

Characteristics of phosphorus sorption at the sediment–water interface in Dongting Lake, a Yangtze-connected lake

Wei Huang, Kun Wang, Hongwei Du, Ting Wang, Shuhang Wang, Zhuoma Yangmao and Xia Jiang

ABSTRACT

Phosphorus in sediments plays an important role in lake eutrophication. This study investigated the phosphorus sorption characteristics of sediments in a river-connected lake and identified the phosphorus source or sink areas in the lake. Sediment samples with different physicochemical characteristics were collected in 2011 and 2013 from Dongting Lake, which is connected to the world's third longest river, the Yangtze. Batch incubation experiments were conducted to determine the phosphorus sorption characteristics of the sediment samples. The sediment sample from Luzui (D3) exhibited the highest sorption capacity in 2013 (0.75 mg g^{-1}) because of its large proportion of fine particles ($<63 \mu\text{m}$). Results of sorption isotherms illustrated that the modified Langmuir model can effectively describe the sorption isotherms ($R^2 > 0.91$). The calculated results (equilibrium phosphorus concentration, $0.025\text{--}0.032 \text{ mg L}^{-1}$) indicated that the estuary from Dongting Lake to the Yangtze River (D1) served as a phosphorus sink because of the large proportion of fine particles and low total phosphorus content in the sediments. The east Dongting Lake (D2 and D3) with a high phosphorus concentration served as a phosphorus source. Yugong Miao (D4) and Nanzui (D5) had a low phosphorus concentration in water because of their location and flow field, respectively.

Key words | kinetics, modified models, phosphorus, sediment, sorption

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INTRODUCTION

Phosphorus is one of the main nutrients in soil, sediments, water, and organisms (Baldy *et al.* 2006; Huang & Zhang 2011). However, in the 1970s, Schindler (1974) indicated that phosphorus is the key limiting nutrient in lake eutrophication. Thus, the control of phosphorus concentrations is one of the most important methods to manage eutrophication. Phosphorus in sediments, which exists in the form of different chemical compounds (e.g., calcium, iron, aluminum complex salts, and organic species), can be adsorbed

on the surface of minerals. Phosphorus is an important part of many structural and biochemically functional components for cell growth in plants (Dorich *et al.* 1984; Zhou *et al.* 2005; Yan *et al.* 2013). In freshwater lakes, sediments can act as a phosphorus source or sink to the overlying water column. Thus, understanding the sorption characteristics of phosphorus at the sediment–water interface is significant.

The main interaction between sediments and water is expressed by the sorption and desorption of sediments together with several microbial processes in the sediments. Thus, understanding sorption and desorption behaviors is important to control pollution in sediments. In previous

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studies, simple Langmuir and Freundlich models were extensively utilized to describe the sorption features of phosphorus in sediments (Machesky *et al.* 2010; Kerr *et al.* 2011; Jalali & Peikam 2013). However, sediments, which differ from homogeneous sorbents, have complex components. Furthermore, native adsorbed phosphorus (NAP) can immediately participate in the sorption or desorption process. Thus, the traditional sorption model cannot effectively describe sorption behavior and NAP should be considered in the process of model description (Hiemstra & VanRiemsdijk 1996; Lai & Lam 2009).

The interaction between a river and a lake strongly affects lake water resources, flood, and drought potential and determines the occurrence of other environmental problems in the lake basin. Researchers have studied this phenomenon in recent years. Changes in the discharge or water level of a river can change the blocking force of the river on outflows from the lake (Hu *et al.* 2007) and thus affect lake level, water storage, and seasonal variations. A previous study examined and quantified the effects of a dam on river discharge and the influence of such effects on the interactions between rivers and lakes (Guo *et al.* 2012). The influence of dam operation and climate change on the interaction between rivers and lakes was evaluated in a previous study (Guo *et al.* 2011). These studies have provided important information on the interaction between rivers and lakes. Dongting Lake, which is the second largest freshwater lake in China, is located in Hunan Province (E 111°40'–113°10', N 28°38'–29°45'). This water body plays a significant role in regulating the amount of water in Yangtze River. The inflow from Yangtze River carries an average of four million MT of sediment load per year (Chang *et al.* 2010). Thus, exchange of nutrients at the sediment–water interface frequently occurs because of the rapidly changing hydrological and hydrodynamic conditions between the river and lake (Wang *et al.* 2014).

Dongting Lake is composed of a series of lakes and has three major lake districts, namely, eastern, southern, and western. The lake is the main water source of Lishui River (388 km long with a catchment area of 18,740 km²), Yuanjiang River (1,022 km, 88,451 km²), Zishui River (713 km, 28,027 km²), and Xiangjiang River (844 km, 93,376 km²). Water from the Yangtze River flows into Dongting Lake via two outfalls (Hudu and Ouchi), and water drained

from the outlet in the eastern part of Dongting Lake to the Yangtze River (Hayashi *et al.* 2008; Pan *et al.* 2009). During the flooding season, Dongting Lake exhibits a low lake surface gradient because of the direct connection between Dongting Lake and Yangtze River. This phenomenon leads to the discharge of sediments to the outlet in the eastern part of Dongting Lake. The relationship between Dongting Lake and the Yangtze River has been investigated from different perspectives. Many studies have examined the relationship between the Yangtze River and its connected lakes (Wan *et al.* 2014), the changes in runoff diversion from the Yangtze River to Dongting Lake (Li *et al.* 2009), and the changes in water quality or nutrient concentration in Dongting Lake under the effect of the Three Gorges Project in the Yangtze River (Li *et al.* 2013). However, only a few studies have focused on the sorption characteristics of phosphorus at the sediment–water interface and the phosphorus source or sink of sediments in Dongting Lake, a Yangtze-connected lake. In addition, the physicochemical characteristics of sediments such as particle size can affect the turbidity (Meral 2016). The largest area of water blooms in low frequency (<1.9%) was observed in 2011 (104 km²), and the largest area of water blooms in high frequency (>26.9%) was observed in 2013 (11.06 km²) (Xue *et al.* 2015). Lake eutrophication status exhibited obvious differences in 2011 and 2013.

