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Response of sediment organic phosphorus composition to lake trophic status in China

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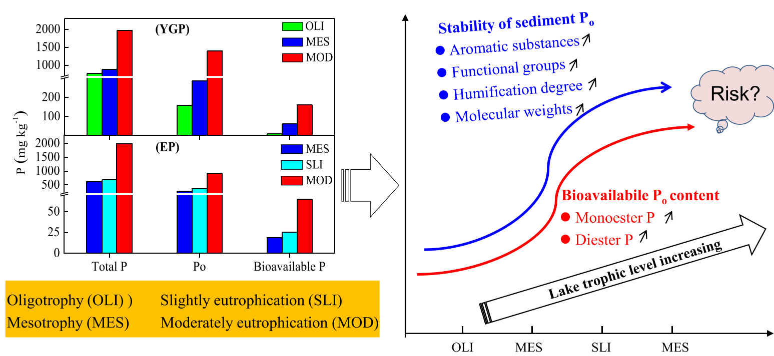
HIGHLIGHTS

- Multiple methods were used to characterize sediment P_o.
- Sediment P_o may be a superior indicator of lake trophic status than TP.
- Sediment bioavailable P_o increased with increasing trophic status.
- Abundant aromatic substances, functional groups, and high humification enhance sediment P_o stability in eutrophic lakes.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic phosphorus (P_o) constitutes the most important fraction of P in lake sediments, and the compositional properties of P_o affect its behavior in lake ecosystems. In this study, ^{31}P NMR, FT-IR spectroscopy, and UV–visible absorbance spectroscopy were combined to identify the dynamic composition of sediment P_o across two sets of lakes in China ranging from oligotrophic to eutrophic, and their possible effects on lake eutrophication were evaluated. The results showed that sediment P_o content (accounting for 24–75% of TP) was positively correlated with trophic status in both Eastern Plain and Yun-Gui Plateau lakes of China, and the linear relationship was more stable compared to total P (TP), implying that sediment P_o may be a superior indicator of trophic status than TP. The P_o component, phosphonate accounted for only 0.4% or less of P_o, while the monoester P and diester P, accounted for 2–24% and 0.5–5% of P_o, respectively, and were the main factors causing P_o to increase with the increasing trophic status. The factors were closely related to the enhanced organic sewage load and intensification of contemporary sedimentation of phytoplankton. As trophic status increased, sediment P_o might integrate into larger amounts of aromatic substances and functional groups, which could enhance the stability of P_o in sediments. Furthermore, sediments from lakes with higher trophic status exhibited a higher degree of humification and molecular weights, which impart resistance to biodegradation, and therefore, reduced the risk of sediment P_o release. However, the massive accumulation of bioavailable P_o (monoester and diester P) allows possible degradation, supporting algal growth and maintains eutrophic status because there is abundant alkaline phosphatase

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in eutrophic lakes. Thus, to control lake eutrophication more effectively, targeted actions are urgently required to reduce the accumulation and degradation of P_o in lake sediment.

1. Introduction

Phosphorus (P) is the most limiting nutrient for productivity in the biosphere, and thus, excessive P loading is associated with increased risk of cyanobacterial bloom formation in many lakes (Schindler et al., 2016). As external P inputs have been gradually reduced, the release of sediment P has become a major source of P that continues to enter into water under certain environmental conditions (Shinohara et al., 2012; Søndergaard et al., 2003). Sediment organic P (P_o), including sugar phosphates, inositol phosphate, nucleic acids, phospholipids, and condensed P, represents an important P source that is similar in magnitude to inorganic P (Turner et al., 2005; Worsfold et al., 2008). However, sediment P_o has long received much less attention than inorganic P because of the limitations of analytical techniques and its complexity of composition (Bai et al., 2009). Sediment P_o is currently recognized as a potential pool for bioavailable P, resulting in extensive studies investigating P_o fractionation, composition, bioavailability, decomposition, migration, and transformation (Zhu et al., 2013; Lu et al., 2016; Zhang et al., 2017; Feng et al., 2018). These studies have demonstrated that the biogeochemical cycle of P_o plays a key role as a source of P in water columns and algal growth. Understanding the compositional characteristics of P_o in sediment from different trophic status lakes is, thus, essential for better evaluation of P_o behavior and its effects on lake eutrophication processes. However, little is known about the relationship between the compositions and bioavailabilities of P_o in sediments and lake eutrophication processes.

The biogeochemical cycle of P_o is usually closely related to its composition and structural characteristics in the sediment. In recent years, various methods have been introduced to characterize P_o, mainly phosphorus-31nuclear magnetic resonance (^{31}P NMR), Fourier-transform infrared spectroscopy (FT-IR), soft X-ray fluorescence spectroscopy, near-infrared spectroscopy (NIR), high-performance liquid chromatography (HPLC), flow injection analysis (FIA), inductively coupled plasma emission spectrometry (ICP-AES) and traditional chemical extraction (Vestergren et al., 2012; Brandes et al., 2007; Cooper et al., 2005; Worsfold et al., 2008; Bünemann, 2008). In comparison, ^{31}P NMR can be utilized to characterize P_o species and provide considerable information to distinguish P compounds, including orthophosphate, polyphosphate, pyrophosphates, monoester P, diester P, and phosphonates (Ahlgren et al., 2006). Fourier transform infrared (FTIR) spectroscopy is widely used to characterize leachate-derived P_o and provide considerable information regarding functional groups containing P (Zhang et al., 2009). Ultraviolet visible light absorbance (UV–visible) can characterize the structure and stability of organic molecule (Matilainen et al., 2011), and thereby indirectly indicates the presence of unidentifiable P_o because some of it is incorporated into humus. Although the compositional characteristics of P_o are important to understanding the behavior of P_o, a single analytical technique is inadequate to characterize the P_o compositional characteristics from different angles. Thus, using multiple combined analytical techniques is beneficial to providing more detailed compositional information.

