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Characteristics of phosphorus components in surface sediments from a Chinese shallow eutrophic lake (Lake Taihu): new insights from chemical extraction and ^{31}P NMR spectroscopy

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Abstract As a primary factor responsible for lake eutrophication, a deeper understanding of the phosphorus (P) composition and its turnover in sediment is urgently needed. In this study, P species in surface sediments from a Chinese large eutrophic lake (Lake Taihu) were characterized by traditional fractionation and ^{31}P nuclear magnetic resonance (NMR) spectroscopy, and their contributions to the overlying water were also discussed. Fractionation results show that NaOH-P predominated in the algal-dominated zone, accounting for 60.1% to total P in Zhushan Bay. Whereas, refractory fractions including HCl-P and residual-P were the main P burial phases in the macrophyte-dominated zone, the center and lakeshore. Recovery rates of the total P and organic P were greatly improved by using a modified single-step extraction of NaOH-EDTA, ranging from 22.6 to 66.1% and from 15.0 to 54.0%. Ortho-P, monoester-P, and pyro-P are identified as the major P components in the NaOH-EDTA extracts by ^{31}P NMR analysis. Trace amount of DNA-P appeared only in sediments from algal- and macrophyte-dominated zones, ascribing to its biological origin. The relative content of ortho-P is the highest in the algal-dominated zone, while the biogenic P including ester-P and pyro-P is the highest in the macrophyte-dominated zone. Moreover, ortho-P and pyro-P

correlated positively with TP and chlorophyll a in the overlying water, whereas only significant relationships were found between monoester-P, biogenic P, and chlorophyll a. These discrepancies imply that inorganic P, mainly ortho-P, plays a vital role in sustaining the trophic level of water body and algal bloom, while biogenic P makes a minor contribution to phytoplankton growth. This conclusion was supported by the results of high proportion of biogenic P in algae, aquatic macrophytes, and suspended particulate from the published literature. This study has significant implication for better understanding of the biogeochemical cycling of endogenous P and its role in affecting lake eutrophication.

Introduction

Lake eutrophication, characterized by surplus nutrients input and excessive phytoplankton growth, has become a global environmental concern (Wetzel 2001; Ahlgren et al. 2005; Smith and Schindler 2009). Phosphorus (P) enrichment is recognized as a main factor responsible for lake eutrophication (Schelske 2009). When external inputs are reduced, sediment-based P recycling would become a major source for P and delay the lake recovery (Bai et al. 2009). However, not all P forms are likely to be released from the sediment and thereby increase eutrophication. The potential contribution of internal P loading to lake eutrophication depends to a large extent on the abundance, speciation, and lability of P in sediments (Ahlgren et al. 2005; Zhang et al. 2008; Shinohara et al. 2012).

Fractionation schemes for P, originally adopted from agricultural science, has been widely applied in understanding the distribution and mobility of various P forms in lake sediments

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(e.g., Hupfer et al. 1995; Ruban et al. 2001; Zhang et al. 2008). Generally, sediment P can be divided into exchangeable P, metal oxides and hydroxides associated P, Ca-bound P, organic P, and residue P based on P fractionation. Although organic P can constitute a substantial pool of internal P, it has received much less attention than inorganic P in the past decades (Zhang et al. 2008; Bai et al. 2009). Due to the limitation in analytical methods, it is usually treated as the refractory fraction or a residue, and possible differences in lability are inevitably ignored among organic P species (Reitzel et al. 2007; Zhu et al. 2015).

Nuclear magnetic resonance (NMR) spectroscopy is a relatively new approach that has the potential to distinguish between different organic P (orthophosphate monoesters, diesters, and phosphonates) and inorganic P (orthophosphate, poly-P, and pyro-P) in sediments. Because of the low natural abundance of P and its heterogeneity in sediment, pretreatment and extraction are considered as two critical steps for solution ^{31}P NMR spectroscopy (Ahlgren et al. 2007). EDTA sodium or calcium salt (Hupfer et al. 1995, 2004) and dithionite (McDowell and Stewart 2005; Reitzel et al. 2007; Bai et al. 2009) were used as a pretreatment to remove excess metal ions and refine ^{31}P NMR spectra before the major extraction. EDTA pretreatment is specially suitable for calcareous sediments with the ratio of Ca/(Fe + Al) > 0.7 (Ding et al. 2010). Various extractants have been used as the main extraction medium, such as NaOH alone or combined with Chelex, NaF, and EDTA (Cade-Menun 2005). Although a uniform standard procedure is difficult to establish for different kinds of sediment samples so far, the single-step extraction with a mixture of NaOH and EDTA (NaOH-EDTA) has been a widely accepted protocol for sedimentary solution ^{31}P NMR study (Zhang et al. 2009; Xu et al. 2012).

