Phosphorus adsorption on natural sediments: Modeling and effects of pH and sediment composition

Aimin Zhou, Hongxiao Tang, Dongsheng Wang[*]

SKLEAC, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract

The classic Langmuir isotherm equation was modified to describe phosphorus (P) adsorption on P-polluted sediments. The P adsorption characteristics of six sediment samples from Chinese Taihu Lake were studied by short-term isotherm batch experiments and related to sediment composition. The maximum P adsorption capacities (PAC) and P-binding energy constant (k) were obtained by nonlinearly fitting sorption data using the modified Langmuir isotherm model. Native adsorbed exchangeable phosphorus (NAP), the zero equilibrium P concentration value (EPC_0), and partitioning coefficients (K_p) were subsequently calculated by corresponding formulae. K_p and PAC were linearly related to the contents of active Fe and Al in sediments by least squares regression analyses ($R^2 \approx 0.9$ for both).

The effect of pH in a wide range on adsorption process was investigated and $H_2PO_4^-$ was presumed to be the preferential sorption species in overall sorption process. The fact that the amount of P sorbed and zeta potential of sediment particles have no necessary relationship reveals that a strong contribution to the P binding still comes from a ligand-exchange process on the $Me-OH_2^+$ and $Me-OH$ sites rather than electrostatic attraction. In addition, the influence of oxidation–reduction potential (ORP) was investigated and discussed and the dual nature of sediments as a pool or source of P in natural waters was evaluated in site T1–T4.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Adsorption; Model; Sediment; NAP; Preferential sorption species; Taihu Lake

1. Introduction

As one of the main nutrients, P can be found in the sediment matrix in the forms of calcium, iron or aluminum complex salts and organic species, or adsorbed onto the surface of minerals and has a predominant role in cellular energetics as ATP and as an important part of many structural and biochemically functional components for cell growth of plants includ-

ing algae (Gibson, 1971; Dorich et al., 1984), but its excess supply can lead to eutrophication. The role of P in the fresh water eutrophication process as the primary limiting factor for algal growth was identified several decades ago (OECD, 1982). Much attention has been paid to P adsorption/desorption processes on natural sediments and pure minerals (Naoml and Patrick, 1991a, b; Yao and Millero, 1996; Zhao and Stanforth, 2001; Kim et al., 2003). Laboratory experiments with Fe(OOH) showed that pH increases produced liberation of P adsorbed onto the iron complexes because of competition with OH^- ions (Lijklema, 1977). But little information about the effects of pH in a wide range on P sorption on natural sediments is available.

*Corresponding author. Tel.: +86 10 62849144; fax: +86 10 62923543.

E-mail address: zheuaimin@yahoo.com.cn (D. Wang).

NAP content and sorption characteristics have been correlated with sediment composition such as active iron, aluminum, and organic matter content, and in turn, sediment composition has been related with lake chemistry, i.e., with hardness, alkalinity, and pH (Naoml and Patrick, 1991a). This fraction of P will certainly participate the adsorption/desorption processes in batch experiments conducted in laboratory. Especially, when NAP is significant, it cannot be neglected in the descriptive model for adsorption/desorption processes.

In the past, researchers had made much effort to develop models to describe P adsorption characteristics on natural sorbents. For instance, Hiemstra and co-orkers have developed CD-MUSIC model to describe the sorption behaviors of P on such pure minerals as goethite (Hiemstra and Van Riemsdijk, 1996; Geelhoed et al., 1998), but this model has difficulty in being applied to heterogeneous sorbents. So far, simple Langmuir isotherm model is still extensively used to describe sorption features of P on natural sediments (Lopez et al., 1996; Bubba et al., 2003). However, as far as NAP-polluted sediments are concerned, the simple Langmuir model cannot work perfectly because it neglected the existence of native adsorbed P (House and Denison, 2000).

The objectives of present study are mainly to model P adsorption processes by modified Langmuir isotherm and understand the influencing patterns of such factors as pH, zeta potential, ORP, and sediment composition.

2. Theory

When sediment contacts with water, P will be exchanged with the water on the interface until a dynamic equilibrium is reached. Sediment and water concentrations are stabilized when sediment-to-water and water-to-sediment rates become equal. Adsorption–desorption and precipitation–dissolution may be involved in these processes. The equilibrium situation is usually described by a Langmuir adsorption isotherm (Stumm and Morgan, 1981; Weber et al., 1991).

$$NSP = \frac{PAC \cdot P_{eq}}{k + P_{eq}}, \tag{1}$$

where NSP is the mass of net adsorbed P per mass unit at equilibrium (mg/g), P_{eq} is the equilibrium concentration of P in solution (mg/l), PAC is the maximum P adsorption capacity at saturation conditions per mass unit of sediment(mg/g). k is the empirical constant with unit of concentration (mg/l) and corresponds to the concentration at which half the maximum sorption capacity is reached and is related to the surface binding energy. The Langmuir model assumes a homogeneous surface, uniform binding energy, and monolayer cover-

age. The model has been used widely to describe anion sorption by soils and sediments (Danen-Louwerse et al., 1993; Lopez et al., 1996; House and Denison, 2000; Bubba et al., 2003), despite their heterogeneous nature. However, in studying P sorption properties on NAP-polluted sediments, adopting directly Eq. (1) is unreasonable because NAP in sediment also takes part in the sorption equilibrium (Aminot and Andrieux, 1996). Taking NAP into account, the equilibrium conditions of adsorption trials can be described as:

$$(NAP + C_{add} \cdot V/w) - P_{eq} \cdot V/w = \frac{PAC \cdot P_{eq}}{k + P_{eq}}, \tag{2}$$

or

$$(C_{add} - P_{eq}) \cdot V/w = \frac{PAC \cdot P_{eq}}{k + P_{eq}} - NAP, \tag{3}$$

