DOI: 10.1007/s11430-006-8107-7

Spatiotemporal variations of internal P-loading and the related mechanisms in the large shallow Lake Chaohu

ZHANG Min, XIE Ping, XU Jun, LIU Bingqin & YANG Hong

Donghu Ecosystem Experimental Station of Lake Ecosystems, State Key Laboratory of Freshwater Ecology and Biotechnology of China, Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, China
Correspondence should be addressed to Xie Ping (email: xieping@ihb.ac.cn)

Received September 16, 2005; accepted February 6, 2006

Abstract Spatiotemporal variations of P species and adsorption behavior in water column, interstitial water, and sediments were investigated in the large shallow eutrophic Lake Chaohu. Orthophosphate (Ortho-P) and total phosphorus (TP) concentrations were significantly higher in the western part than in the eastern part of the lake, due to different nutrient inputs from the surrounding rivers. Moreover, particulate phosphorus (PP) concentration was in a similar spatial pattern to Ortho-P and TP concentrations, and also showed significantly positive correlation with the biomass of *Microcystis*, indicating more uptake and store of phosphorus by *Microcystis* than by other algae. Increase of pH and intensive utilization of P by phytoplankton were the main factors promoting P (especially Fe-P) release from the sediment to interstitial water during the cyanobacterial blooms in Lake Chaohu. Spatial dynamics in TP concentration, P species and adsorption behavior of the sediment, coupled with the statistical analyses, suggested that the spatial heterogeneity of P contents in the sediment was influenced by various factors, *e.g.* human activities, soil geochemistry and mineral composition. In spite of similar TP contents in the sediments, increase in proportion of Fe-P concentration in the sediment may result in a high risk of P release.

Keywords: eutrophication, water column, sediment, phosphorus, species, sorption and release, Lake Chaohu, cyanobacterial blooms.

Dense blooms of phytoplankton, especially cyanobacteria, often occur in the hypereutrophic lakes. Outbreak of cyanobacterial blooms is one of the most important symptoms of eutrophic inland waters. P is considered to be the main factor inducing the nuisance growth of cyanobacteria. Cyanobacterial blooms in eutrophic lakes[1−3] are often coincident with the increase of P in the water column[4−6]. Song *et al.*[7] investigated the relationship between algal blooms and phosphorus status of sediment in ponds, and found that compared with the ponds lacking *Microcystis aeruginosa* the ponds with *Microcystis aeruginosa* blooms showed relatively high concentrations of Ortho-P in the overlying water or different P species in the interstitial water. However, studies on the influence of phytoplankton on P dynamics are very limited. Wang *et al.*[8] studied the effects of the variations of environmental conditions on phosphorus release from the sediments in Lake Taihu, and found a significant increase of P release when both algae and sediment were present in the experiment. Anderson[9] suggested that increased P release from the sediment in summer time might be due to high pH (up to 10.5) caused by active phytoplankton photosynthesis in six shallow Danish lakes. Under laboratory conditions, Seitzinger[10] studied the influence of pH on P release from the sediments sampled from the freshwater tidal portion of the Potomac estuary, and found that the release rate increased markedly when pH of the overlying water was 9.5－10. Xie *et al.*[11] found the different responses of N and P in the sediment to the cyanobacterial blooms in an enclosure experiment conducted in Lake Donghu in the summer of 2000, and they conducted that *Microcystis* blooms selectively induced massive release of P from the sediment.

Although external loading was reduced during the restoration of eutrophic lakes, increase of P concentration in the water column was still observed in summer, which is caused by the potentially mobile P release from sediment pools to lake water. Internal P-loading is the main reason of lake eutrophication after reducing the external loading[13]. Mechanisms of P release are different under different conditions[14]. It is generally believed that aerobic condition promotes P uptake by the sediment, while anaerobic condition is conducive to P release from the sediment[15]. Ortho-P is often bound to clay mineral, iron/aluminum oxide and calcium carbonate in the sediment, among which iron/aluminum oxide has the strongest ability of binding PO_4-P[16]. Different P species usually function differently. Loosely sorbed organic and inorganic fractions as well as the iron-bound and redox-sensitive P are considered potentially mobile, probably contributing to an internal release[17−21]. Zhu *et al.*[22] studied fractionation of sediment phosphorus and their relations to phosphorus concentrations in the water column of shallow lakes in the middle and lower reaches of the Yangtze River, and found that bioavailable phosphorus only accounted for less than 10% of total phosphorus in the sediments of all lakes with the exception of two heavily polluted lakes. Concentrations of TP and TDP in the lake water were also significantly correlated to the exchangeable P concentration and the ratio of iron to phosphorus in the sediment. Therefore, understanding of P forms in the sediments may be important not only for evaluating precisely the potential of P release from the sediment but also for predicting the possible future influences of sediment P on P dynamics in the lake water[23,24].

