ORIGINAL ARTICLE

Phosphorus adsorption characteristics at the sediment–water interface and relationship with sediment properties in FUSHI reservoir, China

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Received: 10 December 2010 / Accepted: 30 November 2011 / Published online: 17 December 2011 © Springer-Verlag 2011

Abstract This study was designed to survey the reservoir sediment properties, assess the phosphorus (P) sorption isotherm, and analyze the relationship between sediment properties and sorption parameters. Physicochemical analysis indicated that sediment from the FUSHI reservoir in Zhejiang Province, China, has similar physical and chemical properties and has been contaminated by P. Sorption isotherm experiments showed that the sorption process could be described by Langmuir and Freundlich models. The parameters of Q_{max} (Phosphorus sorption maximum) and K (Freundlich adsorption isotherm constant) ranged from 618.98 to 825.70 mg kg^{-1} and 114.18 to 170.74 l kg^{-1} , respectively. EPC_0 (zero P equilibrium concentration) ranged from 0.14 to 0.24 mg 1^{-1} , more than the total P concentration in the water of the reservoir. Thus, the reservoir sediment releases P into the water and acts as a ''P resource''. The clay, Fe_o, Al_t, and Fe_t + Al_t content were the main active components in P sorption. Q_{max} had a highly significant positive relationship with some properties and could be estimated by a combination of these.

Keywords Sorption maximum - Sorption isotherm - Sediment - Reservoir - Phosphorus contamination

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Introduction

Nutrients from chemical fertilizers or animal manures are beneficial if retained in the soil for uptake by plants; however, they become environmental pollutants if leached into watercourses, groundwater, lakes, and reservoirs (McGechan and Wu [1998](#page-7-0); McGechan and Lewis [2000](#page-7-0)). Phosphorus (P) is an essential element in the biogeochemical cycle, but excessive utilization in agriculture as well as detergents will lead to environmental and ecological problems. In recent years, attention has shifted from nitrogen as a nutrient and pollutant (McGechan et al. [1997](#page-7-0); Wu et al. [1998\)](#page-7-0) toward the less soluble and non-volatile contaminating nutrient, P. Numerous studies have indicated that heavy use of P results in its accumulation in natural aquatic ecosystems and in sediments acting as P sinks (Jin et al. [2005](#page-7-0); Zhang et al. [2007](#page-7-0)). The consequences of this accumulation will include serious problems for aquatic ecosystems and water environments, and even risks to human health. Developing more efficient nutrient application management strategies has been an important goal of various environmental agencies and farmers to prevent excessive phosphate buildup and protect the ecological integrity of sensitive watersheds (McDowell et al. [2001](#page-7-0)). The efficiency of these strategies relies on better understanding of the transformation processes of P at the soil–water interface. Pollutants such as P may be transferred from the water column to the sediment layer through biochemical, chemical, and physical reactions such as ion exchange, adsorption, and precipitation (Stumm and Morgan [1996\)](#page-7-0). Therefore, pollutants may be adsorbed into sediments and accumulated in the bottom of rivers, lakes, or reservoirs (Kim et al. [2003](#page-7-0)). P may be re-released from the sediment if the overlying water quality changes (Furumai et al. [1989](#page-7-0)). Adsorption and desorption processes

are universal phenomena existing on different interfaces in nature. These phenomena affect not only the characteristics of sediment and water, but also the surrounding environment.

Research into P sorption has been carried out in diverse sediment and soil types, but largely in temperate regions (Appan and Wang [2000](#page-6-0); Zhao and Stanforth [2001](#page-7-0); Kim et al. [2003](#page-7-0); Oguz [2005;](#page-7-0) Auxtero et al. [2008](#page-6-0); Derrick and Kin [2009](#page-7-0)). These studies have almost exclusively focused on soil and lake sediment, while information about P sorption/desorption of sediment in a subtropical reservoir is limited or nonexistent. However, sediment has become a serious problem in reservoirs in recent decades, as it both reduces the effective capacity of reservoirs and releases nutrients into the water (Sallade and Sims [1997](#page-7-0)). Understanding of the P adsorption/desorption in this system is vital as reservoirs are often used as a source of drinking water.