The objective of the study is to illustrate the phosphorus sorption characteristic at the sediment–water interface in the river-connected lake and identify the phosphorus source or sink areas in the lake. This study presents useful information that can be utilized in the control of phosphorus release in the sediments of river-connected lakes.

MATERIALS AND METHODS

Site description and sediment collection

Figure 1 shows the sampling sites in Dongting Lake. D1 is the outlet to the Yangtze River in the eastern part of Dongting Lake. D2 and D3 are located in the eastern part of Dongting Lake, where the water level varies with the season (i.e., the size of the water area can increase and decrease during annual flooding and dry seasons,

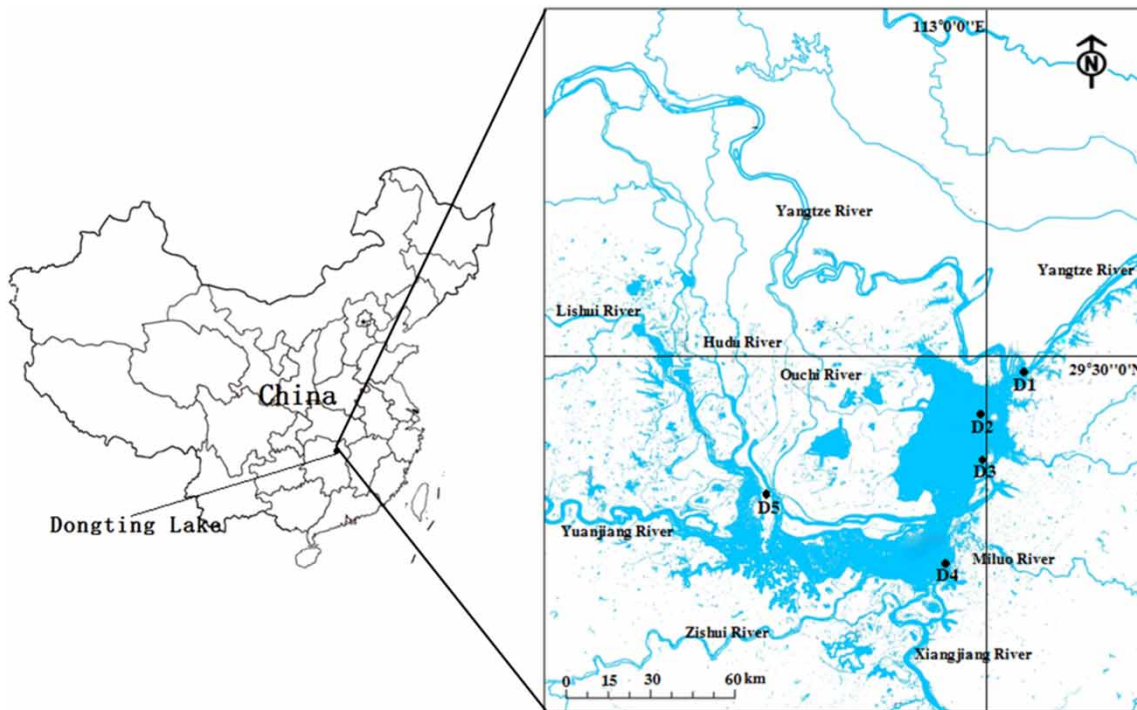


Figure 1 | Location of sampling sites (D1–D5) in Dongting Lake, China.

respectively) (Wang *et al.* 2014). However, in recent years, increased human activity and economic development around Dongting Lake have led to significant changes in the water environment, e.g., large amounts of external pollution have penetrated the water and sediments. D4 and D5 are located in the southern and western parts of Dongting Lake, respectively. Although serious eutrophication has not yet occurred in these lake areas and their water quality is better than that in the eastern part, the sediments in these two parts may accumulate a large amount of nutrients (Chang *et al.* 2010). Five composite surface sediment samples (each $n = 5$) were collected at the sites shown in Figure 1 in 2011 and 2013. The sediment samples were freeze-dried, ground, and sifted through a 100 mesh (0.15 mm) sieve (Jin *et al.* 2005).

Analysis of physicochemical parameters

The total phosphorus (TP) of the sediments was measured using standardized methods and tests (Ruban *et al.* 2001). The phosphorus concentration in the extracted solution or water body was determined with the molybdenum blue

method after the solution was filtered (0.45 μm filtration membrane) (Murphy & Riley 1962). The pH of the sediment was measured in a 1:2.5 (w/v) mixture of sediment with deionized water (Liao *et al.* 2014). Organic matter (OM) content was calculated according to the loss on ignition to constant mass (4 h) at 550 $^{\circ}\text{C}$. The particle size distribution was determined with a particle size analyzer (Hydro2000Mu, Malvern, UK). The main properties of the collected sediments are shown in Table 1.

Study of sorption kinetics and isotherms

Phosphorus sorption kinetics was examined in a solution with four different initial phosphorus concentrations of 1, 5, 10, and 50 mg L^{-1} . Five sediment samples from two different years were utilized. The sediment samples were added to 150 mL conical flasks containing 50 mL of phosphorus solution with different concentrations. The flasks were immediately covered and shaken on a temperature-controlled shaker (200 rpm) at a constant temperature of $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$. At 11 different time intervals (0, 10, 20, 30, 60, 120, 240, 480, 720, 1,440, and 2,880 min), suspensions

Table 1 | Physicochemical properties (mean value ± standard deviation) of five sediments in 2011 and 2013 (each $n = 5$)