The sorption of P by the sediments is mainly affected by the properties of sediment (grain size, and chemical and mineral compositions) and pH of the lake water. Fu (2000)1) found that finer sediment exhibited greater phosphorus sorption index (PSI) in Lake Donghu, and that PSI increased with increasing pH and the maximum occurred about pH5.8 where the adsorption capacity was the largest. Meanwhile, organic molecules can form complexes with metal ions such as iron (Fe) and aluminum (Al), which in turn can sorb phosphorus and reduce its bioavailability[25]. Lopez *et al.*[26] suggested that the concentrations of organic carbon and calcium carbonate could influence the absorption of PO_4-P. Adsorption capacities of tidal flat surface sediments from the Yangtze Estuary showed significantly positive correlation with Fe^{3+} and total organic carbon (TOC) concentration, and the adsorption efficiency of phosphate was mainly affected by TOC concentration. Moreover, environmental factors (*e.g.* temperature, pH and salinity) also exerted significant influences on phosphate adsorption by the sediment[27]. Zhang *et al.*[28] studied the characteristics of phosphorus sorption by surface sediments in three shallow lakes in the Yangtze River Basin, and it is suggested that the P sorption capacities were closely related to the specific surface area, and the concentrations of iron/aluminum hydroxides and organic matter.

Previous studies on the effects of cyanobacteria on internal P-loading are limited to enclosures[11] and small lakes[29], but the possible effects of P species in the sediment are not concerned. In this paper, we studied the P concentration and species in the water column, interstitial water, and surface sediment collected from six sites in Lake Chaohu, one of the five largest freshwater lakes in China. The primary purposes were to evaluate the effects of cyanobacterial bloom on the internal P release, and to describe spatial variation of P in the sediments with discussion on the possible mechanisms underlying these variations.

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1) Fu Yongqing. The forms, behavior and ecological significance of phosphorus in sediments of Lake Donghu, Master Thesis of Institute of Hydrobiology, Chinese Academy of Sciences, 2000.

1 Materials and methods

1.1 Study lake

Lake Chaohu is located in the center of Anhui Province, between 117º16′E and 117º5′E longitude and between 31º25′N and 31º43′N latitude. It has a mean surface area of 770 km^2, a mean depth of 2.7 m and a storage capability of 2.1 billion m^3[30]. The lake is extensively used as water sources for drinking, irrigation, and fisheries. In recent decades, the lake has undergone serious eutrophication with the increase of population and development of economy in its catchments.

1.2 Sampling

Sampling was conducted monthly at six sites (Fig. 1) from October 2002 to September 2003. Water samples were collected from the surface (0 m) and overlying water (0.5 m above the surface sediment). Sites I, II and III are located in the western area, but Site IV in the central area and Sites V and VI in the eastern area. Surface sediments (10 cm) were obtained using a hand-driven stainless steel corer (internal diameter of 3.9 cm). 21 cores were collected at each site, and then grouped randomly into three parts (each part contained seven cores) and mixed thoroughly.

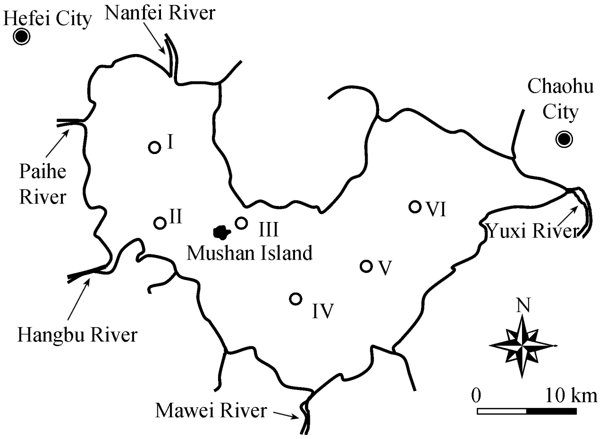

Fig. 1. Locations of sampling sites in Lake Chaohu.