To understand the characteristics and processes of P sorption and the relationship between sediment characteristics and sorption parameters in aquatic sediment of a subtropical reservoir, the sediment characteristics and sorption isotherm were investigated. The objectives of the study were (1) to measure and analyze the characteristics of the sediment samples, (2) to identify the sorption isotherm characteristics and calculate the relevant parameters, and (3) to analyze the relationship between sediment characteristics and sorption parameters.

Materials and methods

Study area description

The FUSHI reservoir is a subtropical reservoir located at 30°38'10.96"N and 119°30'14.60"E in the Zhejiang Province, China. It was formed by damming the Xixi River in 1980. The reservoir has a maximum storage capacity of 218×10^6 m³ and 331 km² upstream areas. It provides $25 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ drinking water, irrigates 8×10^3 ha fields, and generates 5.4×10^3 kW/y power. The area upstream of the FUSHI reservoir consists of low mountains and hills covered with bamboo and Chinese chestnut tree plantations. Soils in these hills are impoverished and easily eroded. Large volumes of fertilizers are used in this area to improve crop growth, leading to heavy nutrient loss and soil erosion. The area experiences a typical subtropical marine-monsoon climate. The mean annual precipitation is 1344.1 mm and the mean annual temperature is 16.6° C. The concentration of P in the reservoir and river which flows into the reservoir ranges from 0.012 to 0.07 mg 1^{-1} .

Fig. 1 Map of sampling sites at the FUSHI reservoir

Sediment samples

Four sediment samples, S1, S2, S3 and S4, were taken from the FUSHI reservoir using a special messengeractivated core sampler (ETC-200) in August 2009 (Fig. 1). Water depths of the sample stations were 6 m for S1 and S3, and 8 m for S2 and S4. Collected samples were stored in an icebox and transported immediately to the laboratory, where they were centrifuged for 10 min at 5,000 rpm to remove most of the water. Subsequently the sample was air dried, passed through a 100-mesh sieve and stored at 4° C.

Sediment analysis

Sediment pH was measured in distilled water (w/v ratio of 1:2.5) and 1 M NaF (pH 8.2) (w/v ratio of 1:50). Particle size distribution of the sediment was determined using the hydrometer method (Bouyoucos [1951\)](#page-6-0). Total nitrogen (TN) was measured by the Kjeldahl apparatus (Kjelflex k-360) after digestion with sulfuric acid $(H₂SO₄)$. Total phosphorus (TP) content was determined using the molybdenum-blue complex method following destruction of P with $HClO_4/H_2SO_4$ at 370°C (Krom and Berner [1981](#page-7-0)). Available phosphorus (Avi-P) was extracted with 0.5 mol/L NaHCO₃ (Bray and Kurtz 1945). The organic matter (OM) was measured by the dichromate volumetric method. Cation exchange capacity (CEC) was measured by ammonium acetate exchanging method. Fe and Mn were measured by flame atomic absorption spectroscopy (SHI-MADZU A-A6300) and Al was measured by xylenolorange photometric method (Bao [2005\)](#page-6-0). Total Fe, Al, and

 Mn (Fe_t, Al_t, and Mn_t) were measured after digestion of the sediment with 30 ml mixture of HF, $HNO₃$, and $HClO₄$ in the ratio of 10:15:5. Crystalline and non-crystalline forms of Fe, Al, and Mn were extracted with dithionite-citratebicarbonate solution (DCB) (Fe_d, Al_d, Mn_d) and 0.2 M ammonium-oxalate solution at pH 3.0 (Fe_o, Al_o, Mn_o), respectively (Wisawapipat et al. [2009](#page-7-0); Mckeague and Day [1966\)](#page-7-0). Inorganic P in the forms of aluminum phosphate (Al–P), iron phosphate (Fe–P), and calcium phosphate (Ca–P) were measured using the molybdenum-blue method after extraction with 0.5 M ammonium fluoride solution at pH 8.2, 0.1 M sodium hydroxide solution and 0.5 M sulfuric acid, respectively (Bao [2005](#page-6-0)).