China has some of the most serious eutrophication in lakes worldwide because of excessive P loading. Indeed, the area of eutrophic lakes in China exceeds 8700 km^2, and almost 25% of all lakes in China are facing the threat of eutrophication (Ni and Wang, 2015). Confronted by the challenge of severe lake eutrophication problems, the state has issued a series of five-year plans and relevant measures to implement watershed load reduction. As a result, external P loading has been reduced to a certain extent in many eutrophic lakes in recent years (Tong et al., 2017). However, the decline of water quality and the frequent outbreak of algal blooms have not fundamentally improved, especially in the Eastern Plain (EP) and Yun-Gui Plateau (YGP) of China. Moreover, the release of sediment P has been found to be a major P source (Li et al., 2015), and P_o could account for 21%–60% of total sediment P (TP) in the EP and YGP lakes (Ding et al., 2010; Ni et al., 2016). This illustrates that sediment P_o might make a vital contribution to the P cycle in these lake ecosystems. Therefore, determination of the relationships and effects of P_o in sediments on lake eutrophication is important to further understanding the biogeochemical cycle of P_o and improving lake sediment remediation strategies. Accordingly, the objective of the current study was to establish the responses of sediment P_o compositional characteristics to lake trophic status and to investigate possible effects of the major classes of organic molecules on lake eutrophication using ^{31}P NMR, UV–visible absorbance, and FT-IR spectroscopy across two set of lakes in China ranging from oligotrophic to eutrophic.

2. Materials and methods

2.1. Study area and background

China has many territories and striking regional differences. The EP and YGP region are characterized by many lakes that have provided resources to millions of people and made important contributions to Chinese civilization and socioeconomic progress. However, these two regions are struggling with the challenge of accelerated water-quality decline and lake eutrophication following the rapid social-economic development that has occurred during the past three decades (Yang et al., 2010). Considering that lake eutrophication in China is primarily a result of anthropogenic activities (Chen et al., 2014), six lakes were selected in the EP and YGP districts of China in accordance with their aquatic ecological characteristics, water quality and intensity of anthropogenic activities. The higher trophic status lakes exhibited more intense anthropogenic activities, higher concentration of nutrient and higher density of phytoplankton in the EP and YGP, respectively (Table 1 and Fig. 1).

The EP district has a densely distributed river network that includes the middle and lower reaches of the Yangtze and Huai Rivers, the lower reaches of the Yellow and Haihe Rivers, and the coastal region of the Grand Canal. The district contains 651 lakes with an area that exceeds 1 km^2 and has a total lake area of 22,900 km^2. The lakes, which are generally tectonic and fluviatile, evolved from fault depressions and riverbeds (Nanjing Institute of Geography and Limnology Chinese Academy of Science, 2015). Most of the lakes are shallow, with an average water depth of <2 m. The regional climate is subtropical monsoon, with a long-term annual average temperature of 4 °C–17 °C and annual precipitation of 600–1500 mm. The altitude of the EP district ranges from 5 to 100 m, and it serves as an important engine of economic growth in China. Lake Poyang, Lake Taihu, and Lake Wuhan-Dong were selected as research subjects in the EP region. Lake Poyang (28°22′–29° 45′ N, 115°47′–116°45′ E) in the north of Jiangxi Province is a typical overflow lake and an internationally important wetland with numerous ecological benefits and environmental regulatory functions. The lake has good water quality because of its frequent water exchange and relatively low level of human activities (Ni et al., 2015). Lake Tai (30°56′–31° 33′ N, 119°54′–120°36′ E), which is in the downstream portion of the Yangtze Delta, is an important drinking water source for surrounding cities, such as Suzhou and Wuxi. The water quality in the lake has gradually changed with the rapid economic development in the watershed over the past several decades (Yu et al., 2013). Lake

Table 1
Comparison of basic feature of different status lakes in the two typical regions of China.

Region	Lake	Altitude (m)	TN (mg L^{-1})	TP (mg L^{-1})	Chl-*a* (μg L^{-1})	Phytoplankton density ($\times 10^5$ a L^{-1})	Summer benthic density (g $m^{2)}$)	Population density (a/km^2)	GDP USD, billion/km^2)	Crops productivity (ton hm^2)	Meat productivity (kg km^2)	TLI	Trophic status
EP	Poyang Lake	21	1.22	0.07	8.3	5	246	350	1.2	5.1	96	46	Mesotrophic
	Taihu Lake	3.3	1.97	0.21	38	260	146	1360	4.4	6.2	153	58	Slightly eutrophic
	Dong Lake	20	2.28	0.25	82	1002	14	3842	8	5.9	358	65	Moderately eutrophic
YGP	Lugu Lake	2690	0.1	0.01	0.4	65	/	47	0.07	1.1	10	18	Oligotrophic
	Erhai Lake	1972	0.55	0.03	11.1	187	8.9	320	1.3	1.5	142	41	Mesotrophic
	Dian Lake	1886	5.13	0.28	127	1398	3.4	1269	5	4.5	210	69	Moderately eutrophic

Data of population density, GDP, crops and meat productivity and production derived from the local statistical yearbook in 2011. Phytoplankton density and summer benthic density from the references of Ouyang et al. (2009), Xu et al. (2015), Wang et al. (2010), Zhang et al. (2011) and G.B. Li et al. (2014).

Wuhan-Dong (30°33′ N, 114°23′ E) in the East of Wuhan is the largest urban lake in China. This area has been undergoing eutrophication since the 1960s because of domestic sewage being randomly discharged along the lake (Yang and Chen, 2016).

The YGP district is in Guizhou Province and Eastern Yunnan Province, which is northwest of the Guangxi Zhuang Autonomous Region, and parts of Sichuan, Hubei, and Hunan Province. This district possesses 60 lakes with areas that exceed 1 km^2 and has a total area of >1199 km^2. Most of the lakes in the region are deep-water small areas and closed or semi-closed lakes because they are primarily distributed in the stratum fracture zone (Nanjing Institute of Geography and Limnology Chinese Academy of Science, 2015). The regional climate is subject to subtropical monsoons, with an annual average temperature of 5 °C–24 °C and a relative uniformity of heat resources in different seasons. The long-term average annual precipitation is 600–2000 mm, and the YGP has a high intensity of ultraviolet radiation because of its high altitude (1000–4000 m). Lake Lugu, Lake Erhai, and Lake Dian were selected as research subjects in the YGP region. Lake Lugu (27°41′ N, 27°45′ E), which is situated on the border of Yunnan and Sichuan Provinces, has good water quality because of the low impact by anthropogenic activities. Lake Erhai (25°35′–25°58′ N, 100°05–100°17′ E) in Dali City is currently undergoing a transformation from mesotrophic to eutrophic status. Lake Dian (24°29′–25°28′ N, 102°29′–103°01′ E), in the southwest portion of Kunming City, has been undergoing serious water-

