Phosphorus sorption and fraction characteristics in the upper, middle and low reach sediments of the Daliao river systems, China

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ABSTRACT

Stream sediments play an important role in the transport and storage of phosphorus in the stream ecosystems. This research investigated the sorption and fraction of P in the sediments of a long-term seriously contaminated river, the Daliao river system, using isotherm sorption and selective sequentially extraction tests. Results indicated that the total content of P in the sediments was 479–1202 mg kg^{-1}, depending on iron content in the sediments. The content of potential bioavailable P, including soluble and loosely bound P, Al bound P, Fe bound P, and reductant soluble P was only 10–20% of total P in the sediments of the Hun river and Taizi river, while it was 40–55% in the sediments of the Daliao river, the downstream of the river system. Equilibrium phosphorus concentration without net P sorption (EPC$_0$) was from 0.05 to 0.54 mg L^{-1}, with an increasing trend from upstream to downstream, indicating increasingly release potential. On the other hand, the upstream sediment generally sorbed more P than the downstream sediment for each river at the same equilibrium P concentration. The binding energy constant of P on the strong sites of the sediments generally decreased from 2.24 to 2.65 L mg^{-1} at upstream to 0.41 L mg^{-1} at downstream or estuary, suggesting that the strong binding sites have been occupied and partly saturated by the phosphate added by point and diffuse sources along the river. On the other hand, molar ratio of Fe to TP contents in the sediments showed sorption capacity of the sediments to P might be under-saturated. The added or sorbed P by the isotherm test was primarily bound to Fe oxides and secondly to Al oxides. Long-term pollution of the river lead to the decrease of P sorption capacity of the river sediment and the increase of P release potential.

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1. Introduction

Worldwide, the increased loading of rivers with phosphorus has been a severe problem starting in the 1960s because P has mostly been the limiting nutrient in streams and rivers [1–3]. The transport and storage of P in the river is important to understand impact of point and nonpoint sources in catchments and subsequently estuaries and coastal waters [4]. The sediments downstream of sewage inflows from urban are generally rich in phosphorus, due to strong interacting of dissolved inorganic P with sediments through its adsorption on mineral surfaces and/or its precipitation with Al, Fe and Ca [5–8].

Stream sediments have the ability to sorb dissolved P from the water column or release P to overlying waters depending on the equilibrium P concentration (EPC$_0$) [9]. The sediment EPC$_0$ is the concentration in the aqueous phase at which net adsorption or desorption of dissolved P from the benthic sediment does not occur [10,11]. The sediment EPC$_0$ concept is often used to determine if

benthic sediments are a potential source or sink to the overlying waters in streams and estuaries [8,12–16].

On the other hand, phosphorus can be found in the sediment matrix in the forms of calcium, iron, aluminum complex salts and organic species, or sorbed onto the surface minerals [17]. Chemical extractions, especially selective sequential extractions, designed to quantify discrete chemical or mineralogical compounds of P in the sediments, are relatively simple and can estimate the potentially bioavailable P in the sediments [18–20]. Therefore, they have been widely used to determine P species in sediments [17,21–25].

The Daliao river watershed in the Liaoning province has been an urban-, industry-, and agriculture-intensive area in China since 1950s. Leading industries include mining and metallurgy, petrochemicals, beer, pharmacy, electronics and telecommunications, and machinery etc. Big industrial cities include Fushun, Shenyang, Benxi, Anshan, Liaoyang, Panjin, and Yingkou, with population of 2.24, 6.98, 1.56, 3.47, 1.82, 1.25 and 2.30 million in 2005, respectively [26] (Fig. 1). The Daliao river system consists of the Daliao river, Hun river, and Taizi river, with 94, 415, and 413 km in length, draining 1390, 11500 and 13900 km^2 of land area, respectively. The watershed is located in the temperate monsoonal zone (E122°–125°10′, N40°30′–42°20′), characterized by long cold winter, hot and rainy

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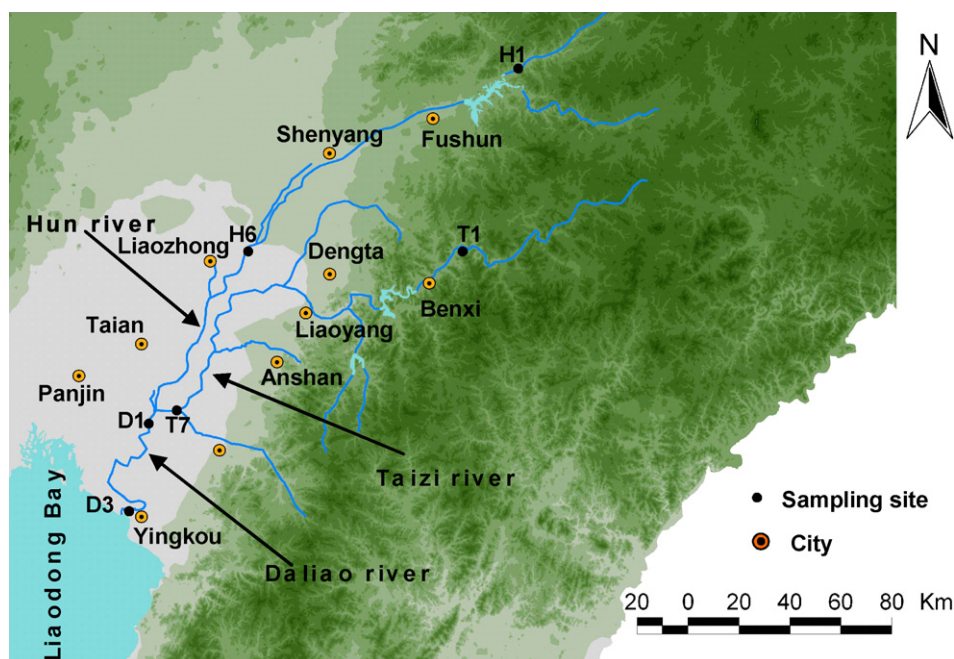*E-mail address:* c.lin@bnu.edu.cn (C. Lin).