Sorption isotherm

For the P sorption study, 0.5 g sediment samples were placed in a series of 50 ml polyethylene centrifuge tubes with 25 ml distilled water containing P at various concentrations. The tubes were shaken at 200 rpm on a rotary shaker at 25 \degree C for 24 h. The initial concentrations (C_0) prepared by analytical pure anhydrous potassium phosphate (K_2HPO_4) were 0, 0.05, 0.1, 0.15, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 5.0, 10, 15, and 20 mg 1^{-1} , respectively. Two drops of toluene were added to restrict microbial activity. After shaking, suspensions were centrifuged at 3,500 rpm for 10 min. Then supernatants were filtered through a 0.45 - μ m filter membrane. Phosphorus equilibrium concentration (C_{eq}) of the supernatant was measured by the molybdate blue method using a UV/VIS (UV-2550) spectrophotometer. The amount of P adsorbed by the sediment was calculated by the difference between C_0 and C_{eq} . The formula was:

$$
Q = (C_o - C_{\text{eq}}) v/w
$$

where Q is the amount sorbed (mg kg^{-1}), C_0 is the initial P concentration (mg 1^{-1}), C_{eq} is the equilibrium concentration (mg 1^{-1}), w is the sample weight (g), and v is the solution volume (ml) of K_2HPO_4 .

Statistical analysis

All data presented were the mean values of three replicates. The softwares of Office Excel and SPSS 13.0 were used for calculation and statistical analysis, and Origin 8.0 was used to fit curves and calculate parameters. Pearson's correlation was used to examine the individual relationship between the P sorption parameters $(Q_{\text{max}}$ and k) and between each physicochemical variable of the sediment. Multivariate stepwise regression was used to analyze and calculate the weights of physicochemical parameters on $Q_{\rm max}$.

Results and discussion

Sediment characteristics

The physical/chemical properties of four sediment samples are summarized in Table 1. Sediment from the FUSHI reservoir generally had a silt clay texture, with a silt content greater than 40%. A considerable portion of the sediment may be derived from decomposed loamy fine-texture and farmland soil upstream of the reservoir. All sediment samples were slightly alkaline with a pH (water) ranging from 7.28 to 7.52. Near neutral pH was typically found in flooded anaerobic sediment, owing to a reduction of $FeCO₃$ in acid soil and production of $CO₂$ in alkaline soil (Vepraskas and Faulkner [2001](#page-7-0)). The pH value measured by the NaF solution ranged from 9.69 to 10.18. Higher values indicated that the soil contained mineral constituents with surface hydroxyl ions, which were exchanged by the fluoride ion (Perrott et al. [1976](#page-7-0)).

Crystalline iron oxides, estimated by DCB extraction $(F_{\rm ed})$, were found to be the major forms of iron oxide in these sediment, though there were large differences between the four sediment samples $(3055.73 - 6312.48 \text{ mg kg}^{-1})$. The value of Fe_o greater than Fe_d indicated that most Fe existed in the form of crystalline Fe-oxide. While the higher value of

Table 1 Sediment characteristics in the FUSHI reservoir

Parameters	S ₁	S ₂	S ₃	S ₄
pН	7.40	7.28	7.36	7.52
pH (NaF)	9.55	9.71	9.69	10.18
Sand $(\%)$	22.69	23.07	23.51	22.39
Silt $(\%)$	42.08	40.91	41.96	45.46
Clay $(\%)$	35.23	36.02	34.53	32.15
TN $(mg kg^{-1})$	415.42	427.91	370.04	423.21
$TP (mg kg^{-1})$	842.84	821.69	581.61	510.13
OM $(mg kg^{-1})$	28.45	29.59	26.41	25.72
CEC (cmol kg^{-1})	54.54	67.01	59.56	52.39
Avi-P $(mg kg^{-1})$	40.29	38.83	31.53	29.34
Al-P $(mg kg^{-1})$	19.8	23.96	21.54	14.9
Fe-P (mg kg^{-1})	139.23	174.6	136.3	104.24
Ca-P (mg kg^{-1})	434.86	259.85	306.02	251.49
Fe _d (mg kg^{-1})	3055.73	5697.08	6312.48	5056.19
Al_{d} (mg kg ⁻¹)	112.99	161.06	121.05	161.35
Mn_d (mg kg ⁻¹)	237.93	219.01	207.35	142.10
Fe _o (mg kg^{-1})	1629.80	1655.90	1587.11	1350.50
Al_{o} (mg kg ⁻¹)	311.45	445.80	487.30	486.74
Mn_o (mg kg^{-1})	328.93	296.03	282.33	193.71
Fe _t (mg kg^{-1})	7851.73	7688.93	7615.06	6107.55
Al_{t} (mg kg^{-1})	26637.41	27794.65	25503.54	24081.85
Mn_t (mg kg ⁻¹)	660.69	614.12	545.14	491.88

Fe_o indicated that there was a substantial amount of both noncrystalline iron oxide and microcrystalline iron oxide in this sediment (Fontes et al. [1992](#page-7-0)).