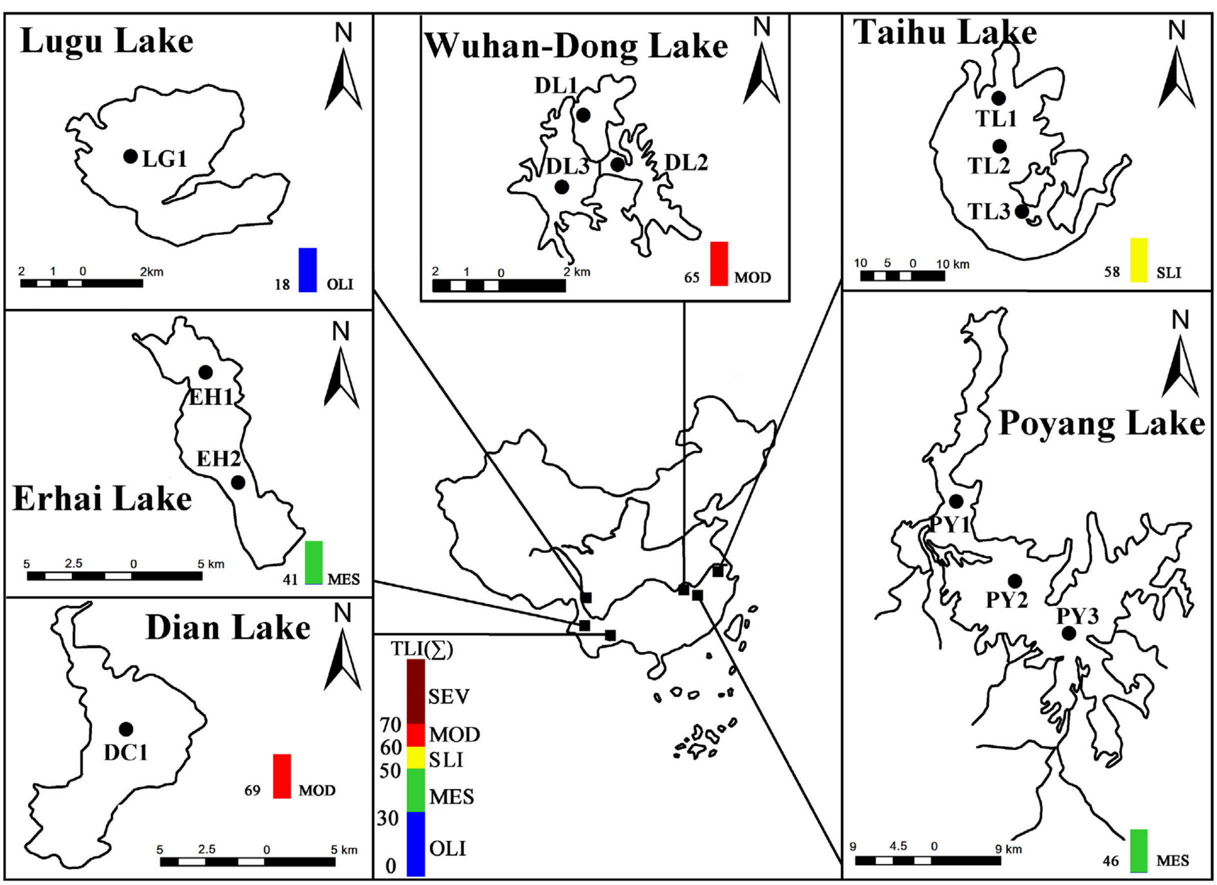

Fig. 1. Location of sampling sites and trophic status of six lakes. Trophic level index (TLI): oligotrophic (OLI), mesotrophic (MES), slight eutrophication (SLI), moderate eutrophication (MOD), and severe eutrophication (SEV).

quality deterioration and sustained algal blooms since the mid-1980s (Liu et al., 2014).

Lake trophic status can be classified as one of four categories (Fig. 1) based on comprehensive trophic level indexes (TLI) of China (Jin, 2001): oligotrophic (OLI: TLI(Σ) <30, Lugu Lake), mesotrophic (MES: 30 ≤ TLI (Σ) ≤50, Erhai Lake and Poyang Lake), slightly eutrophic (SLI: 50 < TLI (Σ) <60, Taihu Lake), and moderately eutrophic (MOD: 60 ≤ TLI(Σ) <70, Wuhan-Dong Lake and Dian Lake).

2.2. Sample collection

Thirteen surface sediment samples (5 cm depth) were collected from different lakes using a core sampler (HL-CN, Xihuayi Technology, Beijing, China) in September 2012 (Fig. 1). Sampling number and sites were selected in accordance with the area and pollution characteristics of the six lakes. Overlying water was also collected during each session. Prior to analysis, the collected samples were immediately sealed in plastic bags and stored at 4 °C in the dark. Upon arrival to the laboratory, sediment samples were freeze-dried, then ground and passed through a 100-mesh sieve for homogeneity.

2.3. Analysis methods

2.3.1. Physicochemical analysis

The content of Fe and Al in the sediment was measured using ICP-AES after microwave digestion by mixing 0.2 g of dried sediments with 10 mL of HNO_3 (68%), 3 mL of H_2O_2 (30%), and 5 mL of HF (40%). The organic matter (OM) content was determined with the K_2CrO_4 external heating method using 0.3 g of dried sediment (Nanjing Institute of Soil, Chinese Academic of Science, 1978). Contents of TP and inorganic P were measured using the Standard Measurement and Testing protocol (Ruban et al., 2001). Briefly, P was extracted using 1 mol L^{-1} HCl for 16 h after the sediment samples were combusted at 500 °C for 2 h. The extracts were then analyzed spectrophotometrically as orthophosphate using the vanadomolybdate method. Inorganic P was directly extracted using 1 mol L^{-1} HCl for 16 h, then analyzed spectrophotometrically as orthophosphate using the vanadomolybdate method. The P_o content was defined as the difference between TP and inorganic P.

2.3.2. NaOH–ethylenediaminetetraacetic acid extraction and ^{31}P NMR analysis

The NaOH–ethylenediaminetetraacetic acid extraction method can efficiently extract P_o from the sediment. Briefly, 5 g of sediment was extracted with 50 mL of NaOH–EDTA solution (0.25 M NaOH-25 mM EDTA) at 25 °C for 16 h. The mixed solutions were subsequently centrifuged at 10,000g for 30 min. The supernatants were then filtered through a 0.45-μm glass fiber filter, after which 1 mL of the filtrate was used to analyze the concentrations of NaOH-extracted TP, inorganic P and P_o.

