

Li Gao¹
Luhua Zhang¹
Hongbo Shao^{2,3}

¹Ocean School, Yantai University,
Yantai, P. R. China

²Key Laboratory of Coastal Biology &
Resources Utilization, Yantai Institute
of Coastal Zone Research (YIC),
Chinese Academy of Sciences (CAS),
Yantai, P. R. China

³Institute of Life Sciences, Qingdao
University of Science & Technology
(QUST), Qingdao, P. R. China

Research Article

Phosphorus Bioavailability and Release Potential Risk of the Sediments in the Coastal Wetland: A Case Study of Rongcheng Swan Lake, Shandong, China

Rongcheng Swan Lake, a natural coastal wetland, is connected to Rongcheng Bay of Yellow Sea, China. In this lagoon, water quality has deteriorated gradually in recent 30 years and filamentous *Chaetomorpha linum* have bloomed during the past five years. In present study, the concentration, fractions, and bioavailability of phosphorus (P) in surface sediments were investigated throughout the lake. In order to evaluate P retention ability of the wetland, six sediment samples from different lake regions were collected to study P adsorption kinetics, adsorption capacity and the relation to sediment properties. In Swan Lake, total P concentrations in sediments varied from 79 to 616 mg/kg, which were significantly higher in northwest region than those in southeast region. Sediment grain size and external inputs were the main factors affecting P distribution. Inorganic P concentration was obviously higher than that of organic P, and Ca-P was the important form in the sediments. Fe/Al-P showed a large spatial variation, with relatively high concentrations occurring at the northeastern corner and the western tip strongly affected by the discharge of wastewater. The adsorption isotherms were well fitted by Linear equation at low P conditions and by Langmuir equation at high initial P concentrations, respectively. The sediments in the northern and central lake had higher P adsorption capacity, while in southern lake the degree of P saturation of the sediments was high. Ammonium oxalate extractable Al, organic matter, and fine particle were important factors influencing P adsorption. In Swan Lake, algae available P (AAP) was the largest form of bioavailable P, followed by Olsen-P; moreover, AAP and Olsen-P showed significant correlations with Fe/Al-P. As a whole, TP concentration in sediments from Swan Lake was low, and the sediments at most regions had buffering ability for P in overlying water; while at the western tip of lake where macroalgal blooms frequently breakout, AAP concentration was relatively high and the sediments had higher potential for releasing P into water column.

Keywords: Bioavailable P; Lake water; Release risk; Sediment composition; Wetland

Received: March 18, 2013; *revised:* June 12, 2013; *accepted:* June 25, 2013

DOI: 10.1002/clen.201300209

1 Introduction

Wetlands, “the kidney of the earth”, are well known for the ability to receive and store nutrients from water bodies [1–3]. The wetland sediments play an important role as a regulator of nutrient fluxes at the sediment–water interface by either adsorbing or releasing

nutrients into the water [4–6]. Phosphorus (P) is a key element of eutrophication processes in many aquatic ecosystems. In coastal wetlands, most of the P from external inputs can be deposited in sediments through adsorption of dissolved P or sedimentation of organic particles before reaching the ocean [7, 8], but the magnitude of P sorption by the sediments is limited. When external P load is reduced, some P in the sediments can be released into the overlying water again depending on P fractions and environmental conditions [9–12]. Sediment internal loading may become a source of eutrophication and have a significant impact on water quality for a long period. Therefore, the knowledge of adsorption capacity and P bioavailability of the sediments is essential for the control of water eutrophication.

P sorption on the sediments is an important process that affects P transport between the sediments and overlying water. P sorption

Correspondence: Li Gao, Ocean School, Yantai University, No. 32 Qingquan Road, Laishan District, Yantai 264005, P. R. China
E-mail: ligao117@126.com

Abbreviations: AAP, algae available P; Al_{ox}, oxalate extractable Al; ANOVA, one-way analysis of variance; BAP, bioavailable P; DPS, degree of P saturation; EPC₀, equilibrium P concentration; ERI, eutrophication risk index; Fe_{ox}, oxalate extractable Fe; IP, Inorganic P; NAP, native adsorbed P; OM, organic matter; OP, organic P; PSI, P sorption index; Q_m, maximum sorption amount; RDP, readily desorbable P; SMT, standards measurements and testing; SRP, soluble reactive P; STP, sediment test P; TN, total nitrogen; TP, total phosphorus; WSP, water soluble P

