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THEMATIC ISSUE

Phosphorus distribution and retention in lacustrine wetland sediment cores of Lake Changshou in the Three Gorges Reservoir area

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Abstract Lake Changshou is a eutrophic reservoir of the Longxi River in the Three Gorges Reservoir area. In this study, we sampled the sediment of the lacustrine wetland to determine phosphorous (P) fractions, their distribution, and retention along the water level, with the overall aim to evaluate biogeochemical P migration. Total phosphorus (TP) concentrations in the water-level zone varied from 106.60 to 1178.86 mg/kg, with highest levels in the shallow-water area. With increasing sediment depth, TP levels decreased. The different wetland zones (land area, area with fluctuating water levels, shallow-water area, and deep-water area) were dominated by different P fractions. Based on our results, the hot spot of P accumulation in the littoral zone is the shallow-water area, possibly because of the significant hydrological changes.

Keywords Lacustrine wetlands · Sediment cores · Phosphorus distribution · Phosphorous retention · Three Gorges Reservoir area

Introduction

Phosphorus (P) is an important part of both terrestrial and aquatic biogeochemical cycles and plays a crucial role in structuring ecosystems in riparian buffer zones (Blake et al. 2005). In addition, it is a key factor of eutrophication of aquatic systems and excessive P amounts, which might cause algae outbreaks (Coelho et al. 2004). High P concentrations can be found in zones with fluctuating water levels and changing hydrological conditions, which are common in riparian subzones of eutrophic lakes (Liu et al. 2008; Spears et al. 2012). Riparian subzones have been recognized as hotspots of P retention. As a phosphorus sink and source, the littoral zone plays an important role in internal phosphorus release which can cause long-time algae bloom after external P input. In eutrophic reservoirs and lakes, large amounts of algae accumulate along the shoreline; after the death of the algae, P is released back into the water, causing high nutrient contents (Cao et al. 2016; Mueller and Mitrovic 2015; Vidal et al. 2014). The concentration is estimated to be 50 times higher than the maximum net P addition contribution for phosphorus of water increase in eutrophicated lake with external load diminished (Tarvainen et al. 2002). The P fractions change dramatically in the riparian ecotone due to the frequent water-level fluctuation, and this area is therefore considered to be the most acetified zone in the aquatic system (Andersen and Ring 1999; Reynolds and Davies 2001). Land areas of littoral zones can effectively reduce excessive nutrients, and the sediments in the littoral zones can significantly contribute to improving the P load (Kalff 2002). In eutrophic reservoirs and lakes, excessive algal growth is an indicator for eutrophication, as P accumulated in the algae contributes to the P load of the water after algae die-off (Feng et al. 2014; Vidal et al. 2014).

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Although lake sediments have been recognized as a phosphorus sink and source, studies on biogeochemical P migration and transformation in lacustrine wetlands of reservoirs are still scarce (Liu et al. 2008; Lu et al. 2012; Tingxi et al. 2007). To provide irrigation for agricultural crops, a large number of dams have been established in China, resulting in significant hydrological changes. The large amounts of nutrients from upper rivers mostly accumulate in the reservoirs, leading to considerable eutrophication. Phosphorus transformation mostly occurs in the ecotone, which is the zone with the highest P accumulation (Feng et al. 2014; Mueller and Mitrovic 2015). A large number of studies have shown that the highest P concentrations can be found in the shallow waters of the ecotone, but it is still unclear whether the water reservoir, being subject to large water-level fluctuations, shows a similar trend. The main factor affecting P cycling in freshwater bodies is hydrology; which differs largely between the lake and the littoral zone (Peryer-Fursdon et al. 2015; Yi et al. 2014).

The objective of this study was therefore to investigate P distribution and fractions in each part of the littoral zone in order to assess overall P retention. We aimed at obtaining detailed information about the P cycling processes in the land–water zone. Such information could then be used to develop adequate nutrient management strategies.

Materials and methods

Study area

Lake Changshou is located in the Changshou district of Chongqing, between E 106°49′–108°05′ and N 29°43′–30°53′. It has been established in March 1957 in the lower reach of the Longxi River which was then an important tributary of the Three Gorges Reservoir. The Changshou Lake covers an area of 6667 km^2 and has an average depth of 15 m. Maximum water depth is 40 m, with an average annual flow of 48.9 m^3/s. It is the largest artificial lake in Chongqing and plays an important role in freshwater aquaculture. The area has a subtropical moist climate with an average annual temperature of 17.7 °C. Maximum temperature is 40 °C in August and minimum temperature is −1 °C in January. At the end of the twentieth century and the beginning of the twenty-first century, sewage and industrial wastewater were directly discharged into Longxi Rvier, resulting in significant eutrophication (Guo et al. 2011). Only recently, a number of policies have been launched to control water quality. For example, fertilization in fish farms has been banned and waste water treatment plants have been established. Although water quality has dramatically improved due to these measures, the water environment is extremely sensitive to phosphorus loads.