1.3 Sample preparation

Interstitial water was separated from the sediment particles by centrifugation at 3000 rpm for 30 min[31]. Sediment samples were treated by passing through 2-mm mesh sieve, and then air-dried to constant weight and sieved through a 0.5-mm mesh.

1.4 Chemical analysis

Orthophosphate (Ortho-P) was measured using Murphy and Riley procedure[32]. Total phosphorus (TP) and total dissolved phosphorus (TDP) were digested with potassium persulfate and measured by molybdenum blue colorimetric method[32]. Particulate phosphorus (PP) concentration was difference between TP and TDP concentrations. TP in the sediment was measured by H_2SO_4-$HClO_4$ digestion-molybdenum blue colorimetric method[33]. P fractionation was carried out according to an improved method[33], which divided sediment P into aluminum-bound phosphate (Al-P), iron-bound phosphate (Fe-P), occluded phosphate (O-P) and calcium-bound phosphate (Ca-P). Phosphorus sorption index (PSI) was determined using the method described by Sallade and Sims[34]. Iron (Fe) and Aluminum (Al) concentration in the sediment was measured by VARIAN CCD Simultaneous ICP-OES, and Calcium (Ca) was measured by AAS method[33]. Grain size was determined using the method described by Hua and Wang[35].

Statistical analysis was conducted using Statistica 6.0.

2 Results

2.1 Seasonal variations of water depth, Chl.a and pH

Seasonal variation of the mean water depth in the six sampling sites of Lake Chaohu was shown in Fig 2(a). The maximum (5.7 m) was observed in July 2003 because of heavy rainfall. Chl-a concentrations in the water column ranged between 9.4 and 47.9 μg L^{-1} with the maximum observed in June (Fig. 2(b)). pH values of the lake water was higher in summer than in other seasons with the maximum (pH = 9.1) in June (Fig. 2(c)).

2.2 Patterns of temporal and spatial variations of phosphorus concentration in lake and interstitial water

TP and Ortho-P concentrations in the water column were the averages of surface and overlying water.

Seasonal variations of TP (Fig. 3(a)) and Ortho-P (Fig. 3(b)) concentrations of the lake water were not obvious during this study with the range between 0.002 and 0.046 mg L^{-1} and between 0.094 and 0.186 mg L^{-1}, respectively. TP (Fig. 3(c)) and Ortho-P (Fig. 3(d)) concentrations of interstitial water increased significantly in the summer with the maximums in August. The ranges of Ortho-P and TP concentrations in the interstitial water were 0.003—0.094 mg L^{-1} and 0.091—0.424 mg L^{-1}, respectively. Annual average values of Ortho-P and TP concentrations of interstitial water were two times higher than those of the lake water. In August, TP concentrations of the interstitial water were four times higher than those of the lake water.

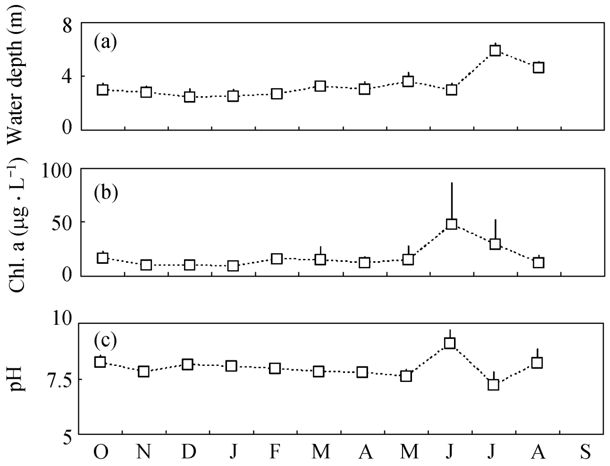

Fig. 2. Seasonal variations of water depth (a), Chl.a (b) and pH (c) in the lake water from Lake Chaohu (n=6, cited from Deng, 2004[1]).

