

Journal of Hazardous Materials A128 (2006) 95-105

*Journal of* Hazardous Materials

www.elsevier.com/locate/jhazmat

## Effects of particle size, organic matter and ionic strength on the phosphate sorption in different trophic lake sediments

Shengrui Wang<sup>a</sup>, Xiangcan Jin<sup>a,\*</sup>, Qingyun Bu<sup>a</sup>, Xiaoning Zhou<sup>a</sup>, Fengchang Wu<sup>b</sup>

<sup>a</sup> Research Center of Lake Environment, Chinese Research Academy of Environment Sciences, Chaoyang District, Beijing 100012, China <sup>b</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

> Received 30 April 2005; received in revised form 29 July 2005; accepted 30 July 2005 Available online 21 September 2005

#### Abstract

The trophic status and development of lake system is significantly influenced by the phosphate sorption at the sediment–water interface. The effects of organic matter, particle size and ionic strength on the phosphate sorption by sediments were investigated in this study. The results show that maximum phosphate sorption capacity ( $Q_{max}$ ), equilibrium phosphate concentration (EPC<sub>0</sub>), phosphate sorption efficiency (k) and phosphate sorption rate decreased as particle size increased for all the studied sediments. But the reliable desorbed phosphorus (RDP) increased.  $Q_{max}$ , EPC<sub>0</sub>, k and RDP of different particle size fractions varied and there were no obvious differences among different trophic lake sediments.  $Q_{max}$ , EPC<sub>0</sub> increased while k and RDP decreased as the pollution level of lake sediment increased. The phosphate sorption mainly occurred within 0.5 h. Power function and simple Elovich models were the best kinetic models for the phosphate sorption of the different particle size fractions.  $Q_{max}$  and phosphate sorption rate decreased with the decreasing of organic matter content of sediments and the increasing of ionic strength. This study suggests that ionic strength and organic matter had similar effects on the phosphate sorption for different trophic lake sediments.

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Keywords: Phosphate sorption; Organic matter; Particle size; Ionic strength; Sediment; Lake

#### 1. Introduction

The phosphate sorption at the sediment–water interface is an important process affecting the phosphorus (P) transport, bioavailability and concentrations in lakes. This process, therefore, has been widely investigated [1,2]. Previous studies in soils showed that the P sorption process was highly nonlinear as energy levels varied among different binding sites on the solid surfaces; high-energy sites were always occupied in the first place [3]. Apparent P sorption was reported to be a combination of two main processes: 'fast sorption' and 'slow sorption' [4]. The sorption capacity on soils varied among different soils and it tended to be high in soils with a high proportion of small size particles such as clay and manure [5]. Clay soils containing high proportions of Fe or Al oxide minerals had particularly high sorption capacity [6] and the P sorption strongly depended on the solution parameters, e.g. ionic strength [7,8]. Similar results were also reported in lake sediments [9–13] and many sediment properties affected the phosphate sorption process, e.g. particle size, organic matter, Fe- and Al-oxides and cationic exchange capacity (CEC), especially the distribution of particle size and organic matter [9]. Different particle size fractions had different specific surface areas and weight [10] and had also different effects on the phosphate sorption by sediments [11]. Many previous studies demonstrated that soils and sediments with different sability to the microbial decomposition, thus having different ent phosphate sorption ability [12,13].

So far, lots of studies have been done on the behaviors and mechanisms of phosphate sorption and particle size fraction

<sup>\*</sup> Corresponding author. Tel.: +86 10 84915185; fax: +86 10 84915190. *E-mail address:* jinxiang@public.bta.net.cn (X. Jin).

<sup>0304-3894/\$ -</sup> see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2005.07.048

characteristics of soils and sediments [12–16]. Although the phosphate sorption mechanism is not well understood, sorption capacity was reported to be closely related to organic matter content [17-20]. Organic matter played an important role in sediments since its mineralization may result in changes in both redox and pH [21-23] and humic substances can stabilize iron particles [24]. But little is known about the effects of organic matter for different trophic sediments in various ionic strength solutions. Ionic strength was also a factor affecting phosphate sorption at the sediment-water interface. The high ionic strength in solution lowered the extent of sorption and shifted the sorption isotherms toward higher equilibrium phosphate concentrations [19]. All factors have to be taken into account when evaluating phosphate sorption by lake sediments [20]. Few investigations, however, have been carried out on the effects of particle size, organic matter and ionic strength on the phosphate sorption in the same experiments and fundamental impact of the distribution of particle size fractions and organic matter content in different trophic lake sediments and various ionic strength solutions is not well understood. Sediments were separated into different particle size fractions and were treated by hydrogen peroxide; those were common and powerful methods to study the effects of particle size and organic matter content on the phosphate sorption by sediments [25,26]. The objective of this study was to elucidate the effects of the particle size fractions, organic matter and ionic strength on the phosphate sorption by different trophic lake sediments.

#### 2. Materials and methods

### 2.1. Sampling and analyses

Sediment cores were collected from the East Taihu Lake, Wuli Lake, Jiangshu Province and Yehu Lake, Hubei Province, using the core Plexiglas sampler with 30 cm length and 5 cm diameter cylinder tub in September 2003. Top 10 cm samples were taken to the laboratory in air-sealed plastic bags and were kept in cool (4°C). They were then freeze-dried and sieved with a standard nylon mesh sieve to obtain different particle size subsamples. Samples were successively passed through 18, 60, 240, 360 and 480 mesh sieves and those subsamples were named 18–60, 60–240, 240–360, 360–480 mesh sediments, respectively.