Sediment sampling

Sediment samples were collected in July 2013 from one sample area which is located in the naturally developed lacustrine wetlands of Changshou Lake without pollution and external water input. We established eight sampling sections along the water level, from deep water to the land area. Due to the high spatial heterogeneity and fluctuating water levels, the lacustrine wetlands could be further divided into four zones: deep-water area (B), shallow-water area (S1, S2), area with water fluctuation (S3, S4, S5), and land area (S6 and S7). Sediment cores (30–40 cm long) were taken from each site using a columnar sediment sampler. Water overlying the sediment surface was carefully siphoned off to minimize disturbance of the sediment. The top 5 cm layer of every core was sectioned immediately on the boat and stored in polyethylene bags. The remaining sediment cores were sliced at 5-cm intervals from top to bottom, packed into plastic bags, frozen, and stored in darkness until analysis.

Analytical methods

Total P content of the sediments was measured by digesting the samples with $HF–HClO_4$ (Liu et al. 2008).The P fractions were determined successively using different solvents and conditions according to the procedure of Fytianos and Kotzakioti (Fytianos and Kotzakioti 2005). We extracted exchangeable P (Ex-P, extracted by 1 M NH_4Cl), iron-associated P (BD-P), calcium-bound P (Ca-P), metal oxide-bound P (NaOH-P), and residual P (Res-P, organic and refractory). The statistical analyses were conducted by parametrical methods. Correlation and regression analyses were performed using SPSS 13.0 and Origin8.0, respectively (Fig. 1).

Results and discussion

As a major nutrient in aquatic ecosystems, phosphorus has been recognized as the most critical nutrient in limiting reservoir productivity. One of the most important factors determining phosphorus concentrations of the reservoir water is phosphorus release from the sediments, with littoral sediments having some of the highest P loads (Liu et al. 2008). Such release may have a significant impact on water quality and may result in continuous eutrophication (Reynolds and Davies 2001; Søndergaard et al. 1996). However, not all phosphorus fractions are easily released from sediments. Therefore, in order to assess internal P loads of reservoir ecosystems, it is necessary to not only gain information about the total phosphorus content, but

