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Phosphorus fractions and alkaline phosphatase activity in sediments of a large eutrophic Chinese lake (Lake Taihu)

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Abstract Spatial, vertical, and seasonal variations in phosphorus fractions and in alkaline phosphatase activity (APA) were investigated in sediments in a large-shallow eutrophic Chinese lake (Lake Taihu) in 2003–2004. The phosphorus content was highest in the most seriously polluted lake area. Iron-bound phosphorus (Fe(OOH) ~ P) dominated (47% on average) among the phosphorus fractions determined according to Golterman (Hydrobiologia 335:87–95, 1996). Notably, organically-bound P comprised a further significant additional portion (acid-soluble + hot NaOH-extractable organic P = 25%), which was highest at the most polluted sites. The Fe(OOH) ~ P content was the lowest in spring (April, 2004), suggesting that degradation of organic matter led to the release of iron-bound phosphates. Sediment APA showed a significant positive relationship with both organically-bound P and Fe(OOH) ~ P. Consequently, organically-bound P is an important portion of the sediment phosphorus in Lake Taihu. It is mainly derived from freshly-settled autochthonous particles and from external discharges. Organically-bound P induces APA and may lead to the release of bioavailable phosphates from the organic sediments, thereby accelerating lake eutrophication.

Keywords P fractionation · Alkaline phosphatase · Kinetics · Distributions · Sediments · Interstitial water · Dredging · Lake eutrophication

Introduction

Eutrophication appears to be a serious environmental problem in a large-shallow Chinese lake (Lake Taihu) in which the concentrations of nitrogen, phosphorus (P), organic pollutants, and water blooms are all increasing at an accelerating rate (Fan et al., 1997). Sediment serves as an important P reservoir, release from which depends on the composition of phosphorus forms (Zhang et al., 2001). Much attention has been paid to the release of inorganically-bound phosphates, but there have been fewer studies on the fate of organically-bound phosphorus. Hua et al. (2000) reported that organic phosphorus is more readily released from the sediment of Lake Taihu and is quickly bioavailable to algae.

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European Large Lakes—Ecosystem changes and their ecological and socioeconomic impacts

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Phosphatase (APA) plays an important role in the hydrolysis of organic phosphorus and consequent phosphate release. In six Finnish lakes with different trophic states, phosphatase activity and levels of organic substances were highest in the top layers of all sediment profiles (Matinvesi & Heinonen-Tanski, 1992), suggesting that microbiological phosphate mineralization from organic substances could determine the internal phosphorus load in those lakes. Phosphatase is an important factor in accelerating eutrophication in Lake Taihu (Song et al., 2006). In this study, the spatial and vertical distributions of P fractions and APA in sediments were investigated during different seasons in Lake Taihu, to address the following issues that have previously remained unclear: (1) Is organically-bound P an important phosphorus component in sediments of Lake Taihu? (2) Does extracellular phosphatase catalyzing the liberation of orthophosphate from organic phosphorus compounds play an important role in phosphorus cycling in Lake Taihu?

Materials and methods

Lake Taihu is situated in the Yangtze River delta (30°05′–32°08′N, 119°08′-121°55′E; mean depth 2.0 m; surface area 2338 km^2), with Wuli Bay being the most polluted area, surrounded by Wuxi City. It functions as a drinking water source, but also as a receiver of untreated domestic sewage (Chen et al., 2003). In 2002–2004, dredging was carried out to remove polluted sediment, using an IHC Holland suction hopper dredger (more details are given in the legend to Fig. 1). Six sites (Sites 1–6) were sampled thrice (in October 2002, January and July 2003) to determine phosphorus fractions and APA, using a 3.5-cm-diameter hand-driven corer. Three or four cores 30 cm in depth was taken from each site. Columns were sliced at 5 cm intervals and the corresponding layers from each core were mixed thoroughly. The samples were stored at 4°C in the dark for 2–4 days before analysis. Each mixed sample was analyzed in triplicate. In 2004, seasonal