Sediments were analyzed for CEC using EDTA-NH<sub>4</sub><sup>+</sup> method and total nitrogen (TN) was measured as nitrate by colorimetry after the digestion of the total samples with  $K_2S_2O_8$  + NaOH [27]. Total P (TP) concentrations in sediments were determined using the SMT protocol [28], water content and losses on ignition measurements were based on weight losses after drying and combustion of the sediments at 105 and 550 °C, respectively. Total organic carbon (TOC) in sediments was analyzed with an Appollo 9000 TOC Analyzer

Table 1		
TOC content of sediments before and after treatment	with	H <sub>2</sub> O <sub>2</sub>

Sediment samples	TOC (%)						
	Before treatment	After treatment					
East Taihu Lake	0.90	0.21					
Yuehu Lake	6.23	1.16					
Wuli Lake	1.67	0.37					

(Tekmar Dohrman Co., USA) after the pre-treatment in warm HCl 50% (v/v) to eliminate carbonate [29]. The contents of major elements were measured by ICP-AES (PE, USA, ICP/6500). The grain size fractions were measured using a Mastersizer 2000 Laser Size Analyzer (Malvern Co., UK) and were classified into clay (<0.002 mm), silt (0.002–0.05 mm) and sand fractions (0.05–2 mm) [30].

#### 2.2. Oxidation of organic matter of the sediment samples

Approximately 200 g sediment samples through 100 meshes were mixed with 300 ml 30% hydrogen peroxide solution in a 1.51 Pyrex beaker. The beaker was allowed to stand for 1 h and was then placed on a sand bath at 400  $^{\circ}$ C to rapidly dry the solution. After cool, the remaining residues were freeze-dried and re-ground to pass through 100 meshes for experiments [26]. The difference of TOC before and after treatment was the oxidation of organic matter in the sediment samples (Table 1).

#### 2.3. Preparation of different ionic strength solutions

Initial sorption experiments were conducted in Milli-Q water and KCl solution was used to adjust ionic strength (0.01 and 0.001 M). Without pH adjustment the equilibrium pH after 24 h of reaction ranged from 6 to 7.

#### 2.4. Sorption isotherms

P sorption isotherms were obtained using a previously reported method [31]. Briefly, 0.5 g dried sediment samples or subsamples were added in a series of 100 ml acid washed centrifuge tubes with 50 ml phosphate solution each (anhydrous KH<sub>2</sub>PO<sub>4</sub>, in different ionic strength condition). The low initial concentrations of 0, 0.05, 0.1, 0.2, 0.5, 1.0 and  $2.0 \,\mathrm{Pmg}\,\mathrm{L}^{-1}$  and high initial concentrations of 0, 2.0, 5.0, 8.0, 10.0, 15.0 and  $20.0 \,\mathrm{Pmg}\,\mathrm{L}^{-1}$  were used, respectively. The tubes were capped and placed at  $25 \pm 1^{\circ}$ C in an orbital shaker at 250 rpm for 24 h to ensure the equilibrium. After equilibrium and centrifugation (5000 rpm for 10 min) the suspension was filtered through 0.45 µm membranes and the phosphateconcentration was measured using the ascorbic acid method [32]. The phosphate sorbed on sediment samples was calculated using the difference between the initial and equilibrium phosphate concentrations [33]. The phosphate sorption isotherm in different initial concentration ranges can be fitted using Langmuir model or Linear model [34]

$$Q = \frac{Q_{\max} \times C}{K_{\rm d} + C} \tag{1}$$

$$Q = K \times C + b \tag{2}$$

where *C* is the phosphate sorption equilibrium concentration  $(mg L^{-1})$ , *Q* the phosphate sorption capacity  $(mg kg^{-1} dry weight)$ ,  $Q_{max}$  the maximum phosphate sorption capacity  $(mg kg^{-1} dry weight)$ ,  $K_d$  the half saturation concentration  $(mg L^{-1})$ , *K* the slope and is a measure of the phosphate sorption efficiency of sediments  $(1kg^{-1})$  [18] and *b* is the constant.

EPC<sub>0</sub> was the phosphate equilibrium concentration when phosphate sorption capacity was  $0 \text{ mg kg}^{-1}$ . In the low concentration range, the sorption isotherms were linear and the intersection of X-axes and the regression curve was EPC<sub>0</sub>, which can be calculated by regressive equations [34]. EPC<sub>0</sub> was higher and the risk of the P releasing onto the overlying water from sediments was bigger [35]. Reliable desorbed P (RDP) was the P releasing from the sediments when no phosphate was added in solution. According to the experiments,  $Q_{\text{max}}$ , EPC<sub>0</sub>, k and RDP can be calculated based on the fitting of Langmuir and Linear models. The triplicate experiments showed high repeatability of the sorption method and the experimental error was within 6%.

#### 2.5. Sorption kinetic measurements

An amount of 0.5 g dried sediments were added in a series of 100 ml acid washed centrifuge tubes with 50 ml phosphate solution containing  $10 \text{ mg L}^{-1}$  P each (anhydrous KH<sub>2</sub>PO<sub>4</sub>, in different ionic strength condition). The tubes were capped and placed at  $25 \pm 1$  °C in an orbital shaker at 250 rpm for various time intervals between 0 and 60 h (0.5, 1, 1.5, 2.5, 5, 9, 13, 18, 24, 36, 48 and 60 h). The super-

 Table 2

 Physical and chemical characteristics of the studied sediments and subsamples

natant was immediately centrifuged at 5000 rpm for 10 min and was then filtered through 0.45  $\mu$ m GF/C filter membranes. The filtrate was taken for phosphate analysis using the molybdenum blue/ascorbic acid method [32]. The phosphate sorbed on samples was calculated by the difference between the initial phosphate concentration and concentration in the supernatant. Triplicate experiments were carried out and the data were expressed as their average in this study.

