Environmental Science Processes & Impacts

Accepted Manuscript

Occurrence and distribution of phosphorus fractions in sediments of Liangzi Lake with typical hydrodynamic conditions

Hailan Li[a], Shuxin Tu[*,a], Guan Guan[b], Zhijian Xie[a,c], Imtiaz Muhammad[a]

[a].Microelement Research Center, College of Resources and Environment, Huazhong Agricultural University,Wuhan 430070, China

[b].College of Life and Environmental Sciences, Gannan Normal Univ. Ganzhou, China 341000

[c].Institute of Soil & Fertilizer and Resources & Environment, Jiangxi Academy of Agricultural Sciences, Nanchang Jiangxi 330200, China

[*] Corresponding author (stu@mail.hzau.edu.cn)

Abstract

Understanding the transformation and chronological accumulation of phosphorus (P) forms in typical hydrodynamic conditions of lake is important for clarifying the process of lake evolution and eutrophication. The occurrence and distributions of sediment P fractions (total, TP; inorganic, IP; and organic; OP), phytate content, and phytase activity at different profile depths (0–8 m) and parent material ages (0.8–11 ka BP) were examined at different ecological locations (inlet, outlet, and center) of the freshwater Liangzi Lake in Hubei Province, China. Sediment P-forms at locations of different hydrodynamic conditions increased from the inlet to the outlet. IP constituted ~40–71% of TP, whereas the OP content was generally lower in the sediment. The two forms of IP extracted by HCl and NaOH varied quantitatively with depth and location: HCl-P ≈ NaOH-P (above 0.8 m) or HCl-P > NaOH-P (below 0.8 m) at the inlet; HCl-P > NaOH-P (above 0.8 m) and HCl-P ≈ NaOH-P (below 0.8 m) at the outlet; and HCl-P < NaOH-P at the center of the lake. Compared with labile and moderately resistant OP, moderately labile OP exhibited substantial quantitative changes and occurred at high levels. The variation trend in phytate content coincided with that of TP, whereas phytase activity varied inversely with location. Low levels of P forms occurred in the sediment below 4.5

m and before 8.6 ka BP, consistent with the oligotrophic period of the lake. During 2–4 ka BP, the P forms first increased rapidly and then stabilized thereafter. From that time period until modern times, TP and phytate increased, whereas IP and OP decreased significantly. The results indicate that the hydrodynamic conditions of the water bodies and the sediments of different ages strongly influenced the occurrence and distribution of sediment P forms, and the sediment TP and phytate contents would be candidate indices to reflect the P input and eutrophication history of freshwater lakes.

Keywords Dating· Ecological niche · Eutrophication · Freshwater lake · sediment · Phosphorus fraction

1 Introduction

Phosphorus (P) is an essential element that participates in metabolic processes. In the Earth's crust, P is a macro-element with a mean content as high as 1200 mg/kg.[1] The P content is 200–5000 mg/kg in soil,[2,3] 218–1640 mg/kg in the sediments of water bodies, and 2–4% in living organisms.[4] P is the most active element in the environment, and more than 90% of P forms exist and circulate in the soil-plant-animal system.[5]

Total P (TP) in the soil and sediment can be classified into inorganic and organic forms. Common inorganic P (IP) includes ferric [Fe(III)], aluminum (Al), calcium (Ca) phosphates, whereas common organic P (OP) includes nucleic acids, phospholipids, sugar phosphates, condensed-P, and phytate (myo-inositol hexaphosphate). Phytate accounts for ~13–70% of OP, which ranks first among all organic forms of P and is widely present in plants.[6] The phytate molecule contains six phosphate groups (28% P) and therefore exhibits strong acidity and chelation capability.[7] Phytase hydrolyzes phytate to phosphoric acid, inositol, and their derivatives. The conversion of phytate-P is an important mechanism for maintaining P nutrients for plants[8] and producing agricultural non-point pollution.[9,10]

The forms of P in lake sediments are derived from both external water bodies and local parent materials. IP is the main form of P in sediments. Wang et al.[4] demonstrated that IP was the main constituent of TP in lake sediments within the reaches of the Yangtze River using a continuous extraction method. Similarly, Zhang et al.[4] reported that Ca-P was the main constituent of IP while Fe/Al-P and OP were the P fractions most easily released in the surface sediment of the Three-Gorges Reservoir Area, China. Multiple studies have investigated the speciation of organic phosphorus in shallow lakes in China[11,12,13]. Based on an extraction method proposed by Psenner and Pucsko,[14] Ribeiro et al.[7] determined that NaOH-extractable P, including Fe(III)-P and OP, was the main P constituent (>50% of TP) in volcanic lake sediment (Azores–Portugal). Sediments are also an important source of nutrients in shallow lakes[15,16], and blooms (mostly caused by P) stimulate the release of nutrients from the sediment[17]. Many P forms can be transformed into an available from via naturally occurring processes[18] at the water-sediment interface. Therefore, elucidating the transformation and distribution of P fractions in sediments is crucial. The contribution of phosphorus fractions to eutrophication is also important in the evaluation of lakes.

In recent decades, the global population has increased rapidly, and intensified agricultural production has improved continuously. The quantity of P entering the soil and sediment has also continued to increase, leading to a series of ecological and environmental problems.[19] More importantly, increased P input into the agricultural-ecological system can directly result in an increase in the sediment P pool of water bodies, ultimately causing eutrophication. Although P pollution in environment/ecological systems has been studied extensively, studies of the distribution of P forms in lake sediments of different ages and at various profile depths have been rare. The study of different P forms and their quantitative variations in lake sediments has implications for elucidating the formation, structure, evolution, and regulation mechanisms of the ecological system of lakes.

In the present study, the content and forms of P and their variations in sediments of different ages and at various profile depths were studied in the ecological system of Liangzi Lake, Hubei Province, China. We hypothesized that different environmental conditions influence the content and distribution of P forms in lake sediment. To test this hypothesis, we examined the following: (1) the forms, content, and transformation dynamics of sediment P at typical ecological locations of Liangzi Lake; (2) to examine the nature/ or availability of P forms in the sediments of natural lake system; and (3) the chronological features of P accumulation in lake sediments. The results would be helpful to understand and elucidate the occurance and mechanisms of the history of P input and eutrophication of freshwater lakes.