Sample	Year	TP in overlying water (mg L ⁻¹)	TP (mg kg ⁻¹)	pH	OM (%)	Particle size distribution (%)				
						< 63 μm	63–125 μm	125–250 μm	250–500 μm	500–2,000 μm
D1	2011	0.062 ± 0.003	710.23 ± 48.23	7.27 ± 0.07	7.12 ± 0.11	39.32 ± 0.52	44.04 ± 2.21	13.95 ± 0.92	2.66 ± 0.23	0
	2013	0.058 ± 0.004	754.24 ± 51.23	7.35 ± 0.06	7.84 ± 0.12	45.01 ± 0.45	16.82 ± 1.23	16.3 ± 1.29	15.77 ± 0.83	6.1 ± 0.58
D2	2011	0.065 ± 0.004	582.48 ± 42.47	7.56 ± 0.11	6.42 ± 0.12	25.38 ± 0.42	2.04 ± 0.87	30.32 ± 2.91	38.76 ± 0.67	3.49 ± 0.28
	2013	0.061 ± 0.005	610.24 ± 52.32	7.87 ± 0.09	7.05 ± 0.10	54.87 ± 1.21	17.7 ± 0.78	11.51 ± 1.28	10.81 ± 0.89	5.11 ± 0.87
D3	2011	0.077 ± 0.005	751.24 ± 64.21	7.12 ± 0.07	4.89 ± 0.10	51.51 ± 0.87	22.36 ± 1.98	15.52 ± 1.26	9.95 ± 1.24	0.65 ± 0.11
	2013	0.063 ± 0.004	772.34 ± 59.72	7.21 ± 0.08	4.32 ± 0.08	65.19 ± 1.45	24.15 ± 1.23	7.38 ± 0.87	2.77 ± 0.45	0.49 ± 0.09
D4	2011	0.081 ± 0.005	600.23 ± 44.73	7.32 ± 0.10	5.62 ± 0.12	50.55 ± 1.82	23.53 ± 2.11	14.76 ± 1.82	9.22 ± 1.02	1.94 ± 0.12
	2013	0.069 ± 0.003	621.24 ± 48.72	7.39 ± 0.09	5.89 ± 0.11	46.8 ± 0.89	30.26 ± 1.28	18.6 ± 0.78	3.91 ± 0.46	0.44 ± 0.07
D5	2011	0.086 ± 0.005	592.37 ± 39.82	7.76 ± 0.06	6.24 ± 0.13	54.33 ± 0.78	25.96 ± 0.87	12.65 ± 0.68	5.16 ± 0.67	1.89 ± 0.08
	2013	0.072 ± 0.006	609.23 ± 42.38	7.81 ± 0.10	6.54 ± 0.12	56.45 ± 1.87	43.46 ± 1.76	0.09 ± 0.02	0	0

were obtained from each flask, centrifuged, filtered (0.45 μm), and analyzed to determine the phosphorus content.

The sorption isotherms of phosphorus in the sediments were obtained through batch experiments. Sediment samples (1 g in triplicate) were added to 150 mL conical flasks containing 50 mL phosphorus solution at different initial phosphorus concentrations (0, 0.5, 1, 2, 5, 10, 20, and 50 mg L⁻¹ as KH₂PO₄). The conical flasks were agitated on a temperature-controlled shaker at 200 rpm under a constant temperature of 25 °C ± 2 °C for a 48 h equilibration period. The suspensions were centrifuged, filtered (0.45 μm), and analyzed to determine P.

Statistical analysis

The phosphorus uptake amount in the different sediment samples at each time, Q_t (mg g⁻¹), was calculated by using a mass balance relationship as follows:

$$Q_t = (C_0 - C_t) \frac{V}{W}, \quad (1)$$

where C_0 (mg L⁻¹) is the initial liquid-phase phosphorus concentration, C_t (mg L⁻¹) is the blank corrected concentration of phosphorus at time t , V (L) is the volume of the solution, and W (g) is the mass of dried sediment.

Sorption kinetics is described by pseudo first- and second-order models, and the models are expressed as follows (Onganer & Temur 1998; Ho & McKay 1999; Ding et al. 2010):

$$Q_t = Q_e(1 - e^{-K_1 t}), \quad (2)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + t Q_e, \quad (3)$$

where Q_t and Q_e are the uptake amounts (mg g⁻¹) of phosphorus adsorbed at time point t and equilibrium (mg g⁻¹), respectively. K_1 (h⁻¹) is the first-order kinetic rate constant, and K_2 is the sorption rate constant of the pseudo second-order kinetic model (g mg⁻¹ h⁻¹).

Modified Langmuir and Freundlich models were used to describe the sorption isotherms. The modified Langmuir

model was obtained from previous studies (Zhou *et al.* 2005; Huang *et al.* 2015), and the isotherm parameters are expressed as follows:

$$Q_e = \frac{Q_m K C_e}{1 + K C_e} - \frac{Q_m K C_e^0}{1 + K C_e^0} - Q_e^0. \quad (4)$$

$$NAP = \frac{Q_m K C_e^0}{1 + K C_e^0} + Q_e^0, \quad (5)$$

$$EPC_0 = NAPK(Q_m - NAP), \quad (6)$$

where Q_e and Q_m are the adsorbed amounts of phosphorus in the sediments at equilibrium and the maximum phosphorus uptake amount (mg g^{-1}), respectively. C_e is the phosphorus concentration in the aqueous phase at equilibrium (mg L^{-1}), and K is the affinity parameter (L mg^{-1}). C_e^0 and Q_e^0 are the equilibrium concentration (mg L^{-1}) and uptake amount (mg g^{-1}), respectively, and C_{add} (initial concentration of newly added phosphorus in the solution of sorption trials) is equal to 0 mg L^{-1} . The zero equilibrium phosphorus concentration (EPC_0) is the concentration (mg L^{-1}) in which no net sorption or desorption of phosphorus occurs, and the original sediment and water phosphorus concentrations are in dynamic equilibrium.

