

Phosphorus fractions and bioavailability in relation to particle size characteristics in sediments from Lake Hongfeng, Southwest China

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Received: 27 April 2011 / Accepted: 18 June 2012 / Published online: 4 July 2012
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Abstract Information on the chemical composition of phosphorus (P) fractions in sediments is fundamental to understanding P bioavailability and eutrophication in lake ecosystems. Phosphorus fractions and its bioavailability in sediments cores of Lake Hongfeng, southwest China, were investigated using a chemical sequential extraction scheme. Relationships between P fractions, P bioavailability and particle sizes were discussed. P fractions concentrations were ranked in the order: Residual-P > NaOH-rP > NaOH-NRP > HCl-P > BD-P > NH₄Cl-P, and all of them decreased with increasing sediment depth. Statistical analysis showed that concentrations of bioavailable P (BAP) which includes the NH₄Cl-P, BD-P, NaOH-rP and NaOH-NRP fractions ranged from 404.68 to 1,591.99 mg/kg and accounted for 26.8–71.8 % of the concentrations of total phosphorus (TP) in the top 5 cm sediments, whereas in the

whole sediment cores, their concentrations ranged from 239.70 to 1,591.99 mg/kg and accounted for 26.8–76.0 % of TP. The results suggested that the sediments were a large potential source of P for algae blooms in Lake Hongfeng. Phosphorus fractions and their potential bioavailability were influenced by the sediment particle sizes, especially the bioavailability of the NH₄Cl-P fraction, which was strongly affected by the presence of fine particle sizes in the sediments.

Keywords Lake Hongfeng · Sediment · Phosphorus fractions · Particle size · Bioavailability

Introduction

Phosphorus is a key limiting nutrient in most of the lake systems (Conley et al. 2009; Schindler 1977). Large phosphorus inputs to lakes result in eutrophication, which severely hinders the beneficial uses of the lake water and becomes a major problem in the lakes of China (Wu et al. 2010). As external P inputs were gradually controlled, release of internal P accumulated in lake sediments becomes the most important source of P in lake systems (French and Petticrew 2007; Zhou et al. 2001; Wu et al. 2001). Phosphorus releases to the overlying water when physico-chemical factors are suitable and/or microbial activities are present in lake sediments (Rydin 2000; Hupfer et al. 1995). Total phosphorus (TP) evaluation may give some information on the pollution status of internal P in lake sediments, but investigation of P fractions in the sediments can better evaluate BAP and its risks to lake systems (Zhou et al. 2005; Golterman 2001; Ribeiro et al. 2008). Chemical sequential extraction methods are appropriate for evaluating P fractions and their bioavailability (Zhou et al. 2001). They allow simple and quick analysis of

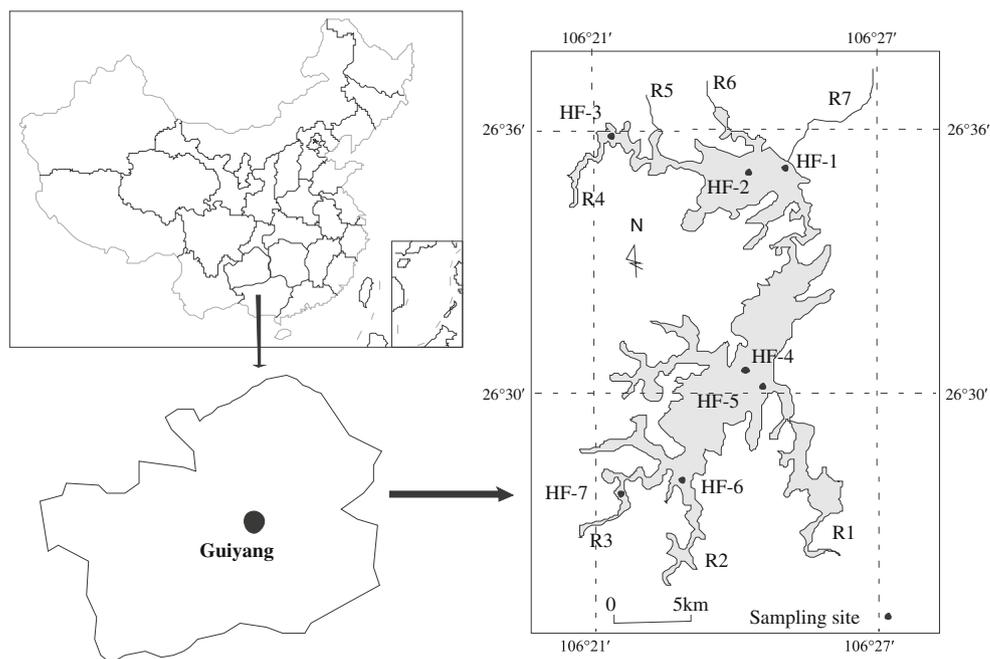
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Fig. 1 Study area: the location of Lake Hongfeng and the sampling sites



numbers of samples at the same time, and have been widely utilized to evaluate the bioavailability of phosphorus in sediments (Hou et al. 2009; Zhou et al. 2001, 2005).

A previous study by Dorich et al. (1984) showed that P fractions (e.g. dissolved phosphate, phosphate extractable with NaOH and HCl, organic phosphorus, and total phosphorus) in size-fractionated eroded soil material increased with decreasing particle size and the algae (*Selanastrum capricorutum*) available P concentration was inversely related to particle sizes of the separates. The eroded soils remain in the lakes and become sediments. Particle size is an important factor which also influences the release and adsorption of phosphorus in sediments (Zhu et al. 2010; Wang et al. 2006a; Andrieux-Loyer and Aminot 2001). The characteristics of particle size influence P fractions and their environmental geochemistry, which alters P bioavailability in sediments (Andrieux-Loyer and Aminot 2001; Zhu et al. 2010; Selig 2003). However, little research has been done on the relationship between particle size and P fractions in lake sediments (Zhu et al. 2010; Wang et al. 2006a; Selig 2003; Stone and English 1993). In order to better understand the geochemical behavior of phosphorus and its bioavailability, the objectives of the present study were (1) to identify the major P fractions in surface and deeper sediments of Lake Hongfeng using a sequential chemical extraction technique; (2) to analyze the particle size characteristics of the sediments and discuss the effect of particle size on phosphorus composition; and (3) to assess the bioavailability of sediment P in the study area.