Recently, the combination of sequential P fractionation and solution ^{31}P NMR spectroscopy has been employed to provide integrated information on P speciation and their labilities in lake sediments (Ahlgren et al. 2005; Reitzel et al. 2006; Zhang et al. 2015). For example, both two methods were used to identify and quantify the biogenic P in sediment cores from different trophic lakes (Ahlgren et al. 2005; Zhang et al. 2015). Pyro-P and phosphate ester are considered as two potentially available forms for supporting the growth of phytoplankton. P species significantly differed in sequential extractions (Reitzel et al. 2006). Hence, it is necessary to investigate the chemical nature of P in various sediment environments, which helps to understand the P dynamics and its contribution to specific lake water.

Lake Taihu is the third largest freshwater lake in China, located in the southeastern part of Yangtze River delta. It is a typical shallow (average depth 1.9 m) and eutrophic lake, with a surface area of 2338 km^2 (Qin et al. 2007). It has experienced accelerated eutrophication over the past three decades; as a consequence, several drinking water crises took place in

recent years, following massive blooms of cyanobacteria (Paerl et al. 2011; Deng et al. 2014). The uneven development of basin economy results in high spatio-temporal heterogeneity of water quality and aquatic ecosystem in Lake Taihu (Qin et al. 2007; Bai et al. 2009; Zhu et al. 2013). The northwest zone is regarded as the most polluted part of the lake and is dominated by algae, due to high nutrient loading derived from the river mouths. The southeastern lake zone on the other hand is covered by macrophytes and keeps good water quality. Kelderman et al. (2005) claimed that 65% of total P input settles into sediment in Lake Taihu. Bioactive P pool in sediment was approximately 5168 tons for the entire lake and was even equivalent to external P loading (Zhu et al. 2013). Sediment P fractions, especially organic P in this lake were previously analyzed using the fractionation scheme (Wang et al. 2006; Zhang et al. 2008). Spatial distribution of P species in sediments from Lake Taihu were also investigated by solution ^{31}P NMR early (Bai et al. 2009), combined with pretreatment of EDTA-dithionite and 0.1 mol/L NaOH extraction. However, extreme low total P recovery (10–19%) might attenuate the practical application of ^{31}P NMR, probably owing to inappropriate pretreatment and extraction procedures. So far, there is a lack of comprehensive knowledge of sediment P speciation in Lake Taihu, and their contributions to the overlying water within different ecological environments remain poorly understood.

In the current study, P composition in the sediment from Lake Taihu was reexamined by P fractionation coupled with a modified single-step extraction of NaOH-EDTA followed by ^{31}P NMR analysis. The lability of various P species among different ecological zones was also evaluated by correlation analysis with total P and chlorophyll a (Chl-a) in the water column. Their source and decomposition behavior were further discussed in combination with latest published results of suspended particulate, algae, and aquatic macrophytes from the same lake. This study aims to better understand the biogeochemical cycle of internal P-loading relevant to lake eutrophication and further remediation.

Materials and methods

Study area and sampling sites

Qin et al. (2007) and Zhu et al. (2013) provided a comprehensive description of socioeconomic conditions, regional hydrogeology, and ecological environment of Lake Taihu basin. Lake Taihu supplies drinking water for 10 million people living within the watershed. It also serves as a repository for sewage from nearby urban households as well as the accelerated industrial and agricultural production activities. Eleven sampling sites were categorized into the following zones

(Fig. 1): (1) sites 1, 2, and 11 are located in the Zhushan Bay and Meiliang Bay, the algal-dominated zones. (2) Sites 7 and 8 are located in the Eastern Taihu Bay, the submerged macrophyte-dominated zone. (3) Sites 3 and 4 are located in Gonghu Bay, a transitional zone between these two types of habitat. (4) Sites 5 and 6 are located in the center of the lake without serious algal bloom during summer. (5) Other sites are located in the west lakeshore with little submerged plants coverage.

Lake water was collected approximately 0.5 m below the surface using a water sampler. Water samples were preserved in acid washed polypropylene bottles. The triplicate samples of surface 10 cm sediment were mixed and selected using a gravity core sampler in August, 2014. This segment represents the sediment accumulated over three decades and is prone to resuspension, based on an average sedimentation rate of 0.33 cm/year estimated by Zhu et al. (2007). These sediments containing pore water were transported to the laboratory in sealed plastic bags that were placed in iceboxes, then freeze-dried, ground, and passed through a 100-mesh sieve for further analysis.

Analysis

The concentration of Chl-a and pH in overlying water were measured in situ using a multisensor sonde (YSI 6600 V2, Yellow Springs Instruments). Total P (TP) in the water was determined after acid-persulphate digestion (Rowland and Haygarth 1997). Total contents of Fe, Al, and Ca in sediments were measured with inductively coupled plasma-optical emission spectroscopy (ICP-OES) after digestion with HNO_3-HF-$HClO_4$. Total P and organic P in sediment were determined according to the SMT protocol (Ruban et al. 2001).

P fractionation was performed according to the scheme of Hupfer et al. (1995) and classified sediment P into loosely sorbed P (NH_4Cl-P), redox-sensitive P (BD-P), NaOH extracted P (NaOH-P), and HCl-P. Residual-P is given by the difference between total sediment P and the sum of the other P fractions. These extracts were centrifuged, and the soluble reactive P (SRP) in supernatants was analyzed by the molybdenum-blue method (Drummond and Maher 1995). All analyses were done in triplicates, and the mean value was reported.