#### 3. Results and discussion

#### 3.1. Sediment characteristics

Elemental composition, particle size distribution, TN, TP, TOC and CEC in the sediments are shown in Table 2. The contents of TP, TN and TOC in the sediments from Yue Lake were the highest and were 1640 mg kg<sup>-1</sup>, 5213 mg kg<sup>-1</sup> and 6.23%, respectively and those from East Taihu Lake were the lowest and were 441 mg kg<sup>-1</sup>, 932 mg kg<sup>-1</sup> and 0.9%, respectively. The sediments in this study represented three different pollution levels with the most serious pollution level in Yue Lake and lightest level in East Taihu Lake: Yue Lake > Wuli Lake > East Taihu Lake.

Al, Fe contents and CEC in the sediments were in the decreasing order in different lakes: Yue Lake>Wuli Lake>East Taihu Lake. But Ca content was different: East Taihu Lake>Wuli Lake>Yue Lake. This is considered to be caused by different pollution sources from the surrounding watershed and the large input of Al and Fe. Silt was the major component in the sediments and the proportion of clay and silt fractions was in the decreasing order in lakes: Yue Lake>Wuli Lake>East Taihu Lake. But the proportion of sand fraction was different: East Taihu Lake>Wuli Lake>Yue Lake. Those results are consistent with their pol-

Sediments	TOC (%)	CEC $(meq(100)^{-1})$	TN (mg kg <sup><math>-1</math></sup> )	$TP (mg kg^{-1})$	Al (%)	Fe (%)	Ca (%)	Clay (%)	Silt (%)	Sand (%)
East Taihu Lake	0.90	13.33	932	441	6.16	3.61	0.98	6.35	74.60	19.05
360-480 mesh	1.45	17.31	1231	872	8.32	5.36	0.79	6.01	78.42	15.57
240-360 mesh	0.95	14.53	902	606	7.56	4.26	0.84	5.46	81.02	13.52
60-240 mesh	0.78	12.32	821	472	5.74	3.01	1.03	6.89	70.63	22.48
18–60 mesh	0.71	11.45	631	336	5.12	2.67	1.12	7.12	63.78	29.10
Yue Lake	6.23	30.12	5213	1640	8.51	6.02	3.71	6.28	81.81	11.91
360-480 mesh	6.50	40.87	6342	2275	10.35	8.53	3.02	5.89	84.32	9.79
240-360 mesh	6.33	36.52	6123	1856	9.43	7.51	3.31	5.23	87.73	7.04
60-240 mesh	6.29	29.42	5832	1763	8.02	5.38	4.15	6.75	76.98	16.27
18–60 mesh	6.03	27.31	5124	1374	7.24	4.89	4.36	7.04	72.16	20.8
Wuli Lake	1.67	22.15	1923	819	6.55	3.44	0.69	7.95	71.00	21.05
360-480 mesh	2.32	26.75	2451	1294	9.32	5.42	0.46	6.75	79.42	13.83
240-360 mesh	1.94	24.63	2013	1037	8.43	4.76	0.53	6.23	83.15	10.62
60-240 mesh	1.69	20.12	2314	892	6.31	4.02	0.74	8.34	68.45	23.21
18-60 mesh	1.68	18.42	1905	608	5.46	3.86	0.93	8.78	65.36	25.86



Fig. 1. Phosphate sorption isotherms of different particle size fractions from various sediments in the high initial phosphate concentration range.



Fig. 2. Phosphate sorption isotherms of different particle size fractions from various sediments in the low initial phosphate concentration range.

lution levels. The 360–480 and 240–360 mesh sediments contained higher contents of clay and silt than 60–240 and 18–60 mesh sediments did (Table 2).

For the three studied sediments, TOC, TN, TP, Al and Fe contents and CEC increased as particle size decreased. This is probably due to the increase of clay mineral concentration in the clay fraction and the larger specific area for the fine fractions [36,37]. As fractions with different sizes had different specific surface areas and weight, they had different effects on the exchange of phosphate between sediments and the overlying water. Finer grain fractions had larger pollutant sorption capacity and high suspension potential. Therefore, sediments with higher proportion of clay and silt fractions were more heavily polluted.

Table 3

P availability and calculated sorption parameter of different particle size fractions from various sediments

Sediments	Particle size (mesh)	$Q_{\rm max} \ ({\rm mg}{\rm kg}^{-1})$	$EPC_0 (mg L^{-1})$	$k (1  \mathrm{kg}^{-1})$	RDP (mg $g^{-1}$ )
East Taihu Lake	360-480	302.9	48.2	800.6	-43.6
	240-360	275.1	41.3	701.9	-41.3
	60-240	226.3	34.2	390.6	-31.2
	18-60	208.4	30.1	223.2	-25.8
Yue Lake	360-480	740.4	634.1	176.1	-51.4
	240-360	683.3	588.5	172.4	-45.8
	60-240	506.7	562.7	168.6	-41.7
	18-60	352.7	531.3	117	-37.2
Wuli Lake	360-480	545.6	214.8	196.6	-54.1
	240-360	414.1	194.4	150.9	-46.8
	60-240	300.8	212.3	97.2	-27.3
	18-60	237.6	87.9	91.7	-14.8



Fig. 3. Phosphate sorption kinetic curves of different particle size fractions.

#### 3.2. Effects of particle size on phosphate sorption

Particle size distribution in sediments is an important factor affecting the phosphate sorption at the solid–liquid interface. In order to study the dependence of phosphate sorption on sediment particle size, experiments were conducted with four different particle size fractions at constant pH (6–7) and ionic strength (0.02 mol  $1^{-1}$  KCl) conditions. Figs. 1 and 2 show the phosphate sorption isotherms in the low and high initial concentration ranges. For different particle size fractions of various trophic sediments, the sorption isotherms in the high and low initial concentration ranges can be best-fitted using Langmuir model and Linear model, respectively.

