Phosphorus sorption capacities in a headstream landscape— The pond chain structure

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Abstract: Understanding phosphorus sorption phenomena in different wetland sediments is important in controlling the P output in headstream watersheds. The pond chain structure (PCS) is widespread in the headstream agricultural watersheds in the southeast of China. Phosphorus sorption characteristics were determined for pond surface sediments (0—12 cm) along a pond chain structure in Liuchahe watershed of Chaohu Lake. Results showed that P sorption capacities (expressed by P sorption index (PSI)) varied both with the landscape position of the ponds and sediment depth. From foothill ponds to riverside ponds the P sorption capacities indicated a significant gradient variability. The higher elevation ponds showed greater sorption capacities, and with the pond elevation decline, P sorption capacities gradually decreased. Some physico-chemical properties, such as pH, oxalate-extractable Fe (Fe$_{\text{ox}}$), organic matter (TOC) and Mehlich I-extractable Ca, Mg of pond sediments also indicated significant gradient variability from high elevation ponds to low elevation ponds. Fe$_{\text{ox}}$ was the sediment parameters most highly positively correlated with PSI and was the key factor in controlling P sorption capacity in the pond chain structure ($r=0.92$, $p<0.001$). Long-term hydrologic and sediment inputs can affect the distribution of sediment constituents and further affect the P sorption capacity. Making the best of the spatial difference of sorption capacities of ponds in watersheds to control nonpoint source P pollutant is necessary.

Keywords: pond; sediment; adsorption; spatial variability; nonpoint source

Introduction

The nonpoint source P pollutants play a significant role in eutrophication processes in the southeast of China. Nonpoint sources pollution from agricultural regions account for more than half of the phosphorus load in many water bodies (Linker *et al.*, 1996). Wetlands in watersheds are known to improve water quality by removing both particulate and dissolved P from incident surface and subsurface waters (Walbridge, 1993; Wang *et al.*, 2002).

The multipond system is an artificial pond system, which has existed for a long time in China. It is distinguished by its water retention and wide-distribution in Chinese agricultural watersheds (Yin *et al.*, 1993). As a traditional hydraulic engineering, its main function has been irrigation. Studies have shown that the multipond system can effectively retain nutrients from agricultural lands and reduce the nonpoint source pollution (Yin *et al.*, 1993; Jin *et al.*, 1992; Yan *et al.*, 1998).

As the basic linking units of the multipond system, the pond chain structures (PCS) are composed of several large ponds and linked by ditches, like a pond chain. Their situations are generally from foothill to riverside. It has been shown that such arrangements of ponds could create special hydrological conditions (Shan *et al.*, 2002), under which, P sorption capacity should be further researched.

In wetlands, long-term P retention is generally believed to be controlled by two main processes: a physical process, i.e. deposition of sediment and particulate organic P; a chemical process, i.e. sorption of dissolved phosphate (Axt and Walbridge, 1999). Amounts of P can be stored with the sedimentation of soil particles in the multipond system (Yan *et al.*, 1998), and these sediments can also further adsorb nonpoint source P pollutants.

Some researches have shown that P sorption capacity is variously related to sediment constituents. Such as in the acid wetland sediments, P sorption was significantly correlated with amorphous Fe and Al content (Richardson, 1985; Lockaby and Walbridge, 1998). Hydrated Fe oxides associated with Al and organic matter in gel complexes have been shown to control inorganic P sorption in sediments (Axt and Walbridge, 1999; McCallister and Logan, 1978). In alkaline soil, the P sorption was probably controlled by Ca or Mg minerals (Goldberg and Sposito, 1985). However, there has not been any research to analyze the controlling factor and spatial variability of P sorption in the multipond system in the southeast of China.

Spatial variability of P sorption capacities of wetland sediments in watersheds has not been well researched. The key factor controlling P sorption capacity in the multipond system was also not clear. In this study, we used the PCS to research (1) the spatial variability of P sorption capacity in PCS under the long-term hydrological conditions in the experimental watershed, and (2) the main controlling factors of P

sorption capacity in PCS.

1 Materials and methods

1.1 Study sites

This study was conducted in an experimental agricultural watershed called Liuchahe watershed in Chaohu Lake in 2003. Chaohu Lake is one of the 5 largest freshwater lakes in China and has suffered from intense eutrophication for a long time (Tu *et al.*, 1990). The Liuchahe watershed is located on the northern bank of Chaohu Lake, and covers 691.6 hm^2 with a typical landscape of a multipond system. There are 193 artificial ponds with a 43.2 hm^2 of area of the ponds. The mean depth is 1.5 m and surface area is from 0.01 to 1 hm^2. These ponds can store the nonpoint source runoffs coming from ambient land uses.

