LOP in resuspended sediments was extracted by 0.5 M NaHCO_3 under constant shaking for 16 h. MLOP is extracted with 1 M HCl and then by 0.5 M NaOH. Finally, NLOP was obtained by burning washed-residue at 550°C for 1 h, followed by leaching for 24 h with 1.0 M H_2SO_4 .

2.2.3. ^{31}P NMR analysis

P_o species in the resuspended sediment pre- and post-sunlight irradiation was extracted using a mixture of 0.25 mol/L NaOH and 50 mmol/L EDTA for 16 h at room temperature (Cade-Menun and Preston, 1996). After lyophilizing the extract at -80°C , 0.3 g lyophilized sample was re-dissolved in 0.6 mL D_2O with 0.1 mL 10 M NaOH. The sample was then centrifuged for 15 min at 12000 rpm before NMR testing (Zhang et al., 2015). The ^{31}P NMR was measured on a Bruker 600 MHz spectrometer (Bruker, Billerica, MA, USA) operating at a frequency of 242.95 MHz and at 25°C with a 5 mm BBO probe. The scans were performed $\sim 40,000$ times. Chemical shifts were recorded relative to an 85% H_3PO_4 standard ($\sigma = 0 \text{ ppm}$). The P_o species were determined with reference to previous studies (Cade-Menun, 2005; Turner et al., 2003a, 2003b). Manual integration was used to determine the concentration of orthophosphate, monoester, diester and pyrophosphate. The concentrations of P species in monoester were quantified by spectral deconvolution after spectral smoothing (Doolette et al., 2011).