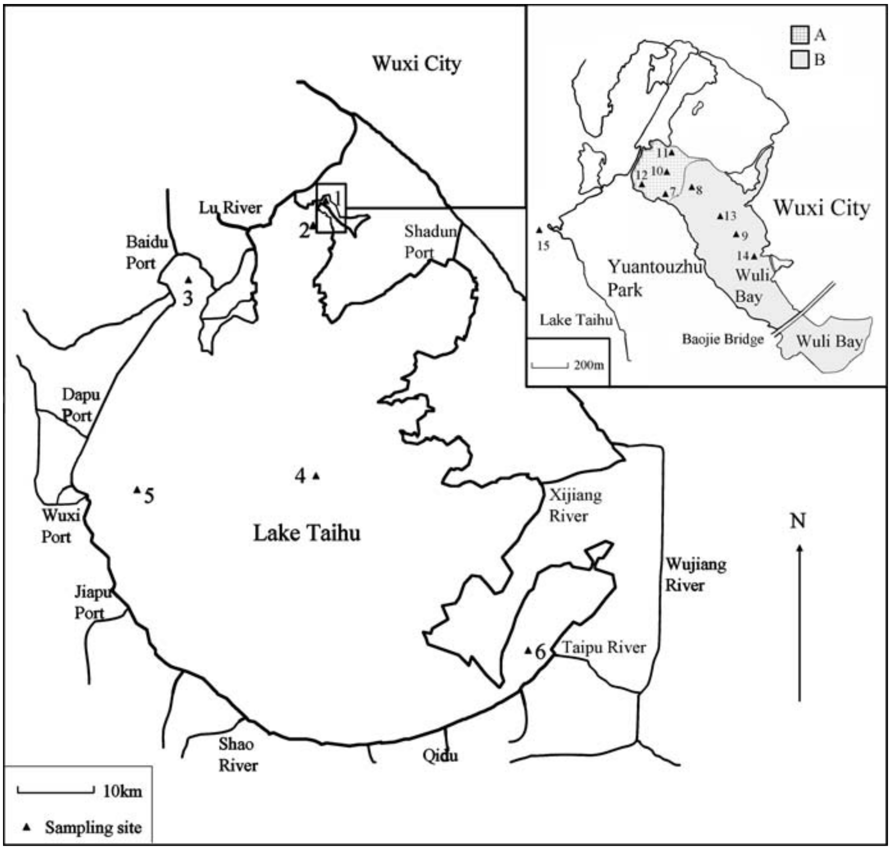

Fig. 1 A map of Lake Taihu showing the sampling sites. Almost the whole of Wuli Bay (Area B) with a total area of 8 km^2 was dredged in 2002–2003. From November 2003 to February 2004 the remaining part in the bay with a total area of 0.2 km^2 (Area A) was dredged. The dredging depth was 0.5 m on average

samples were collected for P fractionation by a Peterson dredge (Buresh & Patrick, 1981) from the area of sediment removal (Sites 7–14) and from Site 15 where sediment was not removed (Fig. 1).

Sediment P fractionation was carried out according to Golterman (1996). This method groups sediment P into iron-bound P (Fe(OOH) ~ P), calcium-bound P ($CaCO_3$ ~ P), acid-soluble organic P (ASOP) and hot NaOH-extractable organic P (P_{alk}). Later in this article, the sum of ASOP and P_{alk} is considered to represent the organically-bound P.

APA was assayed by p-nitrophenylphosphate (pNPP), which is hydrolyzed by the enzyme to yield p-nitrophenol; with this system, enzyme activity is indicated by an increase in light absorbance (Sayler et al., 1979). Sediment samples were suspended in Tris buffer (pH 8.9). The pNPP was added to slurries at six final concentrations ranging from 0.0625 to 1.0 mmol l^{-1}. Samples were incubated at 37°C for 1 h, then 1.6 ml of slurry were centrifuged for 10 min at 3000 rpm. Supernatant (1 ml) was mixed with 4 ml 0.1 M NaOH to stop the reaction. The absorbance of the final solution was measured at 400 nm using a spectrophotometer (Model 721) made by the Shanghai Third Factory of Analytical Instrument, China. The pNPP was added to the reagent blanks after the NaOH. APA was converted to absolute units using a standard curve based on enzymatically hydrolyzed p-nitrophenol. V_{max} and K_m values were estimated by fitting the linearized Michaelis-Menten equation (Dick & Tabatabai, 1984), and the Lineweave-Burk plot was used (Zhou et al., 2001).