The Liuchahe watershed can be divided into 12 subwatersheds. The subwatershed is an independent geographical unit in the watershed. Only when the great irrigation events happen (such as pumping water from the Chaohu Lake), the water exchange between the subwatersheds can happen. Generally, surface runoffs can flow only between the ponds in the subwatershed. In the subwatershed, from foothill to subwatershed outlet (near the riverside), 3—5 large ponds are distributed like a chain at the valley plain

and usually surrounded by rice fields. There are several ditches between these ponds used for irrigation. These ponds and ditches form a pond chain structure in the subwatershed. PCS is the basic unit of the multipond system and is widespread in the headstream agricultural watersheds in the southeast of China.

In this study, Baojiatang subwatershed was selected to research the sorption abilities of the pond chain structure. This subwatershed has an area of 38.4 hm^2. The types of land use are forests (21%), nonirrigated farmlands (17.4%), ricefields (53.6%), and ponds (8%). From foothill to subwatershed outlet, 5 main ponds are distributed like a chain. There are ditches between these ponds. According to the pond situation, from foothill to the subwatershed outlet, the serial number of these ponds is Pond 1, Pond 2, Pond 3, Pond 4 and Pond 5 (Fig.1). Their characteristics are shown in Table 1.

When rainfall events happen, storm runoffs from the ambient land uses can flow into the pond chain structure. During this process, water, soil particles and phosphorus can be stored, accumulated and adsorbed in the ponds. Only during great precipitation events, the water can effuse from ponds and flow through each pond until flow out of the subwatershed (Shan *et al.*, 2002).

Table 1　The pond characteristics of the pond chain structure (PCS) in Baojiatang subwatershed

| Pond	Area, m^2	Elevation, m	Mean depth, m	TP in pond water, mg/L	Sediment thickness, m	Main aquatic plant and coverage	Ambient land use
Pond 1	2275	36.1	1.51	0.015±0.009	0.10—0.18	*Alternanthera philoxeroide* (10%)	Forest
Pond 2	2480	29.0	1.50	0.067±0.013	0.15—0.25	*Juncellus* (2%)	Rice
Pond 3	7550	23.0	1.48	0.112±0.010	0.20—0.30	No aquatic plant	Rice
Pond 4	5850	17.1	1.43	0.171±0.035	0.20—0.29	*Alternanthera philoxeroide* (44%), *Phragmites communis* (12%)	Rice
Pond 5	6500	13.8	1.45	0.142±0.062	0.15—0.28	*Alternanthera philoxeroide* (51%), *Phragmites communis* (2%)	Rice
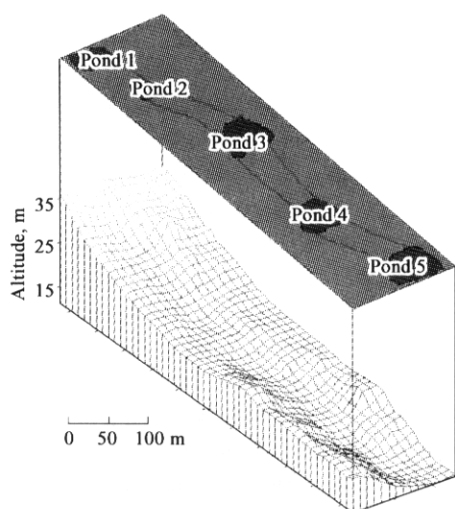
Fig.1　Multipond system in Liuchahe watershed and the pond chain structure (PCS) in Baojiatang subwatershed

1.2 Sample collection

Triplicate sediment cores (ca.12 cm depth) were obtained from representative locations of each pond in Baojiatang subwatershed using polyvinyl chloride pipe. Undecomposed organic debris on the surface of the sediments, such as leaves or plant residue, was removed. From top layer to bottom layer, a plastic knife was used to divide the sediment cores into 2 layers, the top organic layer (0—3 cm) and subsurface layer (3—12 cm). The sediment samples were then immediately homogenized and air-dried. The dry samples were crushed to pass through a 20-mesh sieve to form the initial sediment samples. The samples were placed in sealed plastic bags and kept in darkroom until chemical analysis.

1.3 Physico-chemical analysis

Oxalate-extractable Fe, Al and P were determined by the method described by Bao (2000).

1 g sediment samples were extracted with 50 ml of 0.1 mol/L oxalic acid and 0.175 mol/L ammonium oxalate (pH=3.5). After 4 h continuously shaking on an end-over-end mechanical shaker, the supernatant was filtered through a 0.45-μm membrane filter. The filtrates were analyzed for P, Fe and Al using inductively coupled argon plasma spectrometry (Optima 2000 DV).

Mehlich I-extractable Ca and Mg were determined by the double acid method (Bao, 2000). The sediment samples were extracted with a weak acid mixture (0.05 mol/L HCl +0.0125 mol/L H_2SO_4) at a sediment/solution ratio of 1 : 5. After 5 min shaking on a mechanical shaker, the suspension was filtered through a 0.45-μm membrane filter. The filtrates were analyzed for Ca and Mg using atomic absorption spectrophotometer (Murphy and Riley, 1962).