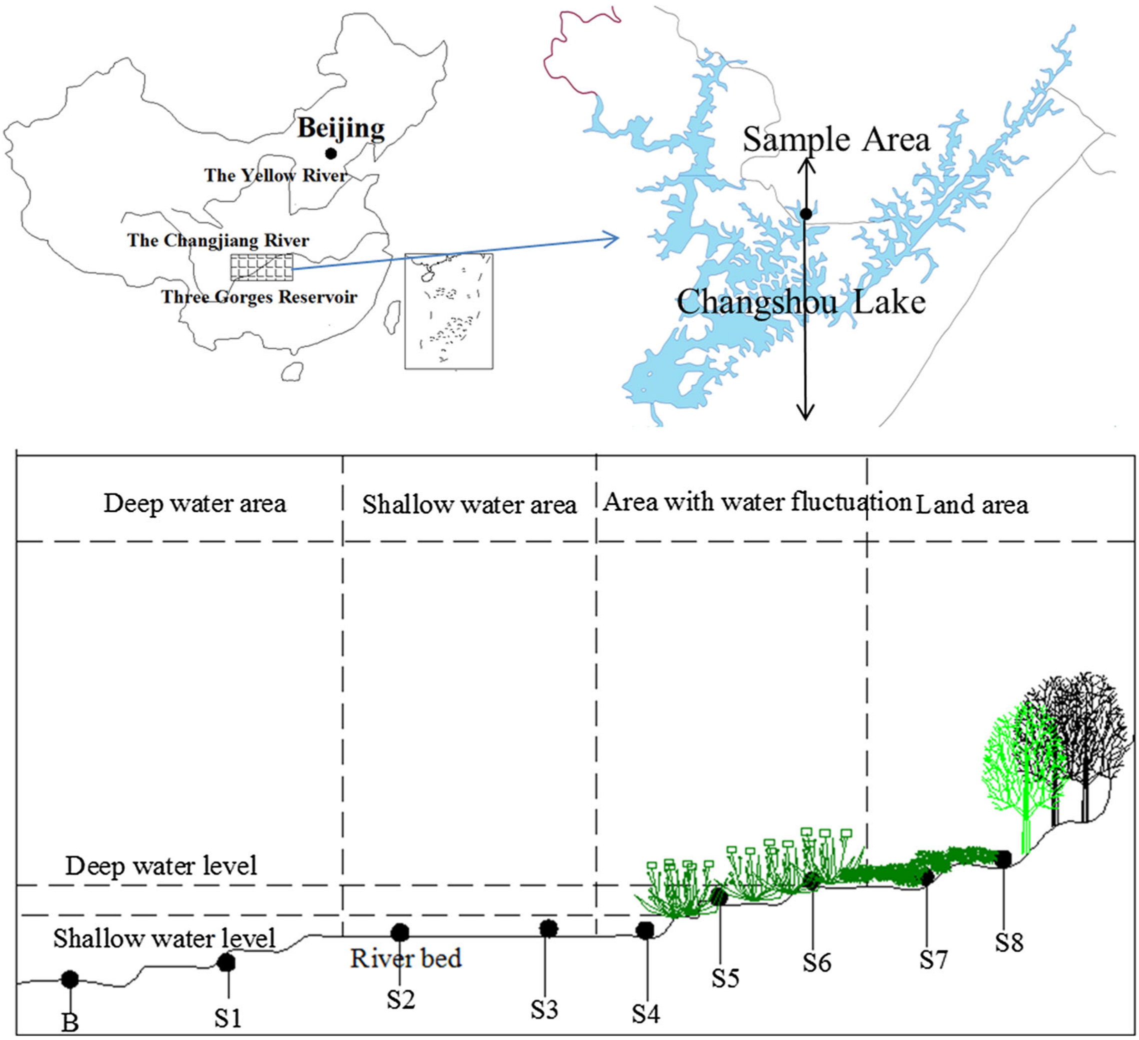

Fig. 1 Sample sites along the water level in the lacustrine wetlands of Lake Changshou

also the concentrations of the different phosphorus fractions. Previous studies have shown that P uptake by biota mainly depends on the specific chemical P forms (Marsden 1989; Tingxi et al. 2007; Zhang et al. 2012a).

Total and fractions of phosphorus distribution

Figure 2 shows the distribution of total phosphorus (TP). The TP concentration in this area varied from 106.60 to 1178.86 mg/kg. The P contents in the deep-water area ranged between 361.65 and 437.08 mg/kg in the 5–20-cm layer. On a horizontal scale, TP concentrations varied drastically between dry land and deep-water areas. The TP values in deep-water area varied between 433.98 and 524.50 mg/kg, with an average concentration of 471.54 mg/kg. In shallow water, P levels reached the highest concentration of 1178.86 mg/kg, with an average of 813.66 mg/kg. In the area with fluctuating water levels, P concentrations decreased and reached an average level of only 242.18 mg/kg, with a range between 145.06 and 564 mg/kg. In the land area, P concentrations range from 106.60 to 608.46 mg/kg, with an average value of 243.83 mg/kg. On a vertical scale, P levels were higher in the surface sediment than at the bottom. However, this trend could not be observed in the deep-water area. In shallow water, P levels were highest in the surface sediment format a depth between 5 and 15 cm and then sharply decrease with depth. The same trend could be observed in sediment of land areas and areas with high water fluctuation. Surface sediment had higher P levels than bottom sediment, and levels were highest in the 0–5-cm layer. Between 10 and 15 cm, P levels sharply decreased, indicating lower P enrichment in these areas.

Based on these results, we assume that the sediment in the littoral zone accumulates P; in contrast, the sediment in the deep-water area showed the lowest P accumulation. Previous studies have indicated that areas with high water fluctuation largely accumulate P (Spears et al. 2006; Zhang