The ratio of different types of sediment P varies at the four sample sites. The TP content in the sediment ranged from 510.13 to 842.84 mg kg^{-1} . Percentages of TP constituted by Ca–P ranged from 31.62 to 51.29%, accounting for around half of TP. Percentages of Al–P and Fe–P ranged from 2.35 to 3.70% and 16.52 to 23.43%, respectively. The Avi-P value ranged from 29.34 to 40.29 mg kg^{-1} , accounting for 4.73–5.75% of TP. There are two possible explanations for the difference in P fraction. Firstly, the four substrate samples, S1–S4, were collected from different rivers (Fig. [1\)](#page-1-0). Secondly, the rinse action during the sediment movement and transportation by flood or undercurrent almost certainly differs at the four sites.

Sorption isotherm

Sorption isotherms are useful for summarizing sorption data and illustrating the relationship between aqueous concentration of the adsorbate and the amount of adsorption by the solid phase sorbent at constant temperature (Stumm and Morgan [1996\)](#page-7-0). House and Denison ([2000\)](#page-7-0) and Zhou et al. ([2005\)](#page-7-0) called the P included in sediment as native adsorbed exchangeable phosphorus (NAP) and the NAP in sediment cannot be neglected in sorption (Zhou et al. [2005\)](#page-7-0).

Figure 2a shows the P sorption isotherm of NAP-polluted adsorbent. It can be divided into two sections where "D" denotes the desorption area and "A" denotes the adsorption area. As shown in the figure, when adsorbed P fell to zero, and C_{eq} (equilibrium P concentration) was equal to $EPC₀$ (concentration at which no net adsorption or desorption of P occurs). When C_{eq} was less than EPC₀, the net effect of sorption was the release of NAP from the natural sediment (denoted by D). Reversely, when C_{eq} was greater than EPC_0 , the net effect of sorption was P uptake by the sediment (denoted by A). When C_{eq} equaled EPC₀, the system was at equilibrium, with no net adsorption or desorption.

Figure 2b shows the P sorption isotherm of sediment in the FUSHI reservoir. From this figure it can be concluded that the P sorption isotherm was similar to that of some reports on soil and lake sediment (Appan and Wang [2000](#page-6-0); Derrick and Kin [2009](#page-7-0)). Moreover, the P adsorption isotherms were generally L-shaped, indicating that P adsorption increased with a greater magnitude at low C_{eq} than at high P loadings where P sorption sites were mostly saturated.

P sorption data could be fitted to the nonlinear equation of the Langmuir isotherms. The Langmuir adsorption isotherm is expressed here as Eq. 1 (Voice and Weber [1983](#page-7-0); Weber et al. [1991\)](#page-7-0):

$$
Q = \frac{Q_{\text{max}} k C_{\text{eq}}}{1 + k C_{\text{eq}}}
$$
 (1)

where \hat{O} is the amount of net adsorbed P at the equilibrium stage (mg kg⁻¹). Q_{max} is the maximum P adsorption capacity (mg kg^{-1}), k is the half-saturation concentration $(mg l^{-1})$, and C_{eq} is the P adsorption equilibrium concentration (mg 1^{-1}). This model has been used widely to describe anion sorption by soil and sediment (Del et al. [2003](#page-6-0); Tian and Zhou [2008](#page-7-0)). However, it is not appropriate to use Eq. (1) when native adsorbed exchangeable phosphorus (NAP) plays a significant role in the adsorption process (Aminot and Andrieux [1996](#page-6-0); Zhou

et al. [2005\)](#page-7-0). Therefore, the modified Langmuir adsorption isotherm equations (Eqs. $2, 3, 4, 5$) (Zhou et al. 2005) were used to model the P adsorption of sediments in the FUSHI reservoir.

