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Research Article

Potential Retention and Release Capacity of Phosphorus in the Newly Formed Wetland Soils from the Yellow River Delta, China

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There are few researches on the characteristics of phosphorus (P) in the newly born wetland soils from Yellow River Delta of China. Meanwhile, whether the wetland soils can protect the aquatic ecosystem from excessive P input or not and the risk of P release from the soils to the water quality have generated considerable interests. Through isothermal batch static equilibrium sorption experiments followed by six subsequent extraction steps, the present study assessed the variations in P sorption and desorption properties of the newly born wetland soils in Yellow River Delta. It is found that the P sorption isotherms were nonlinear and the amount of P sorption reached a steady state as P initial concentration added increased in the studied soils. Though the capacity of P retention differed strongly among the studied zone, the soils can protect the aquatic ecosystem from excessive P input to a certain extent degree. From the desorption experiments, it is found that the newly sorbed P was easily desorbed in higher initial added concentration and the desorption P significantly decreased with successive extraction in all samples. The release of P from soil proposed a significant contribution to the water quality and eutrophication of coastal zone. Correlation and regression analyses showed that the amorphous and free Fe/Al oxides, correlated with clay content in the studied soils, were the crucial chemical factors ascribed to the soil P retention and release capacity.

Keywords: Fe- & Al-oxides; Fluvo-aquic soil; Seaside wetland; Sorption–Desorption

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1 Introduction

The phosphorus (P) which has been regarded as one of the most limited nutritional factors can have an impact on plant growth and biological processes [1, 2]. However, as the excessive nitrogen and phosphorus was input into the water bodies, the aquatic environmental quality was getting worse and worse, especially in the Yellow River [2]. Some researchers suggested that the wetland soil functioning as a sorption sink for phosphorus moving and flooding could immobilize phosphorus from water with high phosphorus concentration and protect the ecosystem, at least temporarily, from external phosphorus inputs [3–5]. However, the desorption of phosphorus also brought higher risk of phosphorus from soils to adjacent water bodies [5, 6]. The conditions of phosphorus retained in or released from the wetland soil have not yet been completely carried out, especially in Yellow River Delta. Therefore, it is essential to assess the variations in phosphorus sorption and desorption characteristics of the soil along the Yellow River Delta.

So far, many studies have demonstrated that P sorption–desorption capacity in different soils was related to soil composition, such as clay and organic matter content [7, 8], Fe- and Al-oxides content [9–11], Ca active species content, cation exchange capacity, pH colloidal specific [12], and so on. The content of metals was thought to be the main factor that determined sorption capacity because of the high specific surface of Fe/Al hydroxides. For example, Villapando and Graetz [10] found that the organic matter bounded Al (CuCl₂-extractable) accounted for more than 60% of the variability in phosphorus sorption by studying 16 Florida Spodosols. Sharpley thought that the ratio of extractable Al- or Fe-organic C explained more than individual soil properties in phosphorus sorption. P adsorption and desorption by soil material is dominated by sesquioxides or mineral surfaces with organic matter blocking P sorption sites [13]. This is corresponding with Wang et al. [14] who reported that the maximum P sorption capacity enhanced with the increase of the content of (Fe + Al + Ca). Besides that, Wang et al. [15] suggested that soils with higher proportion of clay and silt fractions may be heavily polluted in the presence of pollutions because finer grain fractions had larger pollutant sorption capacity and higher suspension potential. In addition, Millero found that the salinity also was important in the aggregation and sedimentation of P in soils and the apparent effect of salinity on the sorption of PO₄ was largely due to changes in

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Abbreviations: DCB, dithionite/citrate/bicarbonate solution; MBC, maximum phosphorus buffer capacity

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the concentration of HCO_3^- in the solution [16]. These factors mentioned above must all be taken into account when evaluating P sorption and desorption characteristics.

The objectives of this paper were to analyze soil properties which contribute to the retention and release of P in new-born coastal wetland by making use of the isothermal static sorption and desorption experiment method. Meanwhile, quantitative descriptions was made with the Langmuir and Freundlich equations in order to estimate the effects of long-term pollution on the P sorption properties of the soils along the Yellow River Delta.