2 Materials and methods

2.1 Study area

Liangzi Lake is located in the southeast of Wuhan, Hubei Province, China (Fig. 1). This freshwater lake has a large water capacity and covers an area of 227.96 km^2 in the dry season and 499.77 km^2 in the wet season. The mean water depth is 2.44 m, and the length of the lake shoreline is 636.5 km. The inflow area is 2,085 km at a constant water level of 1.8 m. The water quality is generally good in Liangzi Lake, with eutrophication in select areas. Large-scale farmlands are present around the lake.

Liangzi Lake is a typical natural freshwater lake that is free from pollution by industrial urban life, but portions of the lake may be influenced by agriculture and aquaculture. Four sampling points were selected to represent three ecological locations and four water quality levels, including the outlet (Sed_{out}), the inlet (Sed_{in}), two centers close to the inlet (Sed_{mid1}, under ecological protection) and a net-cage crab breeding base (Sed_{mid2}, in still water from the base).

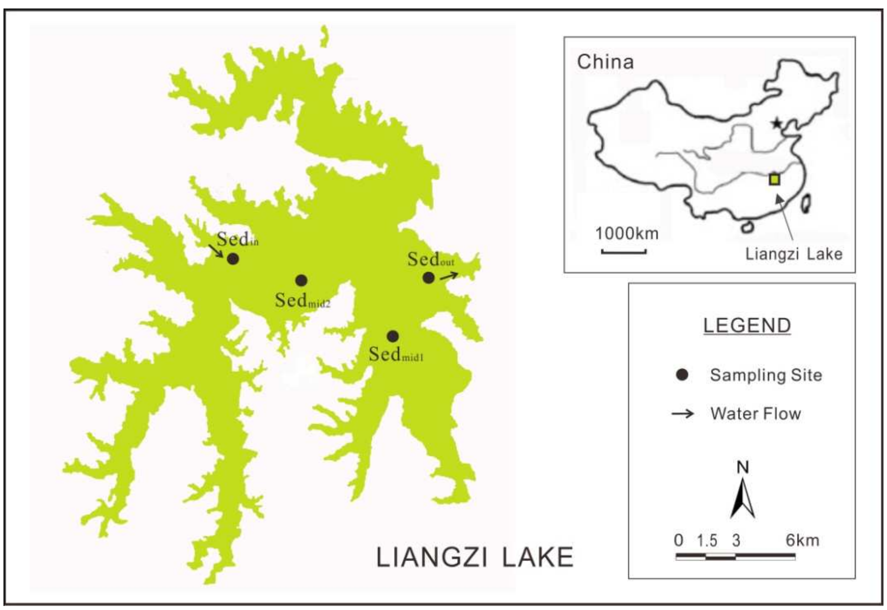

Fig. 1 Distribution of four sampling points in Lake Liangzi. Sed_{in} and Sed_{out} are at the inlet and outlet of the lake, respectively; and Sed_{mid1} and Sed_{mid2} are at the center of the lake, close to the inlet and a crab breeding base, respectively

2.2 Sampling collection

In May 2011, samples were collected from the inlet, outlet, and center of Liangzi Lake at the indicated locations (Table 1). At each location, sediment profiles were collected at depths of 3 m (Sed_{in}), 2 m (Sed_{out}), 4 m (Sed_{mid1}), or 8 m (Sed_{mid2}). Sediment cores with a length of 20 cm (diameter=10 cm) were taken using a drilling platform equipped with a low-speed oil-pressure drilling machine (Type 100, ZhongYin Machine Tool LTD. LingBo, ZheJiang, PRC).

Core samples were placed in individual clean plastic bags; the air was expelled, and the bags were immediately transported to the laboratory. The samples were air-dried, grinded, and passed through a 100-mesh sieve. The sieved samples were sealed in plastic bags and stored at -80°C before analysis.

2.3 Chemical analysis

TP was extracted from sediment using H_2SO_4-$HClO_4$.[20] Two forms of IP were separated using the approach for freshwater sediment developed in the framework of the Standards, Measurements and Testing Program of the European Commission (SMT)[21]: Fe/Al-P (NaOH-P) was successively extracted with 1 mol/L NaOH and 3.5 mol/L HCl; and Ca-P (HCl-P) was successively extracted with 1 mol/L NaOH and 1 mol/L HCl.

OP was fractionated based on the Bowman-Cole method.[22] Briefly, labile OP (LOP) was extracted with 0.5 mol/L $NaHCO_3$ (pH 8.5), and moderately labile OP (MLOP) was extracted with 1 mol/L H_2SO_4. Moderately resistant OP (MROP) was soluble in 0.5 mol/L NaOH without precipitation at pH 1–1.8. The remaining P was defined as highly resistant OP (HROP).

Different P forms, including TP, IP, and OP, were determined using the phosphomolybdate blue colorimetric method.[23]

Phytate was extracted using a mixture of 0.25 mol/L NaOH and 0.05 mol/L EDTA, then determined using a method proposed by Hayes.[24] Sediment phytase activity was determined with the $FeSO_4$-molybdenum blue method.[25]

Tab. 1 The longitude and latitude of typical sampling points of lake and surrounding soil

Samples	Locations	longitude	latitude	sampling depth
LZH4 Sed_{in}	inlet	N30°11′13.2″	E 114°34′19.5″	1.8 m
LZH2 Sed_{out}	outlet	N30°15′47.1″	E 114°35′63.5″	2.0 m
LZH1Sed_{mid1}	Lake center	N30°14'21.8"	E114°27' 56.9"	4 m
LZH3 Sed_{mid2}	Lake center	N30°15′30.8″	E 114°30′04.7″	8.0 m

2.4 Chronological analysis

Sediment chronology was determined by ^{14}C dating with a Xi'an 3MV isotope accelerator mass spectrometer (AMS, HVEE from Holland; Xi'an Accelerator Mass Spectrum Center, Shaanxi, China). The results of the chronological analysis indicated that the age of the sediment in Liangzi Lake was between 0.8 and 11 ^{14}C cal.kyr BP (Table 2).