Fig. 1. Schematic graph of the Daliao river system (Daliao river, Hun river, Taizi river) and sampling sites.

summer, and dry windy spring, with annual average temperature and precipitation of 7 °C and 800 mm, respectively. The average annual water discharge to Liaodong Bay is 6.3 km³ through the Daliao river system, which receives about 1200 million ton of industrial and domestic wastewater annually. Annually average concentration of total P in the water of the Hun river near Shenyang city was 0.33, 0.55, 0.63 and 0.24 mg L^{-1} in 2002, 2003, 2005 and 2006, respectively [27], while it was 0.31 mg L^{-1}, in the range of 0.08 to 0.93 mg L^{-1} for the Taizi river near Anshan city in 2005 [28]. Hence, the Daliao river system has been one of the most contaminated rivers in China, resulting in increasing occurrence, duration and extent of red tide events in the period of July–September in the last 20 years [29,30]. Therefore, it is necessary to investigate the potential sorption and release of phosphorus to/from the sediments of the Daliao river system to understand transport and storage of phosphorus in the seriously contaminated river on the world.

The objectives of this paper were to study the variations in phosphorus sorption and fraction characteristics of the sediment along the river system and assess the effects of long-term pollution on the P retention characteristics of the river sediments.

2. Materials and methods

2.1. Sediment sampling and analyses

In August 2006 (flood season), six surface sediment samples (c.a. 0–15 cm depth) were collected in the Daliao river system (Fig. 1), using cable operated sediment samplers – Van Veen grabs (Eijkelkamp), put into the plastic bags, and bring back to laboratory, where these sediment samples were freeze-dried, slightly crushed, passed through 2 mm sieve, and stored in glass bottles.

The content of organic matter (OM) in the sediment was determined by potassium bichromate-dilution heat colorimetric method [31]. The granularity of the sediment samples was measured by a LS 230 laser diffraction particle analyzer (Beckman Coulter) and percent contents of clay (<2 μm) and silt (2–20 μm) were calculated. The pH value of sediment samples was analyzed in the suspension of 1:10 solid:liquid ratio by using combination pH electrode (Orion, U.S.). Aliquots of the sediment samples were digested

with HNO$_3$–HF–HClO$_4$ and concentrations of P, Al, Fe and Ca in the extracts were measured by ICP-OES (IRIS Instrepid II, Thermo Electron) [32]. Four reference materials (GSS1, GSS2, GSS3, GSS4), provided by Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, were also digested and analyzed to check the analytical quality. Average relative errors of P, Al, Fe and Ca in the four reference materials were −2.40% to 0.95%, −0.21% to 3.92%, −0.29% to 8.16% and −1.40% to 10.71%, respectively.

2.2. Sorption isotherm measurement

Accurately weighed duplicate samples (∼1 g soil each) were mixed with 25 mL solution with varying concentrations of KH$_2$PO$_4$·2H$_2$O. The initial concentration of phosphate in the solution was varied in the range of 0 (blank)–100 mg L^{-1} of P. The suspensions were gently shaken for 7 days at 25 ± 1 °C. At the end of this equilibration period, suspension pH was measured using combination pH electrode. Then the suspensions were centrifuged at 12,000 rmp for 10 min using Xiang Yi centrifuge (H-1650, China). The supernatant was decanted and filtered through 0.45 μm filter. Phosphorus in the solution was measured employing the Malachite green method [33]. The total and net sorbed P was calculated by

$$q_t = (C_i - (C - C_0)) \times V/W_s \tag{1}$$

$$q_n = (C_i - C) \times V/W_s \tag{2}$$

where q_t and q_n are total and net sorbed amount of P, respectively (mg kg^{-1}); C_i is the initially added concentration of P (mg L^{-1}); C_0 is the measured concentration of P in the equilibrium solution at $C_i = 0$; C is the measured concentration of P in the equilibrium solution, V is solution volume, L, W_s is oven-dried (105 °C) soil weight (kg). The isotherm data, $q_t =$ fun $(C - C_0)$, were fitted by the linear form of the Langmuir equation:

$$\frac{1}{q_t} = \left(\frac{1}{q_{max}k}\right)\frac{1}{C} + \frac{1}{q_{max}} \tag{3}$$

where q_{max} is the maximum sorbed amount of P (mg kg^{-1}), and k is a constant related to the binding strength (L mg^{-1}), and the respective adsorption parameters were calculated. Noting two

linear segments were generally observed in the isotherm, the stepwise q_{max} and k parameters were calculated for each segment separately.