The remaining filtrates were frozen and lyophilized until they completely dried to a powder. The lyophilized extracts were subsequently re-dissolved in 2.5 mL of NaOH (1 mol·L^{-1}) with 0.1 mL of D_2O to lock the signal before detection by ^{31}P NMR spectroscopy. Next, the solutions were transferred into a 5-mm tube, and the solution ^{31}P NMR spectra were determined using a Bruker Avance III 600 analyzer (Bruker LC, Switzerland) operating at 161.98 MHz for ^{31}P. Samples were analyzed using a 12.00 microsecond pulse and a relaxation delay of 2 s, with 24,000 scans acquired for each sample. All of the chemical shifts of ^{31}P were analyzed using 85% H_3PO_4 as an external criterion. The chemical shifts appeared to differ from the results of Turner (2008) and Turner and Engelbrecht (2011) by 0.5 ppm.

2.3.3. UV–visible absorbance spectroscopy

The compositions of P_o were analyzed through NaOH extraction using a 1-cm quartz cuvette in a Hach DR-5000 spectrophotometer at wavelengths ranging 200–700 nm. The analysis parameters included A_{253}/A_{203}, specific ultraviolet absorbances at 254 nm ($SUVA_{254}$), and the spectral slope ratio (S_R). A_{253}/A_{203} is the ratio of UV–visible absorbance at 253 and 203 nm. $SUVA_{254}$ is the 100× ratio of the UV absorbance at 254 nm to the corresponding dissolved organic carbon (DOC) concentration. Dissolved organic carbon was analyzed using a TOC analyzer (Shimadzu TOC-500, Japan). The S_R was the ratio of the spectral slope of a short wavelength (275–295 nm) to that of a long wavelength (350–400 nm).

2.3.4. FT-IR spectroscopy

One milligram of sediment was mixed with pre-dried KBr (kept under vacuum in a desiccator until use), then pressed into a mold. The spectra were then analyzed using a Perkin-Elmer Spectrum 100 FT-IR spectrometer (Waltham, MA, USA), after which the blank was corrected with a clean KBr pellet. The spectra were evaluated over a scan range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}.

2.4. Data analysis and quality control

Solution ^{31}P NMR spectra, UV–visible absorbance spectroscopy, and FT-IR spectroscopy were analyzed by MesReNova software 9.0 (Forrester Research Inc., Spain), uvprobe 2.42 software (Shimadzu CO., LTD, Japan) and OMNIC 8.0 (Thermo Nicolet Corporation, USA), respectively. Data were presented and analyzed using Origin.8 (OriginLab, USA) and SPSS 21 (IBM, USA). Field duplicate samples, spiked samples, and method blanks were used to control data quality in this study. Triplicate measurements of each sample were conducted and reported as their arithmetic mean values. The relative percent difference for each value was <10% in the duplicate samples. Precision was assured by determining all samples in triplicate, with a relative standard deviation of <8%. The spectra were blank subtracted.

3. Results

3.1. Composition of sediment P_o investigated by ^{31}P NMR with different trophic status lakes

The EP and YGP regions have very high spatial heterogeneity because of the significant differences in limnological, geographic, and climate characteristics and anthropogenic activities (Nanjing Institute of Geography and Limnology Chinese Academy of Science, 2015). Such differences were deemed to result in great variations in accumulation of nutrients among lakes in the two regions. Therefore, the dynamics of P in the sediments of different trophic status lake sediment are illustrated as two separate panels in the figures.

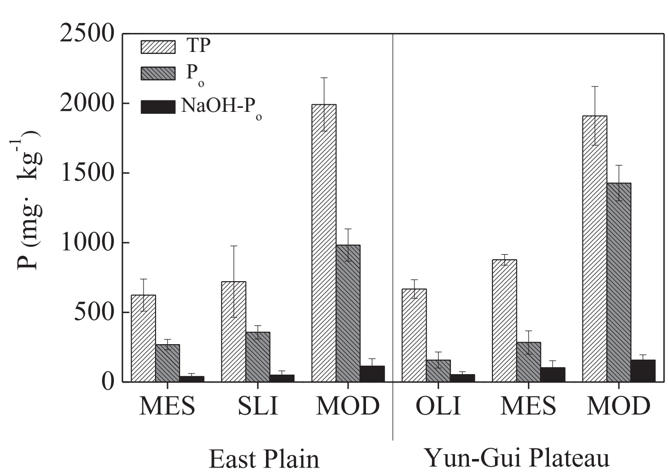

Fig. 2. Contents of P_o and TP of the EP and YGP lake sediment with different trophic status.

As lake trophic status increased, the contents of sediment TP increased in both regions (Fig. 2). The mean contents of TP were 624, 720 and 1992 mg kg^{-1} in the MES, SLI and MOD from EP lake sediment, while they were 667, 877 and 1910 mg kg^{-1} in the OLI, MES and MOD from YGP lake sediment, respectively. The P_o showed a similar trend as TP in the sediments, with mean values of 268, 357 and 983 mg kg^{-1}, while they accounted for 43%, 50%, and 49% of the TP in the MES, SLI, and MOD from EP lake sediment, while these were 158, 284, and 1427 mg kg^{-1}, and accounted for 24%, 32%, and 75% of the TP in the OLI, MES, and MOD from YGP lake sediment, respectively. The contents of NaOH-extractable P_o were 40, 51, and 114 mg kg^{-1} in the MES, SLI, and MOD from EP lake sediment, while they were 67, 101, and 116 mg kg^{-1} in the OLI, MES, and MOD from YGP lake sediment, respectively, and these all showed an increasing trend with increasing lake trophic status.

Our analysis using ^{31}P NMR revealed mainly monoester P, diester P, phosphonates, orthophosphate, and pyrophosphate in the sediments (*SI* Fig. S1). The concentration of P groups in descending order was as follows: orthophosphate > monoester P > diester P > pyrophosphate > phosphonate. For the inorganic P fraction, 11%–80% was orthophosphate and <1.6% was pyrophosphate. For the P_o component, only 0.4% or less was phosphonate, while 2%–24% and 0.5%–5% were monoester P and diester P, respectively. As lake trophic status increased, orthophosphate, pyrophosphate, monoester P, diester P, and phosphonate all increased in the sediments (Figs. 3 and S2).