Tab.2 The dating results of different depths of sediments sampled at Sed_{med2} of Liangzhi Lake

Lab.Code	Sub.Code	Martials	Depth(m)	$\delta^{13}C$（‰）	^{14}Cyr	^{14}C cal. yr BP	（1sigma）
XA8085	LZH3-3	bulk sediment	0.5	-37.54	4763	786	29
XA8054	LZH3-6	bulk sediment	1	-43.38	6250	2414	54
XA8081	LZH3-16	bulk sediment	2	-27.37	7779	4321	54
XA8082	LZH3-26	bulk sediment	3	-28.69	8054	4704	49
XA8083	LZH3-35	bulk sediment	4	-37.11	8624	5478	43
XA8084	LZH3-47	bulk sediment	5	-33.29	9361	6273	46
XA8057	LZH3-67	bulk sediment	6	-28.07	12134	9222	75
XA8086	LZH3-87	bulk sediment	7	-32.92	12787	10012	76
XA8087	LZH3-103	bulk sediment	8	-29.40	13424	10883	77

2.5 Statistical analysis

Data were reviewed for deviations from normality of variance before analysis. SigmaPlot 10.0 (Systat Software Inc., San Jose, CA, USA) was employed for mapping, and SAS 8.0 (SAS Institute Inc., Cary, NC, USA) was adopted for correlation analysis.

Pearson correlation analysis was conducted among sediment TP, NaOH-P, HCl-P, LOP, MLOP, MROP, and phytate contents in addition to phytase activity in relation to different hydrodynamic locations. A *P* value of 0.05 or less was considered to indicate statistical significance.

3. Results

3.1 Content and distribution of TP in sediment

The sediment TP content at the inlet (Sed_{in}) ranged from 34.1 to 128.8 mg/kg, with a mean value of 74.1 mg/kg [coefficient of variation (CV) 47.6%] (Fig. 2); the sediment TP content at the outlet Sed_{out} varied from 53.5 to 457.9 mg/kg, with a mean value of 214.4 mg/kg (CV 54.1%). The TP content of Sed_{out} was 189% higher than that of Sed_{in}, suggesting that P mainly accumulated near the outlet of Liangzi Lake.

The mean values of the sediment TP content at the two centers of the lake (Sed_{mid}) were between those of Sed_{out} and Sed_{in}. However, different environmental conditions significantly affected the TP content of Sed_{mid} in the surface layer (Table 2). Because Sed_{mid2} received water from a crab breeding farm, the sediment TP content was relatively high at the 0–1 m depth, i.e., 60.4–282.4 mg/kg. By contrast, Sed_{mid1} was under completely natural ecological conditions, with 46.6–121.5% lower TP content in the surface layer, i.e., 109.4–127.5 mg/kg.

Relation analysis of the sediment chronology and TP content indicated that the P contents of Sed_{mid} could be divided into three stages along with chronological changes: 1) the primitive P accumulation stage (11–6.3 ka BP), in which the sediment P content substantially increased by 3.6-fold (68.1 to 247.1 mg/kg) over ~5000 years; 2) the P balance stage (6.3–2.4 ka BP), in which the sediment P content moderately varied between 161.8 and 290.2 mg/kg over ~4000 years; and 3) the modern P accumulation stage (2.4 ka BP to modern times), in which the sediment P began to accumulate again and reached an obviously higher value than previously in the history (Fig. 2).

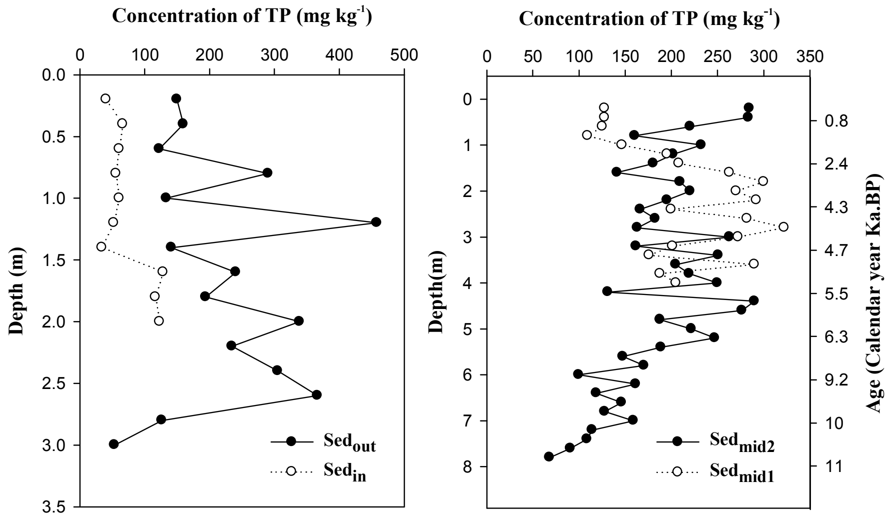

Fig. 2 Distribution of total phosphorous content along sediment profiles in Lake Liangzi. Sed_{in} and Sed_{out} refer to the inlet and outlet, respectively; Sed_{mid1} and Sed_{mid2} stand for two centers of the lake.

3.2 Content, forms, and distribution of IP in sediment

The IP content of Sed_{in} was low (Fig. 3). With respect to different IP forms, the HCl-P content ranged between 5.6–90.1 mg/kg, with a mean value of 24.5 mg/kg (CV 121.3%); the NaOH-P content was 2.8–10.3 mg/kg, with a mean value of 5.3 mg/kg (CV 5.3%). Because HCl-P was higher than NaOH-P (3.6-fold difference between the means), IP in Sed_{in} mainly occurred in the form of Ca-P, notably in the upper layer (0-1 m) of the sediment.