Total organic C (TOC) content of sediments was determined by wet oxidation (Bao, 2000). The sediment pH was determined in a 1 : 2 (sediment/ water) mixture after a 30-min equilibration. The particle size distributions of the sediments were determined with the Lasae Particle Sizer (Mastersizer 2000, Malvern, U.K.).

1.4 Adsorption isotherms

Batch incubation experiments were performed to determine P sorption characteristics of pond sediments. 1 g of each sediment was placed in a 50-ml plastic centrifuge tube and treated with 20 ml of 0.01 mol/L KCl solutions containing several levels of P (0, 0.05, 0.1, 0.5, 1.0, 5, 10, 50, 100 mg/L) as KH_2PO_4. Two drops of chloroform were added to each tube during the equilibration period to eliminate the effects of microorganisms. Thereafter, the tubes were sealed, and shaken for a 24-h equilibration in the dark using an end-over-end mechanical shaker at (25 ±3)°C. Following equilibration, sediment samples were allowed to settle for about 1 h, and then the supernatant was removed and filtered through a 0.45-μm membrane filter. Filtrates were determined for soluble reactive phosphorus (SRP) by the ascorbic acid method (Murphy and Riley, 1962). Phosphate that disappeared from the solution was considered to be adsorbed by sediments.

The P sorption index (PSI), a rapid means to estimate P sorption capacity (Bache and Williams, 1971) was determined for the pond sediments. The method was: 20 ml of a 75-mg/L solution, prepared by dissolved KH_2PO_4 in 0.01 mol/L KCl, was added to 1 g of sediment and equilibrated for 24 h (Sims, 2000). After equilibration for 18 h filtrates were determined for SRP by the ascorbic acid method (Murphy Riley, 1962).

1.5 Sorption parameter calculations

Sorption parameters were calculated using Langmuir isotherms as follows (Reddy *et al.*, 1998):

$$C_t/S = 1/k \times S_{max}+C_t/S_{max} \qquad (1)$$

Where S_{max} is P sorption maximum (mg/kg) and k is a constant related to P bonding energy (L/mg). C_t is the solution P concentration measured after a 24-h equilibration (mg/L). S is the total adsorbed P in sediment (mg/kg).

$$S = S'+ S_0 \qquad (2)$$

Where S' is the amount of added P adsorbed by sediment (mg/kg), and S_0 is the initial or native sorbed P in sediment (mg/kg).

By plotting C_t/S vs. C_t, the slope is equal to $1/S_{max}$ and the intercept is equal to $1/k \times S_{max}$. The phosphorus sorption index (PSI) was calculated as follows (Sims, 2000):

$$PSI (L/kg) = X/\log C \qquad (3)$$

Where X is the amount of added P adsorbed by sediments (mg/kg); C is P concentration at equilibrium (mg/L) after equilibration of a 1-g of sediments with 20 ml of 75 mg/L phosphate solution on an end-over-end shake for 24 h.

Statistical analysis and regression analysis were done using the Origin software.

2 Results

2.1 Physico-chemical characteristics of PCS sediments

Pond sediment pH in PCS ranged from 4.2 to 6.5 indicated significant acidity (Table 2). There was no significant difference between the top organic layers and subsurface layers.

Fe_{ox} of the pond sediments in PCS were very high (> 5000 mg/kg), with the top Fe_{ox} concentrations generally higher than the subsurface layer values. The oxalate-extractable Al (Al_{ox}) concentrations were lower than Fe_{ox} concentrations and generally only 20% of the Fe_{ox} suggesting that Fe_{ox} was probably the more important factor than Al_{ox} in regulating P sorption in the pond chain structure (Reddy *et al.*, 1998).

Total organic carbon (TOC) contents of pond sediments ranged from 9.7 to 20.9 g/kg, and the top TOC concentrations were higher than the subsurface layer values. The highest TOC content was found in the sediments of Pond 1, and the lowest was in the Pond 5, whether the top layers or the subsurface layers. A strong correlative relationship was observed between TOC and Fe_{ox} (Fig.2), suggesting that Fe-organic matter complexes could probably play an important role in controlling P sorption capacity in these pond sediments (Darke and Walbridge, 2000).