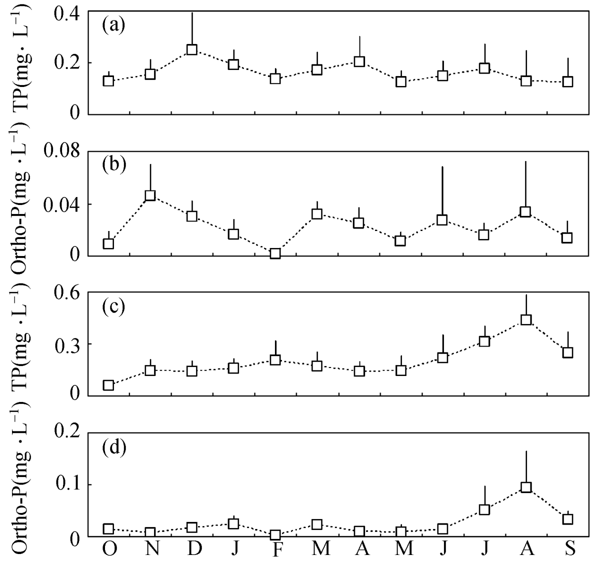

Fig. 3. Seasonal variations of Ortho-P and TP in the lake and interstitial water in Lake Chaohu (n = 6). (a) TP concentration in the lake water, (b) Ortho-P concentration in the lake water, (c) TP concentration in the interstitial water, (d) Ortho-P concentration in the interstitial water.

Spatially, TP concentrations of the lake (Fig. 4(a)) and interstitial (Fig. 4(b)) water were significantly higher in the western than in the eastern part, with the maximum at Station I. The PP concentrations of the lake water showed a similar spatial pattern (Fig. 4(c)). PP concentrations were significantly correlated with the biomass of *Microcystis* (n = 70, r = 0.27, p < 0.01), while the relationship between PP concentrations and biomass of *Anabaena* was not significant (n = 70, r = 0.16, p = 0.09, Fig. 5).

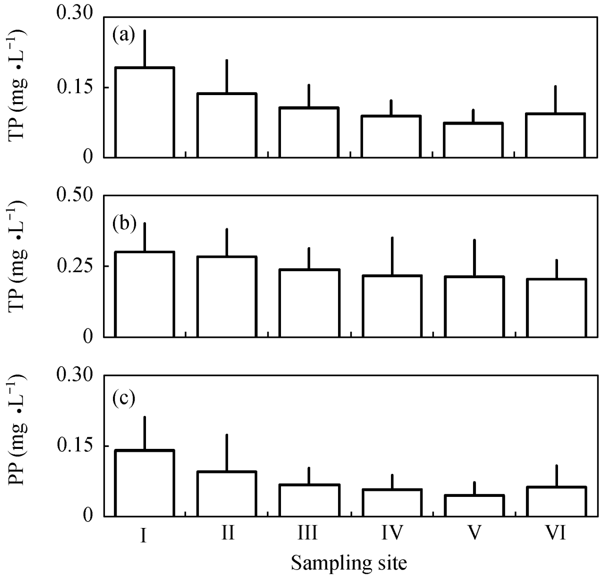

Fig. 4. Spatial variations of TP and PP in the lake and pore water in Lake Chaohu (n=12). (a) TP concentration in the lake water, (b) TP concentration in the pore water, (c) PP concentration in the lake water.

2.3 Spatial variations of TP, Al, Fe, and Ca concentrations, percentage of clay, and PSI in the sediments

TP concentrations of the sediments at Stations I and VI were 482.1 μg g^{-1} and 488.4 μg g^{-1}, respectively, significantly higher than those at the other four stations (Fig. 6(a)). TP concentration of the sediments at Station IV was the minimum. Al (Fig. 6(d)), Fe (Fig. 6(e)) concentrations, percentage of clay (Fig. 6(c)), and PSI (Fig. 6(b)) were significantly higher at Sites I

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[1] Deng Daogui, Ecological studies on the effects of eutrophication on plankton communities in a large shallow lake, Lake Chaohu, Doctoral Thesis of Institute of Hydrobiology, Chinese Academy of Sciences, 2004.