Materials and methods

Study area

Lake Hongfeng (N 26°26′–26°36′, E 106°19′–106°28′) is located about 32 km West of Guiyang City, the capital of Guizhou Province in Southwest China (Fig. 1). It is an artificial reservoir built in 1960, and it is one of three drinking-water sources for the approximately one million people in Guiyang City. The area of its basin is 1,596 km² and the lake area is 57.2 km², with an average water depth of 10.5 m (max. 45 m). The mean residence time of water in the lake is 0.325 year. The main rivers flowing into Lake Hongfeng are the Houliu River (R1), Maxian River (R2), Yangchang River (R3), Taohuayuan River (R4), Huafeichang River (R5), and Maibao River (R6). The only river which drains water from the lake is the Maotiao River (R7) flowing into the Wujiang River, a major tributary of the Yangtze River. Lake Hongfeng is a multi-functional water body used not only for drinking-water provision, but also for flood control, hydro-power, shipping, commercial aquaculture and recreation. However, excess nutrient inputs to the lake occurred as a result of the development of industry, agriculture, tourism and cage culture (aquaculture) systems in the city, which have led to several serious pollution incidents in Lake Hongfeng. For example, large numbers of fish died suddenly in 1994 and 1997 because of the rapid release of nutrients and pollutants arising from seasonal anoxia developing in water at the bottom of the lake. Total nitrogen (TN) and TP concentrations of water in

Table 1 TN and TP concentration of the water from Lake Hongfeng in recent years (mg L⁻¹)

Years	2001–2002	2004–2007	2009	2010
TN	2.79	1.94–3.33	1.04–1.69	1.06–3.07
TP	0.022	0.064–0.350	0.047–0.115	0.011–0.047

Shang et al. (2011)

TN total nitrogen, TP total phosphorus

recent years were shown in Table 1. Cyanobacterial blooms occur frequently, aggravating the oxygen deficit and causing deterioration of the water quality (Wang 2009). In recent years, external phosphorus inputs have been controlled to a certain extent, but algal blooms still occur every year. Research on phosphorus in the sediments has indicated that Lake Hongfeng has a large internal phosphorus load in the sediments, which significantly influences the lake ecosystem (Wang 2009; Jiang et al. 2011). The characteristics of sediments in Lake Hongfeng were showed in Table 2.

Sediment collection and pretreatment

Seven typical core sediment samples were collected from Lake Hongfeng in August 2008 using a plexiglas cylindrical tube sampler (30 cm length, 5 cm diameter). Areas of the lake sampled included the main estuaries (HF-1, HF-3, HF-5, HF-6, HF-7), and the center of the northern and southern parts (HF-2, HF-4) (Fig. 1). The sediment cores were sliced in situ into depth increments of 0–5, 5–10, and 10 cm increments below that. The samples were transported to the laboratory in air-sealed plastic bags and stored in ice. All samples were freeze dried and the subsamples were ground to powder with a pestle and mortar prior to analysis. The remaining non-ground samples were stored in the air-sealed plastic bags for particle size analysis.

Sequential extraction

Phosphorus fractions in the lake sediments were sequentially extracted according to Psenner et al. (1984) with modifications following Hupfer et al. (1995) (Fig. 2). Phosphorus in the sediments was divided into six fractions; loosely sorbed phosphorus (NH₄Cl-P), reductant-soluble phosphorus (BD-P), metal oxide-bound phosphorus (NaOH-rP), alkali-soluble organic phosphorus (NaOH-NRP), calcium-bound phosphorus (HCl-P) and residual phosphorus (Residual-P). Residual-P was calculated as the difference between TP and the sum of other five extractable phosphorus fractions. All extracts were centrifuged and the supernatants were filtered through a 0.45 μm GF/C filter membrane. The supernatants for NaOH-TP determination were not filtered, but digested. Soluble reactive phosphorus (SRP) in each sample was determined by the molybdenum blue/ascorbic acid method (Murphy and Riley 1962). NaOH-NRP was determined by the difference between NaOH-TP and NaOH-rP. TP in the sediments was determined by the method harmonized and validated in the frame of the standards, measurements and testing (SMT) programme (Ruban et al. 1999).

Particle size analysis

For the particle size analysis, 0.24 g of the non-ground sediment samples were treated with H₂O₂ (30 %) and HCl (1/3, V/V) in order to remove organic matter and carbonate. This treated particle could represent the terrigenous clastic composition. After 150 mL of deionized water was added to the samples, they were heated to boiling, cooled, and left standing for 24 h, after which the supernatant was carefully removed. Then 10 mL of 0.05 mol/L Na(PO₃)₆ was added as a dispersant, 200 mL of deionized water was added and the mixture was heated to boiling for 5 min. After cooling the samples to room temperature, a Malvern Mastersizer 2000 laser particle size analyzer was used for

Table 2 The characteristics of sediments (0–5 cm) from Lake Hongfeng

Sampling area	pH ^a	TN (%) ^a	TOC (%) ^a	Fe _t (mg/g) ^b	Mn _t (mg/g) ^b	Ca _t (mg/g) ^b	Al _t (mg/g) ^b
HF-1/HF-2	7.3	0.604	3.306	44.81	0.92	74.82	95.04
HF-3	6.5	0.809	1.978	63.93	2.13	26.63	78.38
HF-4	6.8–7.4	0.551–0.620	2.978–4.234	–	–	–	–
HF-5	7.8	0.429	1.276	38.76	0.57	76.64	85.52
HF-6	7.0	0.701	2.260	45.13	1.54	31.27	95.72
HF-7	–	–	–	40.73	1.61	43.72	64.50

For sampling area see Fig. 1

TOC total organic carbon, Fe_t total iron, Mn_t total manganese, Ca_t total calcium, Al_t total aluminum

^a Ye et al. (2010)