In Sed_{out}, the HCl-P content was 41.2–116.8 mg/kg, with a mean value of 79.9 mg/kg (CV 28.6%); the NaOH-P content was 31.3–162.1 mg/kg, with a mean value of 71.6 mg/kg (CV 57.3%) (Fig. 3). The HCl-P and NaOH-P contents of Sed_{out} were nearly identical. In the surface layer, the NaOH-P (Fe/Al-P) content was substantially increased and was significantly higher than HCl-P (Ca-P) content. These data indicate that the inorganic matter content of Sed_{out} was relatively high, similar to the trend in the TP content. A comparison of different IP forms among the ecological locations revealed that Sed_{out} was 226.1% higher than Sed_{in} in terms of HCl-P content; the former was 1276.9% higher than the latter in terms of NaOH-P content. These results suggested that the accumulation of sediment IP (notably NaOH-P) was mainly concentrated at the outlet of Liangzi Lake.

The content of NaOH-P at the center of the lake was higher than the content of HCl-P in the sediment (Fig. 3). For Sed$_{mid1}$ in the natural state, the HCl-P content varied from 21.8 to 89.4 mg/kg, with a mean value of 43.8 mg/kg (CV 40.5%); the NaOH-P content varied from 39.6 to 138.8 mg/kg, with a mean value of 75.5 mg/kg (CV 31.7%). Because Sed$_{mid2}$ was seriously influenced by the nearby aquaculture, the HCl-P content varied from 8.2 to 93.5 mg/kg, with a mean value of 38.6 mg/kg (CV 39.2%); the NaOH-P varied from 21.6 to 160.8 mg/kg, with a mean value of 67.6 mg/kg (CV 51.7%). In the 0–1-m surface layer, the NaOH-P content of Sed$_{mid1}$ (80.4–138.8 mg/kg) was 110.6–131.1% higher than that of Sed$_{mid2}$ (34.8–65.9 mg/kg).

The accumulation of IP in sediment could be divided into three chronological stages. First, 6000 years ago, sediment NaOH-P and Ca-P contents increased over time. Second, sediment NaOH-P and Ca-P contents entered a balanced state from 6000 to 4000 years ago. However, in the third stage, both NaOH-P and Ca-P contents declined in the profile of the sediment, in contrast to the TP accumulation trend in modern times (Fig. 2).

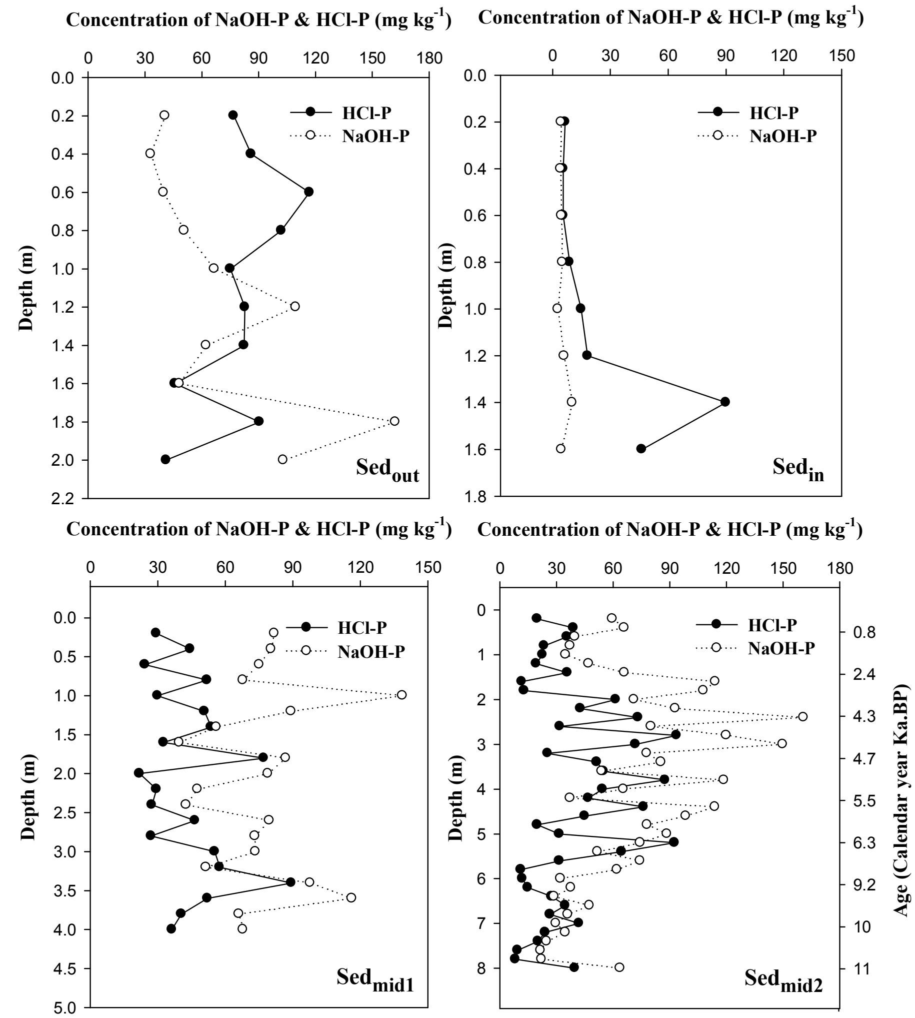

Fig. 3 Distribution of inorganic phosphorus (IP) along sediment profiles in Lake Liangzi. Sed$_{in}$ and Sed$_{out}$ refer to the inlet and outlet, respectively; Sed$_{mid1}$ and Sed$_{mid2}$ stand for two centers of the lake. The IP fraction consists of NaOH-extractable Fe/Al-P (NaOH-P) and HCl-extractable Ca-P (HCl-P). Scale-plates on the right side of the drawings represent the chronology of sediment at the corresponding depth

3.3 Content, forms, and distribution of OP in sediment

Among the OP forms analyzed, the sediment MLOP content was substantially higher than the sediment LOP and MROP contents (Fig. 4). At different locations, the mean LOP, MLOP, and MROP contents of Sed$_{in}$ were 0.9, 10.2, and 3.1 mg/kg, respectively, whereas the mean values of Sed$_{out}$ were consistently higher, i.e., 1.7, 15.8, and 4.1 mg/kg, respectively. The MLOP content indicated substantial changes, primarily at the outlet. A similar distribution pattern of OP forms was observed at the center of the lake. The mean contents of LOP, MLOP, and MROP were 2.2, 27.3, and 2.3 mg/kg, respectively, in Sed_{mid1} and 1.7, 17.3, and 2.2 mg/kg, respectively, in Sed_{mid2}. At both Sed_{mid1} and Sed_{mid2}, the MLOP content was ~10-fold higher than the LOP and MROP contents.

