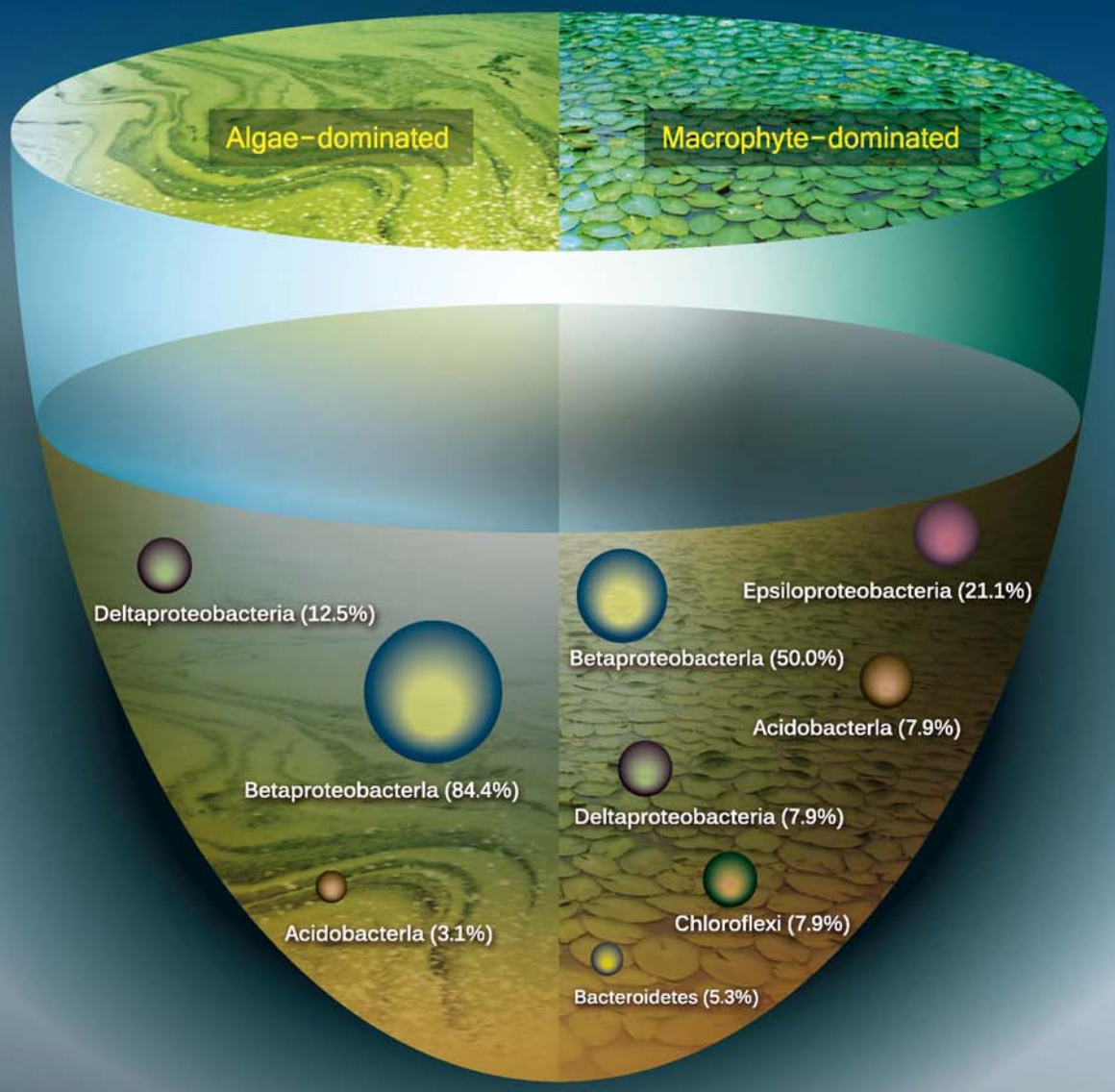
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Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and ^{31}P NMR

Runyu Zhang[1,*], Liying Wang[1], Fengchang Wu[2], Baoan Song[3]

1. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
2. State Environmental Protection Key Laboratory for Lake Pollution Control, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
3. Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Guiyang 550025, China