2.3. Phosphorus fractionation

To investigate the partition of native and added P into various minerals, selective sequential fractionation of P was performed in the native sediment samples and P-added sediment samples immediately after 7 days of sorption isotherm test. Following stepwise extraction was performed: soluble and loosely bound P (S/L–P), Al bound P (Al–P), Fe bound P (Fe–P), reductant soluble P (RS–P), and Ca bound P (Ca–P) were selectively extracted, respectively, by NH_4Cl, NH_4F, $NaOH$, $Na_2S_2O_4$, and H_2SO_4 solutions [34]. Residual phosphorus (RES–P) is given by the difference between the total phosphorus content (TP) and the sum of reactive (inorganic) fractions and mainly consists of organic phosphorus. Phosphorus in the supernant was measured employing the same method as sorption isotherm test. Average detection limits were 0.72, 2.93, 0.33, 0.46 and 0.32 mg kg^{-1} for S/L–P, Al–P, Fe–P, RS–P and Ca–P, respectively, estimated by five blank analyses without sediment. All reagents are analytical grade.

3. Results and discussion

3.1. Sediment properties and phosphorus partition in the native sediment

The pH values of the sediments generally were higher than 7.5, while it was only 6.9 at H6 site (Table 1). The contents of sediment organic matter (SOM) were in the range of 0.23–7.57%. Sediment texture was sandy loam for D1 and D2 sites, and loamy sand for H1, H6, T1, T7 sites. The contents of Al, Fe, and Ca were in the ranges of 6.77–7.35%, 1.67–4.60%, and 1.09–2.16%, respectively, similar to Al (7.20%) and Fe (4.10%) contents, but lower than Ca (6.60%) content in the world sediment [35]. The total content of P ranged from 479 to 1202 mg kg^{-1}, while the mean content of P in the world sediment is 670 mg kg^{-1} [35]. TP was positively correlated to the content of Fe in the sediments of the Daliao river system, with $R^2 = 0.841$ (Fig. 2).

The content of S/L–P was very low, less than 1% of TP (Table 1, Fig. 3). RS–P was about 7–14% of TP. The sum of Ca–P and RES–P was about 80–90% of TP in the sediment of the Hun river and Taizi river, while it was only 45–60% in the sediment of the Daliao river. On the other hand, the contents of Fe–P and Al–P were much higher in the sediment of the Daliao river than the Hun river and Taizi river, possibly because most part of the Daliao river is in the tidal zone of estuary with more reactive clay content in the sediment.

3.2. The sorption isotherms

The isotherms generally showed two-step sorption process: an initial steep increase in sorption at low equilibrium concentrations and moderate increase approaching a steady state sorption at high equilibrium concentrations (Fig. 4). This shape of the sorption isotherm suggests an initial surface adsorption/complexation,
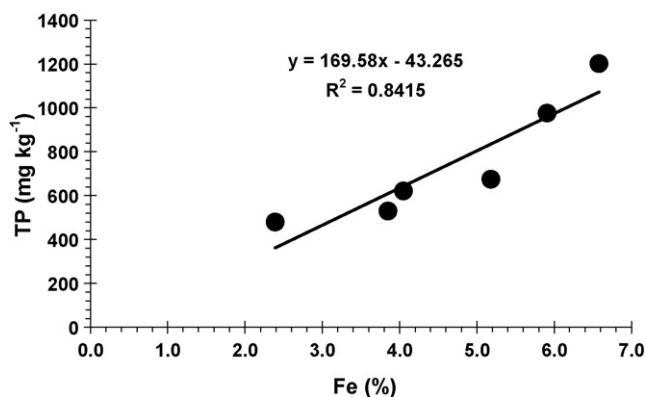

Fig. 2. Relationship between total phosphorus (TP) and Fe contents in the surface sediments of the Daliao river system.
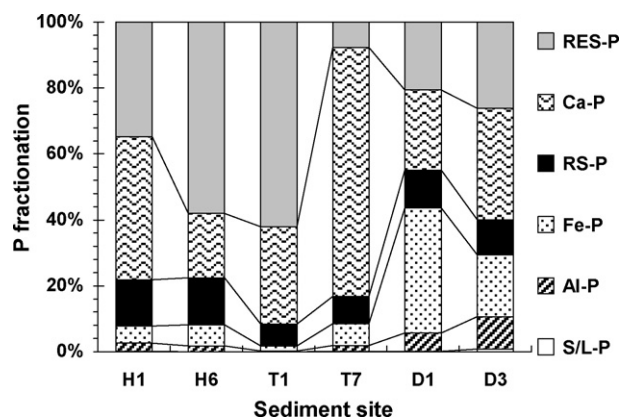

Fig. 3. P fractionation in the surface sediments of the Daliao river system.