$$
(\text{NAP} + C_{\text{add}} \, \nu/w) \, C_{\text{eq}} \, \nu/w = Q_{\text{max}} \frac{k \, C_{\text{eq}}}{1 + k \, C_{\text{eq}}}
$$
 (2)

NAP =
$$
Q_{\text{max}} \frac{k C_{\text{eq}}^0}{1 + k C_{\text{eq}}^0} + C_{\text{eq}}^0 \nu/w
$$
 (3)

$$
(C_{\text{add}} - C_{\text{eq}}) v/w = Q_{\text{max}} \frac{k C_{\text{eq}}}{1 + k C_{\text{eq}}} - \left(Q_{\text{max}} \frac{k C_{\text{eq}}^0}{1 + k C_{\text{eq}}^0} + C_{\text{eq}}^0 v/w\right)
$$
(4)

$$
EPC_0 = \frac{Q_{\text{max}} \frac{k C_{\text{eq}}^0}{1 + k C_{\text{eq}}^0} + C_{\text{eq}}^0 \nu/w}{k \left(Q_{\text{max}} - \frac{Q_{\text{max}} k C_{\text{eq}}^0}{1 + k C_{\text{eq}}^0} + C_{\text{eq}}^0 \nu/w\right)}
$$

=
$$
\frac{\text{NAP}}{k \left(Q_{\text{max}} - \text{NAP}\right)}
$$
(5)

 C_{add} is C_{o} (mg kg⁻¹) and C_{eq}^{0} is the equilibrium concentration (mg l^{-1}), while C_0 is equal to 0 mg l^{-1} .

The P sorption data of the sediments can be described by Langmuir and Freundlich equations. The parameters are listed in Table 2.

The Langmuir adsorption isotherm assumes the occurrence of monolayer adsorption, while the Freundich adsorption isotherm assumes the presence of chemosorption processes in addition to surface adsorption (Rhue and Harris [1999;](#page-7-0) Sundareshwar and Morris [1999\)](#page-7-0). The values of R^2 in Table 2 suggested that more complex mechanisms other than surface adsorption were involved in P sorption in the FUSHI sediment.

The Langmuir adsorption isotherm provided a good estimate of both theoretical adsorption maxima and the capacity of the sediment–water system to remove P. Langmuir adsorption maxima (Q_{max}) of the FUSHI sediment ranged from 618.98 to 825.70 mg kg^{-1} . These values are much lower than the 4,770–10,3400 mg kg^{-1} reported in sediment from the Kranji reservoir (Appan and Wang 2000 , and the 930–3,751 mg kg⁻¹ reported from Balearic Islands (Spain) (Lopez et al. [1996\)](#page-7-0). However, the

values were higher than $150-260$ mg kg⁻¹ and 196–281 mg kg^{-1} reported in constructed wetland sediments in Florida (Gale et al. [1994](#page-7-0)) and Korea (Yoo et al. [2006](#page-7-0)), respectively. This could be attributed to the concentrations of amorphous Fe and Al in the FUSHI reservoir sediment providing abundant specific surface area for P adsorption to take place (Paludan and Jensen [1995\)](#page-7-0). Thus, increasing the proportion of completely decomposed granite in the substrate is expected to enhance the P sorption capacity considerably, as it contributed to the majority of the non-crystalline Fe and Al in the sediment. The EPC_0 value in FUSHI reservoir sediment ranged from 0.14 to 0.24 mg l^{-1} with an average of 0.19 mg l^{-1} , and more than 0.012 mg I^{-1} (the concentration of P in the FUSHI reservoir water). According to the adsorption/desorption mechanism, this suggests that soluble P can easily be rereleased into the reservoir water. Thus, the FUSHI reservoir sediment acts as a P source.

Phosphorus sorption coefficients in relation to sediment properties

The relationship between the Q_{max} and k were evaluated and sediment properties were selected to obtain information about main sediment properties responsible for P retention.

Phosphorus sorption maximum Q_{max} had a highly significant ($P = 0.05$) positive relationship with clay, Fe_t, Al_t, $Fe_t + Al_t$, Fe_o , $Fe_o + Al_o$, Al–P, and Fe–P (Table [3](#page-5-0)). Some bivariate plots for Q_{max} illustrating the relationships are shown in Fig. [3](#page-5-0).