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Abstract

The distribution characteristics of phosphorus (P) forms in the sediment profile of Lake Erhai, in southwestern China has been investigated by sequential extraction and ^{31}P nuclear magnetic resonance spectroscopy (NMR) of NaOH extracts to understand P dynamics and its potential contribution to lake eutrophication. Contents of P fractions varied in the order of NH_4Cl extracted P (NH_4Cl-P) < bicarbonate-dithionite extracted P (BD-P) < HCl-P, Residual-P < NaOH extracted P (NaOH-P). The highly available NH_4Cl-P represented less than 1% of total P (TP). BD-P and NaOH extracted reactive P (NaOH-rP) averaged 39%, while the ratio of Fe/P was higher than 15, indicating low P release from the sediments under permanent oxic condition. The less bio-available HCl-P, NaOH extracted nonreactive P (NaOH-nrP) and residual-P contributed 61% of TP. Regression analysis revealed that BD-P, NaOH-rP and HCl-P were positively correlated with the contents of Fe and Mn, Al and Fe, and Ca, respectively. The investigation of P compound groups in NaOH extracts by ^{31}P NMR showed that ortho-P and monoester-P were the largest two constituents of the P pool, followed by diester-P, phosphonate and pyro-P. A comparison of vertical variations of P groups in the sediment profile suggested that these compounds were involved in the P recycling to different extents in Lake Erhai. In particular, the lake exhibits high potential for labile P release from the surface sediments, which should be taken into consideration even after the outsourced P runoff ceased.

Key words: phosphorus; speciation; fractionation; ^{31}P NMR; sediment; eutrophication

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Introduction

Lake sediments are considered a sink as well as a source for nutrients and, therefore, play a decisive role in eutrophication. The supply of phosphorus (P) which in most cases is the growth-limiting nutrient initiates phytoplankton blooms as well as the development of cyanobacteria, thus deteriorating the water quality severely. Changes of physical, chemical, and biological conditions can induce transformation and release of inorganic and organic P from lake sediments (Pettersson, 1998; Lau and Lane, 2002; Ahlgren et al., 2011). The release of P will often determine the trophic status of the lakes and the time lag for recovery even after the reduction in external loading (Rydin, 2000). Therefore, the long-term behavior of sediment P in lake eutrophication requires efficient evaluation of P fractions (Kaiserli et al., 2002).

Usually P forms are physically adsorbed onto sediment surfaces, chemically bonded in minerals, biologically assimilated in cells and detritus originating from the sediment infauna, which measured by different sequential extraction schemes, so-called P fractionations (Hupfer et al., 1995a; Ruban et al., 1999; Zhang et al., 2008). In view of the potential P-bioavailability, the extracted fractions may be characterized as water-soluble P, readily desorbable P, algal available P or ecologically important P (Zhou et al., 2001). Organic P, which earlier were regarded as the refractory part of P pool, are recently known to contain many labile species which play an important role in sustaining eutrophication (Ahlgren et al., 2005; Zhang et al., 2008).

Nuclear magnetic resonance spectroscopy (NMR) is an efficient way of assessing the P composition in the sediments (Hupfer et al., 1995b; Carman et al., 2000; Ahlgren et al., 2005; Zhang et al., 2009). This technique has successfully revealed structural features of sediment P,

* Corresponding author. E-mail: zhangrunyu@vip.gyig.ac.cn

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and differentiated P bound as orthophosphate (ortho-P), orthophosphate monoesters (monoester-P), orthophosphate diesters (diester-P), pyrophosphates (pyro-P) and phosphonates. Carman et al. (2000) found diester-P was much higher in the reduced sediments from three Swedish lakes than that in the oxic/suboxic conditions. Reitzel et al. (2007) reported the half-life times of common P species in sediments from Lake Erken in the order of ortho-P (1 year) < poly-P (2 year) < DNA-P (22 year) < monoester-P (29 year). Zhang et al. (2009) stated that the relative abundance of ortho-P was higher in hypertrophic and shallow lake sediments than in eutrophic and mesotrophic and deep lake sediments, whereas the relative content of monoester-P was the opposite. Hence, it is necessary to investigate the distribution characteristics of P forms within different sediment environments, which helps to understand P dynamics and release risk into specific lake water.

Lake Erhai (100°5′–17′E, 25°35′–58′N) is the largest fault lake in China. Geochemists have made a great deal of efforts to identify paleosedimentary environment using various geochemical indicators in sediments, such as Fe speciation (Zheng et al., 2001), ^{137}Cs and ^{210}Pb (Wan et al., 2003) and radiocarbon concentration (Kitagawa et al., 2007). However, little is known about P composition in surficial sediments of Lake Erhai (Wang et al., 2005; Zhang et al., 2008), although this lake is experiencing a transition from the mesotrophic to eutrophic condition due to anthropogenic inputs, with P being recognized as the primary pollutant (Wang et al., 2005).