Fig. 1 A sketch map of the sampling sites in Lake Taihu
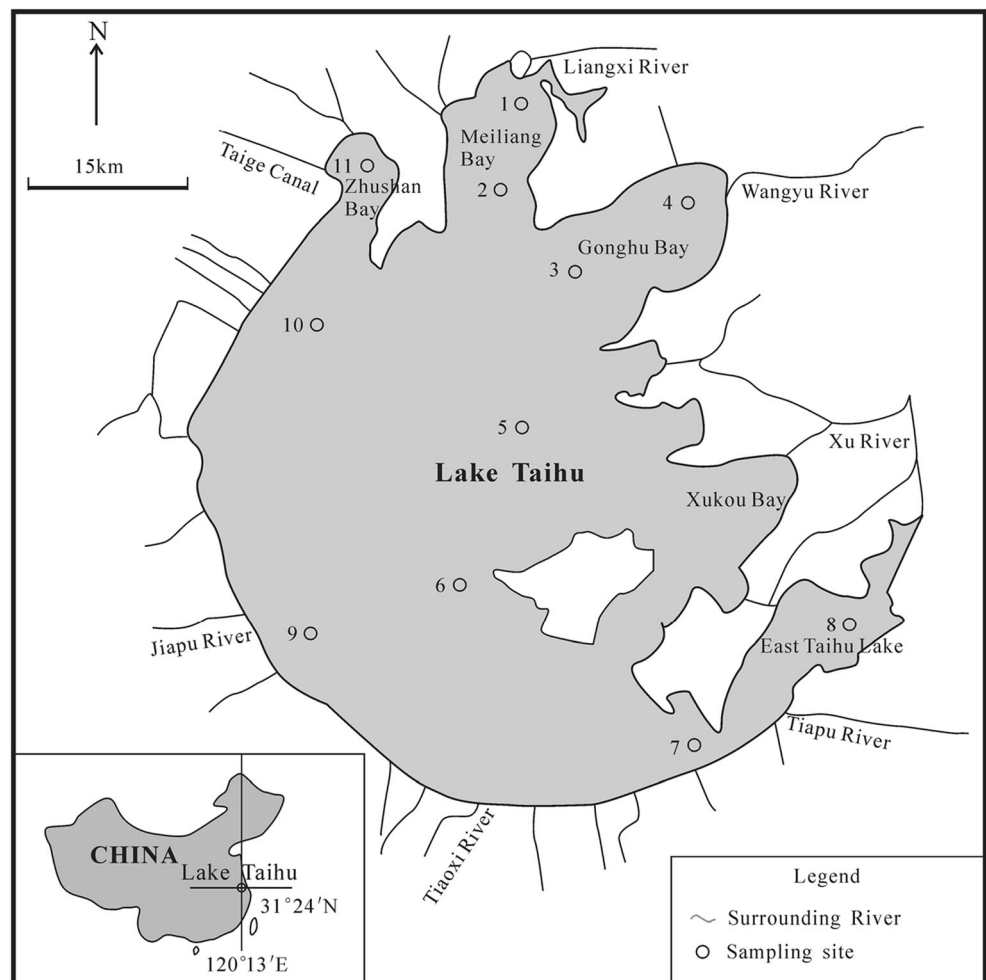
Four grams of sediment was extracted using a mixed solution containing 0.25 mol/L NaOH and 0.05 mol/L EDTA (NaOH-EDTA) for 16 h at 25 °C with the ratio of 1:30 (*w/V*), which produced a high P concentration enough for ^{31}P NMR analysis (Zhang et al. 2015). Total P and SRP in all extracts were analyzed spectrophotometrically after dilution of at least 25-fold to avoid EDTA interferences. The remaining solution was concentrated 20–30 times by rotary evaporation at 30 °C and was frozen at −18 °C until analysis. Before ^{31}P NMR measurement, 5% (vol.) of BD solution was added in order to reduce interference from paramagnetic ions such as Fe and Mn. Approximately 300 mg of NaOH-EDTA extracts was diluted into 0.2 ml of 10 M NaOH and 0.5 ml D_2O, then vortexed and centrifuged at 10,000×*g* for 10 min. The supernatant was transferred into a 5-mm NMR tube. Solution ^{31}P NMR spectra were performed at 202.5 MHz for ^{31}P on a JEOL ECX 500 MHz spectrometer (Japan) at 25 °C in the same manner as described previously (Zhang et al. 2009). Chemical shifts were indirectly referenced to external 85% H_3PO_4 standard. The contribution of individual P compound group was calculated based on its relative peak area. Due to the time-consuming and high cost of ^{31}P NMR scans, replicate analyses were not performed.