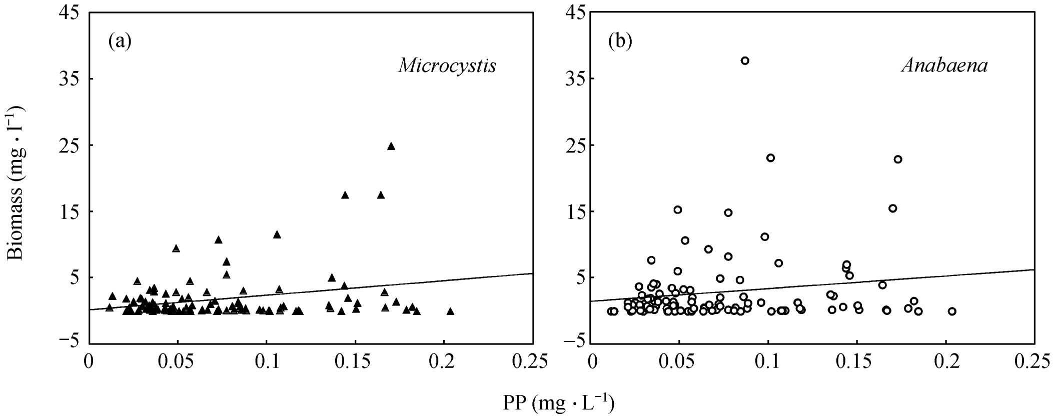

Fig. 5. Relationship between PP concentrations in lake water and biomass of *Microcystis* and *Anabaena* (PP: *Microcystis*, $n = 70$, $r = 0.29$, $p < 0.01$, PP: *Anabaena*, $n = 70$, $r = 0.16$, $p = 0.09$, biomass of *Microcystis* and *Anabaena* was cited from Deng, 2004[1]).

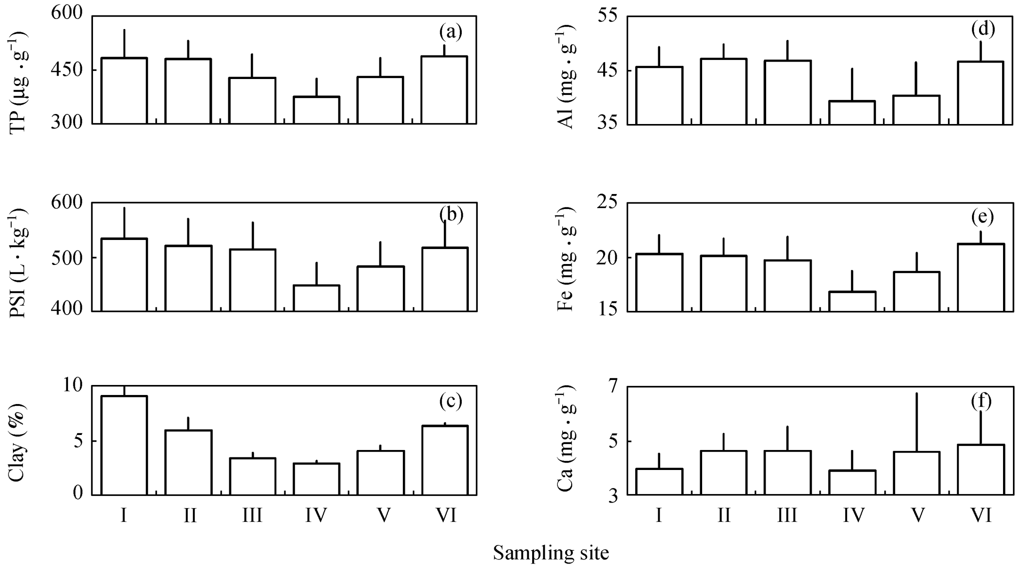

Fig. 6. Spatial variations of TP (a), PSI (b), clay (c), Al (d), Fe (e) and Ca (f) concentrations ($n = 12$).

and VI than at the other stations, while spatial variations in Ca concentration were not observed (Fig. 6(f)).

2.4 Spatial variations of various P species

Al-P concentration was the lowest among the four P species (Fig. 7(a)), accounting for about 6% of TP. Al-P concentration was relatively high in the western part. Fe-P was significantly higher in the western than in the eastern parts (Fig. 7(b)). Fe-P concentrations at Stations I and II were 128.5 µg g^{-1} and 130.6 µg g^{-1}, respectively. Spatial variation of O-P concentration in the sediments was not significant (Fig. 7(d)). Ca-P concentration was relatively lower in the western than in the eastern parts of the lake (Fig. 7(c)), with the maximum (143.6 µg g^{-1}) at Station VI and the minimum (95.7 µg g^{-1}) at Station I.