In the present study, the P fractionation with ^{31}P NMR spectroscopy were combined to investigate the P speciation in the sediment profile from Erhai Lake and to evaluate its potential contribution to the overlying water column.

1 Materials and methods

1.1 Study area

Total water area of Lake Erhai is 249.8 km^2, with an average depth of 10.5 m and a residence time of 2.75 year. The catchment area is mainly underlain by sedimentary and metamorphic rocks, specifically carbonate and siliciclastic rocks and gneisses. The lake water is characterized by a slightly alkaline pH (8.0–8.5) and a low salinity (Wan et al., 2003). This lake serves as the principal water resource of Dali City, and also receives large quantities of industrial wastewater and municipal sewage. Consequently, the lake had been seriously deteriorated since the 1990s, and algal blooms ever occurred in 1996 and 2003. The lake water quality has recently been better in recent ten years, with total P (TP) content of the overlying water ranged from 0.034 mg/L in 2003 to 0.020 mg/L in 2009 (Zhao et al., 2011).

1.2 Sampling and analysis

Three sediment cores from the profundal zone of the Lake were sampled with a gravity corer in June 2009. The cores were sliced into 2 cm segments in the field, and selected layers were analyzed sequentially. Segments from the same cores depth were incorporated and homogenized to obtain a representive sample of sufficient size for extraction. All samples were transported quickly to the laboratory, then were freeze-dried and sieved with a standard 100-mesh sieve for experiments.

Water content was analyzed based on weight loss after drying the sediments at 105°C. Sediment TP and organic P (OP) were determined according to the procedures described by Zhang et al. (2008). Total organic carbon (TOC) and total nitrogen (TN) was analyzed using the elemental analyzer (PE2400-II, Perkin-Elmer Company, USA) after pretreatment in 0.5 mol/L HCl to remove inorganic carbon. Atomic ratios among TOC, TN and OP were calculated on the basis of their concentrations in the sediments. Total concentrations of Fe, Al, Ca and Mn were measured with inductively coupled plasma-optical emission spectroscopy (ICP-OES) followed by digestion with HNO_3-HF-$HClO_4$ (Zheng et al., 2001).

The P fractionation in the sediments was performed using the scheme of Hupfer et al. (1995a), with sequential chemical extraction by NH_4Cl, bicarbonate-dithionite (BD), NaOH, and HCl. These extracts were centrifuged and the supernatants were filtered through a pre-rinsed 0.45 μm membrane. This extraction procedure fractionates sedimentary P into loosely sorbed P (NH_4Cl-P), redox-sensitive P (BD-P), NaOH extracted P (NaOH-P), Ca bound P, and Residual-P. TP in each fraction was determined as soluble reactive P (SRP) after acid-persulphate digestion (Rowland and Haygarth, 1997). SRP in NaOH extracts was analyzed using molybdenum-blue method (Murphy and Riley, 1962). Molybdate-reactive P fraction extracted with NaOH, mainly Al and Fe bound P, is termed as NaOH-rP. The fraction of molybdate-reactive P only after digestion is classified as NaOH-nrP. For all samples, triplicates were analyzed and the data were reported as the average.

The sediment samples for ^{31}P NMR analysis were extracted in 0.5 mol/L NaOH solution for 24 hr at room temperature (Carman et al., 2000). The following procedures were performed (Zhang et al., 2009): Solution ^{31}P NMR spectra were obtained using a JEOL ECX 500 MHz spectrometer (Japan) operating at 202.47 MHz at 25°C, with a 90° observe pulse, a total acquisition time of 5.6 sec and broadband proton decoupling. Spectra were collected with 30000 scans. Spectra were plotted with a line broadening of 10 Hz. Chemical shifts were indirectly referenced to external 85% H_3PO_4 standard (δ = 0 ppm). Peaks were assigned based on data in the literature (Carman et al., 2000; Ahlgren et al., 2005; Zhang et al., 2009). The contributions of individual P groups were calculated

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relative to TP in the extracts from these peak areas.