where NAP refers to the amount of total native (or original) exchangeable P (mg/g), w is dry weight of sediment in the sorption trials (g), C_{add} is the initial concentration of newly added P in solution of adsorption trials (mg/l). V is solution volume (l). P_{eq}, PAC and k was described in Eq. (1). $P_{eq}V$ refers to the amount of exchangeable P remained in solution of adsorption trials, which should include both NAP dissolved and newly added P that was not adsorbed by sediment. Considering an extreme condition with $C_{add} = 0$, then Eq. (3) will take the form as

$$-P_{eq}^0 \cdot V/w = \frac{PAC \cdot P_{eq}^0}{k + P_{eq}^0} - NAP, \tag{4}$$

or

$$NAP - P_{eq}^0 \cdot V/w = \frac{PAC \cdot P_{eq}^0}{k + P_{eq}^0} \tag{5}$$

where P_{eq}^0 denotes equilibrium concentration of exchangeable phosphorous in the solution with initial $C_{add} = 0$, which actually is solution concentration in desorption equilibrium by fresh water. In this special case, there is no exchangeable P added and thus all of exchangeable P in the system is native exchangeable P. In Eq. (5), when desorption/adsorption processes fall into dynamic equilibrium, the amount of exchangeable P adsorbed is described by the value of the left part. Then NAP can be obtained by

$$NAP = \frac{PAC \cdot P_{eq}^0}{k + P_{eq}^0} + P_{eq}^0 \cdot V/w. \tag{6}$$

When NAP in Eq. (3) is substituted by Eq. (6), the resulting equation will hold

$$(C_{add} - P_{eq}) \cdot V/w = \frac{PAC \cdot P_{eq}}{k + P_{eq}} - \left(\frac{PAC \cdot P_{eq}^0}{k + P_{eq}^0} + P_{eq}^0 \cdot V/w \right). \tag{7}$$

Eq. (7) can serve as a model to describe P sorption properties on lake sediments that contain different amounts of NAP. Using this model, the data of sorption isotherm trials can be nonlinearly fitted properly with the least square method. The values of PAC and k are then obtained. Afterwards, NAP can be calculated by Eq. (6) with corresponding parameters. EPC_0 refers to water phase concentration at which $P_{eq} = C_{add}$ where the original sediment and water phosphate concentrations are in dynamic equilibrium. When $P_{eq} = C_{add} = EPC_0$, the expression of EPC_0 according to Eq. (7) will take the form below:

$$EPC_0 = P_{eq} = \frac{k \cdot PAC \cdot P_{eq}^0/(k + P_{eq}^0) + k \cdot P_{eq}^0 \cdot V/w}{k \cdot PAC/(k + P_{eq}^0) - P_{eq}^0 \cdot V/w},$$
(8)

and K_p can be calculated by

$$K_p = \frac{NAP}{EPC_0},$$
(9)

where PAC, NAP, and EPC_0 are indicated in Fig. 2a.

Virtually, in overall model deducing course it is assumed that: (1) newly added P will have direct competition with NAP and they have the same sorption parameters of PAC and k; (2) All of orthophosphate added are exchangeable P and thus the portion of P combined with or co-precipitated on sediment that can no longer be readily exchanged by other ions has been ignored.

3. Methods

3.1. Description of Taihu Lake area

Taihu lake, located in south of the Changjiang delta, China, is a large, shallow and eutrophic lake in the Yangtze valley, 90 km from Shanghai and subjects to severe blooms of cyanobacteria. It has an area of 2338 km² and a mean depth of 2 m. Trophic states in different areas of the lake vary from hypereutrophic to mesotrophic states related to different extents and manners of anthropogenic activities. It is of great importance for drinking water source of cities like Wuxi, Jiangsu province, and Shanghai, and for fisheries and recreations. Due to the very shallow depth of the lake, wind driven resuspension of bottom sediments has given rise to intensive internal circulation of particulates. The mixing and adsorption/desorption processes of P with particulates are significant.

3.2. Sampling

Six sediment samples (T1–T6) were collected from the Taihu Lake according to the eutrophic extents and positional features in January 2002. The information about all sampling sites is listed in Table 1. In all of these samples, T1, T2 and T4 represent typical trophic states of Taihu Lake. T1 is in the Wuli sublake that is the nearest place to Wuxi city, Jiangsu province. The ecological system of this area is strongly influenced by industrial production, human activities, and shipping business. The pollution situation of this area is rather serious. T2 is in eutrophic state and T4 is almost located at the center of the lake, and is in mesotrophic state. At each sampling site three cores were used to collect the sediment and upper 5 cm sediment of each core was sliced and mixed together to obtain relative homogenized materials. Samples were stored wet in sealed Zip-lock bags at 4 °C until used. Back to laboratory the sediment samples were air-dried at room temperature. To remove large debris in the sediments they were passed through a 60-mesh sieve and subsequently the subsamples were passed through 260-mesh (63 μm) sieve before being used in the adsorption trials. These sampling sites almost represent all the trophic states

Table 1
The characteristics of sampling points

Sample	Site position		Overlying water characteristics				
	E	N	Water depth (m)	pH	DO (mg/l)	Clarity (cm)	Trophic status[a]
T1	120.22°	31.54°	0.9	8.36	10.88	60	Hypereutrophic
T2	120.21°	31.50°	2.2	8.54	11.87	90	Eutrophic
T3	120.06°	31.44°	2.0	7.97	9.47	70	Eutrophic
T4	120.22°	31.23°	2.8	8.16	10.87	20	Mesotrophic
T5	119.96°	31.21°	2.5	8.07	10.15	30	Mesotrophic
T6	120.44°	31.43°	1.2	8.89	10.58	120	Mesotrophic

[a]Factors that influence comprehensively evaluating trophic state include nutrient concentration, chlorophyll *a* content in algae, clarity of lake water and dissolved oxygen, etc. Here the trophic states in different areas of Taihu Lake were evaluated by the biomass of algae observed and reference of the literature (Jing, 1995).

observed in Taihu Lake. Pore water of T1–T4 were obtained by the method of high speed centrifuge for 20 min at 4 °C.