2 Materials and methods

2.1 Soil sample

Five surface soil samples (0–10 cm) classified as fluvo-aquic soil were collected from Yellow River Delta. After air-drying, and passing through 2 mm sieve, these samples were stored for the experiment. Soil pH was analyzed by using combination pH electrode (solid/liquid, 1:2.5). The amorphous and free Fe, Al oxides were dissolved in acidified 0.2 M ammonium oxalate solution (Fe_o , Al_o) and dithionite/citrate/bicarbonate solution (DCB) (Fe_d , Al_d), respectively [17, 18]. Extracted Fe and Al were determined by inductively coupled plasma optical emission spectrometer (Optima 7000DV, Perkin Elmer). The grain size fractions were measured using a Mastersizer 2000 Laser Size Analyser and were classified into clay (<0.002 mm), silt (0.002–0.005 mm), and sand fractions (0.05–2 mm). Total organic carbon (TOC), salinity, total phosphorus (TP), and heavy metal contents were determined by using the method of soil analysis in agricultural chemistry [19].

2.2 Phosphorus sorption experiment

Pre-weighed centrifuge tubes were filled with 1 g of soil plus 10 mL of 0.01 M KCl solution which contains P (as KH_2PO_4) concentrations of 0, 0.05, 0.1, 0.5, 1, 2, 5, 10, 20, 40, 60, 80, 100, 120, 150, and 240 mg L^{-1} . Several drops of chloroform were added to weaken microbial activity. The tubes were shaken at $27 \pm 2^\circ\text{C}$ for 24 h to reach equilibrium. After centrifuged at 5000 rpm for 10 min, the equilibrium solution was measured by spectrophotometry [20]. The difference between the added amount and the measured amount in the equilibrium solution was determined as the net sorbed phosphorus concentration.

The phosphorus sorption isotherm in different initial concentration ranges can be fitted using Langmuir, Eq. (1), Freundlich,

Eq. (2), model.

$$S = \frac{K_L S_m C}{1 + K_L C} \quad (1)$$

$$S = K_F C^n \quad (2)$$

where C is the P concentration after 24 h equilibrium (mg L^{-1}), S is the sorbed P amount (mg kg^{-1}), S_m is the P sorption maximum (mg kg^{-1}), K_L is a constant associated with the binding strength, n the order of reaction, is also an indicator of bonding energy, and K_F is the constant. The maximum phosphorus buffer capacity (MBC), calculated on the product of Langmuir constants S_m and K_L , gives an indicator of the effective buffer to the change of soil solution phosphorus concentration [21].

2.3 Phosphorus desorption experiment

After the sorption experiment, the supernatant solutions containing $C_0 = 20, 100, \text{ and } 240 \text{ mg PL}^{-1}$ were removed and each tube was weighed to figure out the volume of the residual solution. The amount of phosphorus sorbed in sorption experiments is regarded as the starting value in soil for phosphorus desorption. Then, the tubes were shaken for 24 h by adding 10 mL 0.01 M KCl solution, and the supernatants were treated as described above. The desorption was repeated six times and the amount of phosphorus remaining in the soil was calculated for each extractions. The percentage of phosphorus desorption (P_{des}) was calculated from the ratio between the amount of phosphorus desorbed and the amounts of phosphorus sorbed in soil.

3 Results and discussion

3.1 Soil characteristics

The basic properties of the soils are listed in Tab. 1. The fractions of silt and sand in the studied soils accounted for more than 92%, and the contents of clay-sized particles were lower. There's not much difference in the pH value (mean, 8.4 ± 0.2) and Ca content (mean, $5.1 \pm 0.8\%$) among the samples. The contents of soil TOC were in the range of 0.2–0.9%. The total content of P ranged from 558 to 691 mg kg^{-1} , which is lower than the alpine wetland in the Qinghai-Tibet Plateau [22] and Pearl River estuary [23]. The available phosphorus (AP, range: 19–31 mg kg^{-1}) accounted for <6% of TP due to the scarcely vegetation cover in the study area [24].