2 Results and discussion

2.1 Sediment characteristics

The physical-chemical properties of the sediments are presented in **Table 1**. Water content declined from 89% to 68% downward through the core in the upper 10 cm. According to the average sedimentation in Lake Erhai is 0.20 cm/year (Wan et al., 2003), high TP content in the top 2 cm sediments may owed to the P load aggravated with human activities in the catchment area intensified in the last decade. Moreover, OP ranged from 75.1 to 330.0 mg/kg, accounting for 12.4%–33.2% of TP. In addition, the high Al and Fe contents could be attributed to special aquatic environment, such as slightly alkaline pH and high dissolved oxygen (DO) content (Zhao et al., 2011).

As shown in **Table 1**, TOC and TN ranged from 1.65% to 3.02% and from 0.20% to 0.45%, respectively, the C/N ratios were low (7.8–10.1) in the entire core, whereas the C/P ratios varied greatly in the range of 236–635. Commonly, the C/N ratio in lake sediments indicates the relative proportion of the terrestrial and aquatic organic matter. Aquatic plants have C/N atomic ratios of 4–10, whereas terrestrial plants have C/N atomic ratios of > 20 (Meyers et al., 1994). Almost all C/N ratios in the sediments from Lake Erhai are lower than 10, suggesting a higher contribution of autochthonous source for sedimentary organic matter. This result is in agreement with the findings of Kitagawa et al. (2007). In addition, C/P ratios are also often used to trace the degradation of organic matter in the sediments (Stüben et al., 1998). The atomic ratio of C/P for the marine algal protoplasm is typically 106:1, so-called the Redfield ratio. The C/P values are much higher than this ratio with an increasing tendency throughout these sediment cores indicating that OP compounds is preferentially degraded than C in the sediments (Wan et al., 2003).

2.2 Vertical variations of P forms in the sediments profile

The rank order of P fractions were NH_4Cl-P (0.7–5.5 mg/kg) < BD-P (27.6–47.5 mg/kg) < NaOH-nrP (33.1–63.5 mg/kg) < HCl-P (169.3–259.4 mg/kg), residual-P (157.0–299.5 mg/kg) < NaOH-rP (214.8–317.8 mg/kg) (**Fig. 1**). NaOH-rP, residual-P and HCl-P varied similarly with a drastic decrease throughout the sediment profile. The other three P fractions declined gradually with sediment depth.

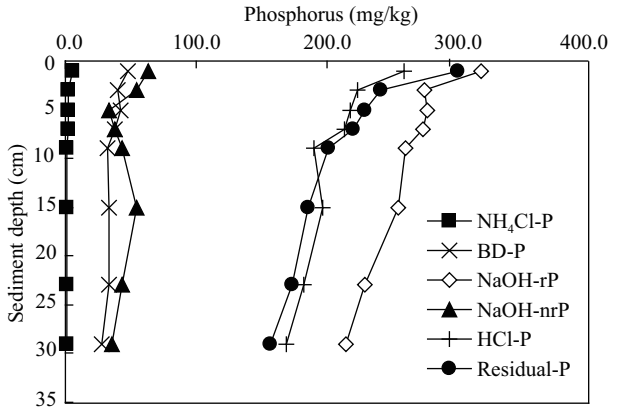


Fig. 1 Vertical profiles of phosphorus fractions in the sediments from Lake Erhai.

NH_4Cl-P represents the loosely sorbed P, which released from $CaCO_3$-associated P or leached P from decaying cells of bacterial biomass in deposited phytodetrital aggregates (Rydin, 2000). This fraction represents < 1% of TP in both sediment segments, agreed with the previous report about Lake Volvi (Kaiserli et al., 2002). The contribution of BD-P to TP are relatively low in comparison to the values reported for other lakes, such as Erken (19%, mesotrophic), Saidenbach (40%, meso-eutrophic) (Kaiserli et al., 2002). This result has been probably associated to high organic matter of the aquatic plant growth in Lake Erhai (Zhang et al., 2008), which might inhibit the formation of BD-P by competitive bonding with Fe (Karthikeyan et al., 2004). Organic matter mineralization also resulted in the changes in redox and pH, thus further affecting the release processes of various P compounds (Wang et al., 2008).