3.3. Sediment analysis

The total contents of metals as Fe, Al, Ca and Mn were measured by ICP-AES method after digestion. The ammonium oxalate-oxalic acid extract is considered to yield active iron and aluminum (Danen-Louwerse et al., 1993). The sediments are shaken with a solution of oxalic acid and ammonium oxalate at pH = 3. The extraction solution reduces the poorly soluble iron (III) ions to the much more soluble iron (II) ions. As light influences the reducing action of oxalic acid, the extraction has to be performed in the dark. The total dissolved iron and aluminum, which are extracted as active iron and aluminum, are determined on a Spectro Analytical Instruments ICP type Spectroflame with AES. More details were provided by Danen-Louwerse et al. (1993). Organic matter measurement, expressed as Loss on ignition (LOI), was based on weight losses after combustion at 550 °C. TOC represents the oxidizable matter after treatment of the sample with chromic acid/H_2SO_4 according to the Walkey–Black method (Tan, 1995).

3.4. Phosphorus analysis

Inorganic soluble P concentration in pore water was measured by the methods of Murphy and Riley (1962) after centrifuged at 5000 rpm for 30 min (4 °C) and filtered by 0.45 μm P-free membrane. Total phosphorus (TP) was determined using the molybdenum-blue complex method after total destruction with $HClO_4/H_2SO_4$ at 370 °C. 1.0 mol/l HCl solution was used to extract the total inorganic phosphorus (IP) proposed by Krom and Berner (1981).

3.5. Adsorption kinetics

To study adsorption kinetics, a series of three 500 ml-capacity conical flasks for each sample site were prepared by mixing 1 g of dried sediment and 150 ml solution with initial P concentrations, 1.5, 2.0 and 3.0 mg/l, respectively. Two drops of 0.1% chloroform was added to inhibit bacterial activity (Naoml and Patrick, 1991a). The suspensions were then placed in a shaking table at 20 °C. Subsequently, 5 ml of slurry was collected from each bottle at 0.17, 0.25, 0.5, 1.0, 1.5, 3, 6, 9, 24, 48, 72, and 120 h and centrifuged immediately at 5000 rpm for 15 min. pH of the slurries were maintained at 7.3 ± 0.05 by adjusting with 0.01 mol/l NaOH and 0.01 mol/l HCl. P concentration in aliquots of clear supernatant was determined using the molybdenum-blue complex method proposed by Murphy and Riley (1962).

3.6. Adsorption equilibrium and pH effect

For each sediment samples (<63 μm) from T1 to T6, similar experimental procedure is done at room temperature. 0.5 g (dry weight) of sediment was added in polyethylene bottles. Each experiment consisted of a series of initial P concentrations of 0, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 mg/l obtained by adding different quantities of 20 mg/l KH_2PO_4 solution to the bottles. 4 ml of 0.04 mol/l NaCl solution was added to make background salinity equate to 0.2‰ which often occurs in natural water column of Taihu Lake. 0.1% chloroform was added to inhibit bacterial activity, and ultimate solution of the trials was diluted with pure water to 40 ml uniformly. The pH was maintained at 8.2 ± 0.02 by additions of 0.01 mol/l HCl or 0.01 mol/l NaOH. No buffer was added to avoid possible competition for sorption sites. Although the concentrations used were considerably higher than occur naturally, they allowed adsorption sites to reach saturation and the maximum adsorption capacity was then calculated. After 48 h of equilibration, the solutions were centrifuged at 5000 rpm for 30 min and 10 ml of supernatants were removed for P analysis (P_{eq}). When $C_{add} = 0$, the dissolved P measured in the supernatant is P_{eq}^0. The amount of P adsorbed on the sediment was expressed by the left part of Eq. (2). The value of the left part in Eq. (7) can then be calculated.

To evaluate the pH effect on P adsorption, pH in a wide range was adopted in the experiments. The samples T1 in hypereutrophic area and T4 in the center of the lake with mesotrophic state were taken for examples. For the two samples similar experimental procedure was conducted. The initial concentration of P added is 0.5 mg/l. In order to get serial pH values with proper gradient, pH was adjusted by adding different drop (s) of NaOH (0.1 or 0.01 mol/l) and HCl (0.1 or 0.01 mol/l) solution to a series of bottles (containing 0.2 g dw T1 or T4) before incubation started and pHs were then determined when adsorption processes reach equilibrium. The final solution volume was 40 ml uniformly. Organic matters (i.e. humic substances) were precipitated in aliquot testing solution before P was determined so as to eliminate their absorbance at 880 nm. Meanwhile, zeta potentials and ORP of particles in suspensions of different pH were determined. The zeta potentials of particles in control experiment suspensions without initial phosphorus added to the solutions in similar pH range were also examined.

4. Results and discussion

4.1. Sediment characteristics and elemental content

Chemical component concentrations measured in the lake sediment samples used for sorption experiments are

summarized in Table 2. Organic matter, expressed as LOI, exhibits concentrations ranging from 4.51% dw (site T6) to 10.20% dw (site T1) in Taihu Lake. The oxidizable matter (TOC) exhibits the lowest content (0.66% dw) in the center of Taihu Lake (site T4) and the highest content (1.97% dw) in the site of T1. T1 has the highest value of LOI and TOC, which may relate to the fact that T1 is the sampling point in Wuli sublake nearest to Wuxi city, Jiangsu Province, from which relative larger amount of industrial and human waste were discharged.

In Table 2, it is noticeable that in Taihu Lake sediment element Fe and Al is the dominant metal content observed from the range of measurement. The metal Fe and Al content has been considered to be the main factor that determines adsorption capacity, because of the high specific surface of the iron/aluminium (hydr)oxides (Lijklema, 1980; Lucotte and D'Anglejan, 1988; Brinkman, 1993). Therefore, further analyses of active Fe and Al were carried out (Table 2). It is obvious that site T1 has the absolutely highest content of active Fe and Al and T6 has relative lower active Fe and Al content. The percentage of active Fe in total Fe ranges from 25.5% in T4 (in central area of the lake and with relative lower trophic state) to 78.5% in T1 (with the most serious eutrophication), with an average of 43.7%. Similarly, active Al accounted for from 3.7% in T4 to 23.3% in T1 of total Al, with an average of 8.3%. The ratio of active Fe and Al is probably related to organic matter, trophic state, and water chemistry in sampling point. Because active Fe and Al are the main factors to retain P dissolved in solution or mineralized from organic matter (e.g. algal debris), the sediment of site T1 has the best ability to trap dissociative P and at the same time establishes the largest pool of available P that can be released when environmental conditions permit. So this mechanism of ephemeral retention rather than permanent burying of P may go against restoration of eutrophication in Taihu Lake.