Results and discussion

Physico-chemical properties in the overlying water and sediment

Sediment properties and concentrations of TP and chlorophyll a in the water are listed in Table 1. The pH in water ranged from 6.95 to 7.89. Both water TP and Chl-a decreased from north to southeast, in the range of 0.07 to 0.24 mg/L and 10 to 73 μg/L. High level of TP and Chl-a exist in the northwest

parts, where these zones are linked with highly urbanized towns with high population density (Zhu et al. 2013). According to the health status report of Taihu in 2014, water quality has slight change since 2007, total P decreased mildly from 0.074 to 0.069 mg/L and total N from 2.35 to 1.85 mg/L between 2007 and 2014 (Taihu Basin Authority of MWR 2014). This is inconsistent with the marked reduction of external P loading in last decade, indicating that sediment P may play an important role in sustaining the eutrophic level in Lake Taihu.

Total P in sediments ranged from 461.3 to 1193.9 mg/g, with high values present in sediments of algal-dominated zones. Organic P in sediments ranged from 152.9 to 243.2 mg/g, accounting for 19.7–42.6% of total P. However, high proportions of organic P present in sediments of Gonghu Bay, the center and East Lake Taihu. This means that organic P in sediment cannot directly contribute to water P level. Total Al, Fe, and Ca, ranged from 58.4 to 71.0 mg/g, from 20.3 to 31.0 mg/g, and from 7.6 to 10.6 mg/g, respectively. Consequently, the ratio of sediment Ca to the sum of Al and Fe [Ca/(Fe + Al)] varied from 0.08 to 0.12, close to previous results (0.06–0.15) (Bai et al. 2009).

P forms in surface sediments among different ecological zones

P fractionation results are shown in Fig. 2. There are highly uneven distributions of various P fractions among different ecological zones in Lake Taihu. NaOH-P predominated in the algal-dominated zone and site 10, with its relative contribution of 35.6–60.1% (average 51.5%) to total P. In contrast, residual-P was the main fraction in sediments from the central zone and Gonghu Bay, accounting for 36.9–45.9% to total P. HCl-P was dominant in the lakeshore zone and contributed 28.0–40.0% to total P.

Table 1 Physical-chemical properties of surface sediments and concentrations of total P and chlorophyll a in the overlying water from Lake Taihu

Sites	Sediment						Water		
	Total P mg/kg	Organic P	Al mg/g	Fe	Ca	Ca/(Fe + Al)	pH	TP g/L	Chlorophyll a μg/L
1	830.0	163.9	70.3	30.9	9.6	0.09	7.31	0.21	49
2	694.9	179.6	66.1	30.6	9.4	0.10	7.83	0.17	31
3	491.3	192.6	68.2	28.0	9.3	0.10	7.72	0.15	29
4	518.7	211.4	66.1	23.7	9.7	0.11	7.43	0.11	18
5	510.1	217.4	58.4	25.6	10.4	0.12	7.87	0.12	37
6	461.3	178.9	65.8	24.9	7.6	0.08	7.76	0.07	10
7	525.5	216.9	66.5	25.3	9.0	0.10	7.65	0.09	16
8	655.1	216.7	60.1	20.3	8.7	0.11	7.42	0.07	10
9	609.3	196.5	66.2	24.6	9.2	0.10	7.27	0.13	21
10	615.6	152.9	65.7	28.3	10.6	0.11	7.89	0.18	46
11	1193.9	243.2	71.0	31.0	9.3	0.09	6.95	0.24	73
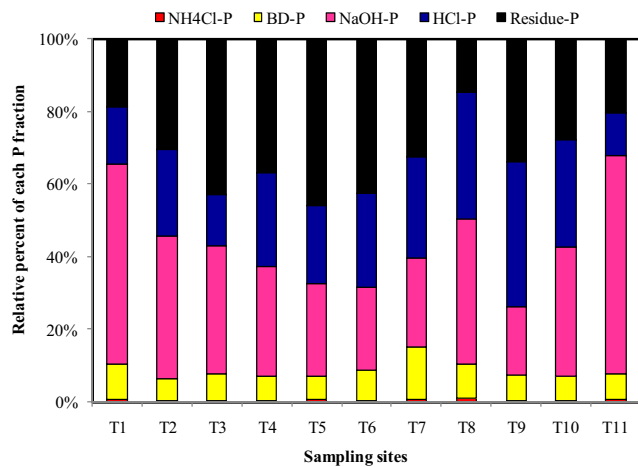
Fig. 2 Relative percentages of P fractions in surface sediments of Lake Taihu