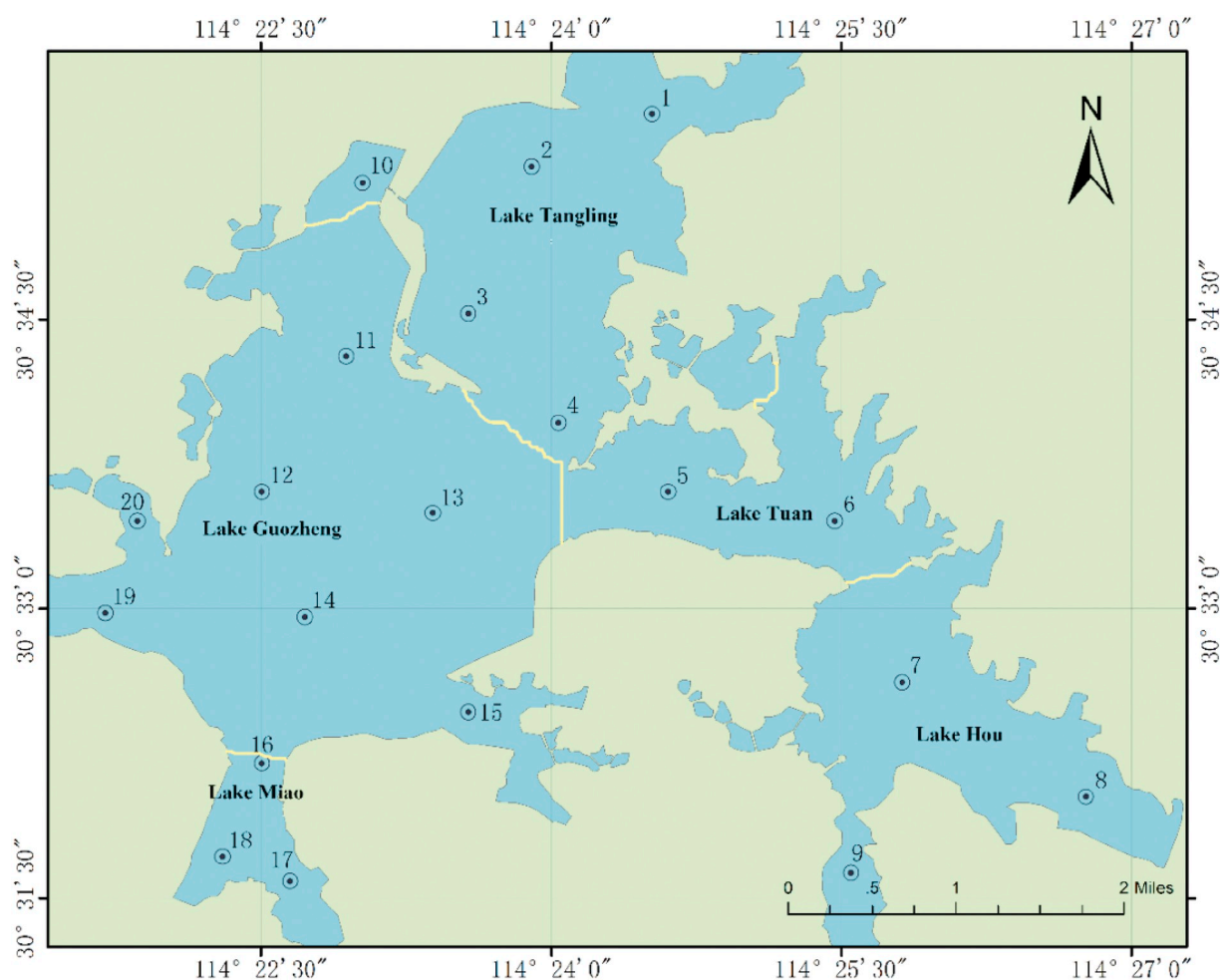


Fig. 1. Location of sampling sites in five sub-lakes of Lake Dong.

2.2.4. The steady-state concentration of hydroxyl radicals ($\cdot\text{OH}$) in sediment resuspension

The steady-state concentration of $\cdot\text{OH}$ in the suspension under simulated sunlight irradiation was determined by fluorescent probe. Coumarin was chosen as a selective probe for trapping $\cdot\text{OH}$ to produce fluorescent 7-hydroxycoumarin (7-HOC). The concentration of 7-HOC was detected by measuring in a Shimadzu RF-5301 PC spectrometer. The steady-state concentration of $\cdot\text{OH}$ was calculated based on the formation rate of 7-HOC as Louit et al. (2005) reported. Due to the complicated condition in the suspension, the results of $\cdot\text{OH}$ steady-state concentration cannot be accurate, while these data provided us with a rough estimate of $\cdot\text{OH}$ production in the suspension.

2.2.5. Sediment particle size and morphology determination

Particle analyzer (CAMSIZER X2, Retsch, Germany) was used for the determination of the average size of resuspended sediment particle from different depths of sediment. Average size value was taken at 50% of the suspension cumulative volume-based distribution which was calculated by the evaluation software. The morphology of resuspended sediment pre- and post-sunlight irradiation was determined by atomic force microscope (AFM, Multimode 8, Bruker). The suspension was dropped on the freshly cleaved mica and dried in room temperature. Double-faced tape was used to attach the mica to a steel sample puck, and then the puck was transferred into the sample stage on the AFM.

2.2.6. Data analysis

Origin 9.1, MestReNova 6.1.1 and Nanosurf easyScan 2 were used for image analysis in the experiment. Analysis of variance (ANOVA) in

IBM SPSS Statistics 20.0 statistical software was used for analysis the significant differences.

3. Results and discussion

3.1. P components in sediment profiles

The contents of P components in sediment profiles in five shallow lakes are shown in Fig. 2. The concentration of TP is 335.88 ± 21.20 , 483.18 ± 18.75 , 590.01 ± 20.11 , 677.05 ± 25.41 , 830.14 ± 28.30 mg/kg in sediment of 0–2 cm depth from Lake Hou, Lake Tuan, Lake Tangling, Lake Guozheng and Lake Miao, respectively. Comparing to the TP concentration in overlying water in Table 1, it could be found that the contents of TP in sediment and overlying water showed similar trend, which was consistent with the results reported by Ni et al. (2016). The concentration of TP in the surface sediment was significantly positively correlated with TP in the overlying water ($n = 5$, $r = 0.891$, $p < 0.05$), suggested that there was exchange of phosphorus between sediments and water column.

It can also be found that the TP contents in sediments generally decreased with the increase of sediment depths (Fig. 2). Similarly, the contents of P_o in sediment profiles also decreased as sediment depths increased:

33.09 ± 2.55 – 96.71 ± 7.60 mg/kg,
 33.55 ± 2.34 – 142.86 ± 5.73 mg/kg,
 57.50 ± 3.46 – 149.69 ± 7.69 mg/kg,
 55.18 ± 4.67 – 168.73 ± 8.31 mg/kg,
 98.75 ± 7.56 – 275.74 ± 10.70 mg/kg for Lake Hou, Lake Tuan, Lake