The most obvious character of sediment physico-chemical changes in the PCS was that the sediment properties indicated significant gradient changes along the elevation of ponds (Fig.3). Patterns

Table 2   Selected physico-chemical characteristics of sediments ($\pm SE$) from the pond chain structure (PCS)

| Type	Depth, cm	Water content, %	pH	TOC, g/kg	Clay, %	Mehlich I extract, mg/kg		Oxalate extract, mg/kg		
						Ca	Mg	Fe	Al	P
Pond 1	0—3	43.3	4.25	20.9	8.0	4830	355	9182	1400	174
	3—12	37.8	4.26	18.3	7.3	4917	330	3572	1139	135
	Mean$\pm SE$	39.2$\pm$2.1	4.26$\pm$0.09*	18.9$\pm$1.2*	7.5$\pm$0.3*	4895$\pm$286*	336$\pm$14*	7974$\pm$471*	1204$\pm$74	145$\pm$10*
Pond 2	0—3	36.5	4.30	17.0	10.7	4945	395	8209	1004	197
	3—12	28.4	4.28	12.4	10.6	4972	338	7355	1296	178
	Mean$\pm SE$	30.5$\pm$2.2	4.28$\pm$0.03*	13.5$\pm$1.8*	10.6$\pm$0.8*	4965$\pm$173*	365$\pm$15*	7568$\pm$364*	1223$\pm$93	182$\pm$15*
Pond 3	0—3	35.3	5.54	13.6	10.7	6280	495	6120	1253	91
	3—12	27.4	5.40	10.5	11.1	6205	455	5228	1100	96
	Mean$\pm SE$	29.4$\pm$2.9	5.44$\pm$0.05*	11.5$\pm$1.2*	10.9$\pm$0.3*	6230$\pm$169*	465$\pm$20*	5451$\pm$273*	1138$\pm$67	95$\pm$1*
Pond 4	0—3	35.5	4.84	13.0	12.9	6745	455	6329	1482	113
	3—12	32.4	4.74	9.97	13.1	5632	472	6475	1433	128
	Mean$\pm SE$	33.2$\pm$0.8	4.77$\pm$0.03*	10.7$\pm$1.1*	13.0$\pm$0.4*	6525$\pm$510*	468$\pm$14*	6438$\pm$103*	1445$\pm$30	124$\pm$8*
Pond 5	0—3	30.7	6.64	10.7	12.6	8520	510	5977	1424	93
	3—12	28.7	5.83	9.7	15.6	7980	560	5511	1431	135
	Mean$\pm SE$	29.3$\pm$0.7	6.27$\pm$0.24*	10.2$\pm$0.5*	14.1$\pm$1.5*	8250$\pm$270*	535$\pm$25*	5744$\pm$233*	1427$\pm$3	114$\pm$21*

Note: * Mean values (0—12 cm) are significant at the 5% level among ponds
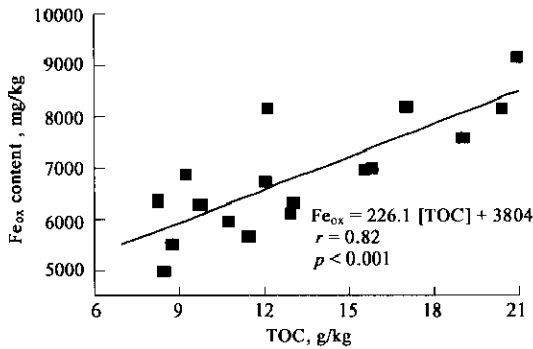
Fig.2   Relationship between oxalate-extractable Fe (Fe_{ox}) and total organic matter (TOC) of the pond sediments

Graph annotation: $Fe_{ox} = 226.1$ [TOC] $+ 3804$, $r = 0.82$, $p < 0.001$

of spatial variation in water content, TOC and Fe_{ox} of pond sediments were similar along the landscape gradient from foothill to riverside. There was a general decline with increasing distance from the foothill pond (pond 1) to riverside pond (pond 5). But pH, Mehlich I-extractable Ca, Mg and clay were just the contrary. From foothill to riverside there was a general rise. However the spatial variation of Al was not significant (Fig.3).

2.2 Phosphorus sorption characteristics of PCS sediments

The main purpose of applying adsorption equations to P adsorption curves is to understand the processes involved in P adsorption and to summarise many results by a few numbers (Barrow, 1984). To achieve this purpose, the concentration of P in the equilibrium solution was related to P adsorption (Fig. 4). As shown in Fig.4, phosphorus sorption characteristics for sediments from the pond chain structure were generally well described by the Langmuir isotherm even though the pond sediments were complex heterogeneous systems ($r^2=0.97$—0.99) (Pant and Reddy, 2001).