The modified Freundlich model can be derived through the same method, and the equations of the isotherm parameters are expressed as follows (Sairam Sundaram *et al.* 2008):

$$Q_e = K_f C_e^m - K_f (C_e^0)^m - Q_e^0, \quad (7)$$

$$NAP = K_f (C_e^0)^m + Q_e^0, \quad (8)$$

$$EPC_0 = \sqrt[m]{\frac{NAP}{K_f}}, \quad (9)$$

$$K_p = NAPEPC_0. \quad (10)$$

where K_f is the sorption coefficient (L g^{-1}) and m is a constant utilized to measure sorption intensity or surface

heterogeneity. K_p (L g^{-1}) is the affinity parameter of the modified Langmuir model.

RESULTS

Phosphorus sorption kinetics

In this study, sorption kinetics was described with the phosphorus sorption behavior. The experiment results corresponding to the phosphorus sorption of the five sediments from two different years fitting the kinetic equations (Equations (2) and (3)) are shown in Figure 2. The kinetic behavior of phosphorus sorption in the five sediments from two different years was examined in a 2,880 min contact time. The phosphorus sorption behavior of all sediment samples reached equilibrium within 240 min, and apparent equilibrium was reached from 240 min to 2,880 min. Figure 2 indicates that the sorption capacity of the sediment samples in 2013 was larger than that in 2011. Furthermore, the sorption capacity of the sediments from D3 (maximum value of 0.75 mg g^{-1}) was the largest among the five sediments. Also, Figure 2 shows that the quantity of phosphorus sorption increased with increasing initial phosphorus concentrations. The sorption capacity of sediment D3-2013 reach 0.75 mg g^{-1} at the initial level of 50 mg L^{-1} , and the lowest value (approximately 0.015 mg g^{-1}) was observed at the initial level of 1 mg L^{-1} . The sorption kinetic behavior of phosphorus fitted the pseudo second-order model better than the pseudo first-order model at a high initial phosphorus concentration ($R^2 > 0.92$).

The value of equilibrium sorption capacity using the pseudo second-order model derived through nonlinear regression is presented in Figure 3. In 2013, the sediments exhibited a relatively high equilibrium sorption capacity at an initial phosphorus level of 50 mg L^{-1} , and had the highest value of 0.75 mg g^{-1} . The sediments from D1 and D3 showed a higher equilibrium sorption capacity than the other sediments. At the initial phosphorus level of 1 mg L^{-1} , the equilibrium sorption capacity of the five sediments was lower than 0.06 mg g^{-1} . In 2011, the sediments exhibited a similar sorption characteristic, and the equilibrium

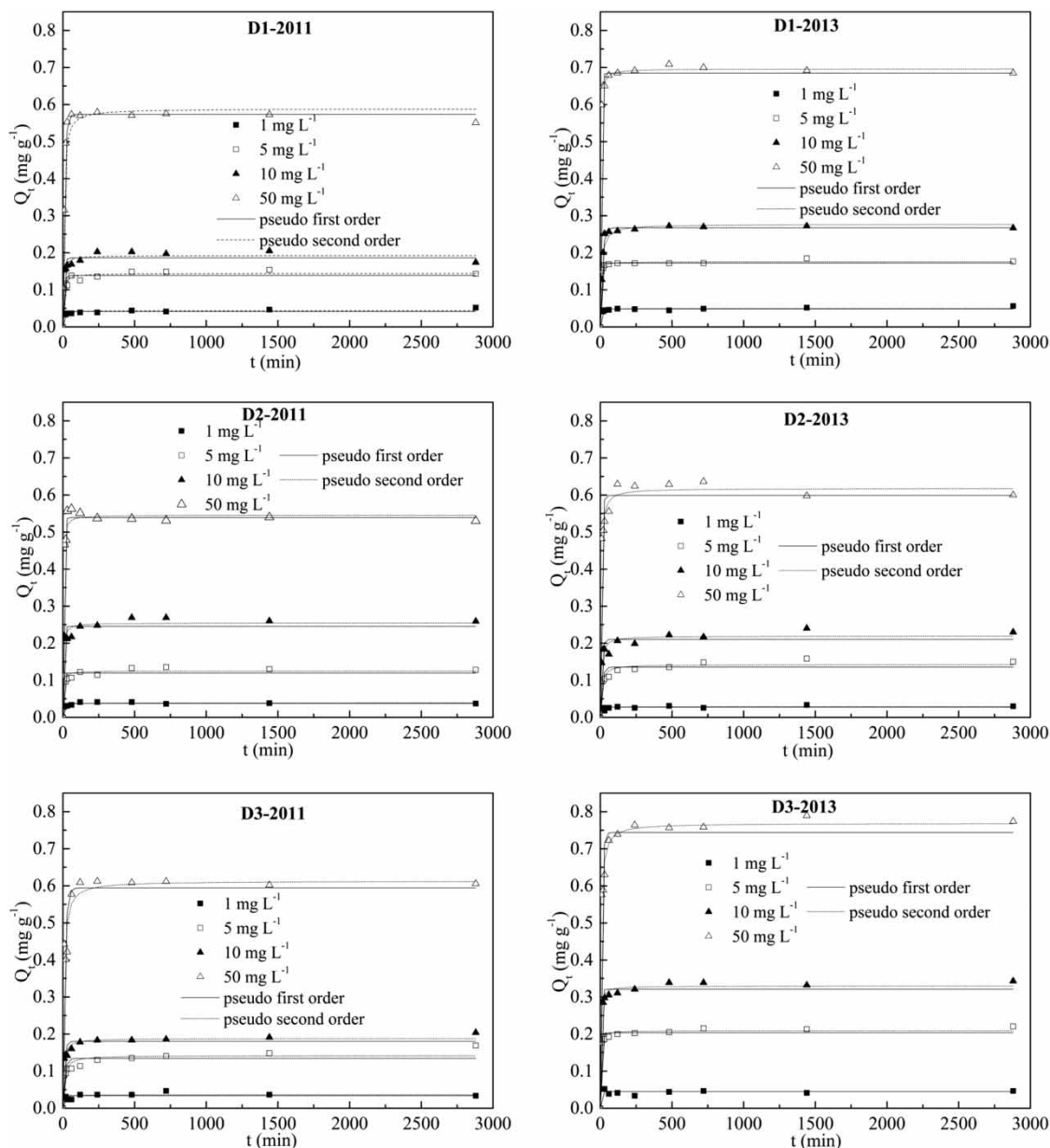


Figure 2 | Sorption kinetics of phosphorus in the five sediment samples obtained from Dongting Lake, China, in 2011 and 2013. (Continued.)

sorption capacity of the sediments was lower than that in 2013.