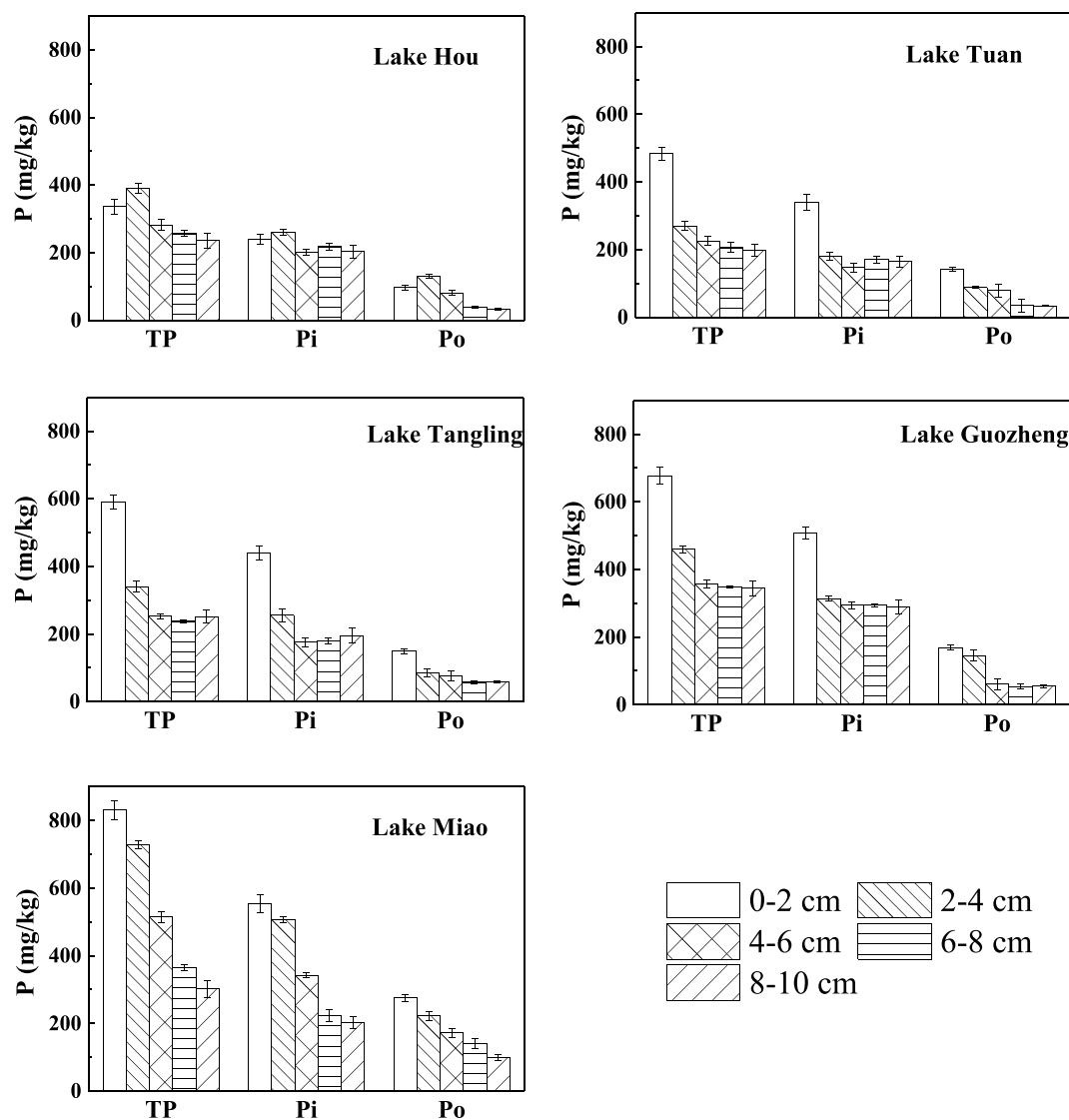


Fig. 2. The content of P components in sediments with different depths. Values are mean \pm SD ($n = 3$).

Tangling, Lake Guozheng and Lake Miao, respectively. These results showed that the distributions of TP, P_i and P_o were surface enriched, and the reason for the phosphorus profiles at different sediment depths may be due to inputs from the surrounding environment, climate and anthropogenic activities (Zhang and Shan, 2008; Lü et al., 2016).

3.2. Photo-release of dissolved P_i during sediments resuspension

The photo-release of dissolved P_i from different sediment resuspension under simulated sunlight irradiation was determined and results are shown in Fig. 3. It can be found that the release of dissolved P_i under simulated sunlight irradiation was observed in all the suspensions prepared in this study with different lake sediments. The release amount of dissolved P_i in Lake Miao is the highest ($30.85 \pm 4.27 \mu\text{g/L}$), while that in Lake Hou is the lowest ($9.20 \pm 2.90 \mu\text{g/L}$). This result shows a similar trend in the concentration of organic phosphorus in the sediments ($181.83 \pm 11.72 \text{ mg/kg}$ for Lake Miao and $76.16 \pm 4.91 \text{ mg/kg}$ for Lake Hou), which indicates that sediments with high content of P_o promote the photo-release of dissolved P_i during resuspension exposed to simulated sunlight. In shallow lakes, sediments could enter the overlying water frequently during sediment resuspension (Håkanson and Jansson, 1983). Hu et al. (2016) also found that dissolved organic

carbon (DOC) and dissolved inorganic nutrients could be photo-dissolved from resuspended lake sediments under simulated sunlight irradiation. The photodissolution of suspended sediment was a potential source of DOC and dissolved nutrients in shallow water ecosystems.