☑ Sorption parameters of ponds for top 0–3 cm layers   —■— Average values of sorption parameters for pond sediments
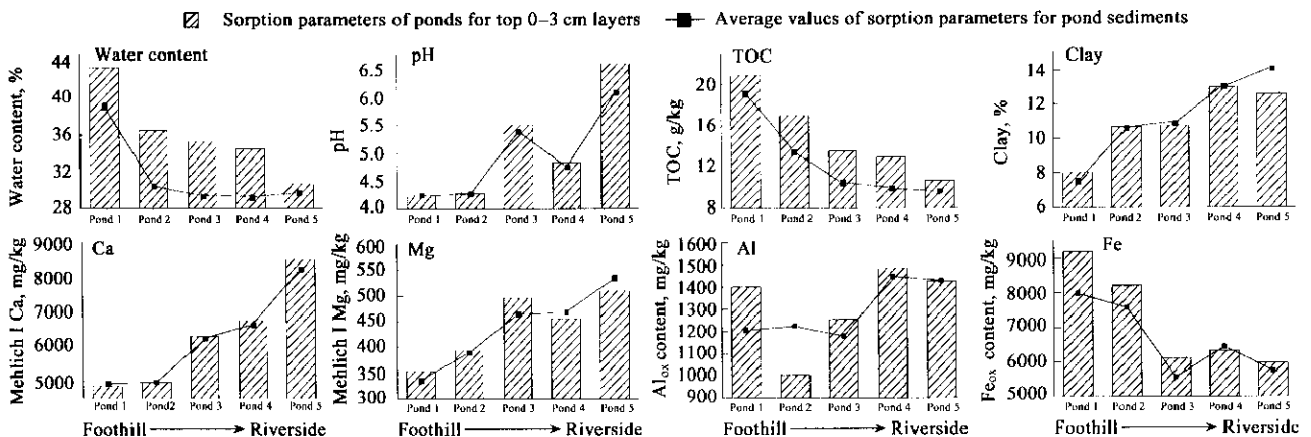
Fig.3   Changes of physico-chemical characteristics of sediments in the pond chain structure (PCS) along a foothill to riverside gradient
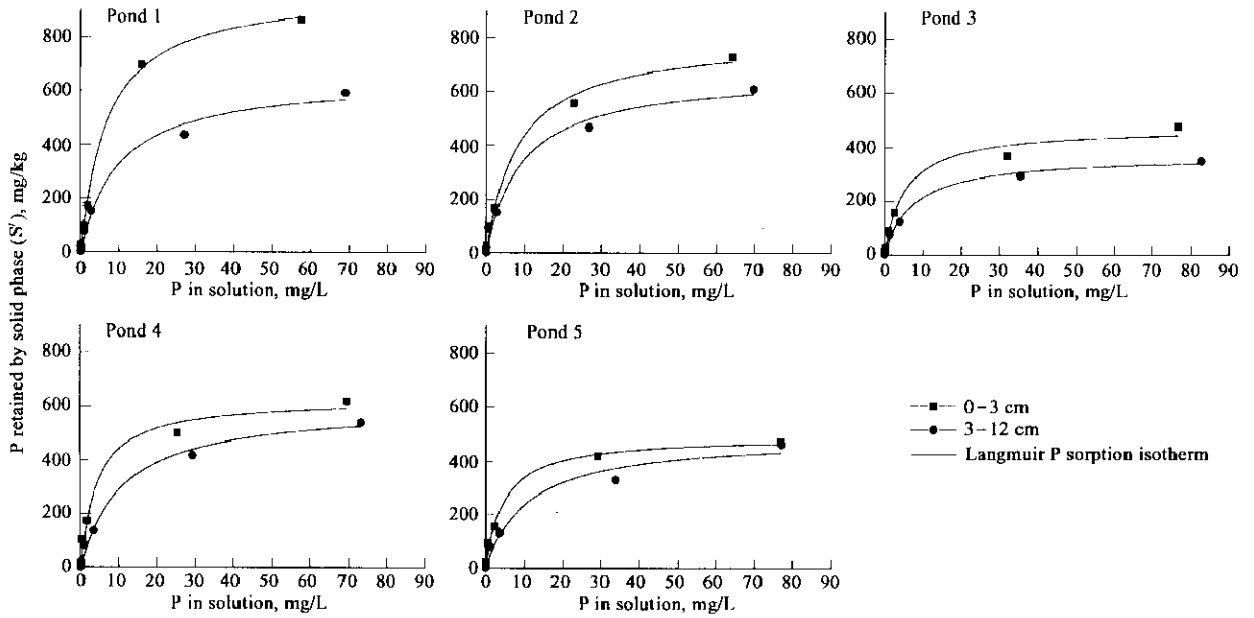
Fig.4　Relationship between P adsorbed by the solid phase and equilibrium P solution for top layer (0—3 cm) and subsurface layer (3—12 cm) of the pond chain structure

In this study, we use P sorption index (PSI) to estimate the P sorption capacities of pond sediments. A strong relationship was observed between the PSI and S_{max} (Fig.5). The PSI was about half of the S_{max}. Mozaffari and Sims (1994) found a similar correlation between the PSI and S_{max} ($r=0.97$, except when $S_{max} >$ 1400 mg/kg). Estimating the PSI is not only less time-consuming than developing P sorption isotherms, it facilitates comparisons with related sediment physico-chemical parameters. Our results indicated that PSI also could be used in researches of pond sediments and could be a reliable and easily used method to rank sediments with respect to P sorption capacity.
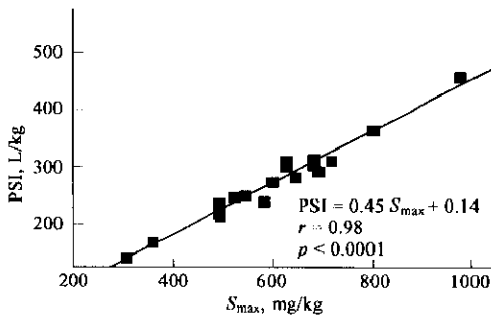

Fig.5　Relationship between the P sorption index (PSI) and sorption maxima (S_{max}) as calculated by the Langmuir equation

For the top sediments PSI values ranged from 238 to 457 L/kg with a mean value of 324 L/kg. In the subsurface sediments the range in PSI was 218 to 301 L/kg and the mean value was significantly lower than that determined for the top sediments (Table 3).