4.2. Adsorption kinetics

The kinetic plots for the adsorption of P are depicted in Fig. 1, taking T4 for example. The plots show an initial fast adsorption step, completed within about 5 h, and followed by a slower second stage. The rate of the initial stage of P adsorption by the sediment increases with an increase in the initial P concentration. The uptake of P by sediments after 20 h is not significant in the case of T4. The similar phenomenon was also observed in other samples. Herein, the amount adsorbed after 48 h was measured in adsorption equilibrium experiments and taken to represent a pseudo-equilibrium condition.

4.3. Model calibration and calculated parameters

All of P adsorption isotherm data shown in Fig. 2 were fitted to the modified Langmuir isotherm (Eq. (7)) with the least square method ($R^2 > 0.90$). Relevant
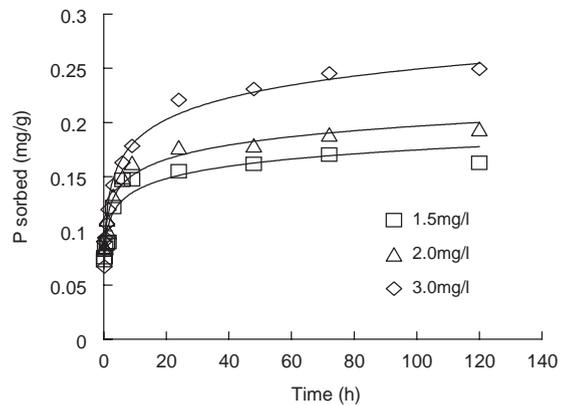

Fig. 1. Kinetics of phosphorus adsorption in site T4 with three initial phosphorus concentrations, 1.5 mg/l, 2.0 mg/l, 3.0 mg/l. The uptake of phosphorus by sediments after 20 h is not significant.

Table 2
Sediment elemental contents

Sample	Metals total contents (mg/g dw)				Active Fe and Al (mg/g dw)				LOI (%dw)	TOC (%dw)
	Fe_T	Al_T	Ca_T	Mn_T	Fe_{act}	Al_{act}	Fe_{act}/Fe_T	Al_{act}/Al_T		
T1	38.57	38.62	5.95	0.46	30.28	8.98	0.785	0.233	10.20	1.97
T2	30.39	37.69	3.24	0.58	16.74	3.49	0.552	0.093	6.95	1.43
T3	32.86	42.54	3.56	1.81	11.60	2.14	0.353	0.050	7.84	1.72
T4	21.61	36.84	3.26	0.45	5.50	1.38	0.255	0.037	4.58	0.66
T5	25.33	38.79	2.40	0.34	8.23	1.55	0.325	0.040	5.08	0.73
T6	12.96	17.85	2.10	0.22	4.61	0.81	0.356	0.045	4.51	1.22

parameters are listed in Table 3. Fig. 2a illustrates the processes of P adsorption on NAP-polluted sediments (T1 for example), where the points are experimental data and the line is the modeled result using Eq. (7). The isotherm can be divided into two sections, where α denotes desorption area and β denotes adsorption area. As Fig. 2a shows, when P sorbed falls into zero, the equilibrium concentration of P in trial solution (P_{eq}) is equal to EPC_0. If $P_{eq} < EPC_0$ the net effect of sorption is the NAP releases from the natural sediment (denoted by α area). Reversely, if $P_{eq} > EPC_0$ the net effect of sorption is P uptake by sediment (denoted by β area). When $P_{eq} = EPC_0$, the system is already equilibrated without net adsorption or desorption. The applied model describes the net effect of sorption. At high concentrations the sorption capacity of the sediments is exceeded and the isotherm will flatten off. At low concentrations the slope of the isotherms may steepen, thus resulting in normal Langmuir isotherms. The crossover-type adsorption isotherm are also found in T2–T6 samples with different intercepts (Fig. 2b).
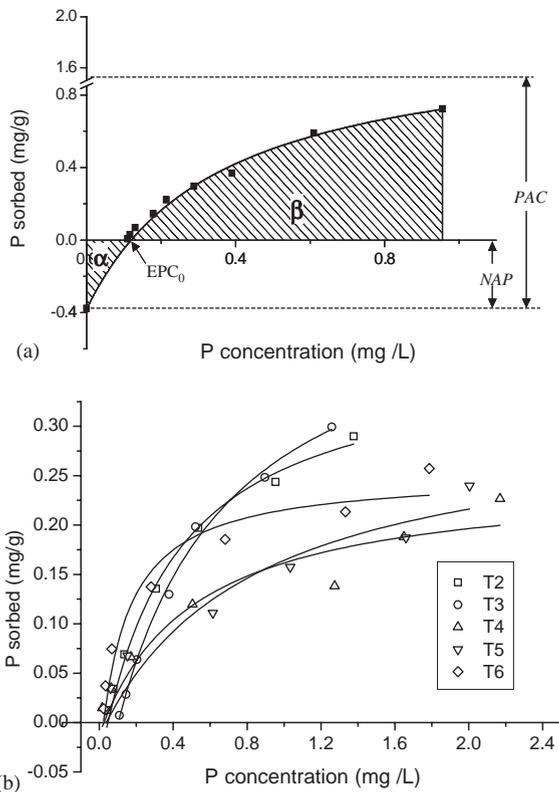

(a)

(b)

Fig. 2. Langmuir adsorption isotherm at pH = 8.2 ± 0.02 with 48-h contact time. (a) T1 for example to demonstrate PAC, NAP, EPC_0 in sorption isotherm diagram. Solid square points are experimental data. Line are modeled result using the Eq. (7). (b) The crossover-type adsorption isotherm were also found in T2–T6 samples with different intercepts.