The selected P availability and calculated sorption parameters of different particle size fractions are shown in Table 3. Those parameters mainly described the transfer ability of P between the sediment and water interface.  $Q_{\text{max}}$ , EPC<sub>0</sub> and *k* decreased with particle size increased for the three stud-

Table 4

Sediments	Particle size fractions (mesh)	Sampling internals (h)								
		0-0.5	0.5-1.5	1.5–3	3–5	5–7	7–12	12–24	24-48	48-60
East Taihu Lake	360-480	97.34	11.32	4.43	0.69	5.67	0.67	0.28	1.04	0.35
	240-360	80.61	14.20	6.98	0.11	0.56	3.00	0.28	0.50	0.91
	60-240	77.00	13.52	7.53	0.63	0.56	1.40	0.49	0.49	0.14
	18-60	71.76	15.30	3.65	1.76	1.74	0.85	0.68	0.28	0.42
Yue Lake	360-480	45.31	0.83	3.40	1.26	0.73	0.02	0.14	0.21	2.75
	240-360	43.64	0.76	0.55	2.12	1.20	0.21	0.07	0.24	2.29
	60-240	35.30	0.90	1.58	2.16	0.42	0.32	0.06	0.29	1.63
	18-60	20.22	1.74	0.45	0.50	0.79	0.69	0.27	0.25	0.70
Wuli Lake	360-480	57.17	6.58	3.34	0.35	1.25	2.23	0.14	0.44	1.44
	240-360	56.98	3.44	0.97	0.11	1.20	1.87	0.46	0.42	0.36
	60-240	50.31	1.76	5.58	1.96	0.90	0.70	0.35	0.30	0.69
	18-60	38.51	6.82	6.61	0.42	0.42	0.03	0.68	0.56	0.19

Table 5

Langmuir parameters of phosphate sorption by sediments before and after treated by H<sub>2</sub>O<sub>2</sub> in different ionic strength solutions

Samples	Ionic strength (M KCl)	Sediments		Sediments treated by H2O2			
		$\overline{Q_{\max} (\mathrm{mg}\mathrm{kg}^{-1})}$	K <sub>d</sub>	$R^2$	$\overline{Q_{\max} (\mathrm{mg}\mathrm{kg}^{-1})}$	K <sub>d</sub>	$R^2$
Wuli Lake	0	352.7	0.014	0.95	326.8	0.003	0.91
	0.001	336.7	0.008	0.93	307.4	0.002	0.99
	0.01	302.1	0.005	0.98	274.8	0.002	0.98
Yue Lake	0	385.6	0.0015	0.91	354.7	0.4126	0.99
	0.001	363.2	0.003	0.92	321.9	0.4658	0.97
	0.01	354.7	0.0091	0.90	301.4	0.5571	0.99
East Taihu Lake	0	310.5	0.0048	0.98	284.8	0.0014	0.97
	0.001	291.6	0.006	0.97	272.3	0.0294	0.94
	0.01	275.3	0.0076	0.91	253.9	0.0098	0.92

ied sediments, but RDP increased.  $Q_{\text{max}}$  and EPC<sub>0</sub> were in the decreasing order in different lake sediments: Yue Lake > Wuli Lake > East Taihu Lake. But *k* and the RDP were different: East Taihu Lake > Wuli Lake > Yue Lake. This suggests that  $Q_{\text{max}}$  and EPC<sub>0</sub> increased as sediment pollution level increased while *k* and RDP decreased.  $Q_{\text{max}}$ , EPC<sub>0</sub>, *k* and RDP of different particle size fractions varied; there were no clear differences among different trophic lake sediments.

The isotherms (Figs. 1 and 2) showed that the sorption tended to reach saturation as phosphate concentration increased and they were best fitted by Langmuir model assuming the homogeneous sorption sites. This probably indicates that there existed one dominant model for the inter-



(Note: E: Experimental results; PFE: Power Function model fitting; SEE: Simple Elovich model fitting; PDE: Parabolic Diffusion model fitting)

Fig. 4. The fitting kinetic curves of phosphate sorption by the various particle size fractions using three different models.

Table 6	
Phosphate sorption rate of sediments before and after treated b	y H <sub>2</sub> O <sub>2</sub> in different ionic strength solutions (mg (kg h) <sup><math>-1</math></sup> )

Ionic strength (M)	Sampling intervals (h)									
	0-0.5	0.5-1.5	1.5–5	3–5	5–7	7–12	12–16	16–24	24–48	
Wuli Lake										
Sediments										
0.01	212.07	25.10	22.91	10.75	12.50	1.20	4.46	5.07	0.44	
0.001	241.17	25.53	9.61	0.15	12.69	1.85	4.64	1.96	0.85	
0	305.95	29.96	13.61	6.02	11.22	1.11	7.35	0.39	0.05	
Sediments treated by	y $H_2O_2$									
0.01	174.62	15.94	13.26	10.15	5.07	1.08	1.27	1.82	1.64	
0.001	186.09	18.40	21.33	9.99	2.70	2.10	6.46	1.86	0.42	
0	200.83	31.18	29.74	10.01	1.50	2.41	2.57	1.06	1.31	
East Taihu Lake										
Sediments										
0.01	93.84	13.26	11.52	7.52	0.28	2.00	2.49	0.66	0.49	
0.001	106.03	14.43	9.95	10.33	2.54	0.97	2.54	1.97	0.46	
0	148.15	19.53	12.30	12.05	6.17	2.60	3.67	3.42	0.27	
Sediments treated by	y $H_2O_2$									
0.01	71.62	38.17	14.43	6.14	2.65	3.96	3.80	7.25	0.41	
0.001	83.88	35.85	16.56	4.99	1.71	1.91	3.74	7.01	0.41	
0	131.67	39.63	11.02	5.47	6.24	4.00	3.24	7.25	0.44	
Yue Lake										
Sediments										
0.01	471.45	25.12	20.74	10.10	9.07	3.37	2.54	1.81	0.00	
0.001	542.78	25.48	22.79	12.76	5.81	2.04	0.70	0.29	1.10	
0	600.33	30.23	20.35	10.26	5.41	4.43	5.24	0.43	0.42	
Sediments treated by	y $H_2O_2$									
0.01	321.67	35.40	10.30	3.86	3.06	3.06	4.71	4.51	0.48	
0.001	331.01	35.34	13.64	9.77	24.06	0.38	5.53	0.38	0.08	
0	411.66	43.12	10.26	9.84	10.32	0.23	6.09	1.68	0.68	