^b Date unpublished

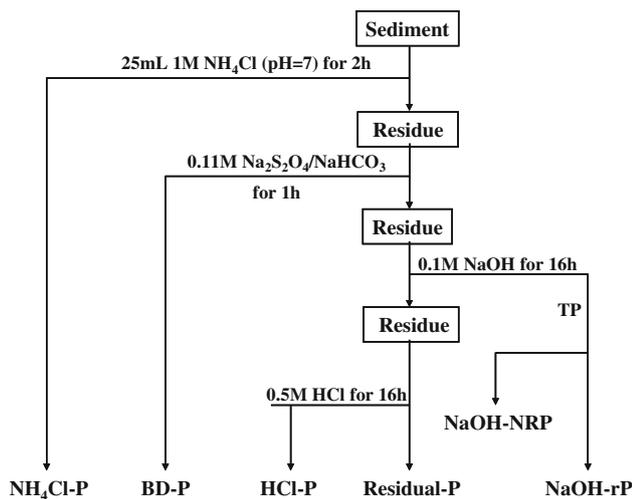


Fig. 2 Sequential extraction method followed in the present study

analysis. The parameter of D_{50} were given and $D[3, 2]$, $D[4, 3]$ were calculated based on formulas (1) and (2).

$$D[3, 2] = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2} \quad (1)$$

$$D[4, 3] = \frac{\sum_{i=1}^n d_i^4}{\sum_{i=1}^n d_i^3} \quad (2)$$

where d_i is the particle diameter, $D[3, 2]$ is the Sauter mean diameter or surface area moment mean, and $D[4, 3]$ is the De Brouckere mean diameter or volume/mass moment mean. The particle size fractions used were clay $<2 \mu\text{m}$, silt $2\text{--}50 \mu\text{m}$ and sand $50\text{--}2,000 \mu\text{m}$ (Das 1990).

Results and discussion

Phosphorus fractions in the sediments

Total phosphorus concentrations in sediments varied from 444.48 to 2,475.69 mg/kg (Fig. 3) and gradually decreased with increasing sediment depth, except for the HF-1 core. The deposition rate of the sediments from Lake Hongfeng was about 0.894 cm/a (Zhu et al. 2006), and 40 cm of sediments cores basically represents sediment accumulation since initial construction of the lake. The vertical variation of TP, especially in the HF-1, HF-2 and HF-7 cores, implied that phosphorus had been continually accumulating in the sediments. The characteristics of P fractions in the sediments were also given in Fig. 3. The order of the contents of the six P fractions was: Residual-P $>$ NaOH-rP $>$ NaOH-NRP $>$ HCl-P $>$ BD-P $>$ $\text{NH}_4\text{Cl-P}$. The concentrations of the six P fractions varied with different sampling sites.

Generally, they decreased with increasing sediment depth in the profiles.

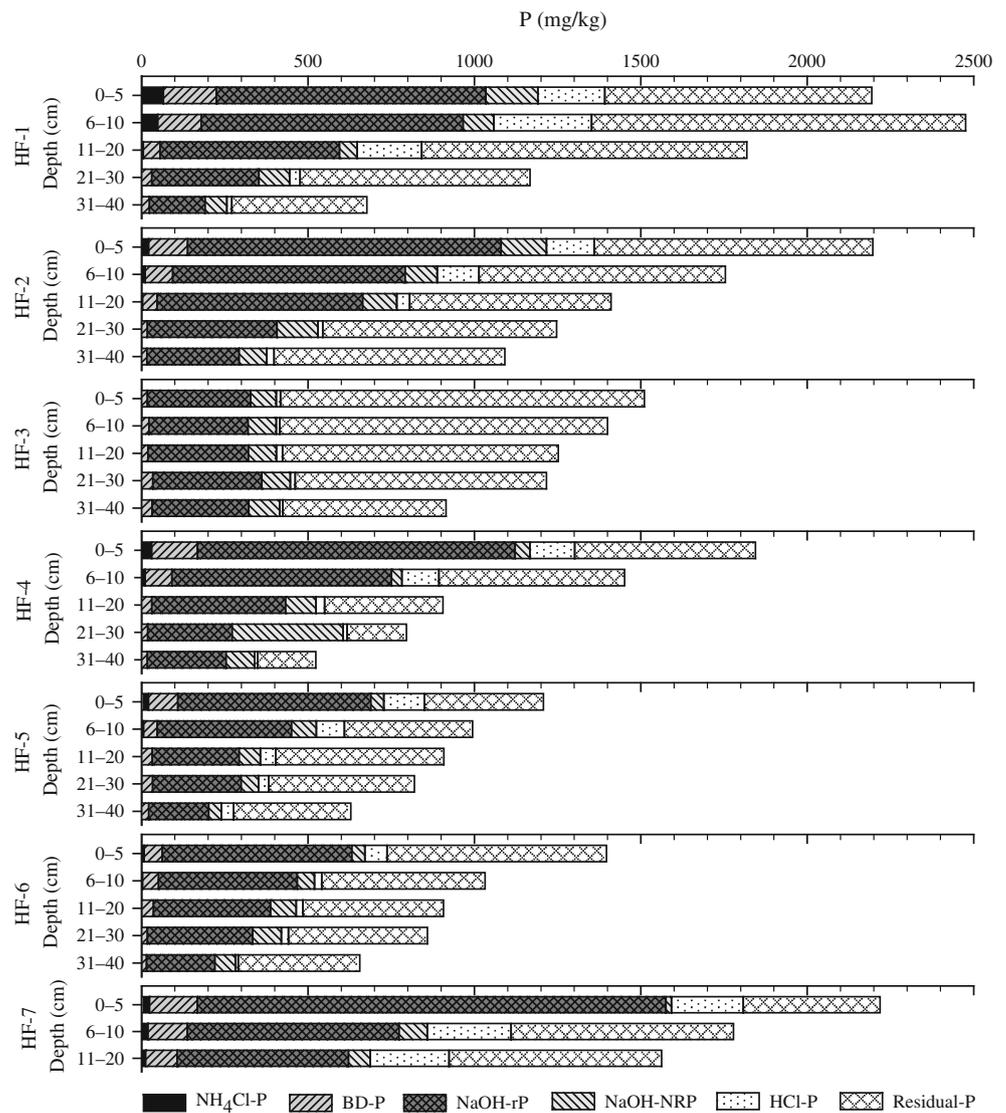
Loosely sorbed phosphorus ($\text{NH}_4\text{Cl-P}$)