Fig.6 indicates a significant gradient variability of P sorption capacities in the pond chain structure from

Table 3　Phosphorus sorption characteristics of the pond sediments (±SE) by Langmuir model

Type	Depth, cm	S_{max}, mg/kg	k, L/mg	PSI, L/kg	r^2
Pond 1	0—3	974.1±60.8	0.15±0.011	456.8±23.2	0.99
	3—12	647.6±52.7	0.10±0.009	289.1±19.1	0.98
	Mean±SE	729.2±89.8*	0.12±0.013	331.0±44.1*	
Pond 2	0—3	799.8±26.3	0.12±0.015	364.9±8.6	0.99
	3—12	666.5±20.4	0.11±0.018	301.4±6.1	0.98
	Mean±SE	700.0±36.3*	0.12±0.013	317.2±16.5*	
Pond 3	0—3	522.2±52.6	0.15±0.010	247.8±21.6	0.99
	3—12	493.9±41.9	0.10±0.018	231.3±20.4	0.98
	Mean±SE	508.1±14.1*	0.14±0.019	239.6±8.3*	
Pond 4	0—3	626.8±20.7	0.24±0.015	311.9±13.5	0.97
	3—12	609.5±18.0	0.09±0.017	265.9±12.7	0.98
	Mean±SE	613.8±14.1*	0.13±0.04	277.4±14.6*	
Pond 5	0—3	492.6±13.5	0.22±0.017	237.9±5.8	0.99
	3—12	491.8±11.3	0.09±0.015	218.1±4.5	0.97
	Mean±SE	492.2±0.4*	0.16±0.065	227.9±9.9*	

Note: * Mean values (0—12 cm) are significant at the 5% level among ponds

foothill ponds to riverside ponds. The sediments of Pond 1 exhibited the greatest P sorption capacity (PSI and S_{max}). From the high elevation ponds to the low elevation ponds, P sorption capacities decreased with the decline of the pond elevation except for Pond 4 (Fig.6). Differently situated ponds in subwatershed might provide different water quality benefits with respect to P retention—higher P sorption capacities were found in the higher elevation ponds sediments, the lowest P sorption capacity was in the ponds near the river.
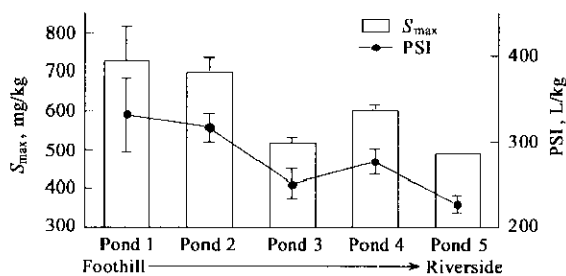
Fig.6   Changes in selected sorption parameters of surface sediment layers along the elevation of the ponds in the pond chain structure

The spatial change of PSI was consistent with the change of oxalate extractable-Fe along the elevation of ponds (Fig.2 and Fig.6). The most striking relationship was found between PSI and oxalate-extractable Fe ($r=0.92$, $p<0.001$; Table 4), which indicated that the distribution of oxalate-extractable Fe in the pond chain structure can probably control the P sorption capacity. Total organic matter (TOC) also was positively correlated with PSI, but correlation coefficient was significant less than Fe_{ox} ($r=0.71$, $p<0.01$) (Table 4), suggesting the importance of Fe_{ox} in regulating P sorption capacity in the pond chain structure. No relationship was found between other sediment properties and PSI, such as Al_{ox}, Mehlich I-extractable Ca, Mehlich I-extractable Mg and clay percentage ($p>0.05$).

Table 4   Correlation coefficients of P sorption capacities and associated physico-chemical properties of pond sediments ($n=17$)

Para-meter	pH	Clay	Mehlich I-Mg	Mehlich I-Ca	Ox-Fe	Ox-Al	Ox-(Fe +Al)	TOC
PSI	NS	NS	NS	NS	0.92**	NS	0.94**	0.71*
S_{max}	NS	NS	NS	NS	0.94**	NS	0.95**	0.74*

Notes: * $p<0.01$; ** $p<0.001$; NS. not significant ($p>0.05$)

3   Discussion

3.1   Physico-chemical characteristics of PCS sediments

The hydrologic linkages of water storage structures in watersheds can influence the biogeochemical processes of sediments, and can further influence the retention characteristics and function of sediments (Darke and Walbridge, 2000).