The P sorption coefficient, k , was the half-saturation concentration (mg l^{-1}) and had a significant ($P = 0.05$) negative relationship with silt, Fe_t, and Fe_o + Al_o + Mn_o. Table [3](#page-5-0) illustrates the correlation between sediment properties and Q_{max} and k separately. Some properties of sediment correlated negatively with Q_{max} , but had positive relationship with k . For example, the coefficient between silt and Q_{max} was -0.99 , but with k it was 0.91. Similarly, if k had a negative relationship with other sediment properties, Q_{max} had a positive relationship, for example, with clay. These results also showed a similar pattern when using the Langmuir formula to calculate Q_{max} and k.

Table 2 Sorption parameters of Langmuir and Freundlich equations

Sample	Langmuir					Freundlich: $Q = K C_{eq}^{n}$		
	Q_{max} (mg kg ⁻¹)	k (L kg ⁻¹)	NAP $(mg kg^{-1})$	EPC_0 (mg L ⁻¹)	R^2	$K(L \text{ kg}^{-1})$	\boldsymbol{n}	R^2
S ₁	769.50	0.28	40.51	0.20	0.97	144.74	0.57	0.93
S ₂	825.70	0.27	38.58	0.18	0.93	156.34	0.57	0.93
S ₃	756.53	0.18	32.65	0.24	0.96	114.18	0.61	0.95
S ₄	618.98	0.58	48.20	0.14	0.97	170.74	0.47	0.91

Table 3 Pearson correlation coefficients of Langmuir P sorption parameters with sediments properties

Properties	Q_{max}	\boldsymbol{k}	
pH	-0.87	0.74	
pH (NaF)	-0.86	0.90	
OM	0.79	-0.86	
CEC	0.80	-0.59	
Sand	-0.003	0.261	
Clay	$0.99**$	-0.825	
Silt	$-0.99**$	$0.91*$	
$AI-P$	$0.97*$	-0.86	
$Fe-P$	$0.95*$	-0.69	
Fe _t	$0.93*$	$-0.93*$	
Al_{t}	$0.95*$	-0.66	
Mn_t	0.79	-0.59	
Fe _d	0.05	-0.17	
$\rm Al_d$	-0.28	0.61	
Mn_d	0.90	-0.85	
Fe _o	$0.98**$	-0.91	
Al_{α}	-0.37	0.24	
Mn_{o}	0.88	-0.84	
$Fet + Alt$	$0.98**$	-0.78	
$Fet + Alt + Mnt$	$0.98**$	-0.78	
$Fed + Ald$	0.04	-0.16	
$Fed + Ald + Mnd$	0.07	-0.19	
$Feo + Alo$	0.86	-0.86	
$Feo + Alo + Mno$	$0.96**$	$-0.94*$	

**** Correlation is significant at the 0.05 and 0.01 levels, respectively

Fig. 3 Examples of significant linear relationships of the Langmuir P sorption maximum coefficient (Q_{max}) with the sediment properties clay, Fe_o, Al_t , and $Fe_t + Al_t$ for the FUSHI reservoir

The relationships of Q_{max} with clay, Fe_t, Al_t, Fe_o, $Fe_t + Al_t + Mn_t$, and $Fe_o + Al_o + Mn_o$ were close, and the sediment properties which are routinely determined by sediment survey could be used with confidence to predict Q_{max} for a subtropical reservoir sediment in China. Multivariate stepwise regression analysis indicated that 98% of the variation in Langmuir P sorption maximum for these sediments can be explained by combinations of clay, Fe_o Al_t, Fe_t, and the sum Fe_t + Al_t (Fig. [4\)](#page-6-0) as follows: $Q_{\text{max}} = -977.21 + 47.04 \text{ (clay)} + 0.06 \text{ (Fe}_0 \text{)} (R = 0.99)$ $Q_{\text{max}} = -1115.09 + 61.44 \text{ (clay)} - 0.01 \text{ (Al}t) \text{ (}R = 0.99\text{)}$ $Q_{\text{max}} = -395.86 + 0.43 \text{ (Fe)} + 0.02 \text{ (Al)} \text{ (}R = 0.99\text{)}$ $Q_{\text{max}} = -383.39 + 0.30 \text{ (Fe)} + 0.02 \text{ (Fe)} + Al$