followed by solid-state diffusion of adsorbed phosphate and/or surface precipitation [9,36]. The pH values of equilibrium solutions generally decreased from about 7.0 to 6.5 for H1, T1, T7, and D1 site, while it decreased from 6.2 to 5.7 for H6 site and from 8.0 to 6.5 for D3 site. This was due to lower pH value of the sediment at H6 site and higher pH value of the sediment at D3 (Table 1). Increase of pH value generally decreases sorption of P on the surface of inorganic minerals, due to competition of OH anion with phosphate anion [37,38]. However, higher pH values of equilibrium solutions for sediment H1 and T1 relative to sediment H6 and T7, respectively, did not lead to less sorption of phosphate on sediment H1 and T1, indicating other factors, such as Fe and P content etc., overpowered pH effect on the sorption. For each river, upstream sediment generally sorbed more P than downstream sediment at the same equilibrium concentration of P.

To estimate the binding strength constant and maximum adsorption capacity of the sediments, the isotherm data were fitted with the linearized Langmuir equation (Eq. (3), Fig. 5). Noting that isotherms showed two parts, the linearized plots of the sorption data exhibit two linear segments (Fig. 5). Previous

Table 1
Properties and chemical composition of the studied sediments.

| Site	pH	SOM (%)	Clay (%)	Silt (%)	Al (%)	Fe (%)	Ca (%)	TP (mg kg^{-1})	S/L–P (mg kg^{-1})	Al–P (mg kg^{-1})	Fe–P (mg kg^{-1})	RS–P (mg kg^{-1})	Ca–P (mg kg^{-1})	RES–P (mg kg^{-1})
H1	7.55	7.57	5.5	15.7	6.77	2.69	1.42	529	0.5	13.1	27.4	74.9	229.3	183.8
H6	6.86	1.73	4.5	11.1	7.35	1.67	1.31	479	0.2	8.1	30.9	68.2	93.4	278.2
T1	7.94	1.79	5.2	14.7	7.06	4.60	2.16	1202	0.0	3.0	18.0	79.2	356.6	745.3
T7	7.56	0.23	4.8	2.9	6.87	2.83	1.43	621	0.8	10.9	41.5	50.8	469.4	47.7
D1	7.45	1.61	13.1	33.1	7.04	4.13	1.10	976	1.2	53.8	370.2	112.6	237.0	201.2
D3	8.12	1.40	15.1	32.7	7.18	3.62	1.09	675	5.3	66.5	127.2	71.5	228.1	176.3
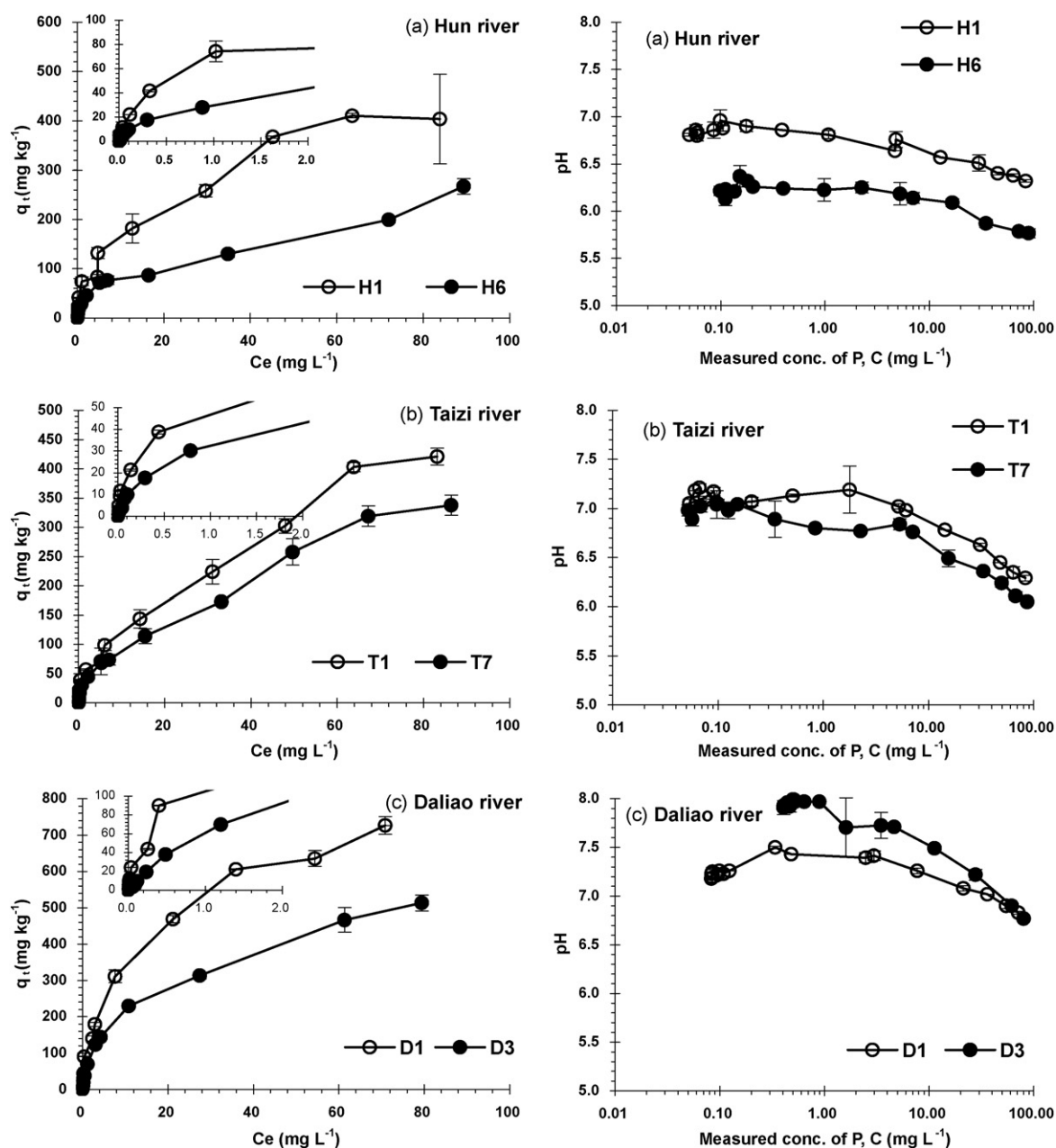
Fig. 4. Sorption isotherms of phosphate by the sediments from the Daliao river system and pH change with equilibrium phosphate concentration ($C_e = C - C_0$, see definition of C and C_0 in the text).