$\text{NH}_4\text{Cl-P}$ content varied from 0.10 to 65.88 mg/kg. This fraction was readily released from sediments and therefore was an estimate of the immediately available phosphorus (Rydin 2000). There was a sharp difference in $\text{NH}_4\text{Cl-P}$ concentrations between the HF-1 (65.88 mg/kg) and HF-3 (0.54 mg/kg) cores in the surface sediment layer (0–5 cm). The highest $\text{NH}_4\text{Cl-P}$ concentration was in HF-1 sampled from the deepest area of Lake Hongfeng. This is possibly due to a lesser degree of disturbance from hydrodynamic forces at the water–sediment interface compared with the other sampling sites. Compared with $\text{NH}_4\text{Cl-P}$ concentrations from Lake Taihu (1.7–4.53 mg/kg, average 3.07) (Zhou et al. 2005), Lake Volvi (4.9–8.2 mg/kg) and Lake Koronia (4.9–8.2 mg/kg) in Northern Greece (Fytianos and Kotzakioti 2005), $\text{NH}_4\text{Cl-P}$ concentrations in Lake Hongfeng were very high, especially in the top 5 cm sediments. $\text{NH}_4\text{Cl-P}$ fraction was immediately bioavailable and seasonally variable in the interstitial water (Kaiserli et al. 2002), which suggested that the high concentrations of $\text{NH}_4\text{Cl-P}$ in the sediments from Lake Hongfeng were a very important source of BAP for algal bloom outbreaks.

Reductant-soluble phosphorus (BD-P)

This fraction represents the redox-sensitive P fraction which is mainly bound to Fe or Mn, and was considered as potentially mobile pool of P (Hupfer et al. 1995; Kozerski and Kleeberg 1998). It can be released from anaerobic sediments and become an internal P source to water bodies utilized by alga (Rydin 2000; Kaiserli et al. 2002). BD-P concentrations ranged from 14.64 to 158.95 mg/kg and the relative contribution of BD-P to sedimentary inorganic P (the sum of extractable inorganic phosphorus) was 4.06–12.87 %. The distribution of BD-P in the sediments was similar to that of $\text{NH}_4\text{Cl-P}$, but dissolved oxygen (DO) was an important factor enhancing P-release from this fraction. The BD-P concentrations in Lake Taihu ranged from 58 to 370 mg/kg and its relative contributions to the sedimentary inorganic P ranged from 24 to 44 % (Zhou et al. 2005), which were much higher than those of BD-P in Lake Hongfeng. Compared with Lake Taihu, a typical shallow lake in China, Lake Hongfeng is a deep lake which shows seasonal oxygen deficits, mostly in summer and autumn. In summer, DO was about 7.5–10.5 mg/L in the surface water, but decreased sharply to almost 0 mg/L about 10 m below surface water from Lake Hongfeng. However, DO was about 9.0–10.0 mg/L from surface to bottom of the water in winter (Shang et al. 2011). In this

Fig. 3 Phosphorus fractions in sediments from Lake Hongfeng



condition, the Fe (III)/Mn (IV) (hydro) oxides would be reduced to Fe (II)/Mn (II) compounds and result in enhanced dissolution of the phosphorus at the water–sediment interface. The phosphorus had a stronger upward diffusion tendency from sediments to the overlying water in summer (Shang et al. 2011). BD-P was a key P fraction in the process of phosphorus upward diffusion from the sediments of Lake Hongfeng in summer, which would accelerate the process of eutrophication and worsen the oxygen deficit situation.

Metal oxide-bound phosphorus (NaOH-rP)

NaOH-rP concentrations ranged from 167.69 to 1408.03 mg/kg and were the main P fraction in the sediments. This fraction of sedimentary P refers to P bound to

metal oxides, mainly Al and Fe oxides, which is exchangeable with OH⁻ and inorganic P compounds dissolved in bases (Kaiserli et al. 2002; Kozerski and Kleeberg 1998). Dorich et al. (1984) found that NaOH-rP was significantly correlated with 2-day and 14-day available phosphorus for alga (*Selenastrum capricornutum*). The relationship between phosphate content in this extractant and algal-available phosphate was also evaluated by Fabre et al. (1996), which showed that NaOH-rP was highly correlated with algal (*Scenedesmus crassus*) available P in the sediments ($r = 0.77, n = 47$). These results suggested that NaOH-rP can be used for the estimation of both short-term and long-term available P in sediments, which is released for the growth of phytoplankton when anoxic conditions prevail at the water–sediment interface (Ting and Appan 1996; Zhou et al. 2001). NaOH-rP mainly

includes Al–P and Fe–P, which is also a good indicator of the pollution status of the sediments (Dai et al. 2006). The concentrations of NaOH–rP in the top 20 cm sediment were extremely high, except in HF-3, which indicates the external P input in the last 20 years. The highest NaOH–rP concentration (1,408.03 mg/kg) in the 0–5 cm sediments from HF-7 suggests an especially large P input to Lake Hongfeng by the Yangchang River (R3). This reflects the serious pollution load input from industry and agriculture carried by Yangchang River flowing to Lake Hongfeng. This inflow occupies about 60 % of the total flow in Lake Hongfeng. The frequent outbreak of algal blooms in the southern part of Lake Hongfeng is likely due to external P inputs. The large amount of P accumulated in the sediments is a potential source of bioavailable phosphorus for the growth of algae.

Alkali-soluble organic phosphorus (NaOH–NRP)

Little variation of NaOH–NRP, which was mainly organic P, such as *myo*-inositol hexakisphosphate, and polyphosphates originating from bacterial cells (Hupfer et al. 1995; Rydin 2000), was found in the profiles of sediments. Its concentrations varied from 16.15 to 332.45 mg/kg. Rydin (2000) reported that NaOH–NRP was released in a short time from sediments. It is possible to explain the transfer of NaOH–NRP that: polyphosphate accumulated by bacteria is likely to be released from sediments under anaerobic conditions, and some organic phosphorus combined with metals becomes more easily transformed under anaerobic conditions, such as *myo*-inositol hexakisphosphate, which is strongly adsorbed on Fe(OOH) (De Groot and Golterman 1993). Liang et al. (2004) reported that organic matter was most intensely degraded by microbes in the upper 9 cm sediments where the microbial activities were very significant, and the organic matter content changed slowly below 11 cm in Lake Hongfeng. These implied that NaOH–NRP fraction would also become quickly bioavailable at the water–sediment interface because of the oxygen deficit and microbial activities.