The removal of P varies considerably according to the type of sediment, and is particularly high for site T1, in which the highest concentrations of Fe, Al and Ca are also found. Compared with T4, T5, and T6, T2 and T3, which were collected like T1 from northern Taihu Lake with more serious eutrophic problem, also have larger PAC values. PAC has been correlated to sediment composition, such as the contents of active Fe and active Al in the case of Taihu Lake. The relationship between them will be further discussed in following section of this paper. Because the estimation of some PAC values is based on extrapolation from the data obtained in the relative low-concentration range, there is some possibility that the value may fluctuate due to the experimental operation. Accordingly, the batch adsorption experiments in present study were doubled for each sediment sample and two series of fitting results were both listed in pairs in Table 3. Calculated parameters in Table 3 were obtained from mean values of PAC, k, and P_{eq}^0. As Table 3 shows, NAP values range from 0.012 mg/g in site T4 to 0.38 mg/g in site T1, with an average of 0.092 mg/g. The relative contribution of NAP to TP and IP ranged from 1.7% in site T4 to 15.2% in site T1 (with and average of 6.4%), and from 4.4% in site T4 to 21.9% in site T1 (with an average of 10.5%), respectively (Table 3).

4.4. The dual nature of sediments as a pool and source of P in natural waters

The usefulness of the EPC_0 concept has been highlighted when applied to understanding the direction and size of soluble reactive phosphorus (SRP) flux (House and Denison, 2002). This parameter is easy to measure and provides useful information about whether sediments will release or extract SRP when placed in contact with water. If the EPC_0 is greater than the SRP concentration in the water, the sediment will release SRP and vice versa, if the EPC_0 is less, the sediment will uptake SRP from the water. The kinetics of the interactions of SRP with natural sediments has been formulated in terms of the EPC_0 of the surface sediments (House et al., 1995). Moreover, the parameter is a useful and rapid means of characterizing the phosphorus status of sediments and has been used to characterize sediments along a eutrophication gradient (Richardson and Vaithiyanathan, 1995).

In the present study, the sorption isotherms produce EPC_0s less than 0.12 mg/l. There is no significant correlation between the EPC_0s and the SRP concentrations (denoted as P_{pw}). The P_{pw} values of T1–T4 are listed in Table 3. Because natural particles often contain NAP before they are used for the experiment, the adsorption isotherms often cross over the aqueous concentration axis. As Fig. 2 shows, the crossover-type adsorption isotherm can be further discussed as follows.

Table 3
Fitting results of adsorption isotherms data and other relevant parameters

Sample	Fitting results			P_{eq}^0 (mg/l)	P_{pw} (mg/l)	Calculated parameters				
	PAC (mg/g)	k (mg/l)	R^2			NAP (mg/g)	EPC$_0$ (mg/l)	Kp (l/g)	NAP/TP	NAP/IP
T1	1.49/1.51	0.30/0.36	0.98/0.87	0.112/0.118	0.029	0.380	0.119	3.200	0.152	0.219
T2	0.40/0.43	0.42/0.37	0.99/0.95	0.045/0.040	0.043	0.044	0.047	0.939	0.050	0.103
T3	0.59/0.51	0.49/0.55	0.99/0.97	0.089/0.095	0.046	0.085	0.102	0.830	0.078	0.136
T4	0.28/0.24	0.50/0.51	0.92/0.93	0.021/0.021	0.039	0.012	0.025	0.486	0.017	0.044
T5	0.36/0.28	0.83/0.80	0.93/0.92	0.030/0.032	—	0.014	0.038	0.367	0.019	0.050
T6	0.28/0.31	0.44/0.48	0.98/0.90	0.018/0.023	—	0.015	0.024	0.625	0.067	0.076

When P_{pw} = EPC$_0$, P sorbed = 0 (neither pool or source); When P_{pw} > EPC$_0$, P sorbed > 0 (denoted by β adsorption area, and sediment serves as pool of P); When P_{pw} < EPC$_0$, P sorbed < 0 (expressed by α desorption area, and sediment serves as source of P); In Table 3, the values of P_{pw} in T1, T2, and T3 points fall into α area of corresponding adsorption isotherm, these sediments thus play a source role of P. Whereas, in T4 point, P_{pw} > EPC$_0$, so sediment of T4 plays a pool role of P.

4.5. pH effect and preferential sorption species of P

It is found that P adsorption on sorbents is determined by the surface charge and the protonation state of P in the bulk solution (Németh et al, 1998). Laboratory studies on soils and sediments have shown that P sorption varies with pH, but little information is available on the direct effects of pH on P sorption by lake sediments, especially within the wide range of pH. The effects of pH on lacustrine P cycling depend in part on the direct, short-term effects of pH on sorption equilibria and kinetics, as well as on the long-term effects of acidification on organic mineralization rates and on sediment composition (Naoml and Patrick, 1991b). In most systems, the sorption of anions like phosphate decreases as pH increases and surface charge becomes more negative.