Fig. S3 shows the concentrations of dissolved P_i in suspension in dark and simulated sunlight treatments. It could be found that the concentration of dissolved P_i in dark treatment increased during treatment process, which can be attributed to the desorption of P_i from the surfaces of sediment particles (Wang et al., 2009). It should be noted that the release amount of dissolved P_i in simulated sunlight treatment was higher than that of dark treatment. Since the potential of biomineralization was removed by the autoclaving process in this study, the increase concentration of dissolved P_i in simulated sunlight treatment should be attributed to the photochemical reaction.

Moreover, it could be observed that the photo-release amount of dissolved P_i gradually decreased as sediment depths increased. For example, as sediment depth varied from 0 to 10 cm in Lake Miao, the photo-release amount of dissolved P_i varied from $35.55 \pm 1.45 \mu\text{g/L}$ to $25.21 \pm 2.86 \mu\text{g/L}$, accordingly. The release amount of dissolved P_i in the resuspension composed of 2–4 cm sediment was higher than that of 0–2 cm sediment, but there is no significant difference (shown in Table S1). Similar phenomena were also observed in other sub-lakes as well. As mentioned above, the concentration of organic phosphorus in the

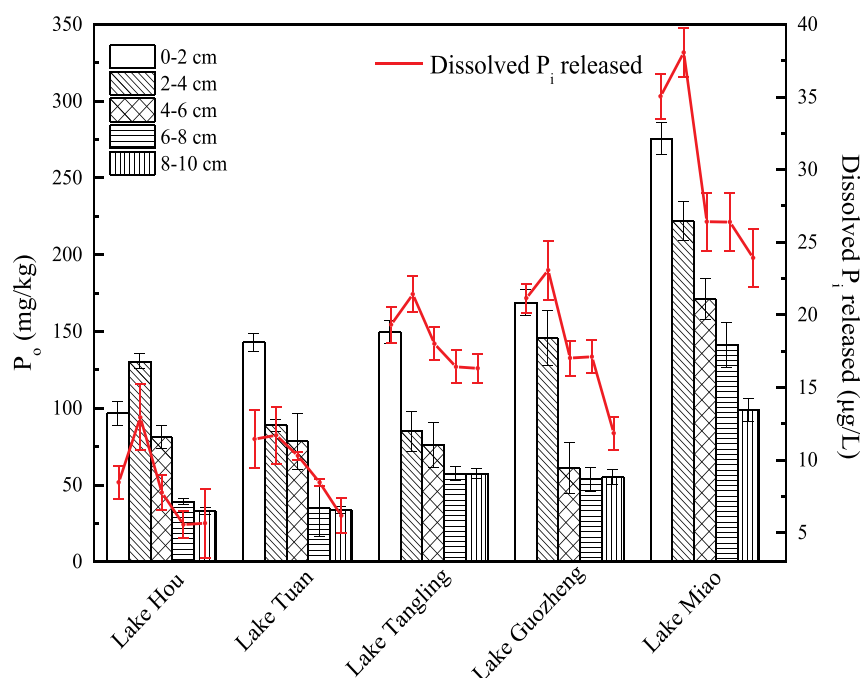


Fig. 3. The relationship between the content of organic phosphorus and photo-release of dissolved P_i during sediment resuspension under simulated sunlight irradiation for 9 h. Values are mean \pm SD ($n = 3$).

sediment profiles also decreased as the sediment depth increased. This indicated that the distribution of organic phosphorus content in the sediment profiles has a potential impact on the photo-release of dissolved P_i during sediment resuspension.

3.3. Photo-release mechanism of dissolved P_i during sediment resuspension

To explore the mechanism of the photo-release of dissolved P_i during sediment resuspension under simulated sunlight irradiation, the surface morphologies of sediments, organic phosphorus species and $\cdot OH$ production in the suspension were determined. Lake Miao was chosen as the research target due to its higher organic phosphorus content, which was more conducive for sequential extraction and ^{31}P NMR analysis.