NaOH-rP is considered as potentially mobile pool of P. It is algal available and can be released for the growth of phytoplankton when anoxic conditions prevail at the sediment-water interface (Zhou et al., 2001). The contents of NaOH-rP in surface sediments was positively correlated to DO level, while Lake Erhai is permanent oxic, with DO contents of the water body varied from 6.61 to 7.42

Table 1 Selected physical-chemical properties of lake sediments

Sediment sections	Water content (%)	TP (mg/kg)	OP (mg/kg)	Al (mg/g)	Fe (mg/g)	Ca (mg/g)	Mn (mg/g)	TOC (%)	TN (%)	C/N	C/P
0–2 cm	89	993.3	330.0	80.8	59.3	21.8	1.7	3.02	0.45	7.8	236
2–4 cm	77	836.6	169.9	76.7	47.9	16.8	1.5	2.57	0.37	8.1	390
4–6 cm	71	801.3	113.2	94.6	50.9	20.1	1.6	2.23	0.31	8.4	508
6–8 cm	71	784.0	140.4	95.6	48.5	16.6	1.4	1.95	0.29	7.8	358
8–10 cm	68	728.9	119.6	99.8	49.2	13.8	1.3	1.86	0.23	9.4	401
14–16 cm	65	725.6	129.0	92.9	47.1	11.5	1.2	1.73	0.20	10.1	346
22–24 cm	56	660.4	91.1	67.7	41.7	9.3	1.1	1.65	0.21	9.2	467
28–30 cm	53	604.8	75.1	60.3	38.6	8.1	1.0	1.85	0.24	9.0	635

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mg/L from 1992 to 2009 (Zhao et al., 2011). The HCl-P represents P forms sensitive to low pH, assumed to consist mainly of apatite P. This P fraction is a relatively stable fraction of sedimentary P and contributes to a permanent burial of P in sediments (Wang et al., 2005). The high HCl-P content was attributed to the calcareous terrain. NaOH-nrP mainly comprised OP in detritus, P bound in humic matrix P and poly-P (Hupfer et al., 1995a). These P fractions may become potential sources of available P for aquatic phytoplankton and bacteria. Based on the study of Zhang et al. (2008), it can be concluded that 35.1% of OP in surficial sediment from Lake Erhai is labile fraction.

Significant correlations between P fractions with matrix metals contents of Fe, Al, Ca and Mn are illustrated in **Fig. 2**. Regression analysis revealed that there have significant correlations between BD-P and sum of Fe and Mn, between NaOH-rP and sum of Al and Fe, between HCl-P and Ca. Jensen et al. (1992) observed that BD-P was positively correlated with Fe content in the sediments of Danish lakes. They suggested that the Fe:P ratio is an indicator of phosphate release from the sediments in shallow lakes, and it may be possible to control internal P-loading by keeping the surface sediment oxidized if the Fe:P ratio is above 15 (by weight). The Fe:P ratio of Lake Erhai (57.3–67.5) was much higher than 15, indicating the low BD-P or NaOH-rP release from the sediments. The links between BD-P, NaOH-rp and extracted Fe, Al in the corresponding fractions have been obvious by Kleeberg and Grüneberg (2005).

Mobile P in sediments often can be used to estimate the potential release of sediment P to the overlying water (Rydin, 2000). The various P fractions in the sediments and special ecological environment are two major factors maintaining the good water quality of Lake Erhai. If the pollution of this lake becomes worse and causes the increase in pH and decrease in DO concentration in the overlying water, the release risk of BD-P and NaOH-rP from the sediments will be significantly increased (Zhao et al., 2011). Additionally, the metal content could be another important factor affecting the phosphate sorption/release capacity due to the high specific surface of the Fe/Al (hydro)oxides (Kleeberg and Grüneberg, 2005).

2.3 ^{31}P NMR spectroscopy

As listed in **Table 2**, NaOH extracted TP ranged from 120.9 to 266.6 mg/kg, with recovery ranging from 16% to 33% of TP, and extracted 10.1–138.7 mg/kg OP, accounting for 11%–42% of total OP. These results showed that both inorganic P (IP) and OP were not fully recovered in the sediments by 0.5 mol/L NaOH (Carman et al., 2000). The residual P not extracted by NaOH might be Ca-bound P (He et al., 2007). Meanwhile, this recovery was obvious lower than the extraction of NaOH-EDTA from Lake Erhai (54% of TP, 63% of OP) as described previously (Zhang et al., 2009). These further proved the result of Ahlgren et al. (2007) who stated the combination of NaOH and EDTA