However, pH effect on P adsorption cannot be simply generalized in a wide range of pH observed in our experiments. In Fig. 3, the figure is mainly separated into three sections by pH$_a$ and pH$_b$. P exhibits a sorption maximum during the range from pH$_a$ to pH$_b$, out of which the amount of surface P decreases rapidly. When the curves of pH effects go below the pH axis the P preadsorbed will be released and then negative NSP can be observed. The fact that T1 has steeper trend to release adsorbed P when pH is out of the range from pH$_a$ to pH$_b$ is interpreted by the speculation that adsorption on T1 is more reversible than on T4, and meanwhile T1 has more pre-adsobed P to release. As is known that
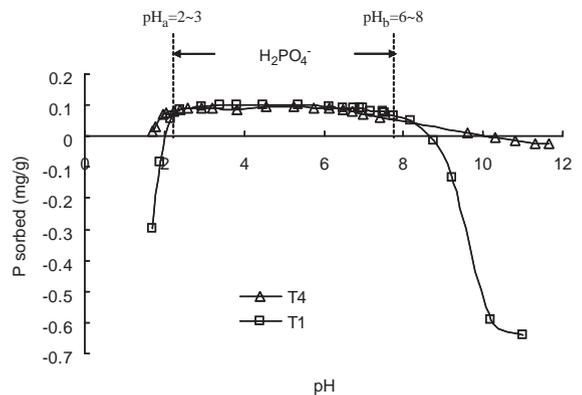

Fig. 3. pH dependence of phosphorus adsorption on sediment T4 (in the center part of the lake) and T1 (in the most serious eutrophic area). It indicates that $H_2PO_4^-$ is the preferential sorption species of phosphorus on sediment. pH$_a$ and pH$_b$ are the threshold values when the amount of P adsorbed decrease. The varying range of pH$_a$ and pH$_b$ are from 2 to 3 and 6 to 8, respectively, observed in experiments of the six samples.

phosphate acid is triprotic acid with pK_{a1} = 2.12, pK_{a2} = 7.20, and pK_{a3} = 12.36. Generally, dissociated species of phosphate acid exist as the pattern of Louis acid-base pairs (i.e. $H_2PO_4^-$/HPO_4^{2-}). Therefore, it is reasonable to regard the sorption solution as buffering acid-base system. The pH calculation of buffering solution was simplified as

$$pH = pK_a + p([HA]/[A^-]), \qquad (10)$$

where [HA] and [A$^-$] refer to equilibrium concentrations of a weak acid and its deprotonized species, respectively. It can be roughly calculated via Eq. (10) that in the range of pH$_a$–pH$_b$, within which the sorbed P maintains at a high level with no significant variation, the anion $H_2PO_4^-$ predominates in phosphate solution and thus is expected to be the preferential species for adsorption. Previous studies had ever discussed the preferential sorption species of P (i.e. $H_2PO_4^-$ or HPO_4^{2-}) on sorbents

(Naoml and Patrick, 1991a), but reasonable interpretations were not available. Herein, when $pH < pH_a$, positively charged sediment surface will compete with H^+ to trap SRP. But in this pH range, H^+ may have much greater ability than surface to trap SRP for its high free concentration. On the other hand, if $pH > pH_b$, OH^- with high free concentration will overcome SRP to adsorb onto sediment surface. Only in the range of pH_a–pH_b, sediment surface can powerfully compete with H^+ to trap SRP and SRP has more ability than OH^- to adsorb onto sediment.

General trend that zeta potential decreases with the increase of pH was demonstrated by curve zeta in Fig. 4(A) and curve (b) in Fig. 4(B). However, the amount of P sorbed and zeta potential of sediment particles have no necessary relationship, that is, when zeta potential goes rapidly negative the amount of P sorbed maintains at the maximum level until $pH > pH_b$ rather than decreases rapidly due to electrostatic repulsion as is expected, which is shown by Fig. 4(A) and (B). Item (c) in Fig. 4(B) refers to the control experiment of pH dependence of zeta potential of T4 sediment particles in solution without adding initial P. Curve (b) was almost overlaid by curve (c), which indicates that P sorption may change the surface charge but is not the significant factor. In fact, P adsorption on sorbents was shown to be chemical in nature, that is, the main adsorption force comes from chemical affinity (or complexation) rather than from electrostatic interaction on sediment-water interface. Especially, a strong contribution to the P binding comes from a ligand-exchange process on the $Me–OH_2^+$ and $Me–OH$ sites. Therefore, it is believed that P sorption, as a function of pH, is more likely to be determined by the stability of phosphate surface complexes than the electrostatic attraction/repulsion from the surface charge (Németh et al, 1998).

4.6. Effect of ORP

ORP is one of the most important parameters to describe the phosphorus adsorption onto iron. Iron-bound-phosphorus is particularly sensitive to redox and pH variations of the system (Gomez et al., 1999). The very low ORP induce the reduction of Fe(III) from the Fe(OOH). As Fig. 5 shows, in the experiments of the two sediments T1 and T4, the ORP decreases at different rate during the pH range observed. When pH is very low (e.g. $pH < pH_a$), ORP is very high, which should, in principle, produce high phosphorus adsorption, but the amount of P sorbed decreases rapidly in this range of pH. Therefore, in this kind of condition, although high affinity to adsorb phosphorus caused by high ORP of particles is produced, H^+ still overcome particles to trap SRP because of its very high concentration as was interpreted in zeta potential effect. As pH further increases (e.g. in the range of $pH > pH_a$), the positive
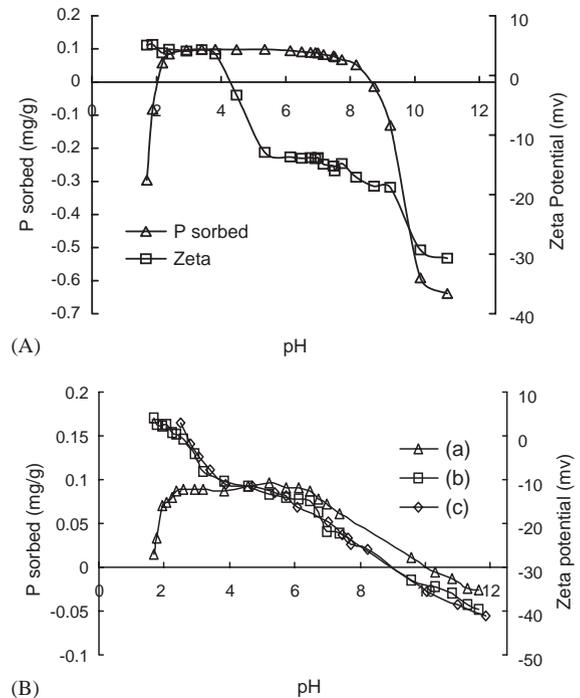

Fig. 4. (A) pH dependence of zeta potential and phosphorus adsorption of sample T1 for example. It indicates that P sorbed and zeta potential have no necessary relationship, although phosphorus sorption maybe influenced by surface charge. (B) pH dependence of zeta potential and phosphorus adsorption of sample T4. (a) phosphorus sorbed. (b) zeta potential determined in the slurry of different pH with 0.5 mg/l phosphorus initially added. (c) zeta potential determined in the pre-incubated suspension of different pH with no initial phosphorus.

correlation between P sorbed and ORP can be approximately observed in the two systems (Fig. 5), but they don't vary exactly in phase, which indicates that ORP will significantly influence P adsorption but cannot completely control the overall adsorption process. With the further increase of pH, the reduction of Fe (III) and the competition from OH^- mentioned above would both hinder phosphorus adsorption onto sediment.