studies reported similar results for P adsorption on soils and some minerals [15,16,39–41]. Stepwise binding strength constants and maximum adsorption capacities for the initial concentration ranges of $1–10\,mg\,L^{-1}$ and $10–100\,mg\,L^{-1}$ of P were calculated (Table 2). The data were well fitted in the initially added P concentration of 1–10 and $10–100\,mg\,L^{-1}$, separately, with regression coefficients of 0.7926–0.9991. On the other hand, at low initially added concentrations of P, desorption of P occurred due to release of P originally present in the sediments. This will be discussed further below. The binding energy constant of P on the strong sites ranged from 0.41 to $2.65\,L\,mg^{-1}$, while it ranged from 0.03 to $0.11\,L\,mg^{-1}$ for the weak sites. Thus, the strong sites had a very much higher (between 4.4 and 58.4 times) binding energy constant than the weak sites. However, maximal sorption by the strong sites was only between 17% and 44% of the total maximal sorption (Table 2), indicating the concentration of the strong sites was lower than that of the weak sites. The total maximal sorption

of P ranged from 204 to $714\,mg\,kg^{-1}$ for the sediment of the Daliao river system. The binding energy constant of P on the strong sites was reported to be $0.01–0.05\,L\,mg^{-1}$ for calcareous soils [42], $0.17–0.23\,L\,mg^{-1}$ for iron coated sorbents [43], and $4.7–10.9\,L\,mg^{-1}$ for the clayey soils with clay content of 16–80% [39]. Lin and Banin [44] reported 0.25–0.26 and $0.02–0.05\,L\,mg^{-1}$ of the binding energy constants on the strong sites and weak sites, respectively, in the clayey sand with 0.02–0.32% of carbonate content. Therefore, the values we measured roughly fall within the same magnitude as those for clayey soils and clayey sand, but much higher than those for calcareous soils. Fox et al. [5] indicated that the bonding of P is weaker in calcareous compared to iron-containing sediments.

The strong sites are mainly strongly reactive sites on amorphous iron oxides in the sediments, while the weak sites may include reactive sites on the surface of other minerals. The binding energy constant of P on the strong sites generally decreased gradually from 2.24 to $2.65\,L\,mg^{-1}$ at upstream to $0.41\,L\,mg^{-1}$ at downstream or
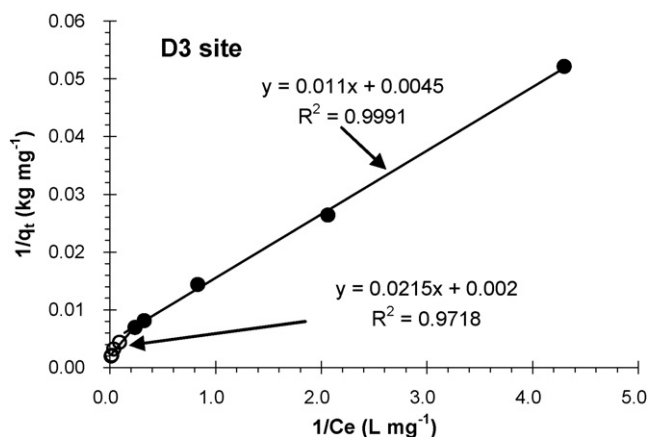
Fig. 5. Adsorption isotherms of P plotted according to the linearized form of the Langmuir equation. Calculated isotherm parameters are given in Table 2.

estuary, while it did not show such changing trend for the weak sites. This indicated that phosphate added by point and diffuse sources along the river appears to have occupied and partly saturated the strong binding sites having the highest binding constant. Whereas maximal sorption of P for each river was higher in the upper reach sediment than in the down reach sediment, the maximal sorption of P in the sediment of the Daliao river was generally higher than that of the Hun river and Taizi river. The high sorption maximal of P in the sediment of the Daliao river may be due to its high clay, Al and Fe contents.