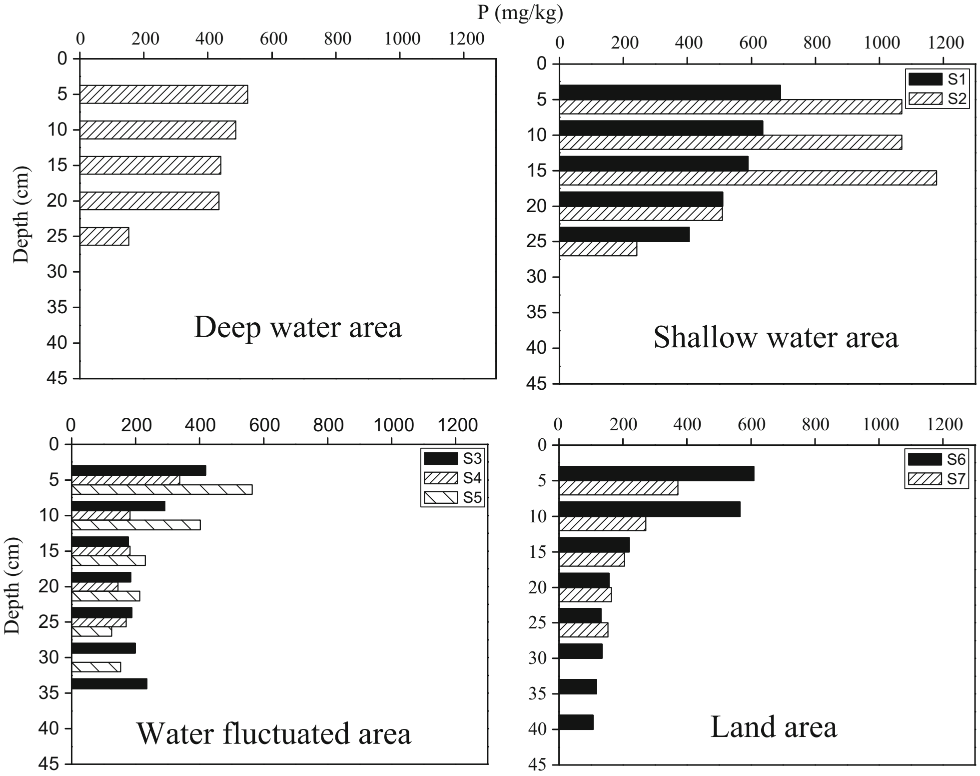

Fig. 2 TP distribution in natural lacustrine wetlands of Lake Changshou

et al. 2012c). In contrast, the sediments of the littoral zone did not show the same behavior as those in the lake. Highest P concentrations were found in shallow-water areas, followed by land areas, deep-water areas, and areas with fluctuating water. The reservoir that got the most obvious difference with lake was its sharply water-level changes to the littoral zone appears to be a water-level-fluctuation zone with water levels controlled by the reservoir. This might be attributed to the hydrological changes in the reservoir, which lead to P accumulation in shallow-water areas rather than in areas with water fluctuation (Furey et al. 2004; Peryer-Fursdon et al. 2015; Watts 2000). Rapid sediment flushes transport P from the areas with water fluctuation to shallow areas where it is then accumulated. Without this hydrological effect, the sediments in the land area would show stable P levels. We therefore assume that the inner P load in the reservoir depends on the P content of the shallow-water zone.

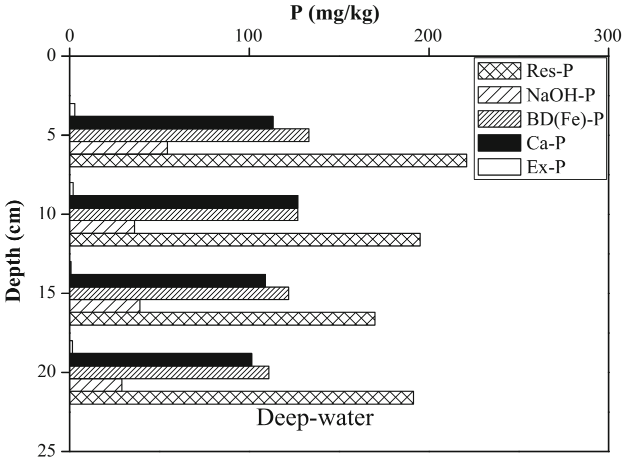

Fig. 3 Distribution of P fractions the deep-water area of Lake Changshou

Figures 3, 4, 5, and 6 and Table 1 show the horizontal distribution of the P fractions in the lacustrine wetlands. The P fractions in the sediments are key factors which determine the mobility and inner load release in water ecosystems (Marsden 1989; Spears et al. 2006). Based on our results, P in the deep-water area was mainly composed of residual P with Ex-P, Ca-P, BD(Fe)-P, NaOH-P, and Res-P ranging from 0.83 to 2.80, 101.23 to 126.97, 110.85 to 133.20, 29.05 to 54.38, and 169.97 to 220.89 mg/kg. Residual P reached nearly 40% of total P in the sediment of the deep water, which indicates P stability. The P accumulated in the residual state indicates the low mobility of P, which results in lower contribution to the P concentration in the water (Spears et al. 2006). The Ca-P and BD(Fe)-P represented 20 and 26% of TP, respectively, indicating that P mobility could be affected by the water–