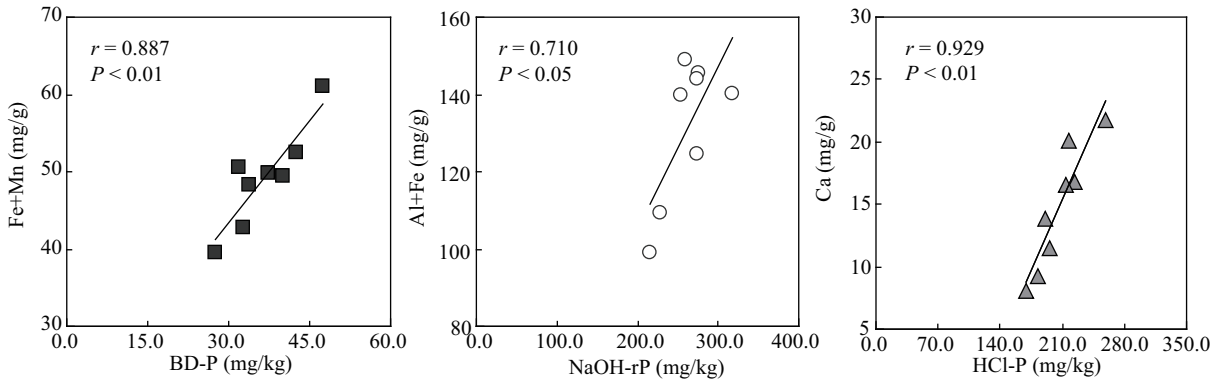


Fig. 2 Correlations between P fractions with matrix metals contents of Fe, Al, Ca and Mn in the sediments from Lake Erhai.

Table 2 Concentrations and relative distributions (in parentheses) of TP, OP and P compounds in NaOH extracts of the sediments from Lake Erhai

Sediment sections	TP in NaOH[a] (mg/kg)	OP in NaOH (mg/kg)	Ortho-P[c] (mg/kg)	Monoester-P (mg/kg)	Phosphonate (mg/kg)	Pyro-P (mg/kg)	Diester-P (mg/kg)
0–2 cm	266.6 (27%)[b]	138.7 (42%)	177.8 (66.7%)[d]	83.8 (31.4%)	1.9 (0.7%)	0.9 (0.3%)	2.3 (0.9%)
2–4 cm	151.0 (18%)	42.9 (25%)	122.5 (81.1%)	27.1 (17.9%)	0.4 (0.3%)	0.4 (0.2%)	0.7 (0.5%)
4–6 cm	130.8 (16%)	27.7 (24%)	107.7 (82.4%)	22.8 (17.4%)	0.3 (0.2%)	n.d.	n.d.
6–8 cm	165.4 (21%)	44.7 (32%)	145.3 (87.8%)	19.6 (11.8%)	0.2 (0.2%)	0.3 (0.2%)	n.d.
8–10 cm	148.3 (20%)	42.5 (36%)	128.5 (86.7%)	19.5 (13.1%)	0.3 (0.2%)	n.d.	n.d.
14–16 cm	152.4 (21%)	28.5 (22%)	132.1 (86.7%)	20.0 (13.1%)	0.3 (0.2%)	n.d.	n.d.
22–24 cm	120.9 (18%)	10.1 (11%)	102.8 (85.0%)	17.8 (14.7%)	0.3 (0.3%)	n.d.	n.d.
28–30 cm	199.1 (33%)	27.9 (37%)	175.2 (88.0%)	23.9 (12.0%)	n.d.	n.d.	n.d.

n.d.: not detected.

[a] detected by colorimetric method; [b] the percentages of NaOH-extracted P for each form; [c] detected by ^{31}P NMR; [d] the percentage of individual P form to total P in NaOH extracts.

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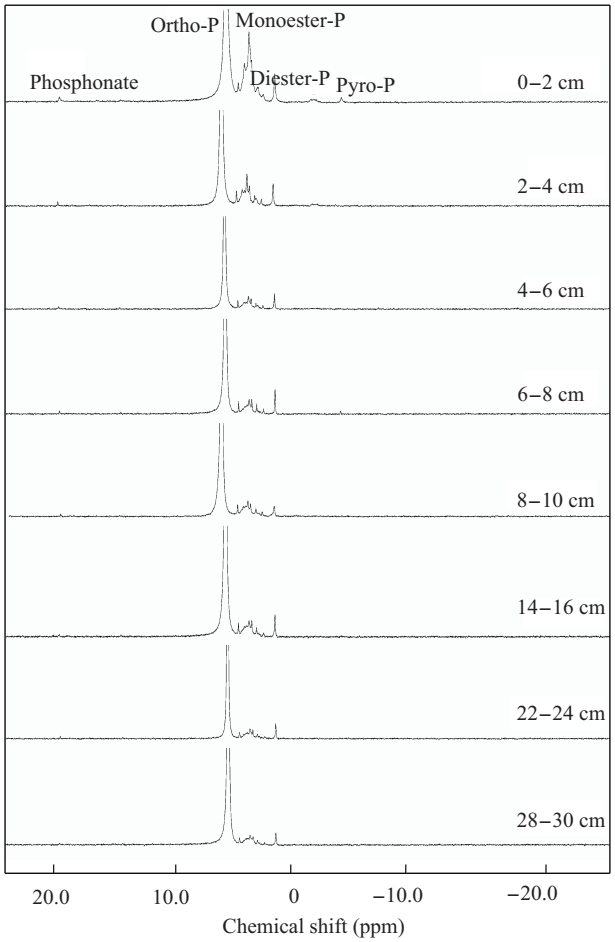