2.5 Statistic analyses

TP concentrations in the sediments did not correlated with the Ortho-P concentrations of the lake and interstitial water, but significantly positively correlated with TP concentrations of the lake and interstitial water (Table 1). Al-P concentrations showed significantly

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[1] See footnote 1) on page 75.

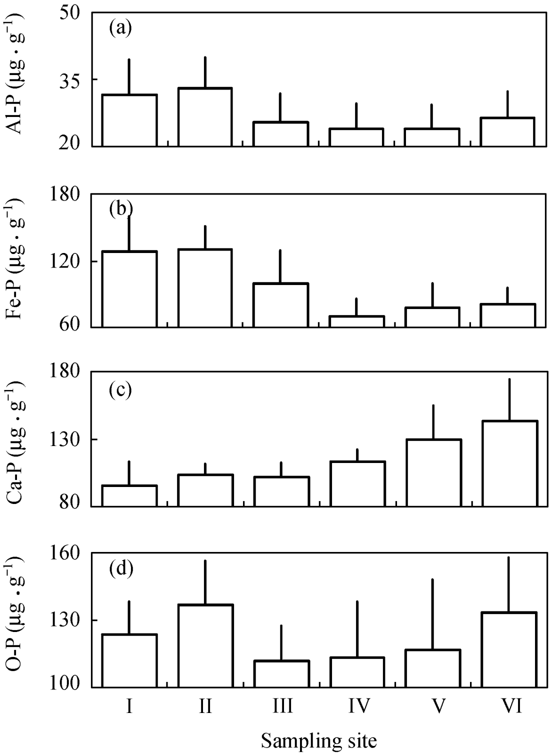

Fig. 7. Spatial variations of Al-P (a), Fe-P (b), Ca-P (c) and O-P (d) in the sediments of Lake Chaohu (n = 12).

positive correlation with Ortho-P of the lake water. TP of the lake water and interstitial water were significantly positively correlated to Al-P and Fe-P, but significantly negatively correlated to Ca-P. Significantly positive correlations were observed between PSI and TP, Al-P, Fe-P and O-P concentrations. PSI (Fig. 8(a)) and TP (Fig. 8(b)) concentrations were significantly positively correlated with Al and Fe concentrations, but not correlated with Ca concentration.

3 Discussion

3.1 Effects of cyanobacterial blooms on temporal and spatial variation of P

Eutrophication in the western part of Lake Chaohu became more serious in recent decades due to heavy discharge of sewage from the surrounding cities (*e.g.* Hefei City). In the present study, TP concentrations of the lake and interstitial water were significantly higher in the western than in the eastern area of the lake. The previous study showed that nutrient discharges from rivers were the main allochthonous sources in Lake Chaohu, accounting for 68.5% in total phosphorous input. TP concentrations discharged from the Nanfei and Sanhe Rivers were relatively high, accounting for 26.9% and 18.9% in total P input, respectively[36]. Therefore, external P inputs contributed greatly to the relatively high P concentration in the western part of the lake. Xu *et al.*[37] reported that suspended particulate materials were mainly composed of phytoplankton, especially in summer when dense cyanobacterial blooms occurred. In the present study, PP concentration was significantly positively correlated with *Microcystis* biomass, but not with *Anabaena* biomass, indicating the importance of the contribution of *Microcystis* to PP concentrations. Generally, P exists in the cell of phytoplankton as the forms of orthophosphate, polyphosphate (cytoplasm), RNA, DNA and phosphoglycride[38]. In the P limited environments, P concentration in the cell of phytoplankton decreases when the growth rate of phytoplankton decreases, and the ability of P uptake by phytoplankton increases. In addition, phytoplankton can assimilate and store excess P in the environment for the convenience of cell growth. The ability of P storage in cyanobacteria (especially *Microcystis*) is considered to be better than that in other algae, and *Microcystis* can sufficiently utilize phosphorus in the lake water[39]. For example, *Microcystis* can assimilate P in the deep layers of the lake water when P is limited in the surface water[40]. Our results also indicate that the ability of *Microcystis* to assimilate and store phosphorus from the environment is better than that of other algae[41].