Calcium-bound phosphorus (HCl–P)

Concentrations of HCl–P ranged from 8.89 to 293.80 mg/kg, which represent a low proportion of TP. This phosphorus fraction is sensitive to low pH, and is assumed to consist mainly of calcium-bound phosphorus, such as apatite P, P bound to carbonates, and traces of P from hydrolysable organic P (Kaiserli et al. 2002; Kozerski and Kleeberg 1998). HCl–P showed an obvious vertical variation in the sediments, except in the HF-3 core. Concentrations of HCl–P were relatively high in 0–20 cm and quickly decreased below 20 cm, especially in the HF-1,

HF-2, HF-4 and HF-7 cores. The increasing inputs of external P in the recent decades and the mineralization of organic phosphorus or the other P fractions could accelerate formation of calcium-bound phosphorus. Calcium-bound phosphorus is a relatively stable fraction of sedimentary P and contributes to the permanent storage of P in sediments. It is released from sediments with difficulty, and is therefore not readily utilized by algae (Kaiserli et al. 2002; Kozerski and Kleeberg 1998). Previous research also showed that HCl–P only contributed small amounts of algae-available phosphorus (Dorich et al. 1984).

Residual phosphorus (calculated, Residual-P)

Residual-P was calculated as the difference between TP and the sum of the extractable P fractions mentioned above. It includes the unextractable organic P or inert inorganic P (refractory P compounds), plus possibly also a small amount of undetermined organic P in the extractable P fractions. Residual-P concentrations in the sediments varied from 174.66 to 1,123.45 mg/kg, with little change in vertical distribution. It is the main phosphorus fraction in the sediments, and is considered to be permanently combined with some minerals to be non-bioavailable (Hupfer et al. 1995; Rydin 2000; Wang et al. 2006b).

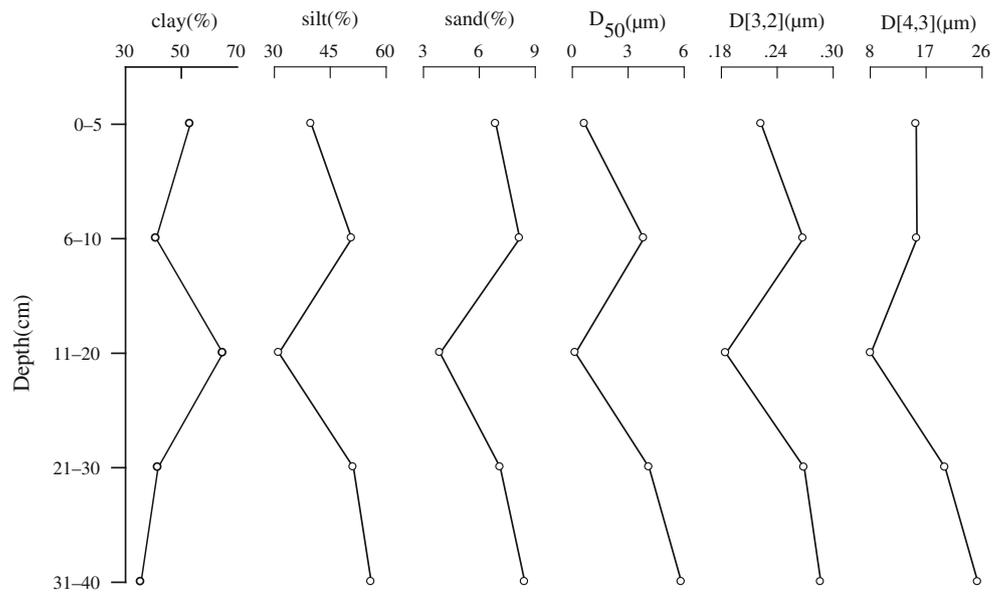
Particle size characteristics of the sediments

The surface sediment samples (0–5 cm) collected from Lake Hongfeng, which are in contact with the overlying water, consist mainly of clay (16.19–34.78 %) and silt (39.94–82.76 %) with smaller proportions of sand (1.05–19.83 %) (Table 3). These were all characterized by a high content of the finer clay and silt size fractions, but the proportions vary with sampling sites. Sites from the northern part of the lake, including HF-1, HF-2, and HF-3, showed high silt and clay contents in HF-1 and HF-2. HF-2 was located in the center part. HF-1 was located in the deepest area (max. 45 m) and had the highest silt plus clay content. The particle size of sediments from sampling sites in the southern part, including HF-4, HF-5, HF-6, HF-7,

Table 3 Particle size characteristics of surface sediments (0–5 cm) from Lake Hongfeng

Parameters	HF-1	HF-2	HF-3	HF-4	HF-5	HF-6	HF-7
Clay (%)	16.19	31.56	34.78	53.17	22.29	33.88	30.82
Silt (%)	82.76	65.45	56.80	39.94	64.85	63.37	49.35
Sand (%)	1.05	2.99	8.42	6.89	12.86	2.75	19.83
D_{50} (μm)	12.20	4.86	6.65	0.67	8.53	5.13	8.01
$D[3,2]$ (μm)	0.59	0.33	0.31	0.22	0.42	0.34	0.36
$D[4,3]$ (μm)	14.44	10.09	18.89	15.41	20.95	9.68	34.54

Fig. 4 Vertical profiles of particle size in the HF-4 sediments



had a similar distribution, with a high silt and clay content in the center sampling site (HF-4). Generally, the fine particles settle in the center of the lake due to their easy movement and the relatively weak hydrodynamic forces there. The coarse particles settle in the estuaries or near the lakeshore (Yin et al. 2008). D_{50} is a parameter that represents the general particle size characteristics. D_{50} values were smaller in the central northern and southern parts of the lake, showing that the proportions of fine particles were high in these areas. $D[3, 2]$ is a parameter related to surface area, and represents the inverse ratio of the surface area. Thus the smaller the $D[3, 2]$, the bigger the surface area. Phosphorus and other contaminants would more probably be adsorbed by the smaller sediment particles, such as HF-2 and HF-4 cores. $D[4, 3]$ is a parameter positively related to the volume or mass of the particles. Under the same conditions, the smaller the $D[4, 3]$ value, the more readily the sediments re-suspend and the more opportunity for phosphorus to be released. The $D[3, 2]$ and $D[4,3]$ values show that the phosphorus accumulated in the sediments from the center of the lake would be released more easily, causing secondary pollution of the water body.