Fig. 3 ^{31}P NMR spectra of NaOH extracts from the sediment profile in Lake Erhai.

can recover more sediment P than NaOH alone. However, it would render the comparison with the fractionation schedule difficult due to some artifacts (Ahlgren et al., 2005).

Five P compounds groups, i.e. ortho-P (6.0–8.0 ppm), pyro-P (–5.0 to –2.5 ppm), monoester-P (3.0–6.0 ppm), diester-P (–1.0 to 2.5 ppm), and phosphonate (17.5–21.0 ppm) were detected in the NMR spectra (**Fig. 3**). Ortho-P and monoester-P were the largest two constituents of the P pool, which almost occupied the total NaOH extracted P (**Table 2**).

The ortho-P vertical profile was S-shaped. The concentration of ortho-P in surface sediments (0–2 cm) was much higher than that in deeper sediments. It is noticeable that the concentrations of ortho-P determined by ^{31}P NMR spectroscopy were consistently greater than those determined by molybdate colorimetry, as the regression model for strong correlation suggested, with an average difference of 15.9 mg/kg (**Fig. 4**). Previous study showed the surface sediment from Lake Erhai contained 75 mg/kg (31% of total OP) of humic substances-bound P (Zhang et al., 2008). Solution ^{31}P NMR analysis reveals the presence of ortho-P in humic and fulvic fractions (He et al., 2006). Therefore, it could be explained that part of P shown as ortho-P in the NMR spectra may denote humic- or fulvic-P (Ahlgren et al., 2005).

Monoester-P made up 11.8%–31.4% of extracted P from the sediment, and declined gradually with increasing sediment depth. Monoester-P represented a wide range of important OP compounds, e.g., sugar phosphates, mononucleotides, phospholipids and phytic acid (Reitzel et al., 2007). Intensive signals at 4.0–5.5 ppm in all extracts might indicate the high concentration of phytic acid (Carman et al., 2000). Phytic acid is considered to be a major component in many types of sediment (De Groot and Golterman, 1993). Using an improved fractionation scheme, Zhang et al. (2008) found that residual OP (mainly comprises phytic acid) occupied 15.1% of TP in surface sediments of Lake Erhai.

Small portion of diester-P was detected only in top 4 cm sediments (**Table 2, Fig. 3**). Diester-P generally consists of DNA-P, P lipids and teichoic-P. OP compounds between 0 and –1 ppm were assigned to DNA-P (Cade-Menun, 2005). DNA-P in sediment originated from bacterial DNA and decomposing phytoplankton, thus it may be used as an indicator of the bacterial quantities in the sediments (Reitzel et al., 2007). Previous studies on the same sampling site showed DNA mainly occurred in the surface sediments (Wei et al., 2004). In our case, the amount of NaOH-extractable diester-P was less than 0.9% of total extracted P and DNA-P was 0.26% of total sedimentary P even in the top sediment. This might reflect that this kind of P was highly degradable. On the other side, DNA-P was also not a major factor in controlling eutrophication from a long-term scale.

Pyro-P may partially originate from esters or poly-P that can be hydrolyzed during alkaline extraction (Hupfer et