Every pond in the PCS has its own catchment (Fig.1). In general, the ponds only receive the nonpiont source runoffs and irrigation runoffs of their own catchments (discontinuous runoff). But when huge precipitations and irrigations happened, the ponds also can receive the runoffs of upstream catchments and effluent of upper ponds (continuous runoff) (Shan et al., 2002). Therefore the pond chain structure is a half-connectivity structure. Because of

the direction of runoffs, higher level ponds had important influence on the lower level ponds, while the lower level ponds had no significant influence on their up-level ponds. With the pond effluents and irrigation runoffs from the above level ponds to lower level ponds, the material exchanges happened between the ponds (Shan et al., 2002). This kind of runoff character has important influence to the characters of pond sediments.

The pond chain structure we researched is located in the typical agriculture watershed in the southeast of China and the soil is typical acidic laterite. The composition of clay minerals is kaolinite, hematite and ilmenite etc. (Zhu, 1982). The main source of pond sediments is storm runoffs from ambient land uses, resulting in the acidity of pond sediments. Higher Mehlich I-extractable Ca, Mg concentrations were found in the lower elevation ponds, which was probably due to the high acidic pH conditions of the sediments (Reddy et al., 1998).

The higher concentrations of TOC found in the top layers were understood because of the decomposition of organic materials under anaerobic conditions (Reddy et al., 1998). As shown in Table 1, there were a lot of aquatic plants in the PCS except for pond 3, and the species and coverage kept approximately steady. The biomass could reach 2×10^5 kg/a in PCS (wet weight, data in 2002). But the difference of pond aquatic plants seemed to have no influence to the spatial changes of sediment TOC (Fig. 2). Although there were no aquatic plants in the pond 3, TOC in its sediment was still higher than in pond 4 and pond 5 which had a mass of plants. This indicated that the influent from ambient land uses had an important influence on the spatial characters of pond sediments. The aquatic plants in the ponds had no obvious influence on the TOC contents of the pond sediments. Be different from other large wetland systems, there was strong interaction between the pond and ambient land uses because the ponds were very small compared with the ambient land uses—the area of ponds was only 8% of the subwatershed. The differences of TOC in the pond sediments were caused by the extraneous sources. Higher TOC contents in pond 1 probably accounted for the high organic matter concentration of influent from the forest soil, which was abundant in humus horizon composed of the decomposed litter of pine trees (Yan et al., 1998). Lower TOC contents in the downstream pond sediments in the PCS suggested that during the storm runoffs flowed from high elevation ponds to low elevation ponds, the pond sediments could function as effective sinks for TOC (Reddy et al., 1998).

Fig.2 indicates TOC had positively correlated with Fe_{ox} in pond sediments, suggesting that TOC may play important role in controlling the biogeochemistry

and spatial distribution of Fe_{ox} in watersheds (Darke and Walbridge, 2000; Reddy *et al.*, 1998). In fact, Fe^{3+} in solution can bind with organic matter(OM) to form an OM-Fe complex, and influence the P sorption capacity of pond sediments. Fig.2 indicates Fe_{ox} generally decreased with the decline of pond elevations. Similarly to TOC, the pond sediments also could function as effective sinks for Fe_{ox} from high elevation ponds to low elevation ponds. The spatial changes of physico-chemical characteristics of PCS were a kind of long-term effects of hydrology (Darke and Walbridge, 2000).

3.2 Phosphate sorption characteristics of PCS sediments

The oxalate-extractable Fe and Al represent amorphous and poorly crystalline forms, which are important in regulating P sorption in the acidic soil watersheds (Reddy *et al.*, 1998; Loeppert Inskeep, 1996). Although Ca and Mg could also adsorb P, the formation of recalcitrant P compounds including apatite permanently sequesters P (Ruttenberg and Berner, 1993), which could be dominant in oceanic systems and estuaries and not important in PCS acidic sediments. Researches had been reported both crystalline and poorly crystalline Fe oxides could sorb P by the same mechanism, but amorphous and poorly crystalline forms tend to dominate sediment P sorption reactions when present in significant amounts because of their greater reactive surface area per unit sediment volume (Axt Walbridge, 1999; Schwertmann and Yaylor, 1989; Freese *et al.*, 1992).