The three OP forms exhibited different relationships with the chronological changes in the sediment (Fig. 4). The trend of variation in the LOP and MROP contents was not significant in the sediment profile. By contrast, the accumulation of MLOP exhibited changes along with chronological changes, similar to IP. However, the corresponding chronologies shifted for MLOP: the accumulation stage was before approximately 9 ka BP; the balanced stage was 9–2 ka BP; and the declining stage started at 2 ka BP and continued to modern times.

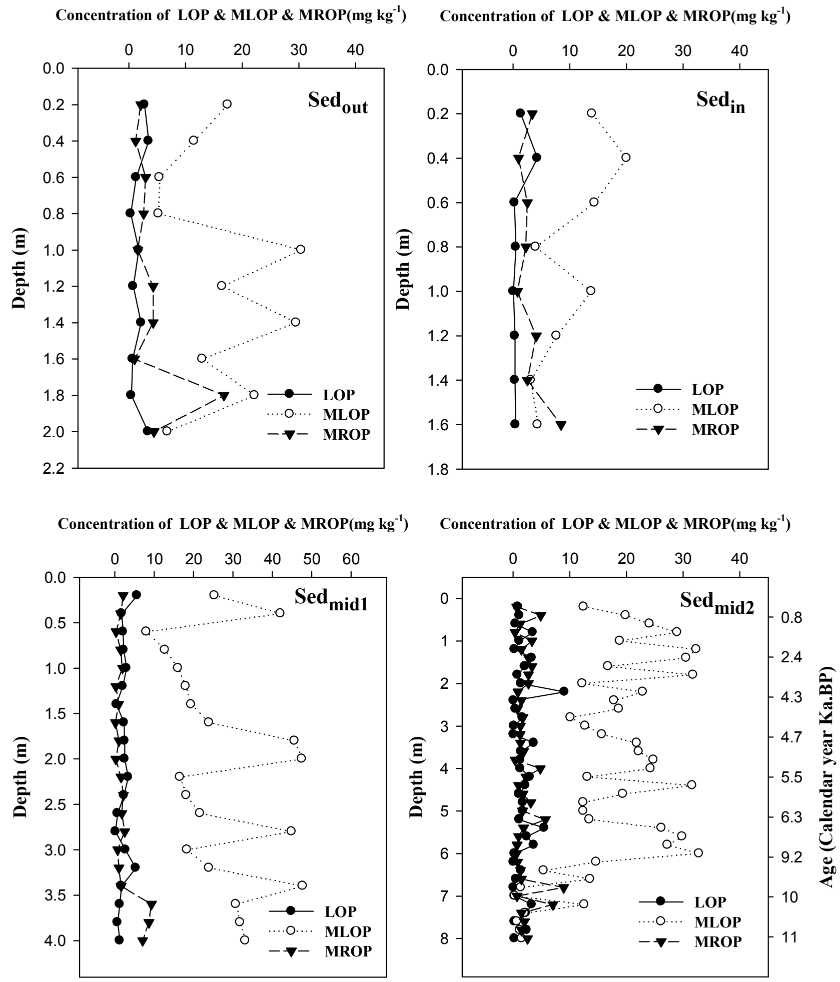

Fig. 4 Distribution of organic phosphorus (OP) along sediment profiles in Lake Liangzi. Sed_{in} and Sed_{out} refer to the inlet and outlet, respectively; Sed_{mid1} and Sed_{mid2} stand for two centers of the lake. LOP stands for labile OP, MLOP represents moderately labile OP, and MROP refers to the moderately resistant OP

3.4 Distribution of the phytate content and phytase activity in sediment

Because of the natural condition of the lake observed, Sed_{out} displayed a significant accumulation of phytate, whereas Sed_{in} was associated with a high accumulation of phytase (Fig. 5). For Sed_{in}, the phytate content varied from 24.1 to 218.1 mg/kg, with a mean value of 93.9 mg/kg (CV 78.8%), and the phytase activity varied from 131.6 to 50.3 U/g, with a mean value of 221.7 U/g (CV 16%). For Sed_{out}, the phytate content varied from 193.3 to 437.1 mg/kg, with a mean value of 345.3 mg/kg (CV 25.3%), and the phytase activity varied from 74.4 to 144.6 U/g, with a mean value of 114.6 U/g (CV 18.2%). A data comparison revealed that the phytate content of Sed_{out} was 267.7% higher than that of Sed_{in}, whereas the phytase activity of the former was 93.4% lower than that of the latter. Thus, a negative correlation was observed between sediment phytase activity and phytate content. In addition, the results suggested that the phytase in sediment was mainly derived from the inlet of the lake.

At the center of the lake, the sediment phytate content and phytate content were intermediate between the values at the inlet and outlet. For Sed_{mid1} in a natural state, the phytate content varied from 24.2 to 169.4 mg/kg, with a mean value of 102.8 mg/kg (CV 49.9%), and the phytase activity varied from 88.9 to 251.4 U/g, with a mean value of 187.9 U/g (CV 28.1%). For Sed_{mid2} influenced by aquaculture, the phytate content increased and varied from 24.1 to 461.9 mg/kg, with a mean value of 164.1 mg/kg (CV 58.4%), and the phytase activity varied from 24.3 to 448.1 U/g, with a mean value of 168.3 U/g (CV 76.6%).

The dynamics of phytate and phytase accumulation in the sediment from different ages and the yearly variations in the sediment phytate content and phytase activity were analyzed, which revealed the following: 1) the sediment phytate content was stable and did not increase with chronological changes before 6.3 ka.BP; and 2) the sediment phytate content increased rapidly at approximately 6.3 ka.BP and significantly increased in modern times, consistent with the variation trend of TP content.