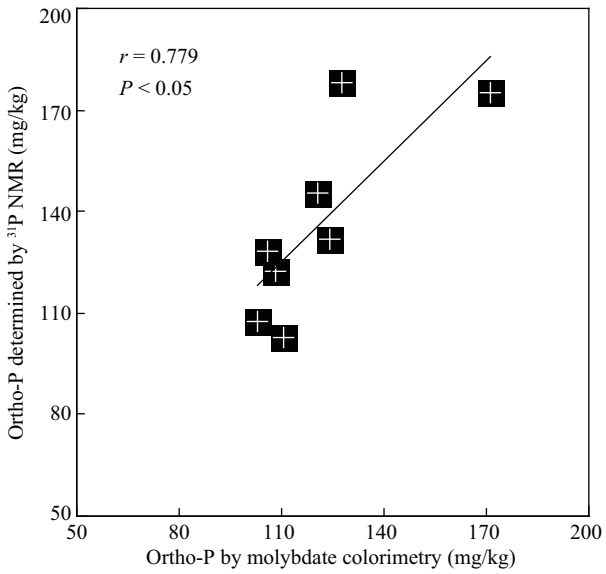


Fig. 4 Relationship between concentrations of ortho-P determined by molybdate colorimetry and solution ^{31}P NMR spectroscopy in NaOH extracts of the sediments from Lake Erhai.

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al., 1995b). Ahlgren et al. (2005) demonstrated that pyro-P was present in the upper 5 cm sediment from Lake Erken. We detected this P groups in our three top sediment samples and the sediment profile decline more rapidly than ortho-P and monoester-P (**Table 2**).

Trace amount of phosphonate was detected and decreased slowly throughout the sediment core. This finding suggested that phosphonates are the chemically stable compounds due to their direct C–P bond (Kittredge and Roberts, 1969). pH may be important to the abundance of phosphonates, because the occurrence of bacteria that possess phosphonatase enzyme seems to be governed by high pH value of Lake Erhai (Wei et al., 2004).

However, NaOH may not extract all of P forms. Due to diagenetic transformation, a part of refractory P becomes hard to extract with the NaOH solution (Reitzel et al., 2007). OP may be converted to apatite without loss of P from the deeper sediment, and Fe-bound P act as an intermediate between OP and apatite P (Ruttenberg and Berner, 1993). Moreover, the percentage of extracted OP decreased with the increase of depth in the sediment, and was significantly correlated with the concentrations of OP and TOC (**Fig. 5**). Thus, the decline in the recovery of OP may reflect release, but also diagenetic transformations resulting in more recalcitrant P compounds not extracted in the deeper sediments. As more than half of sediment P in all the layers were not extracted by NaOH, further identification of their forms could provide more insight about the correlations between the P forms in the sediment profile and diagenetic transformations.

3 Conclusions

The chemical composition of sediment P and its bioavailability are important parameters for predicting future internal loading in lake ecosystems. This study used P fractionation and ^{31}P NMR of NaOH extracts to detect the P forms in the sediments from a meso-eutrophic lake, Lake Erhai, in southwestern China. The TP contents ranged from 604.8 to 993.3 mg/kg. The P fractions in the sediments were in the order of NH_4Cl-P < BD-P < NaOH-nrP < HCl-P, residual-P < NaOH-rP. A comparison of vertical variations of P groups in the sediment profile indicated that these compounds were involved in the P recycling to different extents and diagenetic transformation in this lake. Even though the data presented in this study are limited and cover a relatively small range of sediments of the examined lake, some useful conclusions can be drawn. The highest contents of TP and various NaOH-extractable labile P forms occurred in the surface sediments, which reflected the accelerated P runoff in the relevant catchment area and a potential release from internal P loading in the last decade. Thus this factor should be taken into consideration when a remediation approach is adapted to prevent Lake Erhai from converting to eutrophic condition.

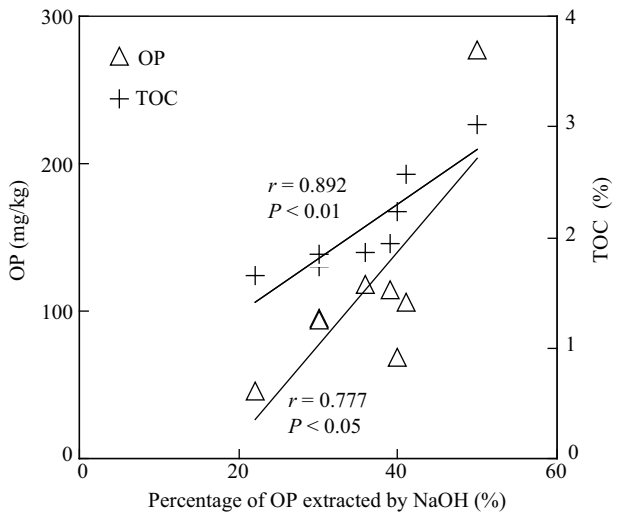


Fig. 5 Relationships between the percentages of OP extracted and the concentrations of TOC and OP.

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