action between phosphate and sediment during the phosphate sorption at the sediment–water interface. Sediment particle size was found to have a significant effect on phosphate sorption capacity. This may be considered that the fine particle size provided most of the sediment mineral surface. This is in agreement with the hypothesis discussed in the earlier section that mineral surface played a dominant role in the phosphate sorption. In addition, higher contents of organic matter, Fe/Al oxides and P in finer particle size fractions may promote the phosphate sorption [34].

Phosphate sorption by sediments was a complex kinetic process usually including quick sorption and slow sorption. As shown in Fig. 3, quick sorption mainly occurred within 0.5 h. Sorption rate was calculated to compare the difference of phosphate sorption in different sediments (Table 4). The average sorption rate within 0.5 h was the highest than that



Fig. 5. Effects of ionic strength in solutions on phosphate sorption by different sediments.

within other times during the experiment period. As particle size decreased, the sorption rate increased for the three studied sediments. This provides further support that the particle size had a significant effect on the phosphate sorption rate in sediments. Phosphate sorption rate was in the decreasing order in lake sediments: East Taihu Lake > Wuli Lake > Yue Lake. This suggests that as sediment pollution level increased the phosphate sorption rate decreased. The sorption rate varied among the different particle size fractions and there were no clear differences among various trophic lake sediments.

As shown in Fig. 4, the sorption kinetic curves can be fitted using several kinetic models, e.g. power function, simple Elovich and parabolic diffusion models. It appears that power function and simple Elovich models can best describe the phosphate sorption kinetics and there was no clear difference among different sediments. But parabolic diffusion model cannot describe the sorption kinetics satisfactorily.

As previously reported, the content and property of organic matter, Fe/Al (hydr) oxides and P in sorbent were considered to be the major factors controlling phosphate sorption by sediments [38,39]. The rank order of  $Q_{\text{max}}$  and EPC<sub>0</sub> possibly reflected the content of organic matter, Fe/Al (hydr) oxides and P as compared with different sediments (Table 2). As particle size decreased,  $Q_{\text{max}}$ , EPC<sub>0</sub> and k increased while

Table 7

Calculated kinetic model parameters of phosphate sorption by sediments before and after treated by H<sub>2</sub>O<sub>2</sub> in different ionic strength solutions<sup>a</sup>

Samples	Ionic strength (M)	Power function model $(q = a \times t^b)$								
		Sediments treat	ed by H <sub>2</sub> O <sub>2</sub>		Sediments					
		a	b	<i>R</i> <sup>2</sup>	a	b	$R^2$			
Wuli Lake	0.01	96.77 ± 3.51	$0.21\pm0.01$	0.98	$131.32 \pm 2.48$	$0.17\pm0.01$	0.99			
	0.001	$116.17 \pm 4.36$	$0.19\pm0.01$	0.97	$136.11 \pm 5.57$	$0.20\pm0.01$	0.97			
	0	$137.3 \pm 10.3$	5 $0.18 \pm 0.03$	0.88	$201.78\pm6.50$	$0.12\pm0.01$	0.94			
East Taihu Lake	0.01	$59.61 \pm 3.12$	$0.21\pm0.02$	0.96	$60.24\pm 6.25$	$0.33\pm0.03$	0.94			
	0.001	$65.13 \pm 3.24$	$0.23\pm0.02$	0.97	$66.00\pm6.52$	$0.31\pm0.03$	0.94			
	0	$121.86 \pm 3.22$	$0.14\pm0.01$	0.97	$177.34 \pm 2.64$	$0.09\pm0.01$	0.97			
Yue Lake	0.01	$175.83 \pm 5.58$	$0.14\pm0.01$	0.96	$265.76 \pm 6.21$	$0.10\pm0.01$	0.95			
	0.001	$202.17 \pm 9.48$	$0.14\pm0.02$	0.91	$296.02\pm6.22$	$0.09\pm0.01$	0.95			
	0	$228.92 \pm 4.63$	$0.12\pm0.01$	0.98	$322.28\pm5.47$	$0.09\pm0.01$	0.96			
Samples	Ionic strength	Simple Elovich mo	$\det (q = a + b \ln t)^{\mathrm{b}}$							
		Sediments treated b	Sediments treated by H <sub>2</sub> O <sub>2</sub>		Sediments					
		a	b	$R^2$	a	b	$R^2$			
Wuli Lake	0.01	93.41 ± 4.21	$28.77 \pm 1.84$	0.97	$129.59 \pm 4.52$	$29.52 \pm 1.97$	0.97			
	0.001	$112.82 \pm 4.98$	$30.66 \pm 2.18$	0.97	$130.48 \pm 5.45$	$40.46\pm2.38$	0.98			
	0	$129.20\pm8.38$	$37.37 \pm 3.66$	0.94	$199.14 \pm 6.20$	$30.85 \pm 2.71$	0.95			
East Taihu Lake	0.01	$56.13 \pm 2.50$	$19.45 \pm 1.09$	0.98	$53.69 \pm 9.87$	$36.29 \pm 4.31$	0.91			
	0.001	$60.76\pm2.25$	$23.16\pm0.98$	0.99	$59.97 \pm 10.20$	$37.02 \pm 4.45$	0.91			
	0	$120.36 \pm 3.70$	$22.49 \pm 1.62$	0.97	$176.49 \pm 2.70$	$19.21 \pm 1.18$	0.97			
Yue Lake	0.01	$196.36 \pm 7.58$	$37.25 \pm 3.31$	0.95	$262.79 \pm 4.88$	$32.38 \pm 2.13$	0.97			
	0.001	$174.95 \pm 7.42$	$31.93 \pm 3.24$	0.93	$293.78\pm5.45$	$31.38 \pm 2.38$	0.96			
	0	$226.05 \pm 3.94$	$35.68 \pm 1.72$	0.98	$320.29\pm4.95$	$34.03\pm2.16$	0.97			
Samples	Ionic strength	Parabolic diffusion m	odel $(q/t = a + b/t^{1/2})$							
		Sediments treated by	H <sub>2</sub> O <sub>2</sub>		Sediments					
		a	b	$R^2$	a	b	$R^2$			
Wuli Lake	0.01	$-6.20 \pm 1.22$	$71.69 \pm 6.53$	0.73	$-8.67 \pm 1.67$	$93.38 \pm 8.95$	0.52			
	0.001	$-7.95 \pm 1.26$	$86.32 \pm 6.76$	0.75	$-9.22 \pm 1.44$	$103.05 \pm 7.72$	0.81			
	0	$-10.19\pm1.36$	$105.26\pm7.31$	0.81	$-14.27 \pm 2.58$	$138.76 \pm 13.83$	-0.03			
East Taihu Lake	0.01	$-4.16 \pm 0.53$	$46.54 \pm 2.84$	0.89	$-3.19 \pm 0.81$	$51.94 \pm 4.36$	0.93			
	0.001	$-4.46\pm0.57$	$51.47\pm3.03$	0.91	$-3.58\pm0.88$	$55.90 \pm 4.73$	0.92			
	0	$-8.14\pm1.68$	$83.96\pm9.00$	0.16	$-12.15 \pm 2.58$	$115.52 \pm 13.86$	-1.74			
Yue Lake	0.01	$-11.43 \pm 2.54$	$119.73 \pm 13.65$	0.08	$-18.88 \pm 3.57$	$178.01 \pm 19.14$	-0.83			
	0.001	$-14.97 \pm 2.19$	$145.28 \pm 11.75$	0.49	$-20.59 \pm 4.28$	$193.53 \pm 22.98$	-1.79			
	0	$-15.86 \pm 3.05$	$156.27 \pm 16.33$	-0.12	$-22.44 \pm 4.58$	$210.94 \pm 24.58$	-1.74			