In contrast to the TP and P fractions, particle size characteristics did not change much with sediment depth, showing that particles at the same sampling site probably have the same source. The vertical variation of particle size in the HF-4 sediment core is an example (Fig. 4).

Relationships between phosphorus fractions and particle size

Statistical analysis was carried out between P fractions and particle size using SPSS 11.5 (Tables 4, 5). The surface

sediments (0–5 cm) were closely related to the overlying water which reflects the short-term release of P fractions. The characteristics of particle size will directly influence the release of P fractions. The correlation matrix between P fractions and particle size in the surface sediments (0–5 cm) is presented in Table 4. $D[3, 2]$ values showed a positive significant correlation with $\text{NH}_4\text{Cl-P}$ concentrations. This indicated that $\text{NH}_4\text{Cl-P}$ concentrations were decreasing with an increase in surface area of the sediments at the water–sediment interface. The increased surface area would enhance the P adsorption capacity of the sediments. According to metastable equilibrium adsorption theory and the crossover adsorption isotherm of phosphorus, the value of the zero equilibrium P concentration (EPC_0) drops with an increase in surface area and consequently enhances adsorption capability (Pan 2003; Pan et al. 2002). EPC_0 would be easily achieved in fine sediments when a low concentration of NH_4Cl solution is used as the extractant. Therefore, when the surface area of sediments increases, $\text{NH}_4\text{Cl-P}$ concentrations decrease. Wang et al. (2006a) also reported that deionized water-extractable phosphorus decreased with increased particle size of sediments. The deionized water-extractable phosphorus fraction is similar to $\text{NH}_4\text{Cl-P}$, which means that the results here are similar to the reported results. The significant correlation between HCl-P and (%) silt is possibly because the HCl-P fraction mainly accumulated in silt-sized particles (2–50 μm) in the sediments. This was supported by Stone and English (1993) who divided the sediments of lake tributaries into six different groups by their particle size, and then extracted the phosphorus in them. The HCl-P concentrations showed an obvious increase with decreasing particle size within the particle size range of 0–64 μm .

Table 4 Pearson's correlation coefficients between phosphorus fractions and particle size parameters from surface sediments (0–5 cm) of Lake Hongfeng

	NH ₄ Cl–P	BD–P	NaOH–rP	NaOH–NRP	HCl–P	Residual–P	Clay (%)	Silt (%)	Sand (%)	D ₅₀ (μm)	D[3,2]	D[4,3]
NH ₄ Cl–P	1.000											
BD–P	0.828 ^a	1.000										
NaOH–rP	0.759 ^a	0.952 ^b	1.000									
NaOH–NRP	0.381	0.808 ^a	0.853 ^b	1.000								
HCl–P	0.548	0.244	0.162	–0.136	1.000							
Residual–P	–0.146	–0.440	–0.500	–0.489	0.616	1.000						
Clay (%)	–0.404	–0.110	–0.302	0.108	–0.429	–0.023	1.000					
Silt (%)	0.475	0.063	0.138	–0.305	0.713 ^a	0.285	–0.872 ^b	1.000				
Sand (%)	–0.267	0.063	0.244	0.436	–0.709 ^a	–0.542	0.040	–0.524	1.000			
D ₅₀ (μm)	0.481	0.162	0.350	–0.047	0.371	0.061	–0.947 ^b	0.773 ^a	0.070	1.000		
D[3,2]	0.698 ^a	0.341	0.451	–0.025	0.550	0.027	–0.921 ^b	0.888 ^b	–0.209	0.930 ^b	1.000	
D[4,3]	–0.037	0.211	0.398	0.515	–0.539	–0.428	–0.096	–0.381	0.945 ^b	0.275	0.003	1.000

^a Correlation is significant at the 0.05 level, $n = 7$ (two-tailed)

^b Correlation is significant at the 0.01 level, $n = 7$ (two-tailed)

Table 5 Pearson's correlation coefficients between phosphorus fractions and particle size parameters from all core sediments of Lake Hongfeng

	NH ₄ Cl–P	BD–P	NaOH–rP	NaOH–NRP	HCl–P	Residual–P	Clay (%)	Silt (%)	Sand (%)	D ₅₀ (μm)	D[3,2]	D[4,3]
NH ₄ Cl–P	1.000											
BD–P	0.893 ^b	1.000										
NaOH–rP	0.703 ^b	0.891 ^b	1.000									
NaOH–NRP	0.050	–0.097	–0.145	1.000								
HCl–P	0.773 ^b	0.874 ^b	0.741 ^b	–0.127	1.000							
Residual–P	0.314 ^a	0.246	0.227	–0.064	0.356 ^a	1.000						
Clay (%)	–0.471 ^b	–0.417 ^b	–0.308 ^a	0.089	–0.525 ^b	–0.152	1.000					
Silt (%)	0.476 ^b	0.387 ^a	0.267	–0.002	0.492 ^b	0.229	–0.942 ^b	1.000				
Sand (%)	–0.091	0.025	0.074	–0.245	0.016	–0.255	–0.017	–0.319 ^a	1.000			
D ₅₀ (μm)	0.515 ^b	0.424 ^b	0.318 ^a	–0.056	0.532 ^b	0.147	–0.964 ^b	0.889 ^b	0.073	1.000		
D[3,2]	0.642 ^b	0.522 ^b	0.381 ^a	–0.021	0.581 ^b	0.201	–0.917 ^b	0.871 ^b	–0.004	0.960 ^b	1.000	
D[4,3]	0.037	0.061	0.057	–0.142	0.093	–0.260	–0.219	–0.095	0.905 ^b	0.262	0.165	1.000

^a Correlation is significant at the 0.05 level, $n = 33$ (two-tailed)

^b Correlation is significant at the 0.01 level, $n = 33$ (two-tailed)