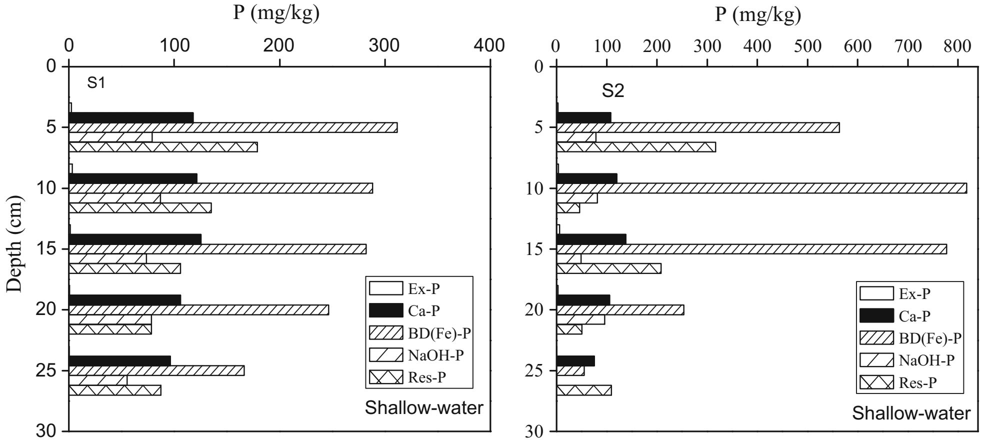

Fig. 4 Distribution of P fractions in the shallow-water area of Lake Changshou

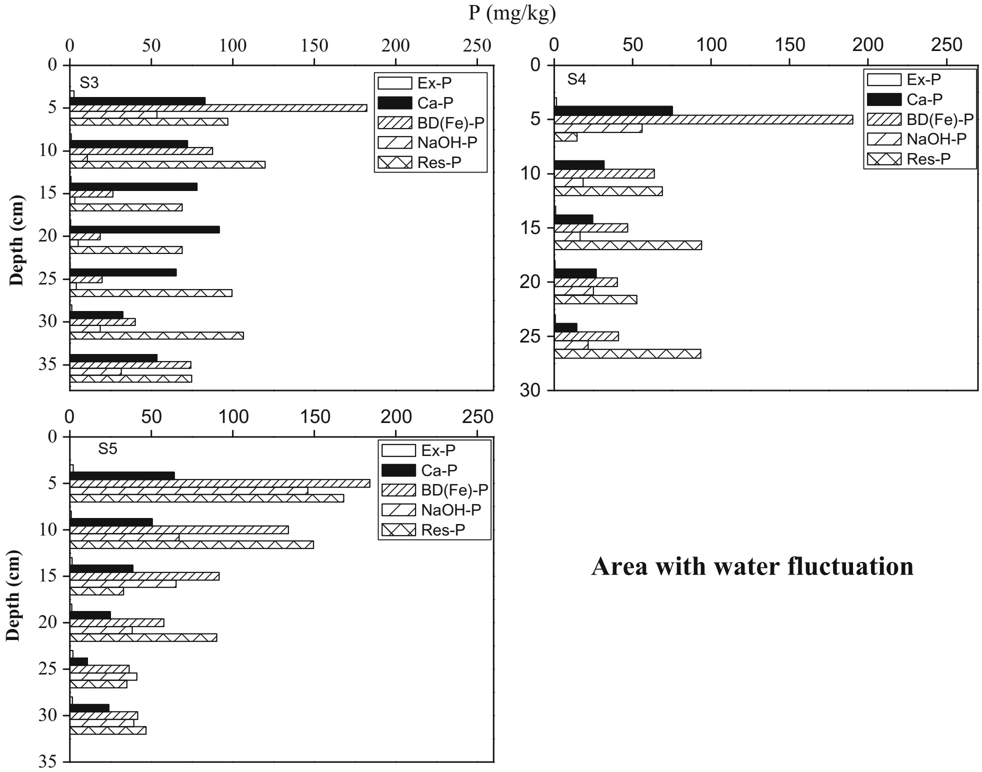

Fig. 5 Distribution of P fractions in the area with fluctuating water levels at Lake Changshou

sediment pH and oxidation–reduction potential (ORP). As it was shown, water of the deep-water area appeared to be alkalescence, which is unsuitable for P release. Due to the high concentration of DO, P binds strongly to iron oxide, which enhances P sink potential rather than P release (Coelho et al. 2004; Rossi and Maciel 2001).

In the shallow-water area, the main P fraction was BD(Fe)-P, which represented over 40% of total phosphorus. The fractions Ex-P, Ca-P, BD(Fe)-P, NaOH-P, and Res-P ranged between 0.29 to 6.23, 75.62 to 138.17, 54.83 to 817.48, 29.05 to 96.01, and 46.38 to 316.65 mg/kg, respectively. The second most represented P fraction was Ca-P, which accounted for nearly 20% of TP. The surface sediment showed the highest concentration of BD(Fe)-P, with depth added to 20 cm, it obviously decrease and Res-P ratio increase. At the same time, the fractions Ca-P and NaOH-P were stable in the sediment core. This indicates that P is first accumulated as BD(Fe)-P, which is easily affected by the physicochemical properties of the water (Wang 2008; Zhang et al. 2012b). When the P from previous accumulation is added, the fractions become stable (Res-P). According to the monitoring data, shallow