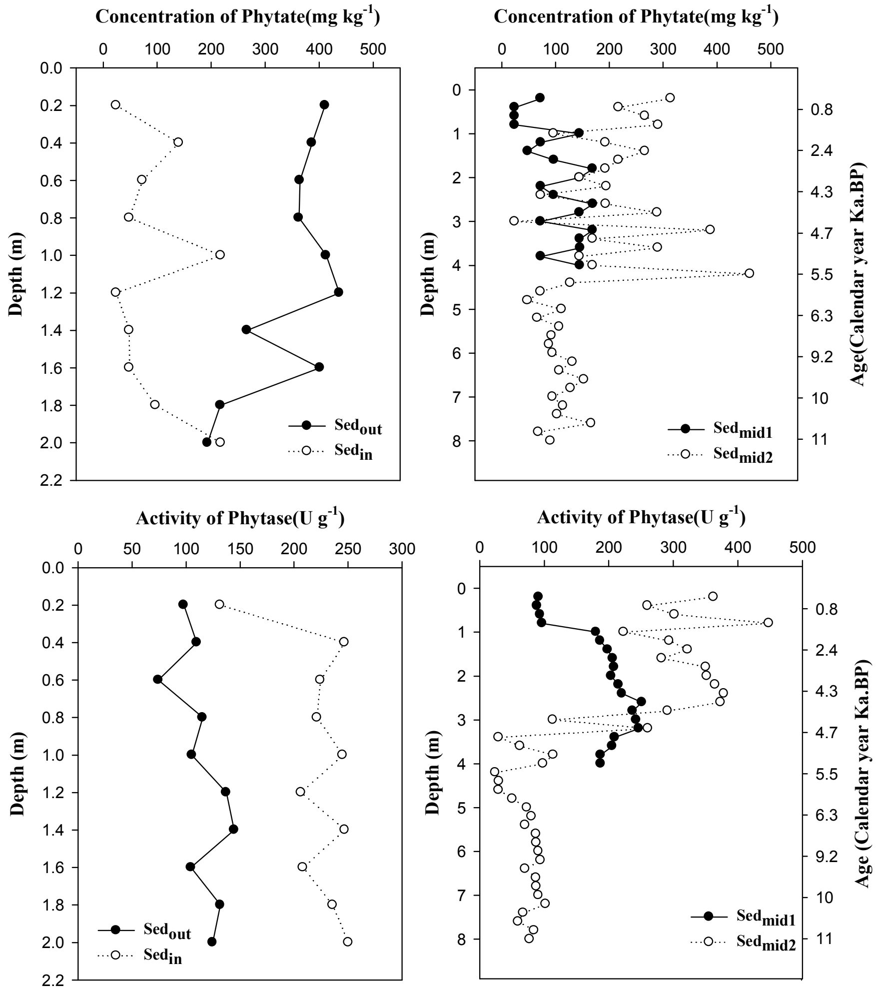

Fig. 5 Distribution of phytate content and phytase activity in sediment profiles in Lake Liangzi. Sed_{in} and Sed_{out} represent the inlet and outlet, respectively; Sed_{mid1} and Sed_{mid2} refer to two centers of the lake. The scale-plates on the right side of the drawings represent the chronology of sediment at the corresponding depth

3.5 Correlations among P forms, phytate content, and phytase activity in sediment

Various P forms were closely correlated in sediment (Table 3). The TP content was positively correlated with the MLOP, MROP, NaOH-P, and HCl-P contents but negatively correlated with the phytate content. Among the three OP forms, the LOP and MROP contents were significantly correlated, whereas the MLOP content varied greatly and was uncorrelated with the other two OP forms. The three OP forms were positively correlated with the TP content, phytate content, phytase activity, and, in particular, IP content (NaOH-P and HCl-P). The contents of IP (NaOH-P and HCl-P) were significantly and positively correlated with each other and with the phytate content, whereas HCl-P content was significantly negatively correlated with phytase activity. The phytase content and phytate activity exhibited significant negative correlations: phytate content decreased significantly as phytase activity increased.

Tab.3 The correlative analysis and test of the TP content, the phytate content, the phytase activity and the contents of different OP and IP forms

	TP	LOP	MLOP	MROP	NaOH-P	HCl-P	Phytate
TP	1.000						
LOP	0.102	1.000					
MLOP	0.254***	-0.046	1.000				
MROP	0.297***	0.291***	-0.006	1.000			
NaOH-P	0.371***	0.126*	0.132*	0.149**	1.000		
HCl-P	0.688***	0.117*	0.308***	0.261***	0.134*	1.000	
Phytate	-0.129*	-0.108*	-0.125*	-0.056	0.146*	-0.059	1.000
Phytase	0.094	0.082*	0.026	0.160**	-0.158	0.151**	-0.114*

Note: data followed by *, **, *** stand for significant difference at $P<0.05$, 0.01, 0.001 respectively.

4 Discussion

In Liangzi Lake, the contents of P fractions, including TP, IP, OP, and phytate, in sediment differed significantly among the different hydrodynamic conditions of water bodies, i.e., $Sed_{out} > Sed_{mid} > Sed_{in}$. The quantitative changes in sediment P forms among the three locations might result from varying flow rates[26] at the inlet and the outlet of Liangzi Lake for the speed of water flow in the inlet was relatively high compared with the outlet. Søndergaard[27] suggested that high P concentrations and high dislocation rates of the weater cause P release in Lake Søbygaard, Denmark. In a study of Lake Apoka, Reddy[28] reported that increases in phosphorus concentrations in the overlaying water were primarily caused by suspension effects, indicating that phosphorus uptake would increase at slower flowrates. Similarly, Søndergarrd[29] observed that the increase in nutrition concentration due to water dynamics was 20–30-fold from the inlet to outlet in Lake Arreso (15 km^2 in area and 2.9 m deep), Denmark. In this experiment, the flow rate at the outlet of Liangzi Lake was relatively slow, consequently enhancing the P accumulation, which might be primarily responsible for the changes in P forms between the Sed_{in} and Sed_{out} sampling points

In addition, at the inlet of the lake, vegetation was sparse, and the associated microbial activities were limited. Therefore, the decomposition and conversion rate of P entering the lake was low, as was the accumulation of P in sediment. By comparison, the flow rates at the centers and outlet were relatively low, whereas associated microbial activities and the vegetation coverage were higher. Thus, the decomposition and conversion rates of P were higher, resulting in massive P accumulation in the sediment. The eutrophication level in lake water is another important influence of P content in sediment, which typically increases with increasing eutrophication.[14] The P content of Sed_{mid2}, which was influenced by crab aquaculture, was higher than that of Sed_{mid1}, which was in a natural state; therefore, Sed_{mid2} exhibited higher P accumulation than Sed_{mid1}.