Correlations between concentrations of P fractions and particle sizes in whole-core sediments were presented in Table 5. The phosphorus fractions transformed into refractory inorganic P during “aging” in the profile of the sediment, where occlusion of P is one possibility (Rydin 2000). The adsorption of phosphorus to sediments was an important process that controlled the early diagenesis of sedimentary phosphorus (Zhu et al. 2006). The characteristics of sediment particle sizes were possibly an important factor influencing the diagenesis of phosphorus in the core

sediments from Lake Hongfeng. Concentrations of NH₄Cl–P were negatively correlated with (%) clay ($R = -0.471$, $P \leq 0.05$, $n = 33$). This indicates that the clay of sediment favors the adsorption of loosely combined P, which was translated into other more stable P fractions in the core sediments. The particle size parameters of D₅₀ and D[3,2] were significantly correlated with NH₄Cl–P, which also showed that the fine particle would strongly adsorb the loosely combined P with “aging” of the sediments. BD–P, NaOH–rP and HCl–P had the similar correlations with (%)

clay, D_{50} and $D[3,2]$. Abundant Si–OH and Al–OH groups are present on the surface of fine particles and the large surface area always has unsaturated charge. Therefore these particles play an important role in translating loosely sorbed P to other more stable P fractions, even refractory P compounds, which influences the bioavailability of P fractions in the process of diagenesis. (%) Silt had a positive correlation with the extractable inorganic P, including $\text{NH}_4\text{Cl-P}$, BD-P , HCl-P , and even NaOH-rP . Andriex-Loyer and Aminot (2001) reported that Fe/Al-bound P and exchangeable P (such as $\text{NH}_4\text{Cl-P}$, BD-P ,) had a significantly positive correlation to the proportion of fine fraction ($<63 \mu\text{m}$). But the sediment were divided into clay ($<2 \mu\text{m}$), silt ($2\text{--}50 \mu\text{m}$), and sand ($>50 \mu\text{m}$) further more. This indicated that the extractable inorganic P was mainly combined with (%) silt in the profile of sediments, which would release or transfer into Residual-P. However, sampling of the core sediment samples with finer depth increments is needed to better interpret the relationships between P fractions and particle size in the sediments.

The observed correlations among different parameters of particle size reflected their interrelationships. Apart from these, there were no other significant correlations among the parameters.

Bioavailable phosphorus

Correlations among P fractions in the surface sediments (0–5 cm) were shown in Table 4. A significant correlation ($p = 0.05$) was observed between $\text{NH}_4\text{Cl-P}$, and BD-P and NaOH-rP concentrations. This showed that the BD-P and NaOH-rP fractions could be released into the pore water or loosely sorbed by the sediments, and thus became part of the $\text{NH}_4\text{Cl-P}$ fraction under the anaerobic conditions of the water–sediment interface in Lake Hongfeng. BP-P concentrations were positively and significantly correlated with NaOH-rP and NaOH-NRP , which indicate that the BD-P , NaOH-rP and NaOH-NRP fractions in the surface sediments may all be controlled by the concentration of dissolved oxygen in the overlying water. This may also explain the significant correlation between NaOH-rP and NaOH-NRP . In order to present an in-depth analysis of the correlations between P fractions and their bioavailabilities, principal component analysis (PCA) was also carried out. PCA is a powerful pattern recognition technique that attempts to explain the variance of a large set of intercorrelated variables with a smaller set of independent variables. PCA has been used to identify the potential bioavailability of phosphorus fractions from Lake Hongfeng. Results of PCA of P fractions in the surface sediments were presented in Table 6. The proportion of the total variance explained by the first two principal components was 90.048 % for the surface sediments, which reflected

Table 6 Principal component analysis for P fractions from sediments of Lake Hongfeng

	Surface sediments (0–5)		All core sediments		
	PC1	PC2	PC1	PC2	PC3
$\text{NH}_4\text{Cl-P}$	0.792	0.485	0.902	0.206	−0.019
BD-P	0.985	0.100	0.974	0.048	−0.167
NaOH-rP	0.986	0.003	0.889	−0.041	−0.192
NaOH-NRP	0.843	−0.281	−0.125	0.979	0.125
HCl-P	0.153	0.965	0.918	−0.022	−0.002
Residual-P	−0.527	0.751	0.410	−0.132	0.899
% of variance	59.706	30.342	59.675	17.057	14.819
Cumulative % of variance	59.706	90.048	59.675	76.732	91.551

the majority of the phosphorus fractions in those sediments. PC1 accounted for 59.706 % of the total variance, and was primarily correlated with the $\text{NH}_4\text{Cl-rP}$, BD-P , NaOH-rP and NaOH-NRP fractions. This showed that bioavailable phosphorus consists of the $\text{NH}_4\text{Cl-rP}$, BD-P , NaOH-rP and NaOH-NRP fractions, which would be released into the overlying water from the surface sediments. PC2 accounted for 30.342 % of the total variance and was correlated with HCl-P and Residual-P fractions. This suggested that HCl-P and Residual-P in the surface sediments were non-bioavailable.

Correlations between P fractions in the whole-core sediments were shown in Table 5. $\text{NH}_4\text{Cl-P}$ was positively correlated with HCl-P and Residual-P, indicating that $\text{NH}_4\text{Cl-P}$ was an intermediate in the process of P fractions transformation in the sediments. P fractions such as BD-P , NaOH-rP and NaOH-NRP initially could be solubilized as $\text{NH}_4\text{Cl-P}$, before being converted into HCl-P or Residual-P. This also explained the significant correlations between HCl-P , BD-P and NaOH-rP . In contrast to Table 4, NaOH-NRP was not significantly correlated with BD-P and NaOH-rP . This indicated that the factors influencing the geochemical cycle of BD-P , NaOH-rP and NaOH-NRP in the sediment cores and surface sediments were different to some extent, with BD-P and NaOH-rP being mainly influenced by physico-chemical factors, but microbial activity being a very important factor in the geochemical cycle of organic phosphorus (NaOH-NRP). HCl-P and Residual-P, both of which are considered to be non-bioavailable, were significantly correlated with each other. With increasing external P inputs and embedding time, BAP can be converted into HCl-P and Residual-P. PCA for the whole-core sediments showed that the cumulative variance of the first three principal components was 91.551 % (Table 6). PC1 accounted for 59.675 % of the total variance and was correlated with $\text{NH}_4\text{Cl-P}$, BD-P ,

NaOH-rP and HCl-P. This factor suggested that the variation in inorganic phosphorus, including $\text{NH}_4\text{Cl-P}$, BD-P, NaOH-rP and HCl-P, was controlled by physico-chemical factors. PC2 accounted for 17.057 % of the total variance and was correlated with NaOH-NRP. This factor reflected the important geochemical process of organic phosphorus being slowly decomposed by microorganisms in the sediment cores. PC3 accounted for 14.819 % of the total variance and correlated with Residual-P. This factor indicated the stability of Residual-P, which was unextractable by solution and non-bioavailable in the sediments.