Additional correspondence: Professor Hongbo Shao,
E-mail: shaohongbochu@126.com

characteristics mainly depend on sediment composition, such as amorphous Fe and Al [13], organic matter (OM) [14], grain size [15], and carbonate [16]. However, the dominant factor influencing P adsorption was different in various aquatic systems. For example, oxalate-extractable Fe (Fe_{ox}) showed the highest correlations with P sorption index (PSI) in Hawaii's Coastal Wetlands [13]. In the newly formed soils in Yellow Sea Delta, the amorphous and free Fe/Al oxides were the crucial chemical factors ascribed to the soil P retention because of the high specific surface area [17]. Studies by Li et al. [14] showed that the sediments rich in fine particles and OM had stronger P buffering capacities in the Yangtze Estuary and Hangzhou Bay. Wang and Li [16] studied the capacities in adsorption and desorption of P by various sediments from Florida state in USA, and found that the high P adsorption in the marine sediment might be related to an abundance of $CaCO_3$ which had an especially high affinity for P, and the high P adsorption potential of wetland sediments may result from abundant hydrated oxides of Fe and Al. In addition, P concentration in water column and the degree of P saturation (DPS) of sediments are also of importance to P retention capacity by the sediments.

P sorption isotherms can be described quantitatively by linear or nonlinear equations, depending on sediment properties and P concentration magnitudes. When at low initial P concentrations, the adsorption isotherms were fitted by the Linear equation very well [18, 19]. At high P concentrations, Langmuir and Freundlich equations were commonly used for characterizing P adsorption [16, 17, 20]. According to the sorption models, some important parameters such as P sorption maxima, the slope related to adsorption efficiency, and equilibrium P concentration (EPC_0) are determined, which can provide useful information regarding the long-term sustainability of sediments in adsorbing additional P.

Sediments serve as an important P reservoir, the release from which first depends on the concentration and fractions of P in sediments [4, 9, 21, 22]. There were great differences in the mobility among various P fractions. Some P forms can be stored in the sediments permanently, while others are immediately available or potentially mobile [11, 12, 23, 24]. P fractions in sediments can provide important information for predicting the release risk to water column. A standards measurements and testing (SMT) fractionation scheme, developed by the European Union laboratories, has been widely used in different types of sediments recently. According to the SMT method, sediment P is divided into P bound to apatite (Ca-P), P associated with Fe, Al, and Mn oxides and hydroxides (Fe/Al-P), organic P (OP) and inorganic P (IP) [25, 26]. Fe/Al-P is potentially mobile, which may be released into overlying water at low dissolved oxygen concentration or high pH conditions [7, 23, 24]. Mayer et al. [11] confirmed the highly significant relationship between Fe/Al-P and sediment P fluxes in Cootes Paradise. OP form is considered to be a potentially mobile P pool, and can be partly converted into algal-available P [9, 12, 23]. In addition, some researchers regarded bioavailable P (BAP) as a predictor for the potential release risk of P in sediments. Zhou et al. [10] proposed that BAP included algae available P (AAP), Olsen-P, readily desorbable P (RDP), and water soluble P (WSP). AAP is potentially available for algal uptake; while WSP and RDP are immediately available P for algae, and easily to release from the sediments particularly when water P concentration is depleted. For the heavily polluted sediments, BAP showed close relationships with IP and Fe/Al-P in Yangtze River [27]. In different aquatic ecosystems, the trophic status and bioavailability of sediment P have marked differences due to external inputs, sediment properties, P forms, and so on.

Rongcheng Swan Lake, a natural lagoon, is located in eastern Shandong Peninsula, China. At present, the quality of lake water becomes worse, and filamentous macroalgae (*Chaetomorpha linum*) have bloomed during the past few years. The knowledge of P sorption characteristics and P mobility of the sediments is essential to understand P cycle at the sediment-water interface. However, few researches on P internal loading of sediments from Swan Lake have been reported, and little is known about their release risk for water column. In present study, the sediments from different lake regions were selected to study P adsorption characteristics and the relation to sediment composition. In addition, the trophic status of total P (TP), P fractions and bioavailable P in surface sediments throughout the lake were investigated. The purposes of this study were to determine P sorption capacity by the sediments, and to evaluate the bioavailability and release risk of sediment P when external P load is reduced.

2 Materials and methods

2.1 Study site

Swan Lake (37°20'N, 122°34'E) is a shallow coastal lagoon, which is connected to Rongcheng Bay of the Yellow Sea by an inlet at the southeastern corner. There are a large area of reed swamp in the northern and western lake wetland, and a great number of swans come for over wintering every year. Along the eastern lake shore, a sand dam occurs, which separates the lagoon from Rongcheng Bay. Due to excessive nutrient inputs and inappropriate utilization, such as the discharge of wastewater and the development of beach aquaculture, water quality has deteriorated gradually and *C. linum* have bloomed in the western area over the past five years.