In the sediment of Liangzi Lake, IP was the main constituent (~40.2–70.6%) of TP. The IP was fractionated into two forms: NaOH-P bound to Al, Fe, and Mn oxides and hydroxides (Fe/Al–P) and HCl-P bound to Ca (Ca-P).[4] Notably, the two IP forms quantitatively varied with the ecological locations of water bodies in Liangzi Lake, i.e., HCl-P ≈ NaOH-P above 0.8 m and HCl-P > NaOH-P below 0.8 m for Sed_{in}; HCl-P > NaOH-P above 1 m and HCl-P ≈ NaOH-P below 1 m for Sed_{out}; and HCl-P < NaOH-P for Sed_{mid}. The quantitative variations in sediment IP forms may be attributable to the effects of parent materials and ecological changes. HCl-P was reported to be the main part of P forms in sediments of mesotrophic lakes in Mexico.[30] Similar results were obtained for most river sediments and polluted lake sediments.[3] In eutrophic lakes, the pH value is generally high, and NaOH-P is exchangeable with OH^- and inorganic P compounds soluble in bases.[31] This NaOH-P fraction can also be released from the growth of phytoplankton when anoxic conditions prevail at the sediment-water interface.[32] Jin[33] observed NaOH-P > HCl-P in sediment from a highly eutrophic region, in contrast to HCl-P > NaOH-P in moderately eutrophic regions. Although the inlet and outlet of Liangzi Lake were associated with no serious eutrophication, the two centers exhibited a tendency of eutrophication due to the influence of crab aquaculture. Therefore, there was NaOH-P > HCl-P at the centers of the lake, our results are correlate with the previous studies that eutrophic lakes contained more IP forms of P.consistent with the distribution of IP forms in highly eutrophic lakes.[33]

OP occurred at lower levels than IP in the sediment of Liangzi Lake. The contents of OP forms at the four sampling points were relatively stable, with MLOP > LOP and MROP. Moreover, the distribution of LOP and MROP did not vary significantly with location or depth, whereas that of MLOP significantly changed across different sampling points and along the sediment profiles. As an active constituent of OP, it can be considered that MLOP was decomposed, utilized, and reduced at the inlet and outlet, regardless of the flow rate (higher flow rates would increase the oxygen content and enhance microbial activities). However, the quantitative variations of MLOP at the center of the lake were intense due to the aquatic vegetation and aquaculture. Meanwhile, the organic matter generated by these factors was accumulated with depth. Consequently, MLOP accumulated in the sediment with increasing depth at the center of the lake.

The variation of the sediment phytate content in Liangzi Lake corresponded to the TP content (Sed_{out} > Sed_{in}) but was opposite that of phytase activity. There were two sources of phytate, the first one might be running water which is entering into the lake from the other sources and the second is the metabolism of plants and activity microorganisms in the lake.[8] Compared with factors at the inlet, relatively slow water flows at the outlet and the center of the lake is the main reason to provide suitable environment/conditions for microorganisms activities, vegetation growth, and for metabolism. Therefore, the phytate content of Sed_{out} was higher than that of Sed_{in}. Similarly, Sed_{mid2} also contained more phytate contents than Sed_{mid1} because microbial activities was higher at earlier than latter age.

In Liangzi Lake, the contents of P forms changed with sediment age in three stages. For example, different P forms exhibited higher accumulation in ancient times before 8 ka BP and entered a balanced stage during 2–4 ka BP; in modern times, IP and OP decreased significantly, whereas TP and phytate increased rapidly. The changes in sediment P contents directly reflect the history of P input and indirectly indicate the eutrophication stages of the lake. Turner et al.[34] demonstrated that the variations in phytate content are relatively stable in the environment and may serve as an index for the history of P input into the lake in ancient environments. In Liangzi Lake, the phytate content and phytase activity in sediments below 4.5 m at the center and before 6.3 ka BP maintained a relatively low, stable level, likely due to a lack of nutrients. The phytate content in sediment increased rapidly approximately 6.3 ka BP and increased significantly in modern times, consistent with the variation of P content. These results suggest that the nutrition accumulation in Liangzi Lake has continued since 6.3 ka BP and that plant growth has contributed to the eutrophication of the lake, particularly the enormous P input in modern times. Further studies are needed to investigate the relationship between phytate content and water eutrophication in the ecological system of Liangzi Lake.

The contents of MROP, LOP, NaOH-P, HCl-P, and phytate exhibited a growth trend during 0–6.3 ka BP. The OP and IP contents also displayed a similar trend of growth during this period. Fang et al.[35] analyzed the composition features of organic matter in the sediment of Liangzi Lake since 8.35 ^{14}Ccal.kyr BP by $\delta^{13}C$ analysis. The resulting $\delta^{13}C$ values were negative before 5.98 ^{14}Ccal.kyr BP in the evolution process of the lake, and organic matter was the main external factor initiating aquatic activities in the lake. The warm and humid climate has continued since the midterm of the long warm period in the brand-new world (5.98–3.67 ^{14}Ccal.kyr BP), when temperature and precipitation reached peak values. A few studies have proposed that the organic Ca isotope is positively correlated with temperature; lake productivity and organic matter content increased in the warm period.[35,36,37] Substantial aquatic plant and organic matter production inevitably results in the elevation of IP and OP contents.

5 Conclusions

In summary, in Liangzi Lake, the occurrence/accumlation and distribution of P forms in the sediments were strongly influenced by the ecological locations with variable hydrodynamic conditions. An increasing trend in sediment P forms and phytate content from the inlet to the outlet of the lake was observed; this trend may reflect the decreasing flow rate. P accumulation exhibited different chronological features in three stages. Accumulation of the P forms experienced an accumulation in ancient times before 8 ka BP and a balanced stage during 2–4 ka BP, followed by rapid increases in TP and phytate but significant decreases in IP and OP until modern times. These quantitative changes in sediment P (notably TP and phytate) reflect the history of P input and the evolution of eutrophication in Liangzi Lake.