3.3. Sorption/desorption equilibrium

The net sorbed P was plotted against P concentration in equilibrium solution (Fig. 6). Simple linear regression of net sorbed P against P concentration in the equilibrium solution was used to estimate sediment EPC_0 (the x intercept) and NAP (native sorbed phosphorus, the y intercept). The slope of this line was used as a measure of the ability of stream sediments to absorb P at low concentration, e.g., $<1.0\,mg\,L^{-1}$ of initial P concentration in this research. For each river, the slope of this line was higher for the upper reach sediment than for the down reach sediment, indicating that the upper reach sediments had a stronger ability to sorb P than the down reach sediment at lower equilibrium P concentration.

Sediment EPC_0 ranged from c.a. $0.05\,mg\,L^{-1}$ at H1, T1 and T7 site to $0.54\,mg\,L^{-1}$ at D3 site (Table 3). EPC_0 was generally higher than the dissolved P concentration in overlying water for flood season, indicating possible release of sediment P to water column. Especially, EPC_0 at the estuarine D3 site was much high that its overlying water P concentration. In addition, soluble and loosely bound P was much higher at D3 site than the other sites (Table 1). The sediment EPC_0 of eight samples at same site of the Blackwater river (UK) for various seasons, six sediments in the Taihu lake (China), six sediments in Three-Gorges reservoir (China), and 22 selected Ozark streams in northwest Arkansas (US) was 0.09–$0.61\,mg\,L^{-1}$, 0.02–$0.12\,mg\,L^{-1}$, 0.04–$0.67\,mg\,L^{-1}$, and 0.001–$0.33\,mg\,L^{-1}$ [8,12,13,16], roughly in the same magnitude as those of the Daliao river system. However, Wang et al. [25] reported 30.1–$634.1\,mg\,L^{-1}$ of EPC_0 for trophic lake sediments with 441–$2275\,mg\,kg^{-1}$ of total P.

Previous researches showed that EPC_0 was positively correlated to the exchangeable P content (P_{exch}) in the sediments [14,45]. Change of EPC_0 as function of P_{exch} in the sediments of the Daliao river system is shown in Fig. 7. Quantitative relationships between EPC_0 and exchangeable P content in the sediments of the Florida Bay [14] and Nansi lake in China [45] are also shown in the Fig. 7. It is clearly shown that the relationships are different, with high, moderate, and low ratios of EPC_0 to P_{exch} for the sediments from the Daliao river system, the Florida Bay, and Nansi lake, respectively. Hence, the sediments of the Daliao river system might have relatively high potential of P release, whereas it contained relatively low P_{exch}.

On the other hand, degree of P saturation (DPS) is generally accepted as a good indicator for the risk of P loss from soils [46]. Although DPS is generally determined by extracting the soil/sediment with an acid oxalate solution and then calculating molar ratio of P to (Al + Fe) [47], Jensen et al. [48] directly used the molar ratio of Fe to TP in the sediments to estimate the P release potential from the sediments. He found that freshwater sediments with molar Fe:P ratios above 8.5 were capable of retaining phosphate in the oxidized surface layer while phosphate released when the ratio was below 8.5. The molar ratio of total Fe to total P generally was 17.32–29.71 in the sediment samples of the Daliao river system, suggesting that sorption capacity of iron oxide/hydroxide with phosphate in the sediments of the Daliao river system was undersaturated. Noting that DPS estimated by the molar ratio of Fe to TP is dependent on both Fe content and TP content in the sediments, it did not show decreasing trend from upstream to downstream.

Table 2
Stepwise and overall maximum isotherm adsorption capacity (q_{max}) and binding strength constant (k) of phosphorous estimated by linearized Langmuir isotherm plots.