2.2 Sediment sampling

In May 2011, 25 sites were chosen uniformly throughout Swan Lake in order to investigate the concentration, fractions and bioavailability of P (Fig. 1). The top 10 cm of sediment sample were collected with a Petersen grab sampler. After being taken to the laboratory, sediment samples were homogenized and then air-dried at room temperature. A portion of the dried samples was used to determine grain size, and the others were ground and sieved through a 100 μ m mesh for analysis. Water content of the sediments was determined by drying at 105°C until stable weight. In present study, the lake area was divided into two regions: northwest (NW) ($n = 12$) and southeast (SE) ($n = 13$).

Additionally, six sampling sites (S1-S6) in different positions of Swan Lake were selected to investigate P adsorption characteristics of surface sediments (Fig. 1). Site 1 is located in the northwestern lake, around the entrance of some small rivers; site 2 was in the north area, near a shrimp pond; site 3 was adjacent to the western tip, where macroalgal blooms break out in recent few years; site 4 was in the central lake; site 5 located in the tidal delta, nearby the sand dam; site 6 was in southern lake, around Tangjia village. The overlying water was taken at four different seasons with a water sampler, and three samples were collected at each site. The basic properties of the sediments and overlying water are shown in Tab. 1. Dried and sieved surface sediments (passed through a 100 μ m mesh) were used in the adsorption experiments.

2.3 Sediment characterization

Total concentrations of Fe, Mn, Al, and Ca were measured using ICP-AES (Optima 7000 DV, Perkin-Elmer) followed by the $HF-HClO_4$ -

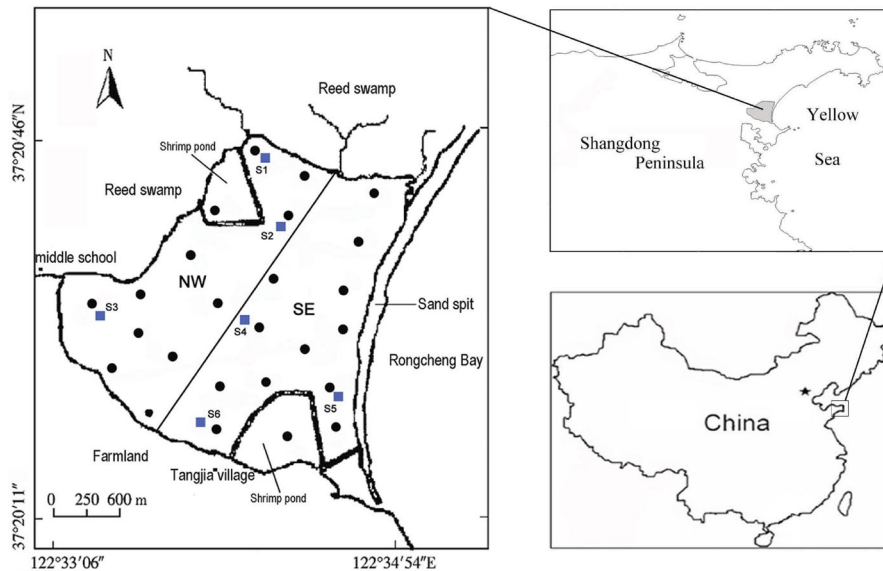


Figure 1. Map of Swan Lake in China and locations of the sampling sites.

HNO₄ digestion. Oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}) were analyzed after the extraction by 0.2 M ammonium oxalate (pH 3) under dark conditions [27]. OM was measured following digestion with K₂Cr₂O₇ [28]. Total nitrogen (TN) was determined using Se-CuSO₄-HNO₃ digestion and distillation method. The grain size, including clay (<2 μm), silt (2–50 μm), and sand (50–2000 μm), was analyzed by the Attenburg cylinders method based on the Stoke's law. The pH value was measured in deionized water by a S20P-K pH meter (Mettler, Switzerland).

The reference materials (GSS3 and GBW07043) were also analyzed to check the analytical quality.

2.4 P fractions and bioavailable P

TP and P fraction in sediments were carried out using the SMT protocol. Five P forms were determined, including TP, Fe/Al-P, Ca-P, IP, and OP [22, 25, 26]. Phosphate concentration in the filtrate was measured by molybdenum blue method.

BAP in sediments includes four fractions in this study. AAP, RDP, WSP, and Olsen P were extracted at 25°C with 0.1 M NaOH (4 h), 0.01 M CaCl₂ (1 h), deionized water (2 h), and 0.5 M NaHCO₃ (0.5 h), respectively [10, 27]. Phosphate concentration in the filtrate was analyzed by molybdenum blue method.