Table 1. Selected physical and chemical properties of the wetland soil used in this study

Sampling sites	Site location	Dominant species	pH	TP (mg kg^{-1})	Clay (%)	Silt (%)	Salinity (%)	TOC (%)	Ca (%)	Fe_d (g kg^{-1})	Al_d (g kg^{-1})	Al_o (g kg^{-1})	Fe_o/Fe_d	Fe_d/Fe_t (%)	Al_d/Al_t (%)
A	N 37°45'48.90", E 119°9'58.00"	River beach	8.7	559	2.2	56.4	0.4	0.3	4.6	2.8	0.3	0.1	0.1	13.2	0.6
B	N 37°45'57.90", E 119°9'55.60"	<i>Tamarix chinensis</i>	8.2	569	7.5	76.0	6.5	0.9	4.9	5.3	0.6	0.3	0.1	22.1	1.4
C	N 37°46'5.22", E 119°9'53.04"	Chenopodiaceae	8.2	564	7.4	78.8	12.2	0.7	4.3	5.8	0.7	0.4	0.1	27.9	1.5
D	N 37°46'26.22", E 119°9'51.06"	<i>T. chinensis</i> and Chenopodiaceae	8.5	586	3.4	70.0	16.0	0.5	5.4	4.0	0.5	0.2	0.1	17.2	1.0
E	N 37°47'52.00", E 119°10'43.60"	Coastal beach	8.5	692	5.8	71.8	24.5	0.2	6.2	4.0	0.4	0.3	0.2	14.1	0.8

Table 2. Parameters of the sorption isotherms described with Langmuir and Freundlich equations

Soil	Estimated by Langmuir equation				Estimated by Freundlich equation		
	K_L (L mg ⁻¹)	S_m (mg kg ⁻¹)	MBC (L mg ⁻¹)	R^2	K_F (mg kg ⁻¹)	n	R^2
A	0.023	293	7	0.94	29	0.41	0.98
B	0.038	845	32	0.94	124	0.36	1.00
C	0.046	1071	49	0.92	162	0.37	0.98
D	0.028	337	9	0.89	44	0.37	0.96
E	0.052	491	26	0.93	95	0.32	0.99

The contents of Al_d , Fe_d in the studied five soils were in the ranges of 0.3–0.7 and 2.8–5.8 g kg⁻¹, respectively, which is in agreement with the report of Georg for the alluvial soils at the Danube River [8]. The freeness of iron oxide (Fe_d percentage of the total Fe content) was 13.2–27.9%, lower than the finding of Villapando and Graetz [10] who reported that more than 60% of the total Fe was DCB-extractable in Florida Spondosols. The reason may be due to the lower weathering of the soils in Yellow River Delta [19].

3.2 The sorption isotherms and parameters

As shown in Tab. 2 and Fig. 1, P sorption increased with increasing P initial concentration until to a stable state sorption in all samples. At lower equilibrium concentrations (0–15 mg L⁻¹), the P sorption to the soil increased significantly because the soil was far from saturated and specific sorption was a dominant factor. While at higher equilibrium concentrations, rate of sorption increase steadily until to a stable state sorption where the physical sorption plays a leading role [24–26].

It can be concluded that the slope of isotherm curves decrease as the initial added P concentration increased. It was almost completely adsorbed when 0.05 mg L⁻¹ P was added in the sampled soils. An earlier study founded that the concentration of P in the Yellow River was in the range of 0.035–0.069 mg L⁻¹ (data not listed). So we can conclude that exposed soils along the coastal zones could be functioned as an efficient buffer to raise the water quality of the Yellow River. As the increase of initial added P concentration, the sorption ratio decreased from 96 to 43% when 100 and 2400 mg kg⁻¹ of P

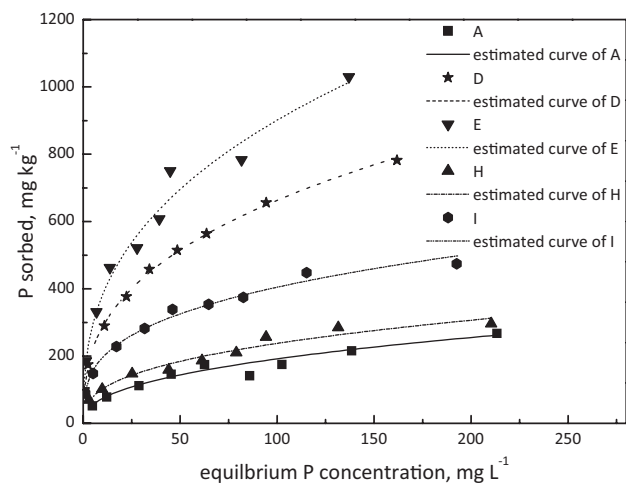


Figure 1. The observed and simulated sorption isotherms of P by Freundlich model on different soils.

solutions were added to the C site, respectively. The values suggest that long-term external P input into the Yellow River may result in the decrease of P retention capacity of the soil.