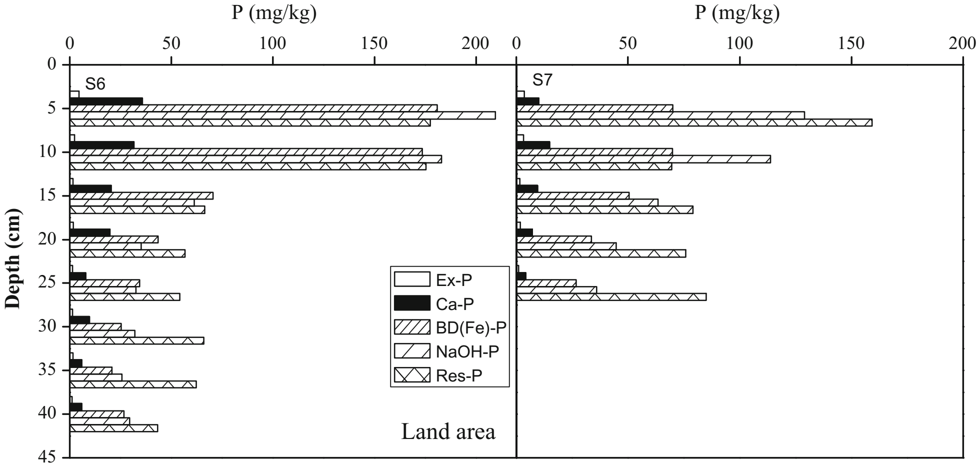

Fig. 6 Distribution of P fractions in the land area of Lake Changshou

water has the highest Chlorophyll A levels and a large in ORP. Phosphorous accumulation might therefore be a result of increased algal growth.

In the areas with water fluctuation, the P fraction ratios were more complex, with Ex-P, Ca-P, BD(Fe)-P, NaOH-P, and Res-P ranging between 0.01 to 2.59, 14.41 to 91.59, 18.61 to 182.29, 2.97 to 145.89, and 33.03 to 168.01 mg/kg, respectively. In the surface sediment (0–5 cm), the dominating fraction was BD(Fe)-P, which accounted for over 40% of TP. With increasing depth, the concentrations of BD(Fe)-P and Res-P converged and in the sediment, Res-P was the dominant fraction, which suggests P inactivation beneath the new sediment. This might be attributed to the dramatic changes of water level in this area. Water-level fluctuation increases ORP values, thereby leading to the reduction of oxidized substances and accelerating P accumulation. Over time, Res-P levels in the surface sediment become stable.

In the land area, the situation was significantly different. The dominating fraction was Res-P, followed by NaOH-P and BD(Fe)-P. The fractions Ex-P, Ca-P, BD(Fe)-P, NaOH-P, and Res-P ranged between 0.93 to 4.58, 4.34 to 64.03, 26.71 to 180.92, 25.64 to 209.58, and 43.20 to 177.58 mg/kg, respectively. The percentage of Res-P stabilized between 30 and 50% of TP, while NaOH-P and BD(Fe)-P accounted for about 25–35%. In terms of P release, it is therefore important to consider metal-bound P in flooded areas. In such areas, higher oxygen and lower water levels stabilize P, which is then more easily bound to metallic oxides. The share of NaOH-P in the land area is therefore higher than in other submerged areas and similar to the one of the nearby soil (Yi et al. 2014).

Generally, the fraction Ex-P increases with decreasing water levels and sediment depth, especially in the littoral zone. With increasing depth, levels of Ex-P increase and reach highest values at 0–15 cm; they then sharply decrease with depth. Calcium-bound P (Ca-P) mainly occurs in shallow-water and deep-water areas, with highest concentrations at medium depths (15–20 cm) of the sediment cores from deep and shallow-water areas, decreasing from the top sediment to the.

Iron-associated P (BD-P) was common across the wetland, especially important in the deep and shallow areas and in areas with water fluctuation. There was a high concentration in the upper 0–10 cm and a sharp decrease with depth. Metal oxide-bound P (NaOH-P) mainly occurred in the land area and the area with water fluctuation, with an obvious decrease with depth. Residual P (Res-P) is usual bound to organic material and mainly appeared in deep-water and land areas, suggesting P stability; it increased with depth.

Previous studies have shown that Ca-P is strongly affected by pH, BD-P strongly correlates with the oxidation–reduction potential in the sediment–water surface, NaOH-P is correlated with Al oxide in the sediment, and Res-P is bound to organic matter (Fytianos and Kotzakioti 2005; Jalali 2010; Jiang et al. 2011; Marie et al. 2014). In submerged sediments, P gets first released into the water, then, with increasing water levels, reaches the main water body. In our study, the sediment of the deep-water area was covered by water with low redox potential. As Fe^{2+} became more soluble in the water, BD-P levels decreased. Given the high concentrations of Ca and algae, increasing pH levels, P can more easily bind to calcium hydroxide and organic matter. With decreasing water levels, dissolved oxygen concentrations in the sediment–water surface increase, with wind and waves which made the Fe became oxidation state and organic matter oxidized, BD-P ratio got obvious increase and the Res-P concentration got decrease (Abdallah 2011; Kaiserli et al. 2002; Søndergaard et al. 1996). Areas with fluctuating water levels showed lowest phosphorus concentrations and highest amounts of Res-P and BD-P, which was associated with redox potential (RP) and pH changes. Total P concentrations decreased after