3.3.1. Morphology difference

Particle size is an important property of sediments that affects their retention time and sunlight exposure time in overlying water (Kitamura et al., 2009; Southwell et al., 2010). As shown in Fig. 4, the mean particle size of sediments in Lake Miao ranged from 6.75 to 15.75 μm with ranging depth from 0 to 10 cm. The results showed that the mean particle size first decreased and then increased with increasing depths. The mean particle size of surface sediment is higher than that of deep sediment, which should be attributed to the accumulation of animal and plant residues without completely mineralized at sediment surface. As the sediment depth increased from 4–6 cm to 8–10 cm, the particle size of the resuspended sediments increased continuously, while the release amount of dissolved P_i decreased. This is consistent with our previous results that the release amount of dissolved P_i from small size sediment particles was higher than that from large size sediment particles during sediment resuspension under simulated sunlight irradiation (Li et al., 2017). Comparing the physicochemical composition of sediments and photo-release amount of dissolved P_i during sediment resuspension, it could be inferred that the distribution of organic phosphorus content may be a more critical factor in dominating the photo-release amount of dissolved P_i during sediment resuspension.

Fig. S4 shows the AFM analysis of the morphologies of resuspended sediments from different depths pre- and post-sunlight irradiation. The

sediment particles have been broken after simulated sunlight irradiation for 9 h due to the physical destruction and photodissolution of resuspended sediment. The morphological analysis of cross-sectional profiles showed that the width and height of sediment particles decreased after simulated sunlight irradiation. It has been found that particulate organic matter (POM) in the sediment may be the main source for the photo-release of dissolved P_i during sediment resuspension under sunlight irradiation (Pisani et al., 2011; Luo et al., 2010). POM is one of the main carriers of organic phosphorus (Niu et al., 2017). Previous studies have also shown that POM can absorb sunlight at similar wavelengths as dissolved organic matter (DOM) and undergo similar photo-induced reactions (Estapa and Mayer, 2010). This reaction can induce a process that breaks down a larger substance into smaller photo-products and generates significant amounts of DOM as well as total dissolved nitrogen (TDN) and soluble reactive phosphorus (SRP) (Mayer et al., 2006; Mayer et al., 2009; Shank et al., 2011; Pisani et al., 2011).

3.3.2. P_o fractions characterization

The amount and composition of organic phosphorus in sediments could affect the transformation processes of organic phosphorus to dissolved P_i during sediment resuspension process (Ussitalo et al., 2000). In this study, the P_o in sediments from different depth was fractionated into LOP, MLOP and NLOP. The content of LOP before and after autoclaved treatment was determined firstly since the autoclaved treatment may have an influence on the content of LOP in the resuspended sediment. As shown in Table S2, there has been no significant change in the content of LOP before and after autoclaved treatment, which indicated that the effect of autoclaved treatment process on the fraction of organic phosphorus in sediment is limited. Fig. 5 shows the content and percentage of organic phosphorus fractions in sediment with different depths. It can be found that the MLOP is the major form of P_o in sediments, accounting for 52.34%, 51.55%, 56.93%, 56.72% and 58.02% of total extracted P_o in the Lake Hou, Lake Tuan, Lake Tangling, Lake Guozheng and Lake Miao, respectively. In addition, the contents of MLOP generally decreased as the sediment depths increased. As our previous report, MLOP is the major contributor to the photo-release of dissolved P_i (Li et al., 2017). This could explain

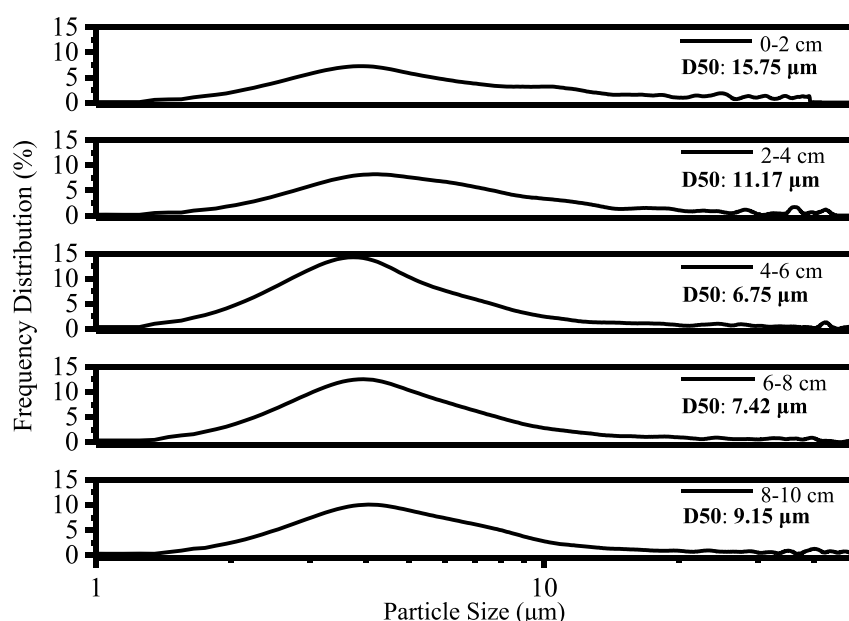


Fig. 4. The particle size distribution of resuspended sediment with different depths from Lake Miao.

the higher release amount of dissolved P_i at surface sediment resuspension.