$$
(R=0.98)
$$

The close relationship of Fe_o with Q_{max} indicates that amorphous or poorly crystalline Fe oxyhydroxides that have a small bulk and big surface provide much of the P sorption, consistent with the findings of a number of studies looking at highly weathered soils (Maguire and Sims [2002](#page-7-0); Agbenin [2003;](#page-6-0) Penn et al. [2005](#page-7-0); Li et al. [2007;](#page-7-0) Lair et al. 2009). As Fe_o was nearly one-quarter of Fe_t and had a significant positive relationship with Q_{max} , whereas Fe_d had no correlation with Q_{max} , Fe_o had an important effect on the relationship between Fe_t and Q_{max} .

 Al_t had a significant positive relationship with Q_{max} , while Al_d and Al_o nearly had no effect on Q_{max} (Table 3). The content of Al_d and Al_o were lower (Table [1](#page-2-0)) in

Fig. 4 Relationship between Q_{max} predicted from the regression equation and the observed Q_{max} for the FUSHI reservoir sediments

comparison to Al_t , suggesting that other Al fractions, such as organic Al, alumina silicate and oxyhydroxide Al, affected the relationship between Q_{max} and Al_t , Al_o and Mn_o did not show significant correlation with P retention. However, a strong correlation was found between the sum of Fe_o, Al_0 , Mn_o, and Q_{max} , as well as between the sum of Fe_t, Al_t, Mn_t, and Q_{max} .

The positive correlation between Q_{max} and clay suggested that there was an association between the colloidal components of the sediment causing the increase of effective surface area of P-sorbing. Organic matter in the soil did not show a significant correlation with Q_{max} , reflecting its low affinity for anions due to negative surface charges in the pH range of the studied sediment.

This study revealed that the clay, Fe_0 , Al_t and $Fe_t + Al_t$ in the FUSHI reservoir sediment were the mainly active components in P sorption. Hence, P adsorption parameter Q_{max} could be estimated by the combinations of clay and Fe_o , clay and Al_t , Fe_o and Al_t , and Fe_o and Fe_t $+ Al_t$, respectively.

Conclusions

These experiments revealed that the sediment in the FUSHI reservoir had similar physical and chemical properties, and that it has been contaminated by P. There was no obvious difference in the capacity for P sorption in the separate samples. Both the Langmuir and Freundlich models can be used to describe and calculate P sorption data, with R^2 ranging from 0.91 to 0.97. The Q_{max} and K ranged from

618.98 to 825.70 and 114.18 to 170.74 l kg^{-1} for Langmuir and Freundlich models, respectively. $EPC₀$ ranged from 0.14 mg 1^{-1} to 0.24 mg 1^{-1} , more than the TP concentration in the FUSHI reservoir waters. Hence, it can be concluded that sediment in the FUSHI reservoir has not only been contaminated by P, but also releases P into the water and thus acts as a "P resource".

The adsorption capacity, Q_{max} , had a highly significant positive relationship with clay, Fe_o, Al_t, Fe_t + Al_t, Fe_o, $Fe_o + Al_o + Mn_o$, Al–P and Fe–P, while the P sorption coefficient, k, had a negative relationship with these sediment properties. Multivariate stepwise regression analysis indicated that Q_{max} can be estimated by the combination of clay with Fe_o, clay with Al_t , Fe_o with Al_t , and Fe_o with $Fe_t + Al_t$. Thus, clay, Fe_o, Al_t, and Fe_t + Al_t contents were the main active components contributing to the P sorption maxima. This indicates that poorly crystalline Fe and Al oxyhydroxides provide much of the P sorption capacity and sorption energies.

As the sediments had similar physical and chemical properties, they did not show obvious sorption trends. The P released from sediment into the reservoir water could reduce the TP content in the sediment. Further studies are needed to calculate the amount of P released into the reservoir, and to analyze and evaluate the effects of this sediment behavior on the reservoir ecosystem and surrounding environment.

Acknowledgments This research was supported by the project: Effect of water loss and soil erosion on FUSHI watershed environment (No. H20092404). Our warmest thanks are also expressed to Miss Colette Matthewman in the Department of Genetics and Biotechnology, Aarhus University, for her assistance in the English presentation.

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