<sup>a</sup> *q*-sorbed phosphate (mg kg<sup>-1</sup>) at time *t* (h). Phosphate was initially added at  $10 \text{ mg L}^{-1}$  P sorbent.

<sup>b</sup> The simple Elovich parameters were calculated without using the origin (q=0; t=0).

RDP decreased. This is probably due to the higher content of organic matter, Fe/Al oxides, clay minerals and P for finer particle size fractions. This is consistent with previous reports [3,38-40]. Therefore, phosphate sorption capacity can be related to many factors and the metal content appears to be the main factor that determines the phosphate sorption capacity due to the high specific surface of the Fe/Al oxides and clay minerals. In some cases, the phosphate sorption sites can be occupied by Fe and Al. Based on the above discussion, the phosphate sorption capacity of sediments with high content of carbon, Fe, Al, nitrogen and P should be high. The obtained results (Tables 2 and 3) agree with this suggestion. There would be a notable accumulation of organic matter, P, nitrogen, Al and Fe when lakes developed from mesotrophic to eutrophic status and that Fe/Al-P precipitation process may occur. A similar result was also reported in other areas [41].

# 3.3. Effects of ionic strength and organic matter on the phosphate sorption

Two different ionic strengths, 0.001 and 0.01 M KCl, were used and the results were compared with those obtained for different samples with no ionic strength experimental control. Sediments with different organic matter content and the samples before and after H<sub>2</sub>O<sub>2</sub> treatment were used (Table 1). For samples with different organic matter content in various ionic strength solutions, the phosphate sorption isotherms in the high initial phosphate concentration range can be best fitted by Langmuir model with regression coefficients ( $R^2$ ) of above 0.9 and the parameters are illustrated in Table 5. As organic matter content decreased and ionic strength increased,  $Q_{max}$ decreased.

For the three studied sediments, as ionic strength increased the phosphate sorption rate increased (Table 6), especially for the sorption rate within 0.5 h. After treated by  $H_2O_2$ (low organic matter content) sediment phosphate sorption rate decreased. As reported, organic matter content was one of the major factors controlling phosphate sorption rate in sediments [17,18,21-24]. The phosphate sorption as a function of ionic strength is shown in Fig. 5. As ionic strength increased from 0.001 to 0.01 mol 1<sup>-1</sup> KCl the sorption capacity increased 20% at a constant pH (6-7). This increase can be attributed to the macromolecular phosphate configuration: In high ionic strength solution, the negative charges on phosphate macromolecules were well screened and consequently the phosphate molecules wounded up like random coils. In this more compact configuration, more phosphate can be sorbed onto a given area of sediment surface. As ionic strength decreased, the unscreened negatively charged function groups repelled each other and consequently the molecule spread out as flexible, linear polymer molecules. In this configuration the molecules more space the surface, resulting in lower sorption density [42–43]. This suggests that organic matter was one of the most important factors affecting phosphate sorption at the sediment-water interface.