The ^{31}P NMR results could provide further insight into the source of dissolved P_i photo-released during sediment resuspension under simulated sunlight irradiation. As shown in Fig. 6a, five components were determined according chemical shift, including orthophosphate (ortho-P), phosphate monoesters (mono-P), phospholipids (lipid-P), DNA (DNA-P)

and pyrophosphate (pyro-P) (Turner et al., 2003b; Cade-Menun, 2005; Cade-Menun et al., 2006; Giles et al., 2015; Zhu et al., 2018). The concentration of different forms of phosphorus pre- and post-sunlight irradiation are shown in Table 2. Lipid-P and DNA-P are summarized to phosphate diesters (diester-P). Ortho-P was the dominant P form in NaOH-EDTA suspensions extracts. The concentrations of ortho-P in resuspended sediments ranged from 191.56 to 535.10 mg/kg with varying depth from 0

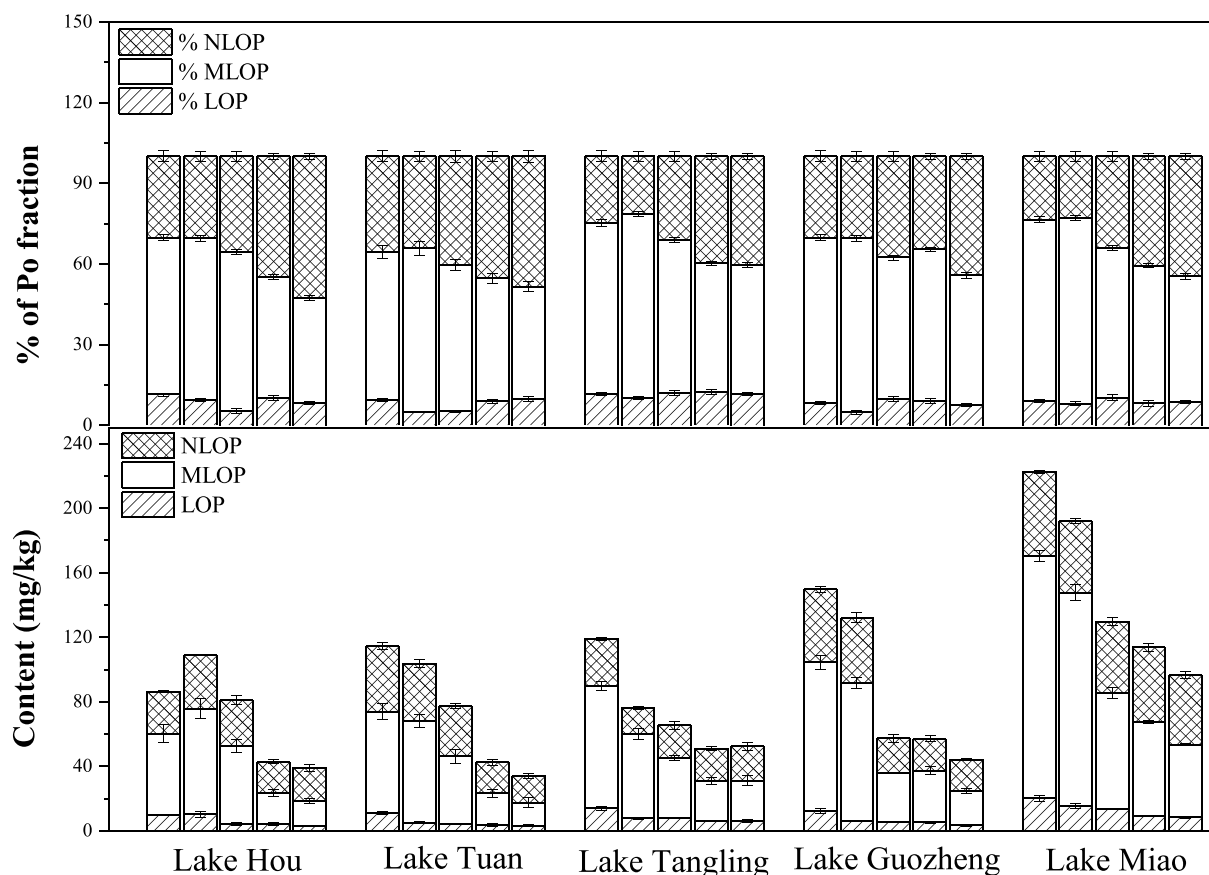


Fig. 5. The content and relative percentage of P_o fractions in the sediment with different depths. Dates are mean \pm SE.