Table 1 Relationship between P species in the sediments and Ortho-P, TP in the lake and pore water and PSI in the sediments of Lake Chaohu

Variable	Ortho-P (LW, n = 70)	Ortho-P (PW, n = 70)	TP (LW, n = 70)	TP (PW, n = 70)	PSI (n = 72)
TP (Sediment)	0.02	–0.10	0.32**	0.45**	0.51**
Al-P	0.28*	–0.06	0.45**	0.50**	0.40**
Fe-P	0.18	–0.29*	0.53**	0.40**	0.51**
O-P	0.01	–0.35**	0.30*	–0.05	0.31**
Ca-P	–0.17	0.05	–0.26	–0.42**	–0.19

* $P < 0.05$, ** $P < 0.01$, LW: lake water, PW: pore water.

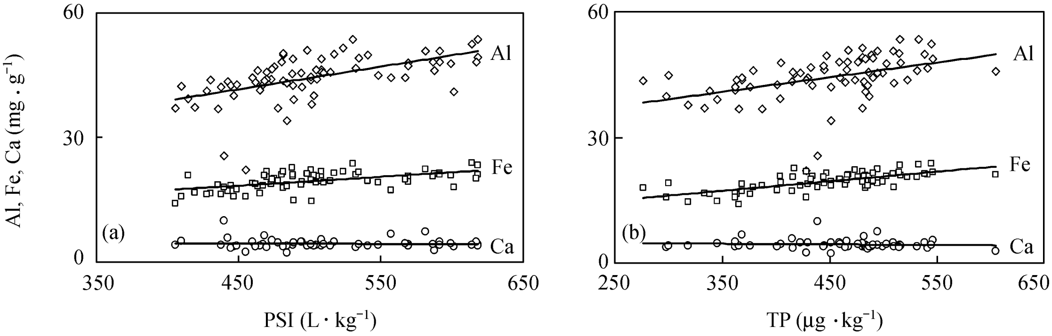

Fig. 8. Correlation between PSI (a), TP (b) and Al, Fe, Ca in the sediment of Lake Chaohu (PSI∶Al, $n = 72$, $r = 0.56$, $p < 0.01$; PSI∶Fe, $n = 72$, $r = 0.54$, $p < 0.01$; PSI∶Ca, $n = 72$, $r = -0.04$, $p = 0.78$; TP∶Al, $n = 72$, $r = 0.44$, $p < 0.01$; TP∶Fe, $n = 72$, $r = 0.71$, $p < 0.01$; TP∶Ca, $n = 72$, $r = -0.08$, $p = 0.55$).

Deng (2004)1) reported that dense cyanobacterial blooms occurred in summer and algal biomass reached the maximum of the year in Lake Chaohu, and the maximum pH (10.4) appeared during the cyanobacterial blooms in the western part of the lake, with a significantly positive correlation between pH and cyanobacteria biomass ($n = 212$, $r = 0.49$, $p < 0.01$). In the present study, no apparent seasonal variations of Ortho-P and TP concentrations in the lake water were observed, while in the interstitial water, both Ortho-P and TP concentrations significantly increased during summer blooms, suggesting that the enhancement algal photosynthesis in summer probably resulted in the increase of pH in the water column, and further promoted the release of P from the sediment to interstitial water. Therefore, the increase of pH and intensive utilization of P by phytoplankton were the main factors promoting P release from the sediment to interstitial water during the cyanobacterial blooms in Lake Chaohu.