The sorption isotherms were best described by Langmuir and Freundlich equations, of which the median R^2 are 0.93 and 0.98, respectively. The coefficient of determination (R^2) is a little higher for the Freundlich equation, in accord with the researches of Sanyal et al. [27] and Dubus and Becquer [28]. However, the P sorption data of Indonesian soils [29] and Thai upland soils [30] were better described by the Langmuir equation. The fitness of the Freundlich model to our soil may be owe to binding affinity decrease as sorption increases which is closer of the real sorption process, while the premise of Langmuir model is correlated with constant binding energy [31].

The maximum sorption amount (S_m) estimated by Langmuir equation for the soils ranged from 293 to 1071 mg kg⁻¹ (mean, 607 mg kg⁻¹), which was lower than the Danjiangkou Reservoir [32]. The P retention capacity (S_m , K_F) was in order of C>B>E>D>A. The soils near the coastal beach (E) and river beach (A) indicated lower P sorption capacities in Yellow River Delta. MBC increased as the amount of sorption increased, indicating that the mobility of P is higher in soils of lower MBC because MBC correlated positively with P retention [10]. The Langmuir K_L coefficient ranged from 0.0226 to 0.052 L mg⁻¹. These data were similar to the low-Fe wetland soils in subtropical reservoir [32], lower than iron coated sorbents [33] and marsh in Korea [34], and related with different soil physical and chemical characteristics (Tab. 2).

3.3 Phosphorus desorption behavior

As shown in Fig. 2, the amount of desorbed P increased as the increase of adsorbed P in soil. P_{des} after six successive desorption increased from 21 to 56% when 20 and 240 mg L⁻¹, respectively, was initially added to the C site. Every single P desorption significantly decreased with successive extraction, and a fraction of P still remained in the studied soils after six desorption times. The reason may be that the form of loosely bound type has shifted to a more tightly bound one when P was held at the surface of the medium [10].

After six successive extractions, more than 90% of sorbed P (except C) was desorbed when 240 mg P L⁻¹ was initially added to the soils (Fig. 2). This indicated that the concentration of strong binding energy sites was lower and the mobility of freshly sorbed P was higher when the initial P concentration was higher [35]. This is consistent with the previous hypothesis that there are two different sorption sites in soils. Therefore the significant load of P to the soil may result in the decrease of P retention capacity and increase the risk of the P release of new-born wetland soil to the adjacent water bodies in the Yellow River Delta.

Among the five sampled soils, over 70% of the added P ($C_0 = 20$ mg L⁻¹) remained sorbed in C site while less than 30% was

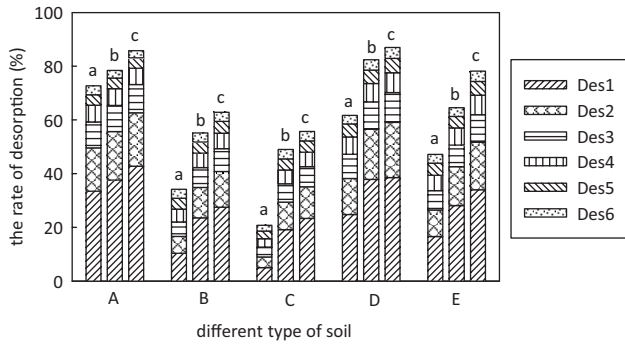


Figure 2. Amount of P successive six desorption times (Des1, 2, 3, 4, 5, 6, respectively) in different soils at $C_0 = 20$ (a), 100 (b), and 240 (c) mg L^{-1} .

remained in A site after six successive extractions (Fig. 2), suggesting the higher P-retention capacity in C site. This may be due to the higher clay and Fe content. For example, the Fe_d value in C site (5.8 g kg^{-1}) is more than twice of that in A site (2.8 g kg^{-1}). The relationship between them will be discussed further below.

3.4 Relationship between P sorption–desorption behavior and soil characteristics

We made a correlation analysis between the experiment parameters and the selected soil characteristics to find out the main soil characteristics which control P sorption–desorption behavior in the studied soils (Tab. 3).