Figure 4 shows the values of the sorption rate constant of the pseudo second-order kinetic model at different phosphorus concentration levels. Evidently, the sediments sampled in 2011 had a higher sorption rate (up to $7.1 \text{ g mg}^{-1} \text{ min}^{-1}$) at low phosphorus concentrations (1 and 5 mg L^{-1}) than at high phosphorus concentrations (10 and 50 mg L^{-1}). The sediments

from 2013 exhibited a higher sorption rate than those from 2011. In 2011 (Figure 4(a)), the sediment from D5 had the highest sorption rate at three phosphorus concentration levels (1, 5, and 10 mg L^{-1}). When the initial phosphorus concentration was increased to 50 mg L^{-1} , the sediment from D2 exhibited the highest sorption rate ($1.4 \text{ g mg}^{-1} \text{ min}^{-1}$). In 2013 (Figure 4(b)), when the phosphorus concentration was 1 mg L^{-1} , the sediment from D2 had the highest sorption

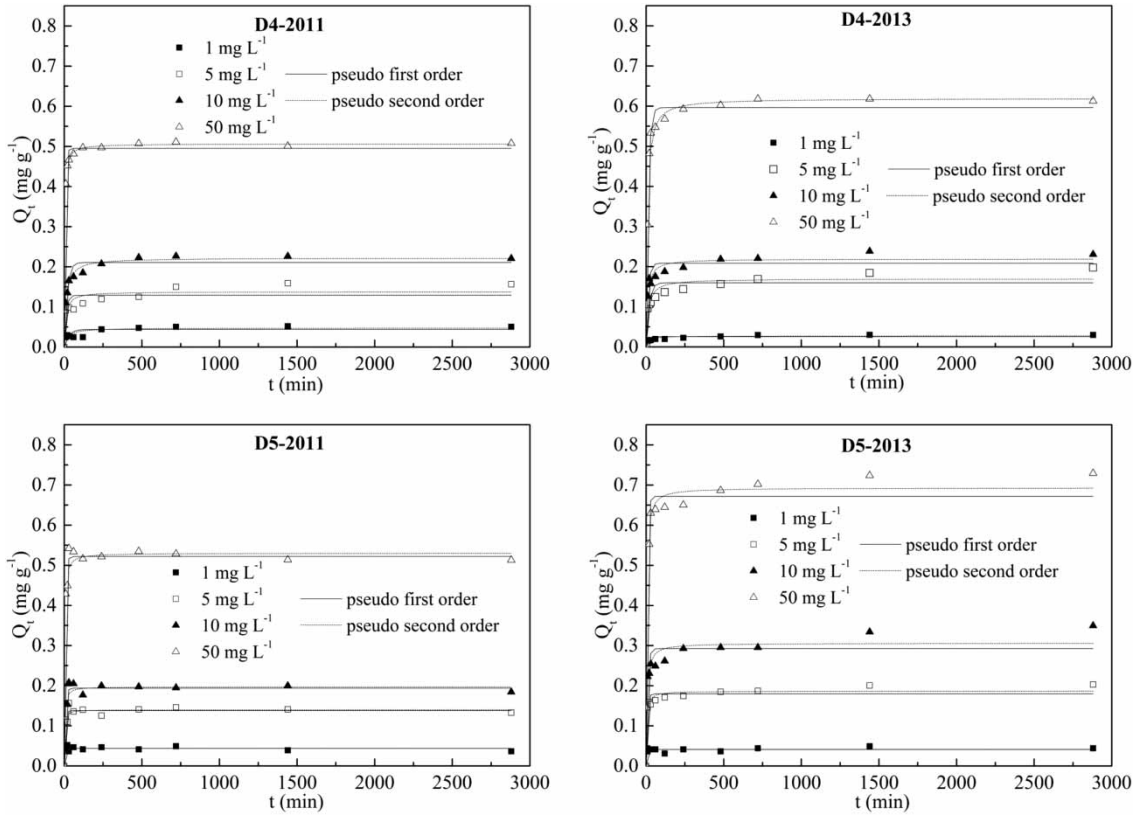


Figure 2 | Continued.

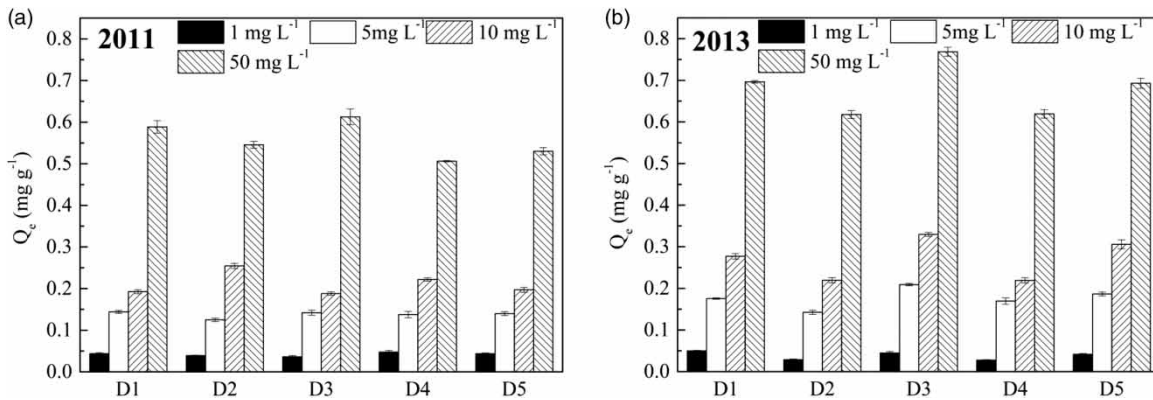


Figure 3 | Equilibrium sorption capacities of five sediment samples obtained from Dongting Lake, China, in 2011 (a) and 2013 (b).

rate; D1 and D5 exhibited higher sorption rates (7.9 and 8.1 $\text{g mg}^{-1} \text{min}^{-1}$, respectively) than the other two sediments. When the initial phosphorus concentration was increased, the sorption rate decreased rapidly. Specifically, when the initial phosphorus concentration increased to 50 mg L^{-1} , the sorption rate decreased to below $0.8 \text{ g mg}^{-1} \text{min}^{-1}$.