3.2 Spatial variations of P in the sediments and the mechanisms underlying these variations

In the present study, TP concentrations in the sediments were higher in the western and eastern parts than in the center part. In a previous study, it is suggested that the high sediments P concentration in the western part of the lake was due to high external P-loading from the Nanfei River, while the high sediment TP concentration in the eastern part might be the result of excessive exploitation of phosphorus mineral deposit existing in the sandstones during Sinina and Cambriam periods in the northern part of the lake[36]. Furthermore, economic development and population increase might be important for the relatively high sediment TP concentrations in the eastern part of the lake since massive sewages were discharged into this part of the lake from the surrounding cities, especially Chaohu City. In the present study, the spatial patterns of clay, Al, Fe concentrations and PSI in the sediments were similar to that of TP concentrations in the sediments, and PSI showed significantly positive relationships with Fe, Al concentrations, but not with Ca concentration, suggesting that spatial patterns of TP concentrations in the sediments were affected by different P adsorption ability due to different mineral compositions and grain sizes. Previous studies indicated that organic matter contents in the sediments were higher in the western than in the eastern part of the lake[36], and there was a positive correlation between clay content and organic matter content in the sediment[42, 43]. The elevated clay contents in the surface sediments of the western part of the lake may be caused by increased sorption sites due to the increase in fine grain of the sediment affected by large amounts of organic matter induced by human activities. However, in the eastern part of the lake, grain sizes of the sediments were affected by both sedimentary origin and organic matter induced by human activities, since previous studies indicated that material sources were complex in the eastern part where grain sizes might be influenced by mud and sand of the Yangtze River. Because

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1) See footnote 1) on page 75.

of the relatively high concentrations of clay, Al and Fe and the greater ability of P adsorption in the sediments of western and eastern parts of Lake Chaohu, a large amount of P deposited in the sediments of these two areas. It is generally known that the ability of phosphorus sorption is relatively high in the mineral-enriched sediments in freshwater[44]. Jugsujinda *et al.*[45] reported that P sorption was positively correlated with the amount of free iron oxide. Sundareshwar and Morris[46] studied the phosphorus sorption characteristics of intertidal marsh sediments, and found a positive relationship between TP and Fe (r^2=0.77) and Al (r^2=0.77) concentrations, but no between TP and Ca concentrations. Our results suggest that the spatial heterogeneity of sediment P in Lake Chaohu was shaped by a variety of factors such as human activities, soil geochemistry and mineral composition.

In the present study, Fe-P and Ca-P are two predominant inorganic P forms in the sediments of Lake Chaohu, and the spatial variations of Fe-P and Ca-P concentrations were different, and TP concentrations in the water column were significantly positively correlated with Fe-P concentrations, but negatively correlated with Ca-P concentrations. Among the sedimentary P species, Fe-P is a very mobile fraction, easily influenced by redox condition and pH especially in shallow lakes. Since redox potential of the surface sediment in shallow lakes is changeable, P in Fe-P undergoes release and adsorption frequently1). For example, when the redox potential is less than 200 mV, Fe (III) in the sediment is reduced to Fe (II), and insoluble $Fe(OH)_3$ to soluble $Fe(OH)_2$, leading to the release of PO_4^{3-} and Fe (II)[47, 48]. In the present study, the ratios of total Fe to TP concentration in the sediments from Station I to VI were 43.2±8.0, 42.3±3.1, 46.4±4.3, 45.5±7.3, 43.6±4.1, 43.5±2.9, respectively, which were similar to those in the surface sediments in the Bay of Seine (54.0)[49], Wadden Sea (21.6—27.0)[50] and Lake Erie (54.0)[51]. These indicate that most iron in the sediment is non-reactive as it is bounded with silicates, and thus cannot react with P[52]. The theoretical and experimental[53, 54] studies indicate that one PO_4-P is absorbed by two Fe (OOH). In Lake Chaohu, the proportion of Fe as Fe-P in total Fe content was calculated to be about 1.8%, indicating that only a small proportion of Fe was involved in P adsorption. Ca-P, a relatively stable fraction of sedimentary P, contributes to a permanent burial of P in the sediment[55, 56], and the amount of Ca in the sediment has no direct influence on the distribution of the various phosphorus pools[57]. In the present study, although TP concentrations in the sediments at Stations I and VI were very close (Station I 482 μg g^{-1}, Station VI 489 μg g^{-1}), TP concentration of the water column was significantly higher at Station I than at Station VI, probably because Fe-P concentration was higher than Ca-P concentration in the sediment of Station I. Our results indicated that in spite of a similar TP content in the sediment, the increase of Fe-P concentration in the sediment may increase the risk of P release.

Acknowledgements This work was supported by a Key Project of the Chinese Academy of Sciences (Grant No. KZCX1-SW-12) and the National Natural Science Foundation of China (Grant No. 30225011).

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