We found a strong positive correlation between the PSI and Fe_{ox} in the PCS (Table 4), but no significant correlation was found between the PSI and Al_{ox} ($p > 0.05$). Even though TOC was also positive correlated with the PSI and Fe_{ox}, while the stepwise multiple regression analysis indicated Fe_{ox} was the most important factor controlling P sorption capacity in the PCS and could explain 85% of the variation of PSI:

PSI=0.056[Fe_{ox}]−106, $p < 0.001$, R^2= 0.85, SE=28.9
(PSI: L/kg; Fe_{ox}: mg/kg)

Two-term model of Fe_{ox} and Al_{ox} was slightly better than Fe_{ox} alone (r=0.94; Table 4). In general, the sum of $Fe_{ox}+Al_{ox}$ was a better predictor of P sorption capacity than either Fe_{ox} or Al_{ox} alone (Darke *et al.*, 2000). The high Fe_{ox} content and high Fe_{ox}: Al_{ox} ratio might be the reason that Fe_{ox} was more important than Al_{ox} in controlling P sorption in PCS.

Fe_{ox} was positively correlated with sediment organic matter (Fig.3), suggesting that organic matter-metal (Fe, Al) complexes, which are also extracted by acid ammonium oxalate, may provide an important component of the P sorption capacity in PCS sediments. Humic Fe complexes provide

important P sorbing sites (i.e., PO_4^{3-} was bound to the organic matter via Fe ligands; Gerke and Jungk, 1991). Fe freshly complexed with humic substances can sorb 10 times more P than noncrystalline Fe_{ox} (Gerke and Hermann, 1992). In addition, organic matter probably could inhibit the crystallization of Fe, which in turn could increase P sorption as noncrystalline Fe_{ox} would sorb more P than well-crystallined (Borggaard *et al.*, 1990). Thus, the presence of OM-Fe complexes could significantly increase the P sorption capacity of the PCS.

The spatial variability of PSI was similar to the Fe_{ox} and TOC of pond sediments (Fig.3 and Fig.6). P sorption capacity in the pond 1 was the highest. The surface runoffs entering pond 1 mainly came from the hill forest, and the P concentration of influent was generally lower than that from rice or nonirrigated farmlands (Yan *et al.*, 1998). Higher P load might decrease the P sorption capacity (Nair *et al.*, 1998). In addition, pond 1 had the greatest Fe_{ox} and TOC. We call these two factors as exterior factor (influent P concentration) and interior (Fe_{ox}, Al_{ox} or TOC contents in sediments). Under the common controlling of exterior and interior factors, pond indicated different P sorption capacity and spatial characteristics. Because the PCS is a half-connectivity structure, the catchments of downstream ponds should include not only their own catchments but also the catchments of upstream ponds (continuous runoff). The downstream ponds had higher potential P loading, in addition, downstream ponds generally had lower Fe_{ox} and TOC contents, resulting in the P sorption capacities of ponds generally declining with the elevations of pond in PCS.

Spatial variability in hydrologic and sediment inputs can affect the distribution of sediment constituents that are important in P sorption (Johnston, 1991). Our data agreed with these studies, and further indicated that under long-term hydrologic and sediment inputs, the different wetland systems arranged in a certain order also showed significant gradient variability of sediment characteristics and P sorption capacities. Spatial variability of P sorption capacity was mainly due to the spatial changes of correlative sediment parameters such as Fe_{ox} and TOC. There was no research about P sorption characteristics of different arrangement structures of wetlands in watersheds. Our research indicated that the situation of ponds had important influence on the P sorption capacity of sediments and the riparian wetlands (such as the PCS) were not homogenous units of P sorption capacity in watersheds. Under the long-term effects of hydrology, they could indicate significant spatial changes, such as physico-chemical properties and P sorption capacities in the PCS (Fig.3 and Fig.6). The P sorption capacities declined from foothill to riverside,

and the higher the ponds are, the stronger the P sorption capacities are. It is not correct to consider riparian wetlands as homogenous units in terms of their ability to remove nonpoint source P pollutant from surface runoffs.

4 Conclusions

As the basic linking units of the multipond system, the PCS can effectively control nonpoint source P pollutant of agricultural watersheds. They can act as a multi-level treatment system in protecting downstream waters from nonpoint source P inputs.

Variation in P sorption capacity was largely explained by a few basic pond sediment characteristics. In PCS, Fe_{ox} was the key factor in controlling P sorption capacity and could explain 85% of the variation in the PSI. The strong correlative relationship between Fe_{ox} and TOC suggests the potential role of Fe_{ox} organic matter complexes in controlling P sorption capacity.

Long-term hydrologic and sediment inputs can affect the distribution of sediment constituents and further affect the P sorption capacity. In PCS, from high elevation ponds to low elevation ponds, Fe_{ox}, TOC generally declined, while pH, Ca and Mg were just the contrary. Under the control of Fe_{ox} and TOC, P sorption capacity (PSI) also indicated spatial variability—decline with the pond elevation decrease. The highest P sorption capacity was in the ponds at the foothill and the lowest value was in the ponds near the river.

The wetlands in riparian areas should not be considered homogenous units when estimating their P sorption potentials. Depending on the different pond spatial connectivity, the pond chain structure (PCS) may act as important buffers between agricultural lands and rivers in watersheds.

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