Acknowledgements

This research was supported in part by the National Science Foundation (Grant No.41071309; 41471407) and Special Fund for Agro-scientific Research in the Public Interest (201303106). The authors gratefully acknowledge Bo Lan for assistance during study and laboratory work.

Author Contributions

Shuxin Tu conceived and designed the experiments. Guan Guan and Hailan Li contributed materials/analysis tools. Hailan Li and Zhijian Xie performed the data analysis. Hailan Li and Imtiaz Muhammad wrote the manuscript.

References

1. G.M. Filippelli, *British Columbia Ma.r Geol*. 2001, **174**, 307–321
2. Y.J. Arai and D.L. Sparks, *Advances in Agronomy*. 2007, **94**,135–179
3. L. Lijklema, A.A. Koelmans and R. Portielje, *Water Sci. Technol*. 1993, **28(7)**, 1–12

4. S.R. Wang, X.C. Jin, P. Yan, H.C. Zhao, X.N. Zhou and F.C. Wu, *J. Colloid Interface Sci*. 2005, **289**, 339-346

5. P.G. Ozanne, (Khasawneh FE, Sample EC, Kamprath EJ, Eds.). 1980,pp 559–589. Soil Science Society of America, American Society of Agronomy, Crop Science Society of America, Madison. W.I.

6. V. Raboy, *Phytochemistry*. 2003, **64**, 1033–1043

7. N.R. Reddy, M.D. Pierson, S.K. Sathe and D.K. Salunkhe, 1989, p. 152, Boca Raton F.L.: CRC Press.

8. H. Marschner, Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press 2012, 1995, **46**, 1977–1978.

9. B.L. Turner, M.J. Papha, P.M. Haygarth and I.D. McKelvie, *Philosophical Transactions of the Royal Society*. 2002b, London, Series B **357**, 449–469

10. B.L. Turner, A.E. Richardson and E.J. Mullaney, 2007, CAB International, Wallingford.

11. W. Ding, R. Zhu, L. Hou and Q. Wang, Environ Sci Process Impacts, 2014, 16(5), 1135-1144.

12. D. Xu, S.M. Ding, B. Li, X.L. Bai, C.X. Fan, C.S. Zhang, Journal of Environmental Sciences-China, 2013, 25(4), 637-644.

13. S.M. Ding, D. Xu, X.L. Bai, S.C. Yao, C.X. Fan, C.S. Zhang, Journal of Environmental Sciences-China, 2013, 25(5), 925-932.

14. K. Peter, W. Zhu and M. Maessen, *Hydrobiologia*. 2005, **544**, 167–175

15. M.W. Marsden, *Freshwater Biol.*, 1989, **21:**139–162

16. M. Søndergaard, J. Jensen, E. Jeppesen, *Hydrobiologia.* 2003, **506**, 135–145

17. L.Q. Xie, P. Xie, H.J. Tang, *Environ. Pollut*. 2003, **122**, 391–399

18. B. Boström, G. Persson and B. Broberg, *Hydrobiologia* 1988, **170**, 155–155.

19. M.I. Stutter, C.A. Shand, T.S. George, M.S. Blackwell, R. Bol, R.L. MacKay, A.E. Richardson and L.M. Condron,; Turner, B.L. *Environ. Sci. Technol*. 2012, **46**, 1977−1978

20. M. Martin, L. Celi and E. Barberis, *Soil Sci. Plant Anal*. 1999, **30**, 1909–1917.

21. V. Ruban, J.F. Lopez-Sanchez, P. Pardo, G. Rauret, H. Muntau and P. Quevauviller, *Fresenius J. Anal. Chem*. 2001, **370**, 224-228
22. R.A. Bowman and C.V. Cole, *Soil Sci*. 1978, **125**, 95–101
23. J. Murphy and J.P. Riley, *Anal. Chim. Acta*. 1962, **27**, 31–36
24. J. E. Hayes, R. J. Simpson and A. E. Richardson, *Plant Soil*, 2000, **220**, 165–174.
25. J.R. Cooper and H.S. Gowing, *Anal. Biochem*. 1983, **132**, 285–287
26. C. Balachandran, S. Dinakaran and B. Alkananda, *Int. J. Adv. Life Sci*. 2012, **1(1)**, 19–33
27. M. Søndergaard, P. Kristensen and E. Jeppesen, *Denmark. Hydrobiologia*. 1993, **253(1-3)**, 345-356
28. K.R. Reddy, M.M. Fisher and D. Ivaoff, *Journal of Environmental Quality*.1996, **25(9)**, 363–371
29. M. Søndergaard, P. Kristensen and E. Jeppesen, *Denmark. Hydrobiologia*. 1992, **228(6)**, 91-99
30. Q. Zhou, C.E. Gibson and Y. Zhu, *Chemistry*. 2001,**42(2)**, 221–225
31. A. Kleeberg and H.P. Kozerski, *Hydrobiologia*. 1997, **342/343**, 9–26
32. D.S. Ting and A. Appan, *Water Sci. Technol*. 1996, **34(7–8)**, 53–59
33. X. Jin, S. Wang, Y. Pang and F.C. Wu, *Environmental Pollution*. 2006, **139**, 288–295
34. D.C. Ribeiro, G. Martins, R. Nogueira, J.V. Cruz and A.G. Brito, *Chemosphere*. 2008, **70**, 1256–1263
35. F. Jin, J.H. Huang, X.Y. Tang, X.Y. Ruan and S.H. Qi, *Geological Science and Technology Information*. 2007**, 26**, 13–18
36. N. Nakai, *Proceedings of the japan academy*. 1972, **48**, 56-521
37. M. Stuiver, *Quaternary Res*. 1975, **5(2)**, 251-262

Environment Impact

Phosphorus (P) has been recognized as one of the most critical nutrients limiting primary productivity and causing eutrophication in lakes. Transformation and chronological accumulation of P forms in the ecological system plays a vital role in P cycling in lake sediments, which is of great significance to clarify the process of lake evolution and eutrophication.