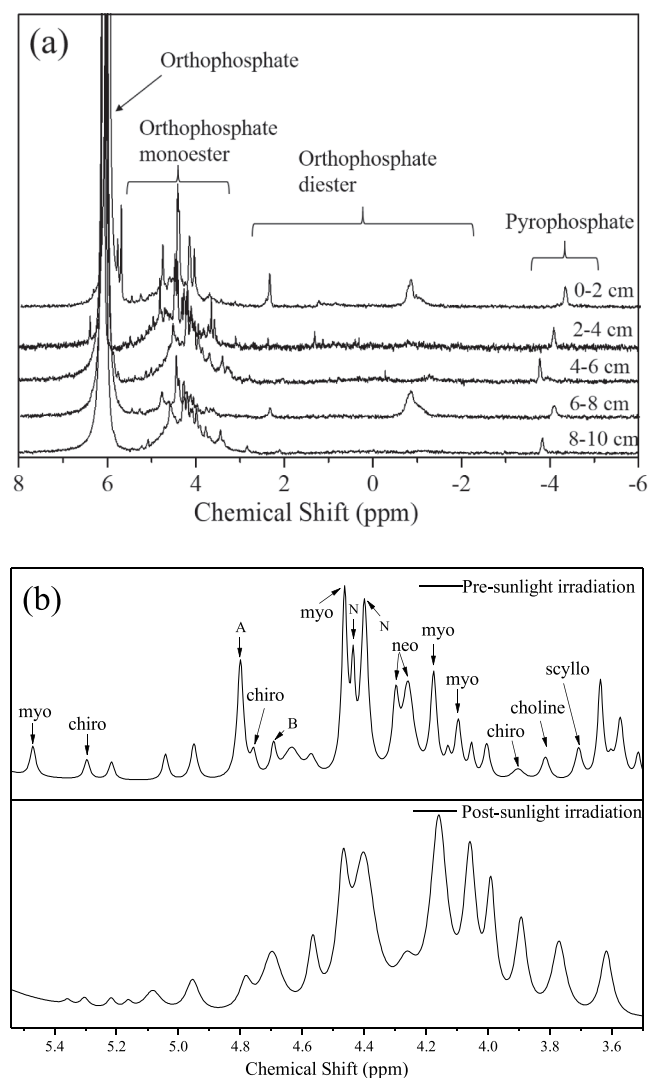


Fig. 6. (a) Solution ^{31}P NMR spectra of NaOH-EDTA extracts of the resuspended sediments with depth of 2–4 cm from Lake Miao pre-sunlight irradiation; (b) a deconvoluted smoothing spectral of phosphate monoester (myo-, myo-IHP; scyllo-, scyllo-IHP; neo-, neo-IHP; chiro-, chiro-IHP; A, α -Gly; B, β -Gly; N, mononucleotides).

to 10 cm before simulated sunlight irradiation. Pyro-P is another form of P_i and showed concentrations varied from 0.45 to 6.83 mg/kg which were much lower than those of ortho-P. Mono-P and diester-P were the dominant forms of P_o in the NaOH-EDTA suspension extracts. After simulated sunlight irradiation for 9 h, the content of mono-P and diester-P decreased, while the content of ortho-P increased generally as shown in Fig. S5. This result should be attributed to the photodegradation of organic phosphorus in suspension.

Table 2

P_o fractions in suspension pre- and post-simulated sunlight irradiation.

Sediment layer	Ortho-P (mg/kg)		Pyro-P (mg/kg)		Mono-P (mg/kg)		Diester-P (mg/kg)	
	Pre-	Post-	Pre-	Post-	Pre-	Post-	Pre-	Post-
0–2 cm	535.10	578.86	3.66	1.93	74.56	55.35	19.75	9.20
2–4 cm	397.76	465.32	6.83	2.27	122.84	77.63	33.25	0
4–6 cm	309.36	317.34	2.16	1.06	54.18	6.03	3.72	4.28
6–8 cm	222.78	233.28	0.45	0.09	13.97	11.17	5.49	3.34
8–10 cm	191.56	189.01	0.90	0.91	35.38	31.39	2.48	0.97

Note: Pre- and post- represent pre-simulated sunlight and post-simulated sunlight irradiation, respectively.