Table 1 Correltion coefficients among the different P fractions and water parameters across all sampling sites in the surface sediment (0–20 cm) of Lake Changshou

	Ex-P	Ca-P	BD-P	NaOH-P	Res-P	Con	pH	DO	Chl.a	Depth	ORP
5 cm											
Ex-P	1.000	0.674	0.557	0.397	0.701	0.241	−0.297	−0.458	0.218	0.563	−0.336
Ca−P		1.000	0.578	−0.145	0.7	0.525	−0.369	−0.569	0.008	0.914**	−0.837*
BD-P			1.000	0.327	0.747	−0.361	0.213	−0.159	0.711	0.237	−0.204
NaOH-P				1.000	0.369	−0.386	−0.199	−0.374	0.401	−0.231	0.348
Res-P					1.000	0.167	−0.426	−0.634	0.397	0.581	−0.579
Con						1.000	−0.781*	−0.596	−0.705	0.805*	−0.784*
pH							1.000	0.894**	0.485	−0.638	0.643
DO								1.000	0.153	−0.717	0.651
Chl.a									1.000	−0.249	0.352
Depth										1.000	−0.917**
ORP											1.000
10 cm											
Ex-P	1.000	0.846*	0.876**	0.808*	0.017	0.175	−0.285	−0.558	0.281	0.667	−0.647
Ca-P		1.000	0.553	0.509	0.283	0.659	−0.585	−0.674	−0.142	0.926**	−0.921**
BD-P			1.000	0.705	−0.334	−0.246	0.076	−0.263	0.673	0.33	−0.337
NaOH-P				1.000	0.163	−0.064	−0.341	−0.656	0.312	0.356	−0.292
Res-P					1.000	0.62	−0.722	−0.593	−0.428	0.408	−0.187
Con						1.000	−0.781	−0.596	−0.705	0.805*	−0.784*
pH							1.000	0.894**	0.485	−0.638	0.643
DO								1.000	0.153	−0.717	0.651
Chl.a									1.000	−0.249	0.352
Depth										1.000	−0.917**
ORP											1.000
15 cm											
Ex-P	1.000	0.529	0.975**	0.401	0.7	−0.365	0.148	−0.207	0.784*	0.212	−0.202
Ca-P		1.000	0.687	0.328	0.72	0.491	−0.385	−0.483	−0.071	0.804*	−0.881**
BD-P			1.000	0.447	**0.765***	−0.199	0.038	−0.305	0.639	0.378	−0.396
NaOH-P				1.000	0.17	0.097	−0.559	**−0.793***	0.082	0.353	−0.282
Res-P					1.000	0.263	−0.143	−0.404	0.43	0.733	−0.64
Con						1.000	−0.781*	−0.596	−0.705	0.805*	−0.784*
pH							1.000	0.894**	0.485	−0.638	0.643
DO								1.000	0.153	−0.717	0.651
Chl.a									1.000	−0.249	0.352
Depth										1.000	−0.917**
ORP											1.000
20 cm											
Ex-P	1.000	0.314	0.714	0.774*	0.134	−0.078	−0.202	−0.512	0.69	0.424	−0.35
Ca-P		1.000	0.573	0.365	0.232	0.596	−0.312	−0.3	−0.251	0.782*	−0.848*
BD-P			1.000	**0.959****	−0.019	0.129	−0.252	−0.584	0.262	0.641	−0.598
NaOH-P				1.000	−0.177	−0.117	−0.136	−0.514	0.452	0.429	−0.405
Res-P					1.000	**0.814***	**−0.807***	−0.675	−0.37	0.635	−0.477
Con						1.000	−0.781*	−0.596	−0.705	0.805*	−0.784*
pH							1.000	0.894**	0.485	−0.638	0.643
DO								1.000	0.153	−0.717	0.651
Chl.a									1.000	−0.249	0.352
Depth										1.000	−0.917**
ORP											1.000

The bold characters suggest these P fractions and water parameters have significant correlation than others

* Correlation is significant at the 0.05 level (two tailed)