For the sediments before and after treatment by  $H_2O_2$  in different ionic strength solution, phosphate sorption kinetic curves were fitted with power function, simple Elovich and parabolic diffusion models by non-linear regression with Microcal Origin Software [44]. The calculated parameters of kinetic models are shown in Table 7. Based on  $R^2$  and SE, it appears that power function and simple Elovich models can satisfactorily describe the effects of ionic strength and organic matter content on phosphate sorption kinetics.

It is apparent that power function and simple Elovich models were the best kinetic fitting models and there was no clear difference between them. But parabolic diffusion model was not the best fitting model. This indicates that the effects of ionic strength and organic matter content in sediments on phosphate sorption were similar for different trophic lake sediments and there was no clear difference among them. More than 75% organic matter was lost when sediments were treated by  $H_2O_2$ . But this only resulted in less than 20% decrease in the sorption capacity. This indicates that both "quantity" and "quality" of organic matter likely varied significantly among various particle size fractions from different trophic sediments, although this aspect needs further investigations.

#### 4. Conclusions

- (1) For the three studied sediments, as particle size increased  $Q_{\text{max}}$ , EPC<sub>0</sub>, k and phosphate sorption rate decreased, but RDP increased.  $Q_{\text{max}}$ , EPC<sub>0</sub>, k and RDP of different particle size fractions varied; there were no clear differences among different trophic lake sediments. With the increase in sediment pollution level  $Q_{\text{max}}$  and EPC<sub>0</sub> increased while k and RDP decreased. The quick sorption mainly occurred in 0.5 h. Power function and simple Elovich models were the best kinetic models for the phosphate sorption of the different particle size fractions and there was no clear difference between them. Parabolic diffusion model was not the best kinetic fitting model.
- (2) As organic matter content decreased and ionic strength increased,  $Q_{\text{max}}$  and phosphate sorption rate of sediments decreased. This indicates that the effects of ionic strength and organic matter content on phosphate sorption were similar for various trophic lake sediments and there was no clear difference among them. Power function and simple Elovich models were the best kinetic fitting models. Parabolic diffusion model was not the best fitting model. Both "quantity" and "quality" of organic matter likely varied significantly among different particle sizes fractions.

#### Acknowledgements

Authors wish to thank for the financial support from China's national basic research program: "Studies on the Process of Eutrophication of Lakes and the Mechanism of the Blooming of Blue Green Alga" (2002CB412304). We also thank the assistance of colleagues of the Research Center of Lake Environment of Chinese Research Academy of Environment Sciences.

#### References

- A.G. Brinkman, A double-layer model for ion adsorption onto metal oxides, applied to experimental data and to natural sediments of Lake Veluwe, The Netherlands, Hydrobiologia 253 (1993) 31–45.
- [2] R. Emil, B. Eugene Welch, Aluminum dose required to inactivate phosphate in lake sediments, Water Res. 32 (1998) 2969– 2976.
- [3] M.B. Mcgechan, D.R. Lewis, Sorption of phosphorus by soil. Part 1. Principles, equations and models, Biosyst. Eng. 82 (2002) 1–24.
- [4] T.M. Addiscott, D. Thomas, Tillage, mineralization and leaching: phosphate, Soil Till. Res. 53 (2000) 255–273.
- [5] P. De Willigen, P.A.C. Raats, R.G. Gerritse, Transport and fixation of phosphate in acid, homogeneous soils. II. Computer simulation, Agric. Environ. 7 (1982) 161–174.
- [6] J.W. Bowden, A. Posner, J. Quirk, Ionic adsorption on variable charge mineral surfaces, theoretical charge development and titration curves, Aust. J. Soil Res. 15 (1977) 121–136.
- [7] M.B. Mcgechan, Sorption of phosphorus by soil. Part 2. Measurement methods, results and model parameter values, Biosyst. Eng. 82 (2002) 115–130.
- [8] J.C. Ryden, J.K. Syers, Rationalization of ionic strength and cation effects of phosphate sorption by soils, J. Soil Sci. 26 (1975) 395–406.
- [9] D.E. Walling, P.W. Moorehead, Spatial and temporal variation of the particle-size characteristics of fluvial sediment, Geografisk Annaler 69 (1987) 47–59.
- [10] C.S. Zhang, L.J. Wang, G.S. Li, S.S. Dong, J.R. Yang, X.L. Wang, Grain size effect on multi-element concentrations in sediments from the intertidal flats of Bohai Bay China, Appl. Geochem. 17 (2002) 59–68.
- [11] L.A. Warren, A.P. Zimmerman, The importance of surface area in metal sorption by oxides and organic matter in heterogeneous natural sediment, Appl. Geochem. 9 (1994) 245–254.
- [12] S. Goldberg, G. Sposito, On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: a review, Commun. Soil Sci. Plant Anal. 16 (1985) 801–821.
- [13] A.N. Sharpley, S.C. Chapra, R. Wedepohl, J.T. Sims, T.C. Daniel, K.R. Reddy, Managing agricultural phosphorus for protection of surface waters-issues and options, J. Environ. Qual. 23 (1994) 437– 451.
- [14] B. Bengt, M. Jens Anderson, S. Fleischer, Exchange of phosphorus across the sediment-water interface, Hydrobiology 170 (1988) 229–244.
- [15] H.X. Tang, Application of surface coordination principle and modeling on aquatic micro-interfacial processes impacting the water quality (in Chinese), Acta Scientiae Circumstantiae 20 (1) (2000) 1–10.
- [16] A. Kaiserli, D. Voutsa, C. Samara, Phosphorus fractionation in lake sediments-Lakes Volvi and Koronia, N. Greece, Chemosphere 46 (2002) 1147–1155.
- [17] M. Liu, L.J. Hou, S.Y. Xu, Phosphate adsorption characteristics of tidal flat surface sediments and its environmental effect from the Yangtze estuary (in Chinese), Acta Geographica Sinica 57 (4) (2002) 397–406.
- [18] P. Lopez, X. Lluch, M. Vidal, J.A. Morguí, Adsorption of phosphorus on sediments of the Balearic Islands (Spain) related to their composition, Estuarine Coastal Shelf Sci. 42 (1996) 185–196.
- [19] K.G. Karthikeyan, A. Mandla Tshabalala, D. Wang, M. Kalbasi, Solution chemistry effects on orthophosphate adsorption by cationized solid wood residues, Environ. Sci. Technol. 38 (2004) 904–911.