4.7. Effects of sediment composition

Researchers have concluded that sediment composition was more significant than pH in affecting P sorption on natural sediments. Exchangeable P content and sorption capacities have been correlated with sediment compositional characteristics such as iron, aluminum, and organic matter content and in turn, sediment composition has been related (qualitatively) with lake chemistry (Naoml and Patrick, 1991b). Linear regression analysis indicated that active (Fe + Al) and PAC
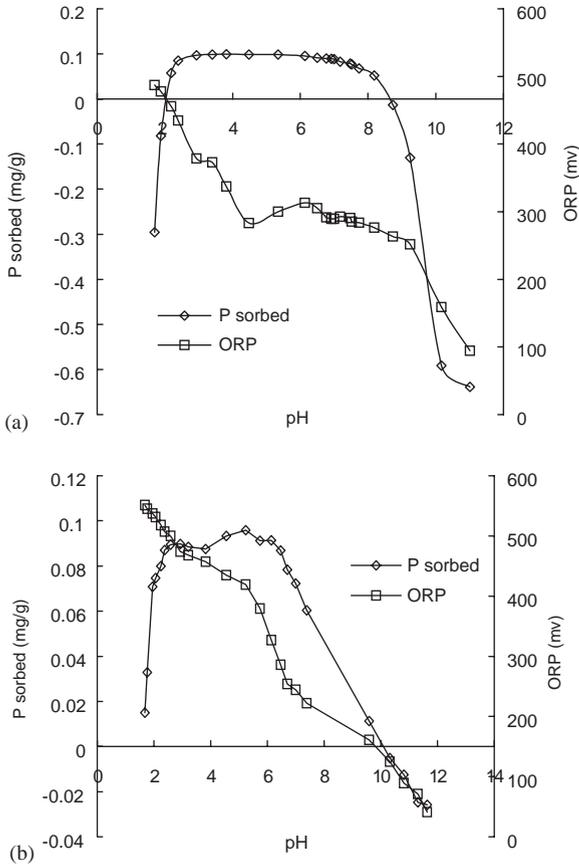
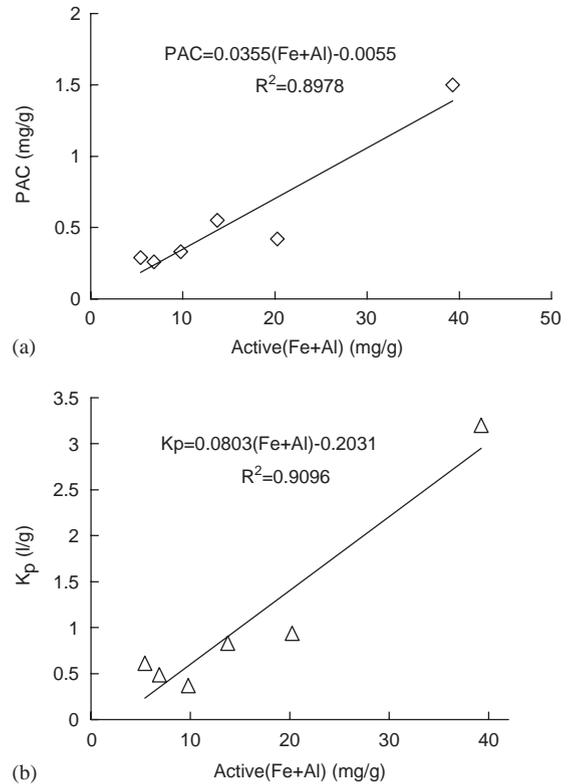Fig. 5. pH dependence of ORP and P sorbed of sample T1 (a) and T4 (b).

Fig. 6. (a) Linear regression analysis for active (Fe + Al) and PAC. (b) Linear regression analysis for active (Fe + Al) and partitioning coefficients of the six samples studied.

were related by the equation showed in Fig. 6(a) ($R^2 = 0.91$). This relation demonstrates that active Fe and Al (i.e., in amorphous forms) play a major role in P sorption and retention on natural sediments, and hence these elements are major variables in the eutrophication process (Lijklema, 1980). In the same principle, partitioning coefficient K_p and active Fe and Al have the similar relationship evaluated by linear regression analysis as Fig. 6(b) shows. K_p value reflects the relative affinities of solid phase and water phase for P. The larger value of K_p indicates the better ability of solid phase to adsorb and retain P. The positive correlation between active (Fe + Al) and the amount of phosphorus adsorption is widely known. However, from general viewpoint, the relationships mentioned above may not be necessarily linear in other water system. This is mainly dependent on the dominant metal hydroxide species the sediment contains. Metal hydroxides of Fe, Al, Ca and Mn are widely known to be the main absorbents for phosphorus. In Taihu Lake Fe and Al has much greater content than Mn and Ca (Table 2). Therefore, the linear relationship between active (Fe + Al) and PAC was observed and used in this specific study area.

5. Conclusion

Although the sedimentary P cycle has been the topic of many previous studies, the dynamics, controls and effects of P sorption in natural sediments are still incompletely understood. Considering NAP the modified Langmuir equation interprets well the sorption data of P on natural sediments, especially when NAP is significant like site T1. When the modified equation could be properly applied, relevant parameters PAC, NAP, EPC_0 and k were calculated. PAC and partitioning coefficient K_p were significantly related with active Fe and Al content, which were interpreted by the leading role of active Fe and Al in the processes of retaining/ releasing P.