3.2. Composition of sediment P_o investigated by UV–visible absorbance spectroscopy with different trophic status lakes

$SUVA_{254}$ values have been confirmed to be an effective index for estimation of the proportion of aromatic compounds in DOM (Weishaar et al., 2003; Yeh et al., 2014). The A_{253}/A_{203} values could reflect the concentration of substitution groups of DOM (Y.P. Li et al., 2014), while variations in S_R are related to differences in the molecular weights of DOM (Helms et al., 2008). In this study, the $SUVA_{254}$ values and A_{253}/A_{203} ratios ranged from 0.34–1.69 and 0.10–0.31, respectively, and they increased steadily as lake trophic status increased (Fig. 4a–b). The S_R value ranged from 0.58 to 1.17 in the sediments, and it showed a declining trend with increasing lake trophic status (Fig. 4c).

3.3. Composition of sediment P_o investigated by FT-IR spectroscopy with different trophic status lakes

The FT-IR spectra of the sediments were similar to each other in terms of the position of the major absorption shoulders and bands in the same region with different trophic status (Fig. 5). The assignments of the principal peaks of the FT-IR spectra of sediments in lakes of different trophic status are shown in Table S1. The assignments of the principal peaks of the FT-IR spectra of sediments in lakes of different trophic status are shown in *SI* Table S1. There were two intense and sharp peaks observed at 3620 and 1031 cm^{-1} in all of the sediments reflecting the O—H and P═O in-plane stretching vibrations. The sediments also showed weak peaks from 2870 to 2890, 1638–1650, and 779–797 cm^{-1}, which corresponded to C—H, C═O, and P—O. The weak peaks at 1427and 874 cm^{-1}, which were assigned to C≡C and P—O stretching in aromatic and arene compounds, only appeared in the YGP lake sediment.

3.4. Relationship of OM and metal to P_o components

Organic matter and metal elements are key factors in the composition and release of internal P. In the present study, as lake trophic status increased, the Fe, Al, and OM contents all increased (Fig. S3), similar to the P_o and P_o components in the sediments. The contents of Fe, Al, and OM were 33–178, 31–37, and 8–94 g kg^{-1}, respectively.

The relationships between P_o and P_o components, as well as Fe, Al, and OM content in the sediments, were analyzed by Pearson's correlation (Table 2). The P_o was significantly positively correlated with monoester P, diester P, orthophosphate, and pyrophosphate, with the correlative coefficients being 0.724, 0.887, 0.708, and 0.698 ($p < 0.01$), respectively. In addition, P_o was positively correlated with OM ($r = 0.590$, $p < 0.05$).

4. Discussion

4.1. Relationships between sediment P_o contents and lake trophic status

The content variations of P_o and P_o components in lakes of different trophic status could be identified by the effects of anthropogenic activities and aquatic ecological characteristics. The levels of sediment P_o

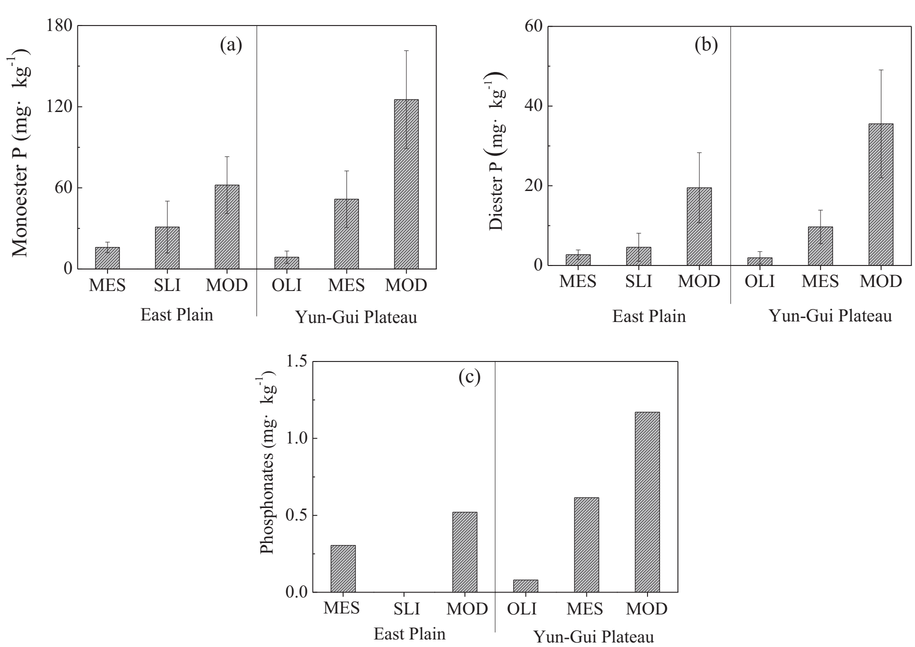

Fig. 3. Contents of monoester P (a), diester P (b), and phosphonates (c) of the EP and YGP lake sediment with different trophic status.

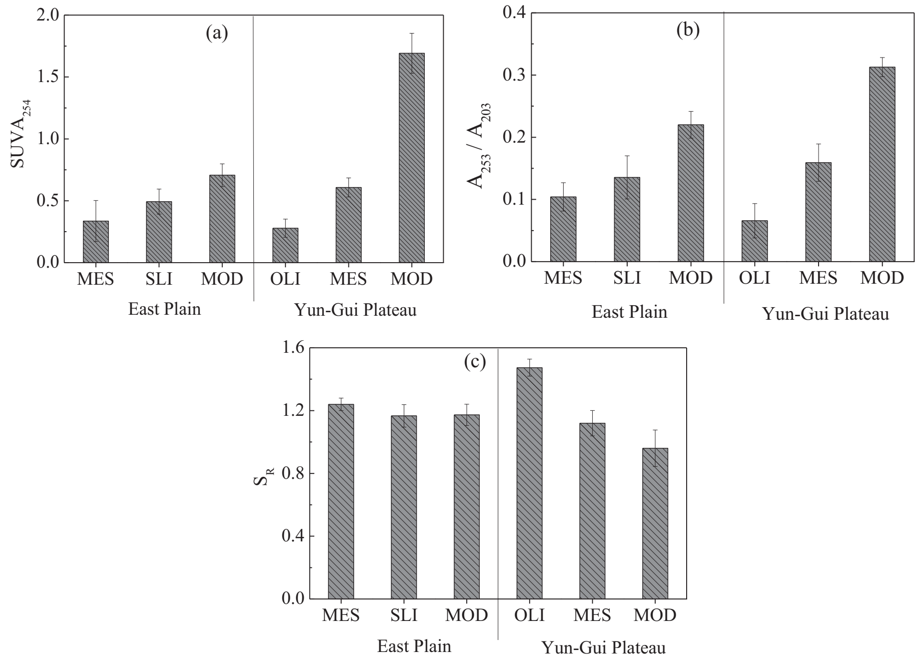

Fig. 4. UV–vis parameters of $SUVA_{254}$ (a), A_{253}/A_{203} (b), and S_R (c) of the EP and YGP lake sediment with different trophic status.