NH_4Cl-P mainly means on surface sediment loosely adsorbed P and interstitial water P. It was readily released from sediments and available for phytoplankton growth (Rydin 2000). This fraction accounted for 0.4–0.9% of the total sediment P, similar to the previous reports of Lake Taihu (Wang et al. 2006). BD-P represents the redox-sensitive P fraction and often considered as a potentially mobile pool of P. High proportion of BD-P was observed in the macrophyte-dominated zone probably due to DO level in the water-sediment interface (9.95 ± 0.22 mg/L) higher than other zones (7.90 ± 1.34 mg/L), which acted as a boundary layer for up-ward diffusing of P (Zhang et al. 2016). NaOH-rP represents metal oxides of Al and Fe bound P, and can be released easily when the sediment-water interface becomes anoxic (Kaiserli et al. 2002). Most of sediment P in the algal-dominated zone was NaOH-P, especially the supreme proportion of 60.1% in Zhushan Bay. Zhu et al. (2013) simulated the dynamic of P by incubation the surface sediments with algal scum and found that Fe-P varied significantly and made a great contribution to water TP. The Fe-P content was 3.2 g/m^2 in the northwestern part of Lake Taihu and higher than the average value of 0.5 g/m^2 for the entire lake. HCl-P often means apatite P and remains refractory under alkaline condition. High abundance of HCl-P in the lakeshore zone was attributed to the calcareous terrain of the recharge area. Residual-P is the most stable phase in sediment, as a result of the dominant fraction in the lake center with weak hydrodynamic force.

Labile P is widely considered as a good index to estimate the potential contribution of sediment P to the overlying water, composing of NH_4Cl-P, BD-P and NaOH-P (Rydin 2000). There are significantly positive correlations between labile P fractions in sediment with TP and chlorophyll a in the water column (for TP, $R^2 = 0.59$, for Chl-a, $R^2 = 0.64$, $P < 0.01$). Wang et al. (2006) found that labile P decreased markedly during algal blooms in Lake Taihu. Among them, over 50%

released P was from NaOH-P, 30% from BD-P, 10% from HCl-P, and below 5% from NH_4Cl-P.

^{31}P NMR analysis in lake sediments

TP concentration in the NaOH-EDTA extracts ranged from 121.7 to 789.2 mg/kg, with the corresponding recovery of 22.6–66.1% (Table 2). These results were slightly higher than the values (27–42%) of Ding et al. (2010) with the ratio of 1:20 (*m/V*), obviously higher than the values (10–19%) using the pretreatment of EDTA-$Na_2S_2O_4$ reported by Bai et al. (2009). EDTA pretreatment was particularly recommended by Ding et al. (2010) for ^{31}P NMR analysis of calcareous sediments with Ca/(Fe + Al) > 0.7, because that broke P-containing organo-metal complexes and increased the extraction efficiency of NaOH alone. On contrary, it is hardly to improve the P yield for the samples with Ca/(Fe + Al) < 0.4. Additionally, EDTA preferentially extracts inorganic P, whereas organic P was inevitably extracted at the same time in the pre-extraction (Hupfer et al. 1995), which leads to the loss of P in the subsequent main extraction step. The ratio of Ca/(Fe + Al) ranging from 0.08 to 0.12 in Lake Taihu (Table 1) confirmed that these sediments were not suitable to adopt the original pretreatment approach for P extraction. In this study, the recovery rate of organic P (15.0–54.0%) was also higher than previous results of 28.7–46.4% (Bai et al. 2009). These findings supported the feasibility of the single extraction of NaOH-EDTA adopted for the studied samples. It was worth mentioning that NaOH-EDTA extracted P is equivalent to labile P in sediment, with a positively correlation between them (Fig. 4), indicating it can be considered as a proxy for evaluating the potential of internal-P loading for lake eutrophication. This suggests that the NaOH-EDTA extracted P likely reflect the inherent composition in non-calcareous lake sediments.

Three main P-containing compound groups were detected and identified by ^{31}P NMR in the extracts, including ortho-P (6–8 ppm), monoester-P (3.5–6 ppm), and pyro-P (−3 to −5 ppm) (Fig. 3; Table 2). Trace amounts of diester-P (0 to − 1 ppm) and phosphonates (17–20 ppm) were present in a few extracts.

Ortho-P was the dominant P form in all sediment extracts, ranged from 97.1 to 552.1 mg/kg, with its relative contribution of 17.9–54.8% to total sediment P. It easily releases from sediment and provides a major nutrients source for algae and phytoplankton utilization, when SRP in the overlying water column is low. Thus, cyanobacteria blooms frequently broke out in the northwestern lake zones, in accordance with high ortho-P content. A small proportion of pyro-P was detected in all extracts, in agreement with previous reports (Zhang et al. 2009; Ding et al. 2010).

Table 2 Contents of TP, OP, and different P species (mg/kg) in the NaOH-EDTA extracts determined by ^{31}P NMR, and their proportions to sediment TP in parentheses (%)