Results

For the samples collected in 2004, Fe(OOH) ~ P made the largest contribution to the sediment P pool, accounting for 22–67% of the sum of extracted fractions (47% on average), while $CaCO_3$ ~ P

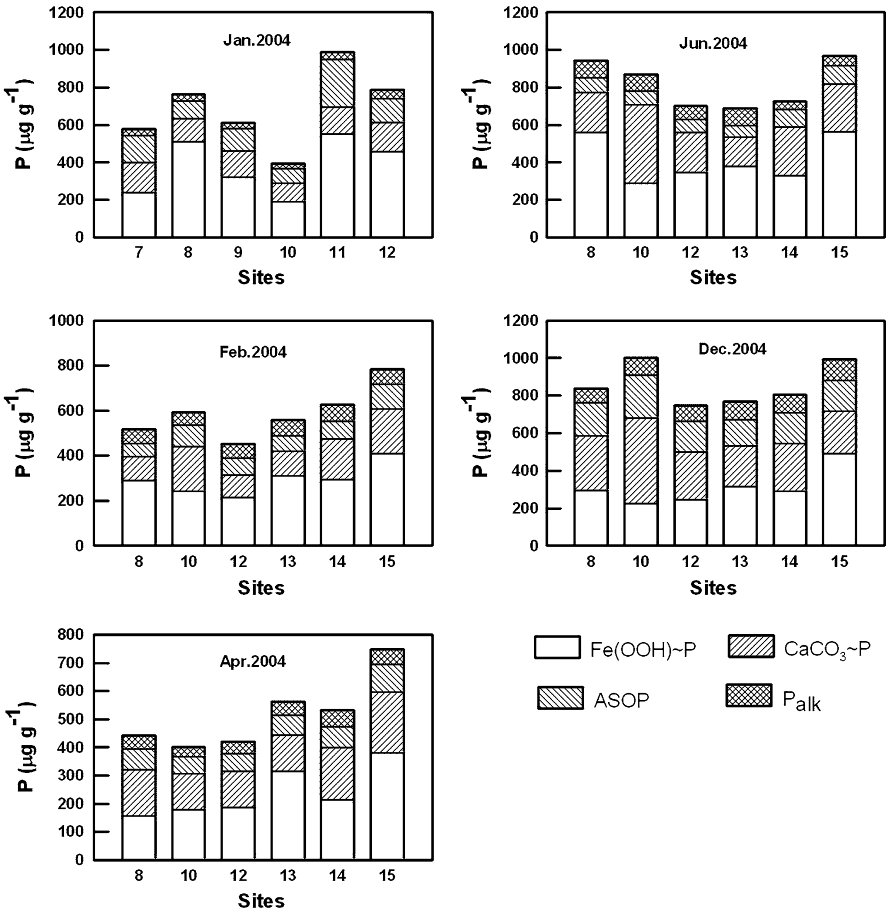

Fig. 2 Distribution of P fractions in surface sediments of Lake Taihu at different sites and in different seasons (the standard errors for each fraction were generally <5%)

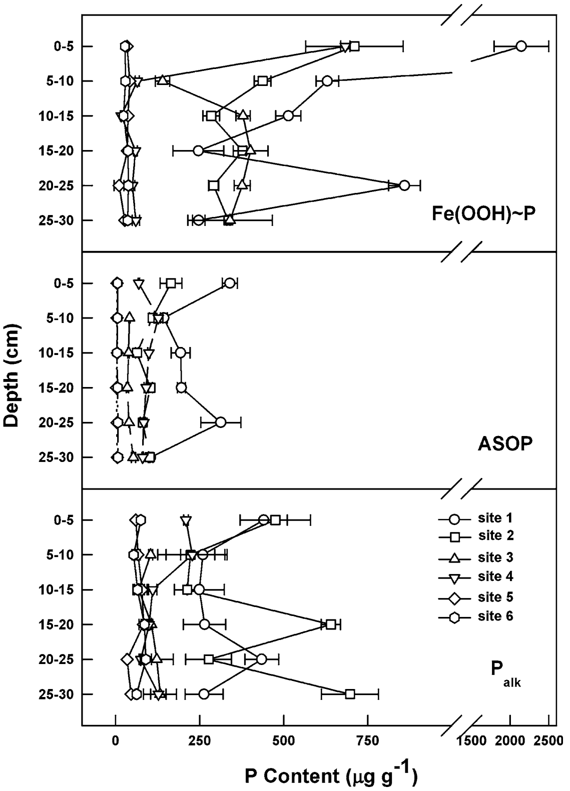

Fig. 3 Depth distribution of P fractions in sediment of Lake Taihu

averaged 28%. ASOP and P_{alk} were estimated on average at 16% and 9% of the total extracted P, respectively. During 2004, Fe(OOH)$\sim$P had the lowest values in April in the sediments from all sites studied (Fig. 2).