Sorption isotherm of P

Modified Langmuir and Freundlich models were utilized in this study to describe the sediment isotherms. Figure 5 presents the fitting of sorption equations with the modified models. The figure indicates that the equilibrium sorption

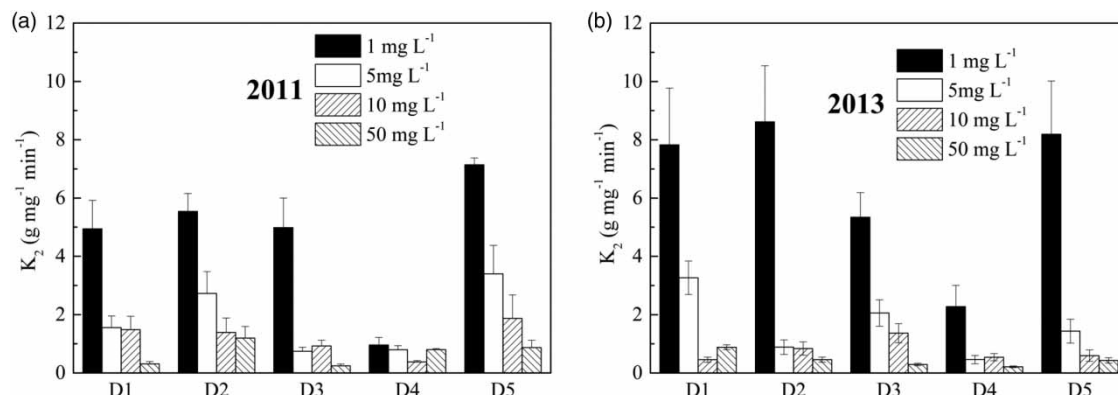


Figure 4 | Sorption rate constant of the pseudo second-order kinetic model of the five sediment samples obtained from Dongting Lake, China, in 2011 (a) and 2013 (b).

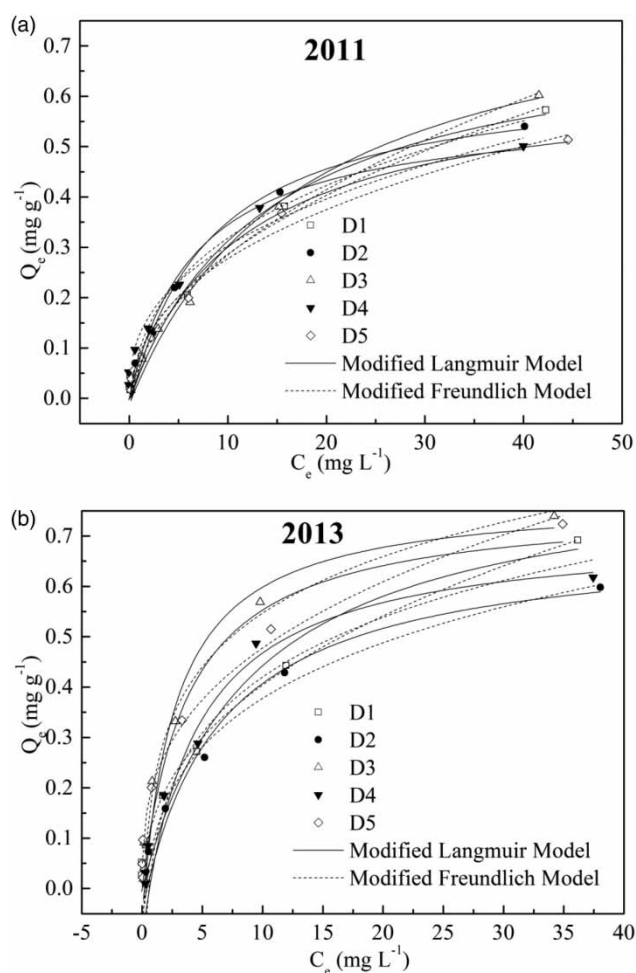


Figure 5 | Sorption isotherms of phosphorus on five sediment samples obtained from Dongting Lake, China, in 2011 (a) and 2013 (b), fitted with modified Langmuir and Freundlich models.

capacity of the sediment in 2013 was larger than that in 2011. D3 exhibited the largest equilibrium sorption capacity in the two years. Table 2 presents the fitting results. The correlation coefficient, R^2 ($0.85 < R^2 < 0.99$), verifies that the modified Freundlich and Langmuir models can effectively describe the sorption isotherms. However, the overall data were better fitted by the modified Langmuir model than by the modified Freundlich model. Table 2 also provides a good estimate of theoretical sorption maxima Q_m and sorption affinity parameter K . The Langmuir sorption maxima and the sorption affinity parameter ranged from 0.578 mg g^{-1} to 0.865 mg g^{-1} and from 0.057 L mg^{-1} to 0.365 L mg^{-1} , respectively. D3 in 2011 exhibited the maximum sorption and minimum K . The calculated results indicated that D4 had the highest EPC_0 and NAP , whereas D1 had the lowest EPC_0 and NAP (Table 2).