| Site	NaOH-EDTA extracts		Inorganic P		Organic P		
	Total P	Organic P	Ortho-p	Pyro-P	Monoester-P	Diester-P	Phosphonate
1	539.0 (64.9)	46.3 (28.2)	454.9 (54.8)	17.2 (2.1)	57.1 (6.9)	9.7 (1.2)	ND
2	290.0 (41.7)	68.4 (38.1)	241.6 (34.8)	5.7 (0.8)	42.7 (6.1)	ND	ND
3	170.2 (34.6)	32.6 (16.9)	144.3 (29.4)	3.3 (0.7)	22.5 (4.6)	ND	ND
4	160.4 (30.9)	61.6 (29.1)	118.8 (22.9)	2.8 (0.5)	38.7 (7.5)	ND	ND
5	141.2 (27.7)	32.6 (15.0)	112.3 (22.0)	2.6 (0.5)	26.3 (5.2)	ND	ND
6	121.7 (26.4)	42.2 (23.6)	97.1 (21.0)	0.9 (0.2)	23.7 (5.1)	ND	ND
7	157.3 (29.9)	71.4 (32.9)	105.5 (20.1)	3.5 (0.7)	45.7 (8.7)	2.7 (0.5)	ND
8	316.0 (48.2)	117.0 (54.0)	195.7 (29.9)	10.1 (1.5)	88.8 (13.6)	21.3 (3.3)	ND
9	137.9 (22.6)	48.7 (24.8)	109.3 (17.9)	2.9 (0.5)	25.7 (4.2)	ND	ND
10	222.1 (36.1)	39.2 (25.6)	169.0 (27.5)	11.9 (1.9)	41.1 (6.7)	ND	ND
11	789.2 (66.1)	73.5 (30.2)	552.1 (46.2)	24.1 (2.0)	167.5 (14.0)	18.0 (1.5)	27.6 (2.3)

Parentheses indicate the percentage of organic P in sediment extracted with NaOH-EDTA

ND not detected

Monoester-P ranged from 22.5 to 167.5 mg/kg, accounting for 4.2–14.0% of total P. It was the dominant component of organic P in the studied samples. Intensive peak signals at 4.0–5.5 ppm in all extracts might suggest high abundance of phytic acid, which has been widely identified by ^{31}P NMR in sediment extracts from other freshwater lakes (Reitzel et al. 2007; Zhang et al. 2009; Zhu et al. 2015). Due to higher charge density, it is less labile to decomposition and hydrolysis through binding with metal cations. Weak peak intensity in the range of 0 to − 1 ppm was assigned as diester-P, mainly DNA-P (Cade-Menun 2005), which exist in sediments from the algal-dominated and macrophyte-dominated zones (including sites 1, 7, 8, and 11). DNA-P in sediment originated from bacterial DNA and plankton degradation debris. This means microorganism activity involved in the biogenic P cycling in these environments (Deng et al. 2014). A small amount of phosphonates exist only in site 11 and are close to

Fig. 3 ^{31}P NMR spectra of the NaOH-EDTA extracts from Lake Taihu
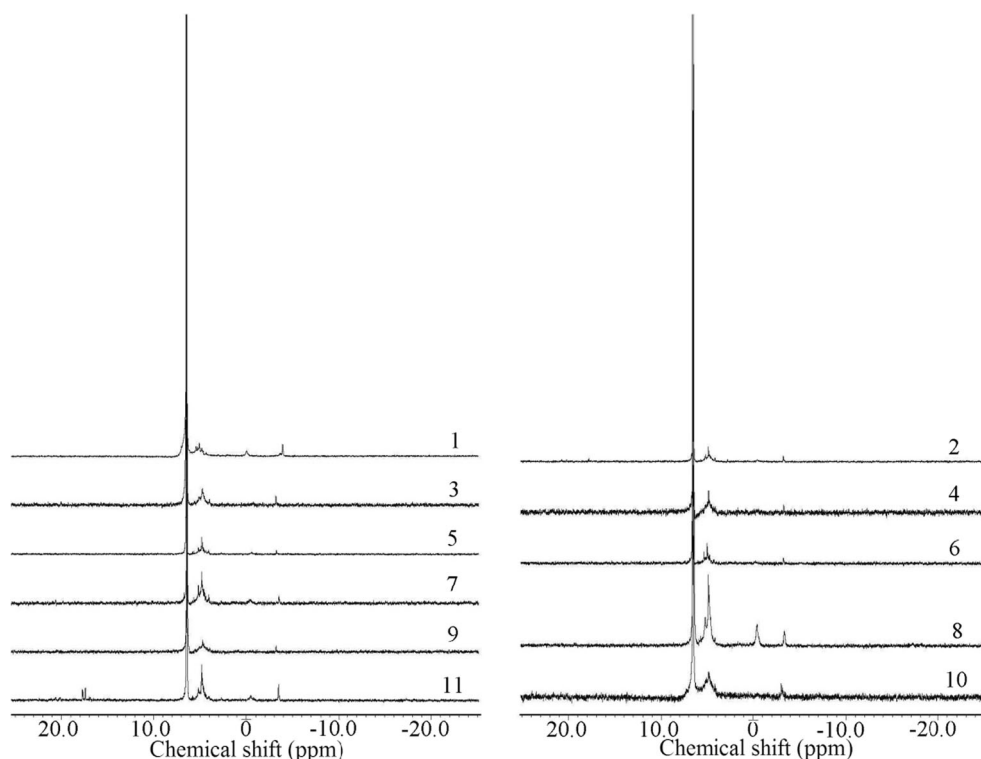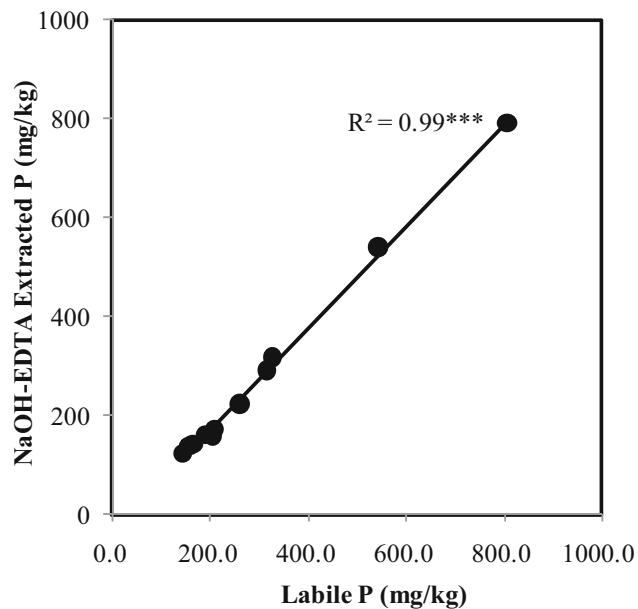
Fig. 4 Correlation of labile P faction and the NaOH-EDTA extracted P ($n = 11$, ***$P < 0.001$)