increased with lake trophic status in both regions, which could be attributed to intensive anthropogenic activities and intensification of contemporary sedimentation of phytoplankton. Higher trophic status lakes are usually associated with higher nutrient loading in watersheds as a result of intensive anthropogenic activities in the watershed, such as domestic pollution, animal excrement, and planting pollution (Table 1). In addition, the increased trophic status would enhance the growth of phytoplankton or death of macrophytes debris (Table 1), thereby increasing sedimentation of P_o.

The results presented above indicate that it is important to explore the relationship between sediment P_o content and trophic status of the EP and YGP lakes. The levels of sediment TP and P_o in 15 EP lakes and 8 YGP lakes from the latest published studies, and our results are summarized in Table S2. Pearson's correlation coefficients of the relationships with the TLI were calculated for the EP and YGP regions separately as shown in Fig. 6a and b. For the EP region, TP and P_o showed a linear correlation with TLI, with correlation coefficients of 0.8289 ($p < 0.01$) and 0.5720 ($p < 0.02$), respectively (Fig. 6a). For the YGP region, sediment P_o was positively correlated with the TLI ($r = 0.6591$, $p < 0.05$). TP is known to be useful as an indicator of lake trophic status (Vaalgamaa, 2004), but its correlation coefficients with TLI varied significantly in the EP and YGP lakes. This was likely because most of the P consisted of mobile inorganic fractions, which are adsorbed onto amorphous iron oxides and will eventually be remineralized and released from the sediment under certain conditions (Jensen et al., 1995). In contrast, the linear relationship between P_o and trophic status was more stable for both the EP and YGP lakes. Sediment P_o decomposes slowly; therefore, it represents less mobile forms of P and is more closely related to sedimentation of macrophytes, phytoplankton, and terrestrial organic detritus (Vaalgamaa, 2004). These findings imply that sediment P_o may be a superior indicator of trophic status than TP in China.

4.2. Relationships between sediment P_o components and lake trophic status

With the increase of trophic status, the monoester P, diester P, and phosphonates contents increased (Fig. 3), similar to the levels of

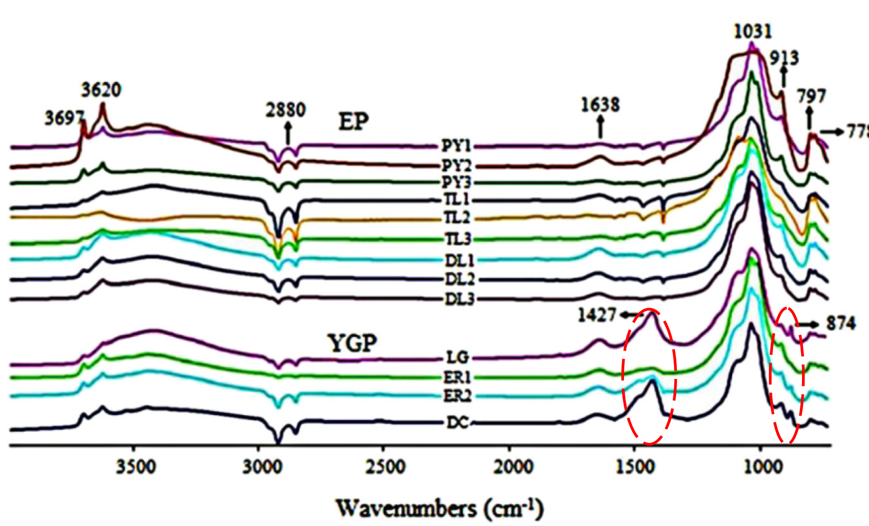

Fig. 5. Typical FT-IR spectra of sediment from the EP and YGP lakes with different trophic status.

Table 2
Pearson correlation coefficients for the relationship between P and the geochemical characteristics of sediment (n = 13).

Unit	TP	P_o	NaOH-P_o	Monoester P	Diester P	Orthophosphate	Pyrophosphate	OM	DOM (NaOH extract)	Fe	Al
TP	1										
P_o	0.882**	1									
NaOH-P_o	0.691**	0.692**	1								
Monoester P	0.641**	0.724**	0.772**	1							
Diester P	0.872**	0.887**	0.820**	0.970**	1						
Orthophosphate	0.776**	0.708**	0.615*	0.370	0.568*	1					
Pyrophosphate	0.844**	0.698**	0.673**	0.296	0.611*	0.789**	1				
OM	0.531*	0.590*	0.662**	0.647**	0.698**	0.278	0.215	1			
DOM (NaOH extracts)	0.382	0.476	0.643**	0.734**	0.686**	0.295	0.014	0.883**	1		
Fe	0.529*	0.384	0.292	0.610*	0.464	0.700**	0.232	0.185	0.295	1	
Al	0.463	0.415	0.558*	0.747**	0.765**	0.751**	0.374	0.440	0.554*	0.829*	1

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level.

orthophosphate and pyrophosphate in sediments (*SI* Fig. S2). The monoester P consisting of labile monoester and phytate-like P (Jørgensen et al., 2011) was the dominant P_o in sediments. The accumulation of monoester P might be closely related to the effects of metal chelates (Fe, Al) and anthropogenic phytate-like materials input. The significant positive correlation of monoester P with Fe ($p < 0.05$) and Al ($p < 0.01$) (Table 2) indicates that higher Fe and Al are beneficial to the formation of more monoester P in sediment. This is because polyvalent cations (Fe^{3+}, Al^{3+}) may increase adsorption onto inositol phosphate to form insoluble and stable Fe_4–phytate that precipitates onto the sediments, thereby increasing the phytate-like P accumulation. On the other hand, phytate-like P is primarily derived from indigestible P-bearing materials, including legumes, triticeae, and cereals, as well as the indigestible excrement of humans and non-ruminant animals (Ravindran et al., 1994; Lantzsch et al., 1992). Higher trophic status lakes usually correspond to higher amounts of farming and livestock breeding and greater population density in watersheds (Table 1), suggesting that loading of these specific organic materials plays an important role in the accumulation of monoester P in lake sediment.