- [20] E. Gomez, C. Durillon, G. Rofes, B. Picot, Phosphate adsorption and release from sediment of brackish lagoons: pH, O<sub>2</sub> and loading influence, Water Res. 33 (1999) 2437–2447.
- [21] H.L. Golterman, Zonation of mineralization in stratified lakes, in: J.M. Anderson, A. Macfayden (Eds.), The Role of Terrestrial and Aquatic Organism in Decomposition Processes, vol. 1, E-Publishing Inc., New York, 1976.
- [22] W. Davison, S.I. Heany, Ferrous iron-sulfide interactions in anoxic hypolimnetic waters, Limnol. Oceanogr. 23 (6) (1978) 1194– 1200.
- [23] H. Verdouw, E.M.J. Dekkers, Iron and manganese in Lake Vechten (The Netherlands): dynamics and role in the cycle of reducing power, Arch. Hydrobiol. 89 (4) (1980) 509–532.
- [24] J. Pizarro, N. Belzile, M. Filella, G.G. Leppard, J.C. Negre, D. Perret, J. Bufe, Oagulation/sediment-tation of submicron particles in a Eutrophic lake, Water Res. 29 (2) (1995) 617–632.
- [25] M.I. Makarova, L. Haumaier, W. Zech, T.I. Malyshev, Organic phosphorus compounds in particle-size fractions of mountain soils in the northwestern Caucasus, Geoderma 118 (2004) 101– 114.
- [26] J. Angus Beck, C. Kevin Jones, The effects of particle size, organic matter, crop residues and dissolved organic matter on the sorption kinetic of atrazine and isoproturon by clay soil, Chemosphere 32 (1996) 2345–2358.
- [27] Institute of soil science Chinese academy of sciences, Soil physics and chemistry analyze, Shanghai science and technology publishing company, Shanghai, 1978.
- [28] V. Ruban, J.F. López-Sánchez, P. Pardo, G. Rauret, H. Muntau, P. Quevauviller, Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments—a synthesis of recent works, Fresen. J. Anal. Chem. 370 (2001) 224–228.
- [29] L. Zanini, W.D. Robertson, C.J. Ptacek, S.L. Schiff, T. Mayer, Phosphorus characterization in sediments impacted by septic effluent at four sites in central Canada, J. Contamin. Hydrol. 33 (1998) 405–429.
- [30] B.M. Das, Principles of Geotechnical Engineering, 2nd ed., PWS-KENT, Boston, 1990.
- [31] M. Sayin, A.R. Mermut, H. Tiessen, Phosphate sorption-desorption characteristics by magnetically separated soil fractions, Soil Sci. Soc. Am. J. 54 (1990) 1298–1304.
- [32] AWWA, APHA, WPCE, Standard methods for the examination of water and wastewater, 18th ed., American Public Health Association, Washington, DC, 1995.
- [33] B. Nwoke, J. Vanlauwe, N. Diels, O. Sanginga, R. Osonubi Merckx, Assessment of labile phosphorus fractions and adsorption characteristics in relation to soil properties of West African Savanna soils, Agric. Ecosyst. Environ. 100 (2003) 285–294.
- [34] X.C. Jin, S.R. Wang, Y. Pang, H.C. Zhao, X.N. Zhou, The adsorption of phosphorus on different trophic lake sediment, Colloid Surf. A: Physicochem. Eng. Aspects 254 (2005) 241–248.
- [35] A.W. Taylor, H.W. Kunishi, Phosphate equalibria on stream sediment and soil in a watershed draining agricultural region, J. Agric. Food Chem. 19 (1971) 827–831.
- [36] Y.M. Zhou, R.R. Liu, H.X. Tang, Sorption interaction of phenanthrene with soil and sediment of different particle sizes and in various CaCl<sub>2</sub> solutions, J. Colloid Interf. Sci. 270 (2004) 37–46.
- [37] N.J. Barrow, The description of phosphate adsorption curves, Soil Sci. 29 (1978) 447–462.
- [38] R.A. Berner, Phosphate adsorption from seawater by adsorption on volcanogenic ferric oxides, Earth Planet. Sci. Lett. 18 (1973) 77– 86.
- [39] M.D. Lucotte, B. Anglejan, Seasonal changes in the phosphorus-iron geochemistry of the St. Lawrence Estuary, J. Coastal Res. 4 (1988) 339–349.
- [40] L. Lijklema, Interaction of orthophosphate with iron III and aluminum hydroxides, Environ. Sci. Technol. 4 (1980) 537–541.

- [41] H.S. Jensen, F.O. Andersen, Importance of temperature, nitrate and pH for phosphate release from aerobic sediments of four shallow, Eutrophic lakes, Limnol. Oceanogr. 37 (1992) 577– 589.
- [42] R. Carman, F.V. Wul, Adsorption capacity of phosphorus in Baltic Sea sediments, Estuarine, Coastal Shelf Sci. 29 (1989) 447–456.
- [43] T. Tiren, K. Pettersson, The influence of nitrate on the phosphorus flux to and from oxygen depleted lake sediments, Hydrobiologia 120 (1985) 207–223.
- [44] S.R. Wang, X.C. Jin, Y. Pang, Z.H. Zhao, X.N. Zhou, The study on the effect of pH on phosphate sorption by different trophic Lake sediments, J. Colloid Interf. Sci. 285 (2005) 448–457.