** Correlation is significant at the 0.01 level (two tailed)

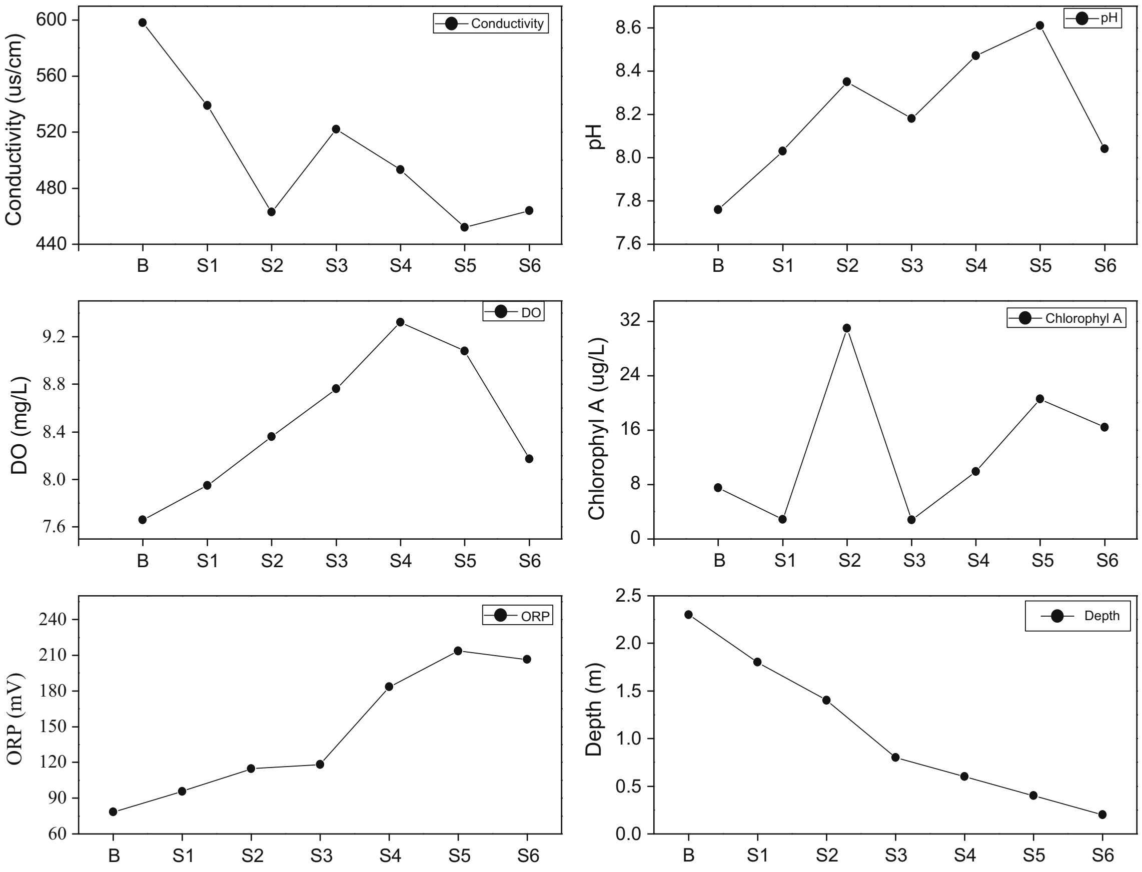

Fig. 7 Water parameters of each site in the littoral zone of the natural lacustrine wetland of Lake Changshou

long-time reaction with active one flushing into the water and inertia ones resented (Liu et al. 2008). Increased levels of NaOH-P in the land area might be correlated with Al oxides, which were considerably decreased in other areas.

Water quality effect analysis

As expected, water parameters were significantly different between the different areas. Highest conductivity values were found in the deep-water area and decreased with decreased water levels. The pH values increased with decreasing water depth, similar to DO and ORP, in the littoral zone. Highest values of Chlorophyll A were found in the shallow water and increased with decreasing water level. The fraction Ex-P was significantly correlated with Ca-P, BD-P, and NaOH-P at a depth of 10 cm. The level of Chlorophyll A obviously affected Ex-P levels at 15 cm, while NaOH-P determined the concentration of Ex-Pin 20 cm. Levels of Ca-P were significantly affected by water depth and ORP in the water column; BD-P was significantly affected by Res-P in 15 cm and by NaOH-P in 20 cm. There was a strong relationship between NaOH-P and DO at a depth of 15 cm and the fraction Res-P was significantly correlated with conductivity and pH levels in 20 cm. Concentrations of Ex-P were determined by other fractions in different depths (Fig. 7).

Conclusions

In natural littoral lacustrine wetlands, phosphorus is most highly concentrated in shallow-water areas which are influenced by sediment erosion and algal growth. Total P levels decrease with increasing sediment depth, with highest concentrations in the 15–20-cm layer, indicating P accumulation.

Based on our results, the hotspot of P accumulation in the littoral zone is the shallow-water area, possibly because of the significant hydrological changes. In the deep-water area, the dominating P fraction is Res-P, while shallow-water areas are dominated by the fraction BD(Fe)-P. In areas with high water fluctuation, P dynamics are relatively complex and differ between sediment depths. In contrast, P dynamics in the land area are relatively stable, and total P is dominated by Res-P.

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