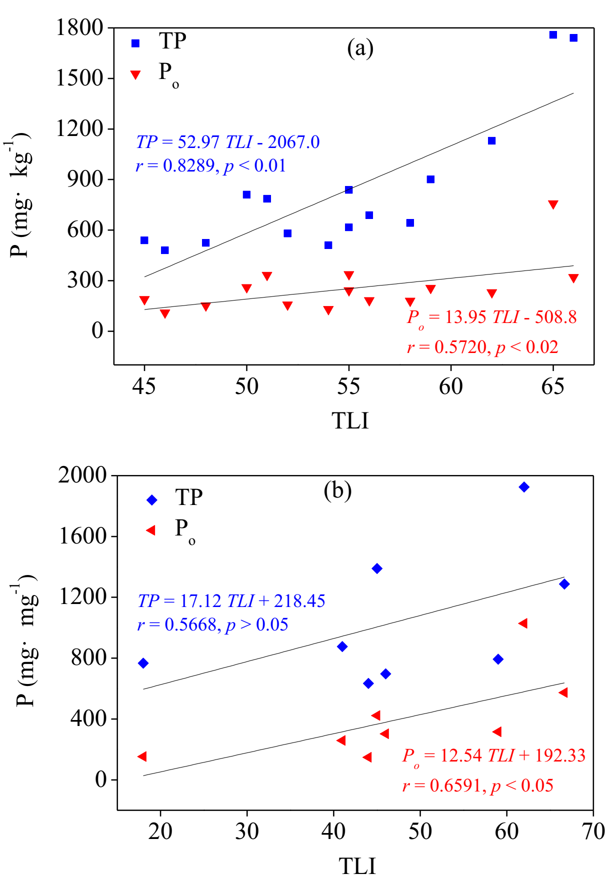

Fig. 6. Pearson correlation coefficients for the relationship between TLI (trophic level index), TP, and P_o content of sediment from the EP lakes (a, n = 15) and YGP lakes (b, n = 8).

The diester P increased as lake trophic status increased, which may be closely related to its source characteristics. Diester P is primarily derived from the sedimentation of OM as DNA and RNA of microorganisms and degradation products of phytoplankton (Ahlgren et al., 2006). In this study, higher trophic status lakes were found to have higher amounts of phytoplankton (Table 1). Diester P was significantly positively correlated with OM ($p < 0.01$), indicating that OM was essential to accumulation of diester P (Table 2).

Phosphonate, which contains a stable C—P bond (Zhang and Shang, 2013), and represents immobile P_o. This material showed an increasing trend with increasing lake trophic status. Sediment phosphonate is primarily derived from the metabolic product of protozoans (Nowack, 2003). However, the biomass of benthos showed decreasing trends as lake trophic status increased (Table 1), illustrating that the chelation of phosphonate and metal ions might an important factor for accumulation of phosphonate in the sediments. As trophic status increases, more divalent and trivalent Fe and Al ions in sediments can integrate more phosphonate, thereby forming an increased amount of metal bond phosphates that are more stable.

4.3. Relationships between sediment P_o stability and lake trophic status

4.3.1. UV–visible absorbance spectroscopy

The stability of P_o is usually closely related to its composition and structural characteristics in the sediment. Values of DOM in the extracts were significantly positively correlated with NaOH-P_o, monoester P, and diester P contents, with correlation coefficients of 0.643, 0.734, and 0.686, respectively (Table 2). These findings suggest that OM plays a significant role in the compositions of P_o in the sediments. $SUVA_{254}$ values have been confirmed to be an effective index for estimation of the proportion of aromatic compounds in DOM, with higher $SUVA_{254}$ values corresponding to greater humification and aromaticity (Weishaar et al., 2003; Yeh et al., 2014). The A_{253}/A_{203} values could reflect the concentration of substitution groups of DOM, with higher ratios indicating higher concentrations of substitution groups of aromatic rings (Y.P. Li et al., 2014; G.B. Li et al., 2014). Variations in S_R are related to differences in the molecular weight of DOM, with higher values corresponding to lower molecular weight (Helms et al., 2008). The significant positive correlations of P_o concentration with $SUVA_{254}$ and A_{253}/A_{203} (Fig. 7) indicate that the UV parameters may indirectly reflect the unidentifiable P_o that is incorporated into humus.

The $SUVA_{254}$ and A_{253}/A_{203} values increased steadily as trophic status increased for both the EP and YGP lakes (Fig. 4a and b), indicating that higher trophic status lake sediment P_o contains more substitution groups of aromatic rings and has a higher degree of humification. This

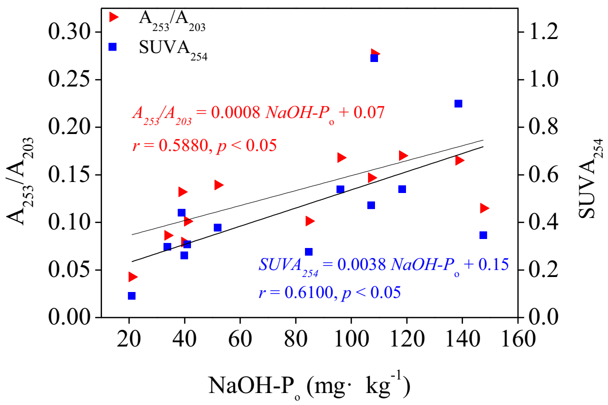

Fig. 7. Pearson correlation coefficients for the relationship between NaOH-P_o content and UV–vis parameter ($SUVA_{254}$ and A253/A203) in sediment (n = 13).

fact is inferred to be attributed to the relatively great mineralization of OM in the sediment because of somewhat larger numbers of microorganisms and enzymes in higher trophic status lakes. Carbohydrates and other labile components of OM are preferred by microorganisms in the mineralization process, resulting in more aromatic OM with a higher humification degree and accumulation of P_o in the sediments (Hur et al., 2011). The S_R value in the EP and YGP lakes all decreased with increasing trophic status (Fig. 4c), suggesting that sediment organic molecules possess a higher molecular weight in higher trophic status lakes. This might be attributed to the greater mineralization in higher trophic status lakes, which increases molecular weight of organic molecules (Guggenberger and Kaiser, 2003).