The highest concentration of phosphate extracted from the sediments was recorded at Site 1. It was greatest at the surface and decreased with depth (Fig. 3). This was a general distribution pattern in all seasons. Site 1 and the surficial sediment layer (0–5 cm) of site 2 showed markedly higher V_{max} values of APA (Table 1). There were significant correlations between the V_{max} values and P species (Fe(OOH)$\sim$P, ASOP and P_{alk}) in the sediments ($P < 0.01$, Fig. 4).

Discussion

Iron-bound phosphate accounted for most of the phosphorus extracted from the sediment of Lake Taihu (Fig. 2). Notably, the organically-bound P comprised a significant additional portion (ASOP + P_{alk} = 25%). It has two major sources, autochthonous and allochthonous. First, the concentrations of organically-bound P were always highest in the 0–5 cm sediment layer (Fig. 3), presumably reflecting the contribution of freshly-settled autochthonous organic particles. Furthermore, in 2004, ASOP concentrations in the intact sediment at the undredged site 15 were higher than those in the dredged sites 7–14, where the newly-formed surface had been a deeper layer prior to dredging (Fig. 2). Second, Site 1 generally showed the highest concentrations of organically-bound P in sediments at different depths (Fig. 3), attributable to the input of untreated domestic sewage from the large city of Wuxi (Qu et al., 2001).

Most of the organically-bound phosphorus in sediments is remineralized by springtime. This has been shown in the upper 10–20 cm of sediments from 32 shallow meso- to hyper-trophic Danish lakes (Sondergaard et al., 1996). In addition, in the Mejean Lagoon in France, the springtime rise in temperature reactivated the decomposition of the macroalgal biomass that had accumulated during autumn. The redox potential fell as a result of this biological activity, leading to the leakage of inorganically-bound P (Gomez et al., 1998). In our results, the content of Fe(OOH)$\sim$P was also lowest in spring (April, 2004; Fig. 2), suggesting that the degradation of organic matter led to phosphate release.

Extracellular phosphatase plays an important role in the degradation of organic matter in sediments. Our most eutrophic Site 1 generally had the highest values especially at the surface (Table 1). In the shallow eutrophic Chinese Lake Donghu, the most eutrophic basin also showed the highest sediment APA (Zhou et al., 2002). As shown in Fig. 4, there was a significant positive relationship between APA and organically-bound P (ASOP and P_{alk}). This may be explained by a mechanism of phosphatase induction by organic matter, as the total organic carbon content correlated significantly with APA (Su et al., 2005). The coincidence of APA with phosphatase-hydrolyzable phosphorus was also observed in the interstitial water of Lake Donghu (Zhou et al., 2002). Increased alkaline phosphatase V_{max} values were measured in the sediments, which were mainly formed from organic wastes of fish (*Oreochromis*

Table 1 Distribution of V_{max} values (μmol g^{-1} h^{-1}) of APA in sediments of Lake Taihu

Depth (cm)	Sites (October 2002)					
	1	2	3	4	5	6
0–5	963.43	1170.99	483.31		328.85	80.99
	247.86	*93.76*	*10.96*		*71.70*	*26.90*
5–10	1065.38	1037.29	250.87		37.04	62.75
	73.09	*201.85*	*72.80*		*16.92*	*39.52*
10–15	687.11	927.87	262.30	205.90	78.03	
	87.65	*28.88*	*30.91*	*22.72*	*9.71*	
15–20	688.88	526.54	169.16	164.17	93.41	115.65
	14.63	*134.34*	*36.74*	*35.65*	*12.11*	*36.96*
20–25	554.16	510.84	223.10		10.36	126.15
	138.90	*57.43*	*14.61*		*32.64*	*24.03*
25–30	581.76	795.38	401.55		71.56	9.21
	2.91	*75.12*	*35.31*		*3.33*	*8.63*
Depth (cm)	Sites (January 2003)					
	1	2	3	4	5	6
0–5	775.68	1308.63	481.12	260.85	494.87	237.08
	5.56	*59.19*	*40.04*	*45.58*	*25.49*	*18.89*
5–10	845.67	852.95	395.36		97.01	285.50
	75.81	*53.90*	*66.74*		*33.57*	*60.06*
10–15	659.97	284.94	218.85		205.93	119.76
	6.99	*76.70*	*40.63*		*20.56*	*32.67*
15–20	707.27	416.83	226.54	109.76	143.94	78.08
	109.60	*95.45*	*22.01*	*34.80*	*9.32*	*15.62*
20–25	530.76	315.22	31.47	99.72	332.47	23.59
	98.80	*44.52*	*16.50*	*24.86*	*34.58*	*6.63*
25–30	780.45	382.51	124.31	40.54	335.56	
	114.89	*41.54*	*21.65*	*21.61*	*2.89*	
Depth (cm)	Sites (July 2003)					
	1	2	3	4	5	6
0–5	426.28	557.58	612.57	475.28	472.16	127.57
	118.20	*59.85*	*100.34*	*60.88*	*3.64*	*27.79*
5–10	829.15	594.48	1604.53	157.04	283.54	167.89
	79.95	*128.47*	*210.35*	*6.34*	*24.15*	*45.89*
10–15	676.55	745.88	579.68	316.65	37.56	82.76
	162.66	*37.45*	*15.55*	*41.82*	*37.66*	*39.35*
15–20	942.78	249.31	609.40		103.06	13.84
	40.05	*76.79*	*15.02*		*26.24*	*25.76*
20–25	1101.12	223.61	254.76		70.52	104.14
	55.79	*29.75*	*21.12*		*25.62*	*14.28*
25–30	928.11	368.65	72.99		139.14	17.12
	113.44	*38.66*	*36.12*		*13.18*	*8.48*