In a wide range of pH values, hat-shaped adsorption curves were found in six samples from Taihu Lake. The surface coverage will maintain with no significant variation during the range of pH_a and pH_b, out of which the P adsorbed decreases rapidly. The slope of decrease is supposed to be related to sediment composition and adsorption reversibility, which will be a task for further studies. In the range of pH_a–pH_b the anion

$H_2PO_4^-$ predominates in phosphate solution and thus is expected to the preferential species for adsorption, but zeta potential of sediment particle is almost neutral or negative in this range of pH, which indicates that the electrostatic interaction may play minor role in the process of adsorption. The stability of phosphate surface complexes is the main factor controlling the adsorption process. ORP would certainly influence the adsorption process significantly, but the two curves showed in Fig. 5 do not necessarily go exactly in phase. In conclusion, P adsorption process has complicated mechanism and would be influenced by various factors. More attempts should be made for further understanding.

Acknowledgements

Reference

Aminot, A., Andrieux, F., 1996. Concept and determination of exchangeable phosphate in aquatic sediments. Water Res 30, 2805–2811.

Brinkman, A.G., 1993. 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, 31–45.

Bubba, D.M., Arias, C.A., Brix, H., 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. Water Res 37, 3390–3400.

Danen-Louwerse, H., Lijklema, L., Coenraats, M., 1993. Iron content of sediment and phosphate adsorption properties. Hydrobiologia 253, 311–317.

Dorich, R.A., Nelson, D.W., Sommers, L.E., 1984. Availability of phosphorus to algae from eroded soil fractions. Agriculture, Ecosystems and Environment 11, 253–264.

Geelhoed, J.S., Hiemstra, T., et al., 1998. Competitive interaction between phosphate and citrate on goethite. Environ. Sci. Technol. 32, 2119–2123.

Gibson, C.E., 1971. Nutrient limitation. Journal of Water pollution Control Federation 43, 2436–2440.

Gomez, E., Durillon, C., Rofes, G., Picot, B., 1999. Phosphate adsorption and release from sediments of brackish lagoons: pH, O_2 and loading influence. Wat. Res. 33, 2437–2447.

Hiemstra, T., Van Riemsdijk, W.H., 1996. A surface structural approach to ion adsorption: the charge distribution (CD) model. J. Colloid and Interface Sci. 179, 488–508.

House, W.A., Denison, F.H., 2000. Factors influencing the measurement of equilibrium phosphate concentrations in river sediments. Water Res 34, 1187–1200.

House, W.A., Denison, F.H., 2002. Exchange of inorganic phosphate between river waters and bed-sediments. Environ. Sci. Technol. 36, 4295–4301.

House, W.A., Denison, F.H., Smith, J.T., Armitage, P.D., 1995. An investigation of the effects of water velocity on inorganic phosphorus influx to a sediment. Environ. Pollut. 89, 263–271.

Jing, X.C., 1995. Chinese Lacustrine Environment, Vol. 2. Chinese Oceanographic Press, Beijing.

Kim, L.H., Choi, E., Stenstrom, M.K., 2003. Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. Chemophere 50, 53–61.

Krom, M.D., Berner, R.A., 1981. The diagenesis of phosphorus in a nearshore marine sediment. Geochim. Cosmochim. Acta 45, 207–216.

Lijklema, L., 1977. The role of iron in the exchange of phosphate between water and sediments. In: Golterman, H.L. (Ed.), Interaction between Sediments and Freshwater. W. Junk. Publ., The Hague, pp. 313–317.

Lijklema, L., 1980. Interaction of orthophosphate with III and aluminium hydroxides. Environ. Sci. Technol. 14, 537–541.

Lopez, P., Lluch, X., et al., 1996. Adsorption of Phosphorus on sediments of the Balearic Islands (Spain) Related to Their Composition. Estuarine, Coastal and Shelf Sci. 42, 185–196.

Lucotte, M.D., D'Anglejan, B., 1988. Seasonal changes in the phosphorus-iron geochemistry of the St. Lawrence Estuary. J. Coastal Res. 4, 339–349.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural water. Analytica Chimica Acta 27, 31–36.

Naoml, E.D., Patrick, L.B., 1991a. Phosphorus sorption by sediments from a soft-water seepage lake. 1. An evaluation of kinetic and equilibrium models. Environ. Sci. Technol. 25, 395–403.

Naoml, E.D., Patrick, L.B., 1991b. Phosphorus sorption by sediments from a soft-water seepage lake. 2. effects of pH and sediment composition. Environ. Sci. Technol. 25, 403–409.

Németh, Z., Gáncs, L., Gémes, G., Kolics, A., 1998. pH dependence of phosphate sorption on aluminum. Corrosion Science 40, 2023–2027.

OECD, 1982. Eutrophication of Waters: Monitoring, Assessment and Control. OECD Publications, Paris.

Richardson, C.J., Vaithiyanathan, P., 1995. Phosphorus characteristics of Everglade soils along a eutrophic gradient. Soil Sci. Soc. Am. J. 59, 1782–1788.

Stumm, W., Morgan, J.J., 1981. Aquatic Chemistry. John Wiley & Sons, New York.

Tan, K.H., 1995. Soil Sampling, Preparation and Analysis. Marcel Dekker, New York.

Weber Jr., W.J., McGinley, P.M., Katz, L.E., 1991. Sorption phenomenon in subsurgace systems: concepts, models and effects on contaminant fate and transport. Wat. Res. 25 (5), 499–528.

Yao, Wengsheng., Millero, F.J., 1996. Adsorption of phosphate on manganese dioxide in seawater. Environ. Sci. Technol. 30, 536–541.

Zhao, Hongshao, Stanforth, R., 2001. Competitive Adsorption of phosphate and Arsenate on Goethite. Environ. Sci. Technol. 35, 4753–4757.