| Sediment	Linear segment	C_e range (mg/L)	Linearized Langmuir equation	R^2	K $(L\,mg^{-1})$	Stepwise q_{max} $(mg\,kg^{-1})$
H1	(I)	0.83–4.80	$(1/q)=0.0042(1/C)+0.0094$	0.9858	2.24	106.38
	(II)	4.80–83.95	$(1/q)=0.0479(1/C)+0.0019$	0.9650	0.04	419.93
	Overall					526.32
H6	(I)	0.40–8.84	$(1/q)=0.0132(1/C)+0.0143$	0.9508	1.08	69.93
	(II)	8.84–88.93	$(1/q)=0.0648(1/C)+0.0049$	0.7926	0.08	134.15
	Overall					204.08
T1	(I)	0.21–6.13	$(1/q)=0.0049(1/C)+0.013$	0.9753	2.65	76.92
	(II)	6.13–84.18	$(1/q)=0.0506(1/C)+0.0023$	0.9471	0.05	357.86
	Overall					434.78
T7						
	(II)	7.10–86.50	$(1/q)=0.0823(1/C)+0.0025$	0.9715	0.03	328.57
	Overall					400.00
D1	(I)	0.34–2.97	$(1/q)=0.0043(1/C)+0.004$	0.8951	0.93	250.00
	(II)	2.97–71.00	$(1/q)=0.0124(1/C)+0.0014$	0.9908	0.11	464.29
	Overall					714.29
D3	(I)	0.64–4.63	$(1/q)=0.011(1/C)+0.0045$	0.9991	0.41	222.22
	(II)	4.63–79.87	$(1/q)=0.0215(1/C)+0.002$	0.9718	0.09	277.78
	Overall					500.00
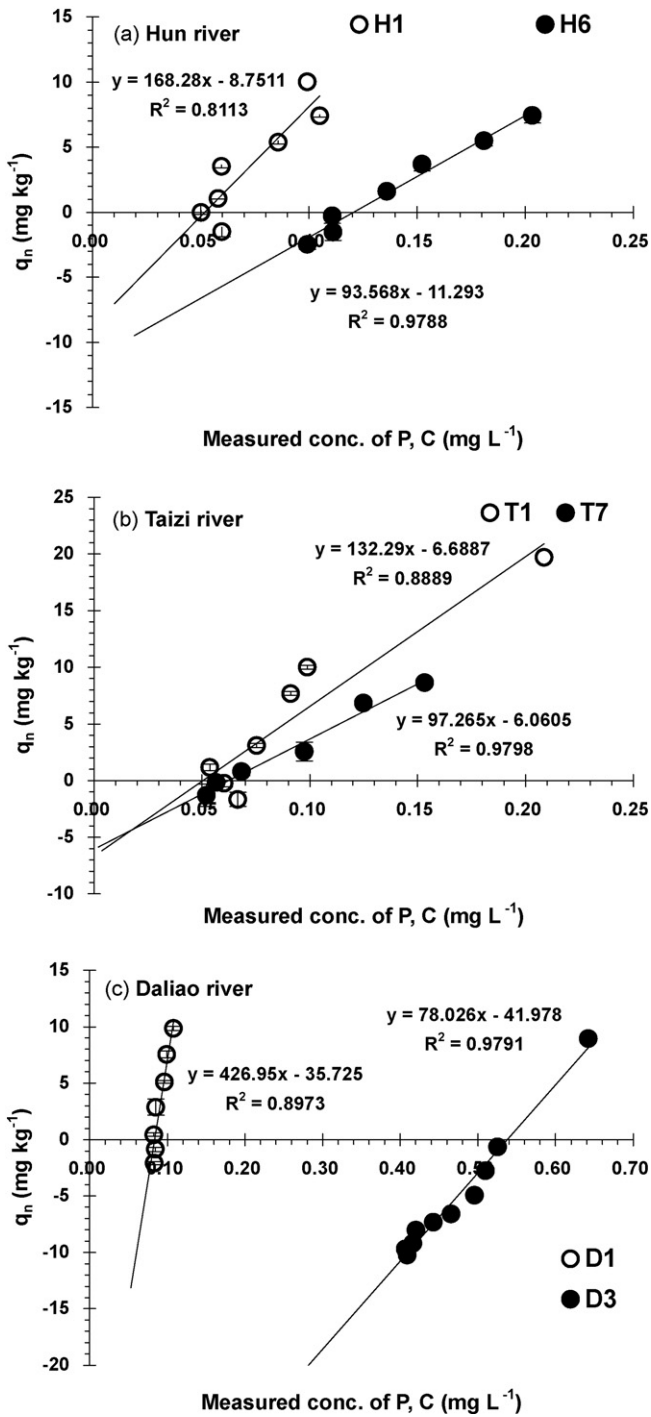
Fig. 6. EPC_0 values of the sediments. EPC_0, measured concentration of P when net sorbed P (q_n) = 0 and signifies the point at which no sorption nor desorption occurs.
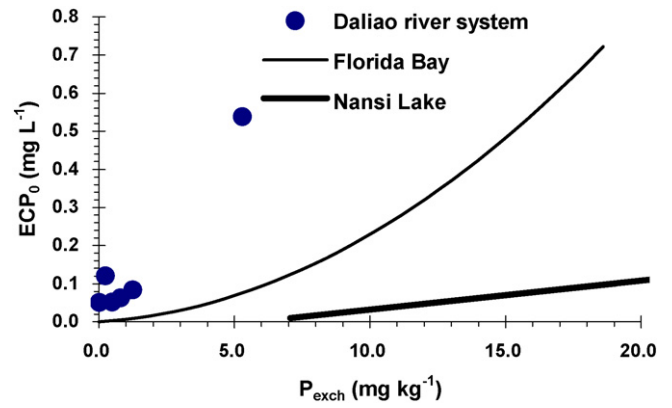