relevant results of less than 1% in from Meiliang Bay and Zhushan Bay (Zhu et al. 2015). Phosphonates are chemically stable compound due to their direct C–P bond. Thus, their absence in other samples might owe to their low abundances (Bai et al. 2009).

Monoester-P, diester-P, pyro-P, and phosphonates are considered as biogenic P, except ortho-P (Ahlgren et al. 2005). These biogenic P collectively contributed 15.2–38.1% (average 23.6%) to total extracted P (Table 3). These values are similar to results from another eutrophic lake, Lake Kasumigaura (Shinohara et al. 2012), and lower than those of a moderately eutrophic lake, Lake Erken (Ahlgren et al. 2005).

Relationship between ^{31}P NMR-detected P species in sediment and TP, Chl-a in the overlying water

Positive correlations of ortho-P and pyro-P in the extracts with TP and Chl-a in the overlying water confirmed that

these two P pools play a vital role in lake eutrophication and cyanobacteria blooms (Fig. 5). In contrast, there were inapparent relationships between monoester-P, biogenic P, and water TP level. Besides that, a significant positive correlations between monoester-P and biogenic P in sediment and Chl-a in the overlying water were also found. It is possible that the biogenic P in surface sediment originate from the sedimentation of suspended particles including detritus, phytoplankton, and bacteria (Shinohara et al. 2012). Another possible explanation is that biogenic P in sediment can provide the potential nutrient source for phytoplankton growth. This finding was supported by the results of Amirbahman et al. (2013), who claimed that the decrease rate of 8.2 mmol/m of the biogenic P in the surface sediment was comparable to the increment of 6. 5 mmol/m of ortho-P during summer from a eutrophic lake, Lovejoy Pond. Hernandez et al. (1997) reported that algae made use of more than 40% of P from monoester-P in a mesotrophic lake, in addition to abundant ortho-P. Accordingly, part of labile biogenic P compounds can be decomposed to ortho-P and recycle into the overlying water column.

Comparison of P composition in surface sediment, algae, aquatic macrophytes, and suspended particulate

Coincidentally, the chemical nature of P in algae, aquatic macrophytes, and suspended particulate in this lake were subsequently characterized by ^{31}P NMR technique (Feng et al. 2016; Zhang et al. 2016). With such knowledge, it can help us to better understand the biogeochemical cycle of endogenous P in lakes. As results listed in Table 3, proportions of major P compound groups in algae and aquatic macrophytes were similar to those from suspended particulate, except of the absence of poly-P. Low content of poly-P in particulate matter is attributed to the debris aggregation of algae and aquatic plants (Zhang et al. 2016). Content of ortho-P in the suspended particulate was the highest in the lakeshore zone, mainly resulting from the large quantity of allochthonous river inflows from

Fig. 5 Relationships of various P compound groups in the NaOH-EDTA extracts detected by ^{31}P NMR with TP and Chl-a in the overlying water ($n = 11$, *$P < 0.05$, **$P < 0.01$)
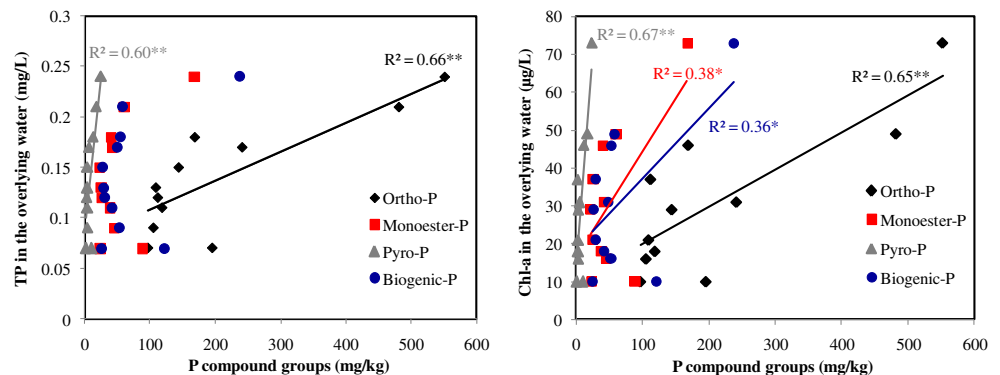
Table 3 Comparisons of extracted P compound groups and their percentages (%) in algae, aquatic macrophytes, suspended particulate, and surface sediment from different lakes determined by solution ³¹P NMR