4.3.2. FT-IR spectroscopy

FT-IR spectroscopy provides information regarding P valence bonds with functional groups in the OM (Yang et al., 2015). The FT-IR spectra of sediments were similar to each other in terms of the position of the major absorption shoulders and bands in the same region of lakes with different trophic status. There were two intense and sharp peaks observed at 3620 cm^{-1} and 1031 cm^{-1} in all sediments because of O—H and P═O in-plane stretching vibrations, indicating that the sediment P_o comprises a large amount of hydroxyls, phospholipids, DNA, and RNA. This was closely related to the large amount of monoester P, diester P, and phosphonate in the sediment detected by ^{31}P NMR. The sediments also showed weak peaks in the range of 2870–2890, 1638–1650, and 779–797 cm^{-1} corresponding to the C—H, C═O, and P—O in-plane stretching vibrations of proteins, amides, and aromatics, respectively. Particularly, the weak peaks at 1427 and 874 cm^{-1}, which were assigned to C≡C and P—O stretching in aromatic and arene compounds, only appeared in the sediment of YGP lakes, implying that sediment P_o in the YGP lakes comprises more aromatic compounds. UV-radiation-induced degradation of organic molecules is an important factor in YGP lakes because of their higher altitude (Table 1), which leads to accumulation of more aromatics into the sediment.

4.4. Possible effects of P_o composition and stability on lake eutrophication

The release and decomposition of P_o are the main routes of recycling of P and thus an important process determining the level of bioavailable P in both water and sediment (Ni et al., 2016). Based on the result of $SUVA_{254}$ values and A_{253}/A_{203} ratios reported in this study, higher trophic status lake sediment P_o contains more aromatic substances and functional groups, and the substances have degrees of higher humification. These functional groups, which include hydroxyl, carboxyl, carbonyl, and ester groups, can potentially absorb and fix nutrients, heavy metals, and organic pollutants (Zhang et al., 2016), having a positive effect on lake water quality. Moreover, higher degree of humification is usually associated with greater conjugation in aliphatic chains complexes or more complex and condensed aromatic structures (Li et al., 2015), both of which stabilize the sediment, preventing P_o release and degradation. In addition, the S_R values indicated organic molecules in sediments of higher trophic status lakes have greater molecular weight. The high molecular weight usually imparts resistance to biodegradation compared to low molecular weight (He et al., 2011). Overall, these findings implied that the risk of release of P_o would be alleviated by increases in lake trophic status because of the more stable structure of P_o in the sediment.

Alkaline phosphatase, which is extensive in water columns and sediments, is the most important driver in the biological geochemical cycle of P_o (Hakulinen et al., 2005). As lake trophic status increase, increases in microorganisms and phytoplankton would enhance the amount and activation of alkaline phosphatase, especially during algal blooms in eutrophic lakes (Barik et al., 2001; Zhou et al., 2002). When combined with the higher content of monoester P, diester P, and phosphonate in higher trophic status lakes, the remarkable increase in alkaline phosphatase reflected that, as an important component of P, the large accumulation of P_o in sediments can be mineralized to bioavailable P, facilitating eutrophication. The positive correlation ($p < 0.05$) between diester P and orthophosphate in sediments (Table 2) indicated that the mineralization of diester P to bioavailable P by phosphodiesterase would be an important P source for supporting algal growth and maintaining long-term eutrophic status, even after external input of P loading has been controlled.

The efforts to control lake eutrophication in China began in the mid-1980s. Since then, great improvements in industrial pollution and erosion and torrent control have resulted in large-scale declines in lake inorganic P and TP concentrations (Ni and Wang, 2015). However, frequent blooms and serious eutrophication still occur and have not been fundamentally solved, particularly in Tai Lake, Chao Lake and Dianchi Lake, which are listed by the Ministry of Environmental Protection of China as priority lakes in which to achieve significant eutrophication improvements. Thus, more effective and flexible actions are urgently required to protect these eutrophic lakes from further deterioration and reverse the process. This study found that the accumulation of P_o in lake sediment was closely related to agricultural and domestic input. Although the risk of sediment P_o release may be alleviated in eutrophic lakes as a result of more stable structures of P_o, the massive storage of sediment bioavailable P_o (diester and monoester P) will degrade as a result of increased enzyme activity with increasing trophic status, leading to increased lake eutrophication or resistance of eutrophic lakes to remediation. Therefore, reducing watershed organic source materials load, advancing sediment P_o degradation control for optimization of key environmental conditions, and strengthening algal removal techniques are essential to restoration of damaged ecological environments in eutrophic lakes.

5. Conclusions

^{31}P NMR, UV–visible absorbance spectroscopy, and FT-IR spectroscopy were combined to identify the dynamic composition of sediment P_o across two sets of lakes ranging from oligotrophic to eutrophic in China. The results showed that sediment P_o content (accounting for 21%–75% of TP) was positively correlated with trophic level index in both EP and YJP lakes of China, and the linear relationship was more stable compared to TP, implying that sediment P_o may be a superior indicator of trophic status than TP. The P_o component, phosphonate, accounted for 0.4% or less of P_o, while the monoester P and diester P accounted for 8%–31% and 2%–9% of P_o, respectively, making them the main factors causing P_o to increase with increasing trophic status, which is closely related to the enhanced organic sewage load and intensification of contemporary sedimentation of phytoplankton. Furthermore, sediment P_o contained more functional groups and aromatic substances with increased trophic status, and substances had a higher degree of humification and molecular weights because of mineralization.

The possible effects of P_o composition on lake eutrophication were also evaluated. The results showed that sediment P_o might integrate into more aromatic substances and functional groups, such as hydroxyl, carboxyl, ester, and carbonyl groups, in higher trophic-status lakes, which could enhance the stability of P_o in sediments. In addition, higher trophic lake sediment exhibited a higher degree of humification and molecular weights, which imparted resistance to biodegradation, and thus, reduced the risk of sediment P_o release. However, the massive accumulation of bioavailable P_o remains subject to possible degradation and has the potential to further enhance eutrophication via dramatic increases in alkaline phosphatase in eutrophic lakes.

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Appendix A. Supplementary data

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