Researchers have concluded that the physicochemical properties of sediments significantly influence Q_m , NAP , and EPC_0 values. Table 3 shows the inter-correlations among Q_m , NAP , EPC_0 , particle size, and OM content of sediments in 2011 and 2013. In these two years, the proportions of fine particles ($<63 \mu\text{m}$) in the sediment had highly significant relationships ($R^2 > 0.92$, phosphorus < 0.01) with Q_m . The relationship between OM content in sediments and Q_m was also significant ($R^2 > 0.89$, $P < 0.05$). EPC_0 and NAP had significant relationships with Q_m in 2011 and 2013. This relationship demonstrates that the proportion of fine particles

Table 2 | Modified Langmuir and Freundlich model parameters for phosphorus sorption

sample	Year	Modified Langmuir: $Q_e = \frac{Q_{mKC}e^0 Q_{mKC}e^0}{1 + KC_e} - Q_e^0$										Modified Freundlich: $Q_e = K_f C_e^n - K_f (C_e^n)^n - Q_e^0$									
		Fitting results					Calculated results					Fitting results					Calculated results				
		C_e^0 (mg L ⁻¹)	Q_e^0 (mg g ⁻¹)	K (L mg ⁻¹)	Q_m (mg g ⁻¹)	R ²	EPC ₀ (mg L ⁻¹)	NAP (mg g ⁻¹)	K _p (L g ⁻¹)	n	K _f (L g ⁻¹)	R ²	EPC ₀ (mg L ⁻¹)	NAP (mg g ⁻¹)	K _p (L g ⁻¹)						
D1	2011	0.017	0.001	0.072	0.753	0.9966	0.032	0.002	0.054	0.471	0.102	0.9863	0.019	0.016	0.837						
	2013	0.017	0.001	0.111	0.844	0.9961	0.025	0.002	0.094	0.391	0.180	0.9867	0.018	0.037	2.106						
D2	2011	0.140	0.007	0.125	0.664	0.9808	0.228	0.018	0.081	0.301	0.225	0.9841	0.168	0.131	0.782						
	2013	0.275	0.014	0.157	0.740	0.9851	0.406	0.044	0.109	0.185	0.527	0.9770	0.328	0.428	1.308						
D3	2011	0.119	0.006	0.057	0.865	0.9831	0.243	0.012	0.049	0.478	0.110	0.9915	0.160	0.046	0.287						
	2013	0.171	0.009	0.365	0.836	0.9630	0.203	0.058	0.284	0.074	1.810	0.9506	0.184	1.598	8.686						
D4	2011	0.089	0.004	0.148	0.578	0.9749	0.137	0.011	0.084	0.386	0.124	0.9629	0.109	0.053	0.485						
	2013	0.459	0.023	0.234	0.813	0.9112	0.612	0.102	0.167	0.094	1.417	0.8511	0.552	1.340	2.428						
D5	2011	0.068	0.003	0.092	0.644	0.9801	0.127	0.007	0.058	0.370	0.142	0.9894	0.081	0.056	0.692						
	2013	0.101	0.005	0.264	0.763	0.9882	0.127	0.025	0.195	0.351	0.213	0.9855	0.117	0.100	0.859						

Table 3 | Pearson correlation coefficients among theoretical sorption maxima (Q_m), NAP, EPC₀, proportion of fine particles (<63 μm), and OM in 2011 and 2013 (five composite surface sediment samples were used, each sample n = 5)

	Particle size	OM	Q_m	EPC ₀	NAP
2011					
Particle size	1				
OM	0.821	1			
Q_m	0.923**	0.962*	1		
EPC ₀	0.821*	0.792	0.819*	1	
NAP	0.872	0.871	0.913*	0.847	1
2013					
Particle size	1				
OM	0.721	1			
Q_m	0.935**	0.897*	1		
EPC ₀	0.791	0.916	0.769*	1	
NAP	0.827	0.851	0.862*	0.671	1

*P < 0.05.
**P < 0.01.

(<63 μm) and OM content in sediments plays major roles in phosphorus sorption.

DISCUSSION

Phosphorus sorption was rapid in the first few minutes (0 min to 120 min) because the active sorption sites of the sediments were occupied rapidly in the first few minutes. In the next few hours, the active sorption sites and phosphorus sorption rate decreased. The other reasons for this phenomenon are the adsorption of phosphorus (PO₄³⁻ or H₂PO₄³⁻) in the solution by active sorption sites, lower TP content of the sediments of Dongting Lake (<800 mg kg⁻¹) than those of sediments of other eutrophic lakes in China, such as Dianchi Lake and Taihu Lake (>1,500 mg kg⁻¹) (Huang *et al.* 2013, 2015), and low pollutant content in the sediments. Thus, sorption equilibrium can be achieved before 240 min in the phosphorus sorption of sediments, and slight desorption may occur.

The sorption rate of the pseudo second-order kinetic (K_2) of the sediments in 2013 was higher than that in 2011 because sediments in 2013 had a higher OM content than those in 2011. From 2011 to 2013, although external pollution was controlled by stringent regulations, owing to

economic development around Dongting Lake, pollution entered the lake and the amount of pollutants in the sediments increased. The East Dongting Lake District, which is the main lake district of Dongting Lake, experienced severe eutrophication from 2011 to 2013. In this area (D3), the proportion of fine particles ($<63\ \mu\text{m}$) in the sediments was high and OM content was low, which resulted in a low sorption rate and high sorption capacity. A previous study also indicated that the sorption rate is affected by the OM content of sediments (Huang *et al.* 2015). Table 1 indicates that the proportion of fine particles ($<63\ \mu\text{m}$) in the sediments in 2011 (25.38% to 54.33%) was lower than that in 2013 (45.01% to 65.19%); this condition could have resulted in the larger sorption capacity of the sediments in 2013 than those in 2011.