Fig. 7. EPC_0 as function of P_{exch} for the sediments of the Daliao river system, Florida Bay [14] and Nansi lake in China [45]. S/L-P is defined as P_{exch}.
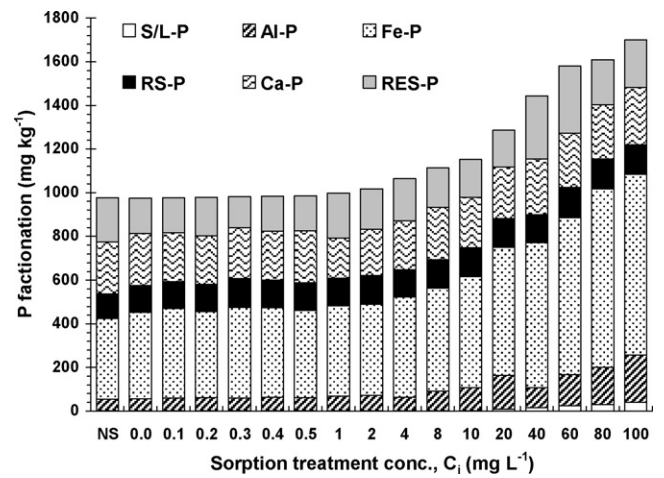

Fig. 8. The fractionation of the native sediment (NS) and P-added sediment immediately after 7 days of sorption isotherm experiment at D1 site. C_i is added initial concentration of P in the sorption isotherm experiment.

Whereas the sediments of the Daliao river system were undersaturated for P sorption, P sorption or release to/from the sediments directly depends on EPC_0 and the concentration of P in the water column. In addition, the decrease of P sorption capacity of the sediments, caused by the long-term pollution, can be further indicated by binding strength constant.

Sediment NAP of the Hun river and Taizi river ranged from 6.1 to 12.3 mg kg^{-1}, while it was 35.7–42.0 mg kg^{-1} for the Daliao river. Sediment NAP in more serious eutrophic and moderate eutrophic areas of the Taihu lake was 44–380 mg kg^{-1} and 12–15 mg kg^{-1}, respectively [13]. Hence, the Daliao river's sediments and the Hun river and Taizi river's sediments had slightly lower NAP than the serious eutrophic and moderate eutrophic area in the Taihu lake, respectively. In addition, sediment NAP of the Daliao river system was significantly correlated to the Al–P content in the sediment.

Table 3
Calculated EPC_0 and NAP of the sediments and measured P concentration in overlying water of the Daliao river system.

Sediment	C_e range (mg L^{-1})	Linearized regression equation	R^2	EPC_0 (mg L^{-1})	NAP (mg kg^{-1})	Water column (mg L^{-1})
H1	0.05–0.11	$q = 168.28 C_e - 8.75$	0.8113	0.05	8.75	0.008
H6	0.10–0.20	$q = 93.56 C_e - 11.29$	0.9788	0.12	11.29	0.126
T1	0.05–0.21	$q = 132.29 C_e - 6.69$	0.8889	0.05	6.69	0.009
T7	0.05–0.15	$q = 97.27 C_e - 6.06$	0.9798	0.06	6.06	0.015
D1	0.08–0.11	$q = 426.95 C_e - 35.73$	0.8973	0.08	35.73	0.011
D3	0.41–0.53	$q = 78.03 C_e - 41.98$	0.9791	0.54	41.98	0.029

3.4. Partition of the added P into the various minerals

The sediment of D1 site by the isotherm batch experiment was fractionated into the S/L-P, Al–P, Fe–P, RS–P, Ca–P, and RES–P. The concentrations of each fraction were plot as against the initial P concentration added in the isotherm experiment (Fig. 8). Results indicated that added or sorbed P was primarily bound to Fe oxide minerals and secondly bound to Al oxide minerals at higher treatment concentration. Only small amount of the P-added was classified as reductant soluble (occluded-bound) P fractions. And extremely low amount of the P-added was bound to carbonate minerals, whereas separate calcite can remove phosphate from solution [49]. In addition, at relatively low treatment concentration, RES–P and Ca–P in the sediment might transform to Fe–P, RS–P and Al–P.

4. Conclusion

The content of P in the sediments of the Daliao river system was 479–1202 mg kg^{-1} and depended on iron contents in the sediments. The content of potential bioavailable P, including S/L-P, Al–P, Fe–P, and RS–P was only 10–20% out of total P in the sediment of the Hun river and Taizi river, while it was 40–55% in the sediment of the Daliao river, the downstream of the river system. In addition, the EPC$_0$ generally increased from upstream sediment to downstream sediment, indicating increasingly release potential.

On the other hand, the upstream sediment generally sorbed more P than the downstream sediment for each river at the same equilibrium P concentration. The maximal sorption capacity was 204–714 mg kg^{-1}. The binding energy constant of P on the strong sites of the sediments generally decreased from 2.24 to 2.65 L mg^{-1} at upstream to 0.41 L mg^{-1} at downstream or estuary, suggesting that the strong binding sites have been occupied and partly saturated by the phosphate added by point and diffuse sources along the river. The added or sorbed P in the isotherm test was primarily bound to Fe oxides and secondly to Al oxides. The molar ratio of Fe to TP in the sediments indicated that sorption capacity of the sediments to P was under-saturated.

Generally, long-term pollution of the river lead to the decrease of P sorption capacity of the river sediment and the increase of P release potential. This might further result in a lagging restoration of overlying water quality.

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