Site and trophic level			Ortho-p	Pyro-P	Poly-P	Monoester-P	Diester-P	Phosphonate	Biogenic-P	Reference
Lake Taihu, eutrophic	Algae		41.4	10.3	ND	47.1	1.2	ND	58.6	Feng et al. 2016
	Macrophyte		56.2	2.0	ND	40.4	1.4	ND	43.8	
	Suspended particulate	Algae-dominated zone	35.98	17.86	5.48	39.11	1.57	ND	64.02	Zhang et al. 2016
		Mid-lake zone	36.05	14.65	7.92	40.46	ND	1.03	63.95	
		Macrophyte-dominated zone	49.37	6.39	1.24	39.61	3.39	ND	50.63	
		Lakeshore zone	82.57	3.84	0.56	13.00	ND	0.03	17.43	
		Average	50.99	10.68	3.80	33.02	2.48	1.06	49.01	This study
	Surface sediment	Algae-dominated zone	79.2	2.7	ND	15.5	1.4	1.2	20.8	
		Mid-lake zone	79.7	1.3	ND	19.0	ND	ND	20.3	
		Macrophyte-dominated zone	64.4	2.7	ND	28.6	4.3	ND	35.6	
		Lakeshore zone	77.7	3.8	ND	18.5	ND	ND	22.3	
		Average	76.4	2.5	ND	19.7	1.2	0.2	23.6	
Lake Kasumigaura, eutrophic	Suspended particulate		27.2	10.3	ND	50	12.5	ND	72.8	Shinohara et al. 2012
	Surface sediment		73.3	0.5	ND	12.6	13.6	ND	26.7	
Lake Erken, moderately eutrophic	Suspended particulate		27	10	ND	62	1	ND	83	Ahlgren et al. 2005
	Surface sediment		45	3	ND	32	20	ND	55	

ND not detected

agriculture, industrial, and domestic wastewater in the basin. In addition, this lake sector is easily disturbed by prevailing south-easterly summer winds (Qin et al. 2007). Surface sediment resuspension markedly elevated ortho-P content in the suspended particulate.

Except in the lakeshore zone, relative content of biogenic P in suspended particulate is obviously higher than that in surface sediment, suggesting it could be partly decomposed and released during or after sedimentation. The phenomenon was also observed in previous studies (Ahlgren et al. 2005; Shinohara et al. 2012). Compared to suspended particles, the proportion of biogenic P in sediment decreased 46 and 28% in Lake Kasumigaura and Lake Erken, respectively (Table 3).

Hitherto, much effort have focused on the degradation mechanism of biogenic P under different environmental settings. It was also reported that the half-life times of common P species in lake sediment ranked in the order of ortho-P (1 year) < pyro-P (13 years) < DNA-P (22 years) < monoester-P (23–29 years) (Ahlgren et al. 2005; Reitzel et al. 2007). Reitzel et al. (2007) showed that diester-P decreased faster than monoester-P in the sediment profile of Lake Erken. Pyro-P also can be rapidly decomposed to ortho-P in Lake Kasumigaura (Shinohara et al. 2012). Carbon substrate was also considered to be an important factor affecting the release of organic P in sediments (Ahlgren et al. 2011; Zhu et al. 2015). However, the exact transforming and releasing pathway of biogenic P in lake remains unclear. More new technologies, such as enzymatic hydrolysis and phosphate oxygen isotope (Jaisi et al. 2011; Zhu et al. 2015), need to be developed for understanding its turnover in lake sediments and the ecological impact in the near future.

Conclusions

This study demonstrates the usefulness of ³¹P NMR technique with the single-step NaOH-EDTA extraction to evaluate P composition and its bioavailability in noncalcareous lake sediments. Results show that distribution characteristics of P forms varied in different ecological zones. NaOH-P and ortho-P predominated in the algal-dominated zone, whereas refractory fractions including HCl-P, residual-P, or biogenic P were the main P forms in the macrophyte-dominated zone. The correlation analysis also indicated that ortho-P and pyro-P are two labile P pools, and play the vital role in regulating the nutrient status for eutrophic lakes. Part of labile biogenic P compounds can be decomposed to ortho-P and recycle into the overlying water column for biological growth. This current study may be beneficial for the deep understanding of the biogeochemical cycle of sediment P and its potential eco-environmental effect in lake.

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