It is noticeable that different form of Fe and Al oxides significantly associated with P sorption–desorption parameters (Tab. 3). Sorption parameter (S_m) correlated with contents of Fe_d ($r = 0.86$; $p < 0.01$) and Al_d ($r = 0.84$; $p < 0.01$), while negative correlations between desorption parameter (P_{des}) and values of Fe_d ($r = -0.91$; $p < 0.01$) and Al_d ($r = -0.88$; $p < 0.01$) were also observed. This is also reported by Georg for alluvial soil derived from Danube River [8] and by Dunne in wetland soils [36]. Fe_d/Fe_t show significant relationship with S_m ($r = 0.94$, $p < 0.05$) and P_{des} ($r = -0.9$, $p < 0.05$). It may be due to the fact that hydroxyl groups on the surface of free iron oxide can be replaced by P in ligand exchange reaction [19, 37].

Clay-sized particles of studied samples was correlated with S_m and P_{des} ($r = 0.91$, $p < 0.05$; $r = -0.92$, $p < 0.05$, respectively), suggesting that clay content is also an important factor affecting P sorption–

desorption property in the studied soil. Soil with high clay content may retain more P and the release of P will largely decrease.

The correlation between pH and S_m was negative ($r = -0.88$; $p < 0.05$) because there are more negative surface charges and more dissolution of Fe/Al phosphates will decrease the pH value of the studied soils [38].

Organic C concentrations did not show closely related to all the P sorption–desorption parameters, implying that the affinity between organic C and anions was lower because of the negative charges in the surface of organic C [8]. However, the effect of organic matter on P sorption is not clear. Yoo et al. [34] and Traina et al. [39] found significant correlation of S_m with organic matter content because organic matter might be associated with Ca, Al, and Fe. On the contrary, Barrow [40] found negative correlation between them due to the competition between organic matter and P for sorption sites on mineral surfaces.

In addition, a significant increase of P sorption was observed at the salinity around 10‰, which was in accordance with the findings of An [12] and Hu [41]. The higher sorption at the salinity around 10‰ may be based on the hypothesis that a nearly complete sedimentation of P aggregates occurred at this salinity [42, 43]. However, the poor correlation between S_m and salinity implies that factors other than salinity have an important impact on the sorption and desorption process of P [44].

4 Conclusions

P sorption increased with increasing P initial concentration in all samples and reached saturation to a fixed value. P retention capacities are best described by Langmuir and Freundlich equations, of which the median R^2 are 0.93 and 0.98, respectively. The P sorption maximum range from 293 to 1071 mg kg^{-1} soil and the maximum P buffer capacity varies between 7 and 49 L kg^{-1} . Among the five studied soils, more than 60% of the input P will be removed, and the exposed soils along the coastal zones could be functioned as an efficient buffer to raise the water quality of the Yellow River. The release capacity varied largely among the five sampled soils and the amount of P single desorption decreased as the increase number of successive extraction, and a proportion of P still remained in the studied soils after six desorption times. The abundance load of P to the soil may result in the decrease of P retention capacity and increase the risk of the P release of new-born wetland soil to the adjacent water bodies in the Yellow River Delta. Different forms of

Table 3. Correlation of P sorption and desorption parameters with selected soil variables for the studied samples

	pH	Clay	Salinity	TOC	Fe_d	Fe_o	Al_d	Al_o	Fe_d/Fe_t	S_m	P_{des}
pH	1										
Clay	-0.94*	1									
Salinity	-0.21	0.26	1								
TOC	-0.83	0.65	-0.32	1							
Fe_d	-0.97**	0.92*	0.15	0.82	1						
Fe_o	-0.72	0.85	0.67	0.21	0.73**	1					
Al_d	-0.95*	0.88	0.11	0.83	0.97**	0.78**	1				
Al_o	-0.82	0.92*	0.47	0.43	0.72**	0.96**	0.74**	1			
Fe_d/Fe_t	-0.84	0.76	-0.74	0.84	0.94*	0.52	0.97**	0.74	1		
S_m	-0.88*	0.91*	-0.01	0.75	0.86**	0.68*	0.84**	0.75**	0.94*	1	
P_{des}	0.87	-0.92*	0.05	-0.74	-0.91**	-0.85**	-0.88**	-0.87**	-0.9*	-0.89**	1

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level ($n = 5$).

Fe/Al oxides, especially the freeness of iron oxide, were regarded as the main factors contributing to the soil P retention and released capacity. C site with higher DCB-extractable Fe oxides has the higher P retention capacity and more external input of P will be retained by this type of soil. This finding will be a good index for planning future management of water pollution and soil reuse in Yellow River Delta.

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