Langmuir and Freundlich sorption isotherms have been widely utilized to describe the anion sorption of soil and sediments (House & Denison 2000). However, NAP in sediments affects the sorption/desorption characteristics of sediments. Furthermore, the Langmuir and Freundlich models are the preferred choice to describe the sorption behavior of phosphorus in homogeneous sediments (Del Bubba *et al.* 2003). Thus, we modified the Langmuir and Freundlich models to evaluate the isotherms of the five sediments in this study. The fitting and calculated results of the two modified models are presented in Table 2. Both models can be utilized to describe the sorption of sediments. The fitting results indicated that D3 had high theoretical sorption maxima in 2011 and 2013. The main reason for this outcome may be the high proportion of fine particles ($<63\ \mu\text{m}$) and low TP content in the sediments. Furthermore, the high proportion of fine particles ($<63\ \mu\text{m}$) had highly significant relationships with the theoretical sorption maxima in the two years (Table 3). Additionally, the sediments in 2013 with high OM resulted in a high sorption rate and elevated K values. The results in Table 3 show that OM contents in sediments had a significant relationship with sediment sorption capacity. The fitting results obtained by the modified Freundlich model demonstrated that the values of m ranged from 0 to 1, thereby indicating that the conditions were conducive to sorption (Fouladi Tajar *et al.* 2009). The values of K_f were relevant to sorption capacity, and the sediments in 2013 exhibited high values of sorption affinity, because of high sorption capacity. Overall, the

sediments in 2013 had higher isotherm parameters than those in 2011.

Depending on the dynamic equilibrium between the solution and solid phases, phosphorus can either be adsorbed or desorbed from sediments. Determining the sediment EPC_0 value can reveal the direction of soluble reactive phosphorus (SRP) flux (House & Denison 2002). In this study, the EPC_0 values of the five sediments were calculated with the modified models. The results of the modified Langmuir model better reflect the relationship between EPC_0 values in the sediments and SRP in the interstitial water than those of the modified Freundlich model. D1 is located in the outlet of Dongting Lake and the estuary of the Yangtze River. The flow velocity in the lake was high (0.42 m/s), and the disturbance of the sediments was severe. Furthermore, the sediments in D1 were arenaceous and clean, with relatively lower TP contents than the other sediments. Thus, the calculated results of EPC_0 for D1 (Table 2) were significantly lower than those of other sediments in 2011 and 2013. The monitoring data (Table 4) indicated that the SRP concentrations of the interstitial water were higher than that of EPC_0 . Thus, phosphorus sorption occurred from the overlying water, and the sediments of D1 served as a sink of phosphorus. This phenomenon could explain why D1 did not undergo eutrophication in the eastern part of Dongting Lake. On the contrary, the TP contents in sediments in D2 and D3 were high, and the values of EPC_0 were substantially higher than the SRP concentration of the interstitial water in the eastern part of Dongting Lake. Thus, the two districts had a high phosphorus concentration in water.

D4 is located in the southern part of Dongting Lake. The value of EPC_0 was larger than the SRP concentration of

Table 4 | EPC_0 and SRP concentration in interstitial water of the study area

Sample	EPC_0 (mg L^{-1})		SRP in interstitial water (mg L^{-1})	
	2011	2013	2011	2013
D1	0.032	0.025	0.126	0.101
D2	0.228	0.406	0.172	0.267
D3	0.243	0.203	0.138	0.141
D4	0.137	0.612	0.091	0.096
D5	0.127	0.127	0.082	0.078

interstitial water ($<0.1 \text{ mg L}^{-1}$) (Table 4). Although the sediment of D4 served as a phosphorus source, the overlying water of D4 did not undergo eutrophication. This result might be explained by the control of external pollution in the southern part of Dongting Lake from 2011 to 2013; the release of phosphorus from sediments did not lead to eutrophication in the lake. D5, which is the district with the smallest area, is located in the western part of Dongting Lake. The values of EPC_0 in 2011 and 2013 did not vary in D5 and were relatively lower than those in D2, D3, and D4. However, the values of EPC_0 in both years were higher than the SRP concentration of interstitial water ($<0.1 \text{ mg L}^{-1}$) (Table 4). This area is the intersection of two large rivers, namely, Hudu River and Ouchi River, which are connected to the Yangtze River. The flow state is complex in this district. The water levels increase in the south or north of this district at different times, and the flow field is unsteady (Lai *et al.* 2006). The monitoring data indicated that the flow velocity of D5 (0.40 m/s) was higher than that of D2 (0.08 m/s), D3 (0.27 m/s), and D4 (0.16 m/s) in 2013 (Liu *et al.* 2015) but lower than that of D1 (0.42 m/s). Therefore, phosphorus exchange between the sediment and water was frequent. These characteristics were the main reasons eutrophication was prevented in this district.

CONCLUSION

The sediment–water interface experiences complex environmental conditions in a river-connected lake. In Dongting Lake, physicochemical characteristics such as proportion of fine particles or nutrient content in sediments, significantly influence the characteristics of phosphorus sorption at the sediment–water interface and the phosphorus source or sink in sediments. The results of this study showed that the sediment sorption rate followed the pseudo second-order, and some sediments in eastern Dongting Lake exhibited the highest sorption capacity because of the high proportion of fine particles ($<63 \mu\text{m}$) and the relationship between the river and lake. The lake phosphorus input in 2013 was more severe than that in 2011, particularly in the eastern part of Dongting Lake. The southern and western parts of the lake had a relatively low phosphorus input in 2011, although the external

phosphorus input increased from 2011 to 2013. The overall data that describe the sorption isotherms were better fitted by the modified Langmuir model than modified Freundlich model. The proportion of fine particles in the sediments caused a change in the phosphorus sorption characteristic of the estuary. In addition, the eastern part of Dongting Lake served as a phosphorus source and had high phosphorus concentrations in water. The location and flow field of the sediments reduced the eutrophication risk in the southern and western parts of Dongting Lake.

Sediments are a potential phosphorus source under certain conditions, especially in a river-connected lake. Understanding the characteristics of phosphorus sorption at the sediment–water interface and the phosphorus source or sink areas in a lake is crucial to clarify the role of sediments during phosphorus release or sorption. With Dongting Lake as an example, this study revealed the sorption characteristics at the sediment–water interface to provide a theoretical foundation for the control of phosphorus release in sediments.

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