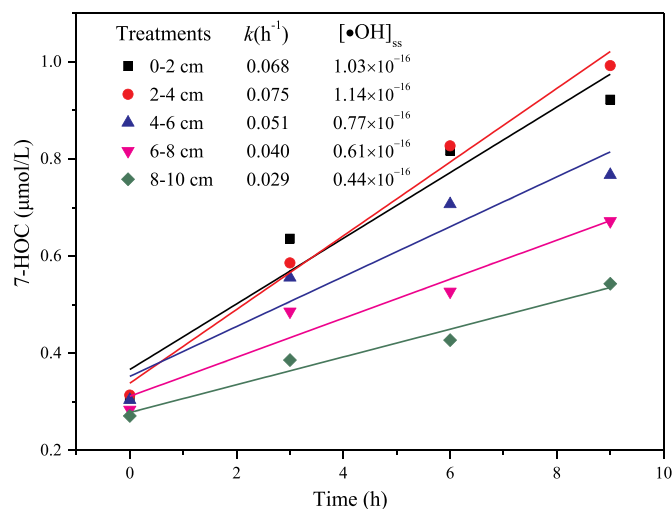


Fig. 7. The formation of 7-HOC in resuspension composed of different depths of sediment under simulated sunlight irradiation.

Further analysis of the phosphate monoesters in resuspended sediment of 2–4 cm depth showed that phosphate monoesters included four stereoisomers of inositol hexakisphosphate (myo-, scyllo-, neo-, and chiro-IHP), glucose-6-phosphate (G6P), degradation products of diester (α - and β -glycerophosphate, mononucleotides), choline phosphate, and other unidentified monoesters (Fig. 6b, Doolette et al., 2009). After simulated sunlight irradiation for 9 h, the contents of phosphate monoester component were changed (Table S3) and myo-IHP, neo-IHP, chiro-IHP, G6P, α -glycerophosphate, β -glycerophosphate and mononucleotides are the main species of phosphate monoesters involved in the photochemical reaction. It is worth noting that the alkali extraction process during the sample preparation results in the hydrolysis of partial labile monoester P, shown in Table S4. This indicated that ^{31}P NMR spectra are not quantitative enough to reveal the contribution of phosphate monoester components degradation to the release of phosphate. Therefore, a better method was needed to characterize the contribution of organic phosphorus photodegradation to phosphate content without destroying the composition of the organic phosphorus.

3.3.3. Steady-state concentration of $\cdot\text{OH}$

The hydroxyl radicals ($\cdot\text{OH}$) plays a critical role in the release of dissolved P_i from the photodegradation of organic phosphorus and the steady-state concentration of $\cdot\text{OH}$ is directly correlated to the release amount of dissolved P_i in the resuspension under sunlight irradiation (Luo et al., 2010). To further understand the photo-release mechanism of dissolved P_i during sediment resuspension, the steady-state concentrations of $\cdot\text{OH}$ in suspensions were determined for sediments collected from different depths of Lake Miao. As shown in Fig. 7, the steady-state concentrations of $\cdot\text{OH}$ in suspensions of sediments from 0 to 10 cm ranged from 0.44×10^{-16} to 1.14×10^{-16} mol/L. The steady-state concentration of $\cdot\text{OH}$ decreased as the sediment depth

increased in resuspension. Results from previous studies have suggested that highly reactive hydroxyl radicals could lead to successive oxidation of organic phosphorus to release dissolved P_i and thus the production of $\cdot OH$ under sunlight irradiation is a direct indication of the photochemical transformation of organic phosphorus to dissolved P_i (Keen et al., 2014; Xie et al., 2015; He et al., 2015). According to the report by Zhang et al. (2019), $\cdot OH$ generated by natural photosensitizers, nitrate, organic matter and Fe(III), played a dominant role in the P_o photodegradation. The natural photosensitizers' contributions to $\cdot OH$ production followed the order: nitrate > organic matter > Fe(III). The contents of nitrate and OM in the sediments also have surface enrichment (He et al., 2016; Tendaupenyu et al., 2018), which was beneficial to the production of $\cdot OH$ in the suspension composed of surface sediments during sediment resuspension, resulting to more photo-release of dissolved P_i from organic phosphorus photodegradation.

4. Conclusions

This study investigated the distribution of organic phosphorus species in the sediment profiles and its effect on the photo-release of dissolved P_i during sediment resuspension under simulated sunlight irradiation. The contents of TP, P_i and P_o showed distinct surface enrichment phenomena and significantly affected the photo-release of dissolved P_i during sediment resuspension under simulated sunlight irradiation. The photo-release amount of dissolved P_i in the resuspension composed of surface sediment was higher than that of deep sediment, which should be attributed to the higher concentrations of organic phosphorus and $\cdot OH$. The results observed in this study contribute to the understanding of organic to inorganic P conversion during lake sediment resuspension process, which could further help understand the eutrophication of shallow lakes.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2019.104916>.

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