Knowledge of P fractions is of great importance in determining the potential BAP in the sediments and in aquatic ecosystems. Figure 5 shows depth trends in potential BAP, viz. $\text{NH}_4\text{Cl-P} + \text{BD-P} + \text{NaOH-rP} + \text{NaOH-NRP}$. Concentrations of BAP range from 404.68 to 1,591.99 mg/kg and account for 26.8–71.8 % of TP in the surface sediments. The concentration and percentage of BAP is highest in the HF-7 core and lowest in HF-3. BAP concentrations in the surface sediments rank in the order of HF-7 > HF-2 > HF-1 > HF-4 > HF-5 > HF-6 > HF-3, which is in good agreement with observed areas of algal bloom outbreaks in Lake Hongfeng. Over all sediment depths, BAP concentrations ranged from 239.70 to 1,591.99 mg/kg and accounted for 26.8–76.0 % of TP. BAP concentrations all declined rapidly in the top 10 cm of the sediment cores, suggesting that external P inputs in recent decades have increased the accumulation of BAP in the upper part of the sediment cores. BAP concentrations were significantly correlated with TP in the sediments (Fig. 6). Thus BAP concentrations can be estimated from TP values,

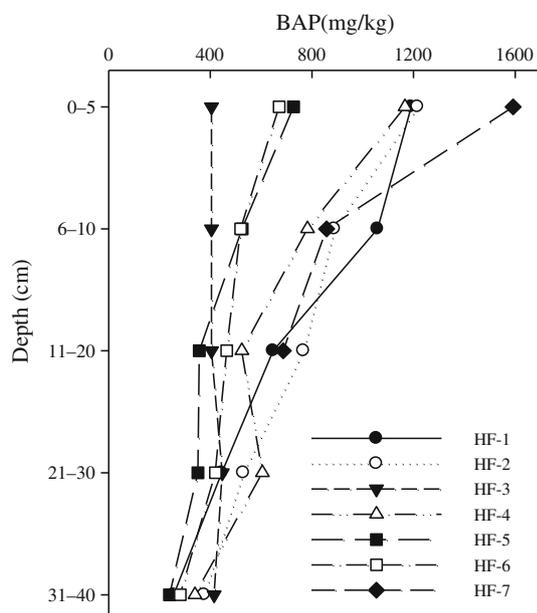


Fig. 5 Vertical profiles of bioavailable phosphorus in the sediments of Lake Hongfeng

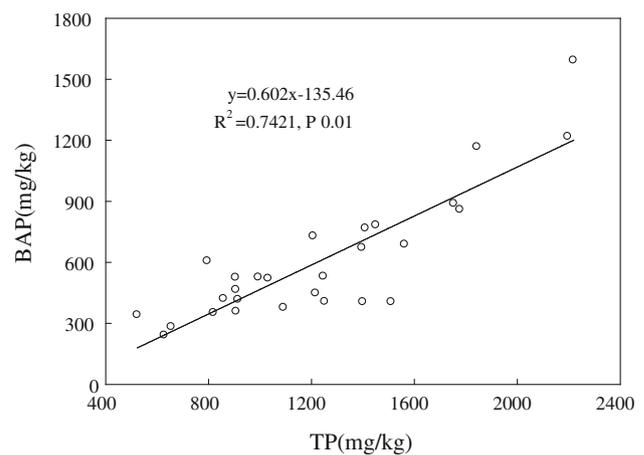


Fig. 6 Relationship between BAP and TP in the sediments of Lake Hongfeng

but knowledge of P fractions is still needed. Compared with Lake Dianchi (Gao et al. 2004) and Lake Taihu (Wang et al. 2006b) in China, the sediments of Lake Hongfeng are a larger sink of BAP. This indicates that the status of eutrophication in the lake will be keeping for a long time.

Conclusions

This study revealed the different P fractions in the sediments of Lake Hongfeng and their bioavailability. TP in the sediments ranged from 444.48–2,475.67 mg/kg and the concentrations of P fractions in them were ranked in the order: Residual-P > NaOH-rP > NaOH-NRP > HCl-P > BD-P > $\text{NH}_4\text{Cl-P}$. The distribution of P fractions in the surface sediments (0–5 cm) varied among sites and decreased gradually with sediment depth. $\text{NH}_4\text{Cl-P}$, BD-P, NaOH-rP and NaOH-NRP were the potential bioavailable P fractions in the sediments. BAP accounted for 26.8–76.0 % of TP in the sediments and the concentrations decreased with increasing sediment depth. The distribution of BAP was closely related to the outbreak of algal blooms. Particular attention should be paid to the accumulation of BAP in the top 10 cm sediments, because of its potential risk to the lake ecosystem.

$\text{NH}_4\text{Cl-P}$ was strongly influenced by the finer particles in both the surface and core sediments. With increasing surface area of the sediments, concentrations of $\text{NH}_4\text{Cl-P}$ decreased at the water–sediment interface. The fine particles favor the adsorption of $\text{NH}_4\text{Cl-P}$ and its transformation to other P fractions. Particle size appears to play an important role on the phosphorus geochemical cycle in the sediments and on P bioavailability. Further work is needed to investigate the coupling of phosphorus fractions with ecosystem processes in the lake and the role of different sediment particle sizes in these processes.

Acknowledgments The authors thank the anonymous reviewer whose constructive reviews significantly helped to improve this work. This study was supported by China's National Basic Research Program (2008CB418200) and the National Natural Science Foundation of China (No. 41130743, No. 40903052, U0833603).

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