Standard errors are given in italics

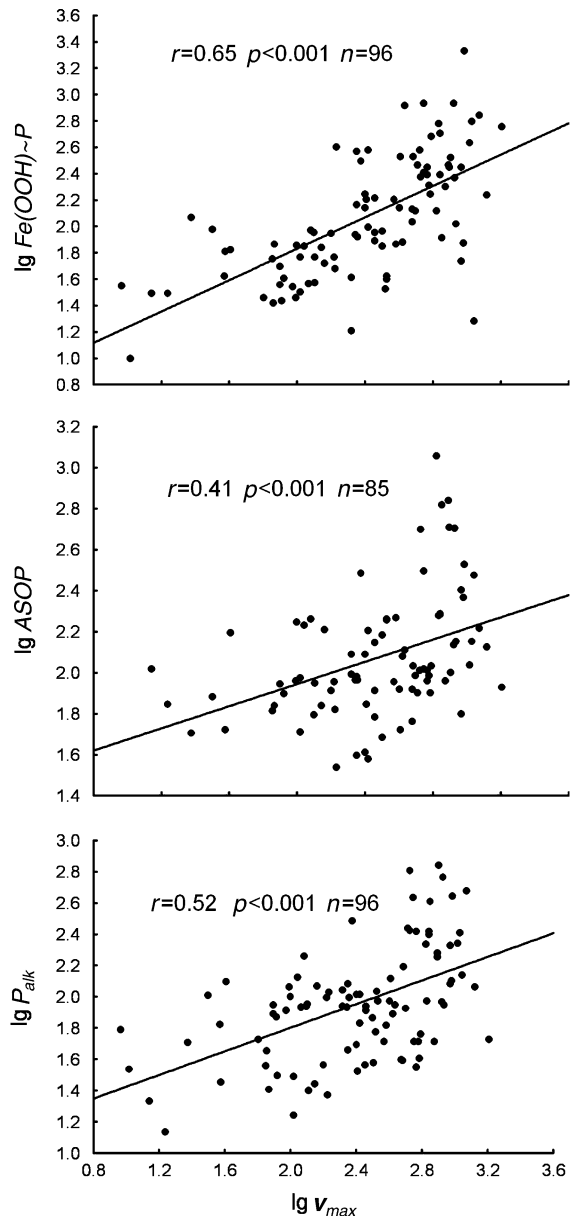

Fig. 4 Positive relationship between V_{max} of APA and P content of organically-bound fractions in sediments of Lake Taihu

niloticus) culture (Zhou et al., 2001). In a reservoir in Morocco, most of the total APA was produced by bacteria that were attached to organic matter (Mhamdi et al., 2003). All this information supports the idea that the activity of extracellular phosphatases is induced by an increased supply of organic matter rather than by a deficiency of phosphates. Nevertheless, the increased activity of alkaline phosphatase(s) enhances the availability of phosphates from both organically-and inorganically-bound sources, since there was also a significant positive relationship between APA and Fe(OOH)$\sim$P (Fig. 4), which is considered to be the most mobile fraction in the sediments (Taoufik et al., 2005).

In conclusion, organically-bound P constitutes an important portion of the sediment phosphorus in the large-shallow eutrophic Lake Taihu. It is mainly derived from freshly-settled autochthonous particles and from external discharges. Organically-bound P induces phosphatase activity and may lead to the release of bioavailable phosphate from the organic sediments, thereby accelerating lake eutrophication. The increased APA is induced to degrade the large amounts of organic matter rather than to compensate P deficiency.

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