2.5 P sorption kinetic experiments

Sediment samples of 0.50 g were given into 100 mL centrifuge tubes, and then 50 mL phosphate solution (KH₂PO₄, containing 30 mg P/L, in 0.01 M CaCl₂ matrix) were added. The centrifuge tubes were shaken at 250 rpm (at 25°C) for different time intervals, varying within 48 h (0, 5, 15, 30, 45 min, and 1, 2, 3, 5, 7, 10, 12, 15, 18, 24, and 48 h). Phosphate concentration in the filtrate was determined as described above. P adsorption amount by the sediments was calculated according to the difference between the initial and the measured P amount.

Table 1. Physico-chemical parameters of the sediments and the overlying water

Parameters	S1	S2	S3	S4	S5	S6
Lake water						
pH	8.15	8.26	8.48	8.19	8.13	8.35
Salinity	34.1	32.2	31.9	30.1	30.0	29.8
DO (mg/L)	9.33	9.87	8.75	10.13	10.29	10.13
Water depth (m)	1.8	1.4	1.2	1.5	0.5	0.7
SRP (mg/L)	0.018	0.011	0.013	0.010	0.010	0.013
TP (mg/L)	0.024	0.022	0.046	0.013	0.026	0.022
Surface sediments						
pH	3.50	6.36	6.94	5.69	8.67	5.44
TN (g/kg)	1.7	1.0	1.2	1.5	0.5	0.3
TP (g/kg)	0.5	0.4	0.5	0.6	0.2	0.3
OM (g/kg)	57.2	19.7	26.2	37.6	7.4	7.6
Clay (%)	45.3	16.6	14.9	37.4	8.3	5.8
Sand (%)	17.4	55.1	57.4	27.7	88.2	87.8
Fe _{ox} (g/kg)	0.9	0.5	0.5	0.5	0.3	0.2
Al _{ox} (g/kg)	2.9	3.0	3.1	3.3	1.1	1.2

2.6 P sorption isotherm experiments

This experiment included two series of initial concentrations of P. The low concentration range (likely to be encountered in natural systems) of 0, 0.02, 0.05, 0.1, 0.15, 0.2, 0.5 mg P/L and the high range of 0, 0.5, 1, 2, 3, 5, 10, 15, 30, and 50 mg P/L were used, respectively. The centrifuge tubes were filled with 0.50 g of sediment samples and 50 mL of solution with various P concentrations, and then shaken at 25°C for 24 h. The experimental conditions and the calculation of P adsorption amount were the same as described in kinetics experiment.

Different models were used to describe the relationship between P concentration at equilibrium and P adsorption amount, respectively. At low initial P concentrations, the sorption isotherms were fitted by the linear Eq. (1); while at high concentrations, the sorption isotherms were fitted using Langmuir Eq. (2) and Freundlich Eq. (3) models, respectively.

$$Q = mC - NAP \quad (1)$$

$$Q = \frac{Q_m k_1 C}{1 + k_1 C} \quad (2)$$

$$Q = k_F C^n \quad (3)$$

where C is P concentration after 24 h equilibration (mg/L), Q is P sorption amount (mg/kg), m is the linear adsorption slope, NAP is

native adsorbed P by the sediments (mg/kg), Q_m is maximum sorption amount (mg/kg), k_1 is a constant related to the binding energy (L/mg), k_F and n are empirical constants.

2.7 Eutrophication risk index

PSI was derived from a single-point P sorption isotherm. 20 mL phosphate solution (75 mg P/L) were added to 1 g of sediment samples, and then shaken at 25°C for 18 h. PSI ((mg/100 g)/(μmol/L)) was calculated by the quotient $X/\log C$, where X is P sorption amount (mg/100 g), C is P concentrations at equilibrium (μmol/L).

STP (sediment test P) was extracted from 2.5 g of sediment sample with 50 mL 0.5 M NaHCO₃ (pH 8.5) (25°C, 24 h). DPS was calculated with the following equation:

$$DPS (\%) = \frac{STP}{Q_m + STP} \times 100\% \quad (4)$$

where Q_m (mg/kg) is estimated by Langmuir equation. The eutrophication risk index (ERI) induced by P was developed as the percentage of DPS divided by PSI. The data were presented as the means of three replicates.

2.8 Statistical analysis

The concentration differences in TP and various P forms in sediments between the NW region and SE region were tested by the independent-sample T test (SPSS 17.0). The correlation analyses were performed by

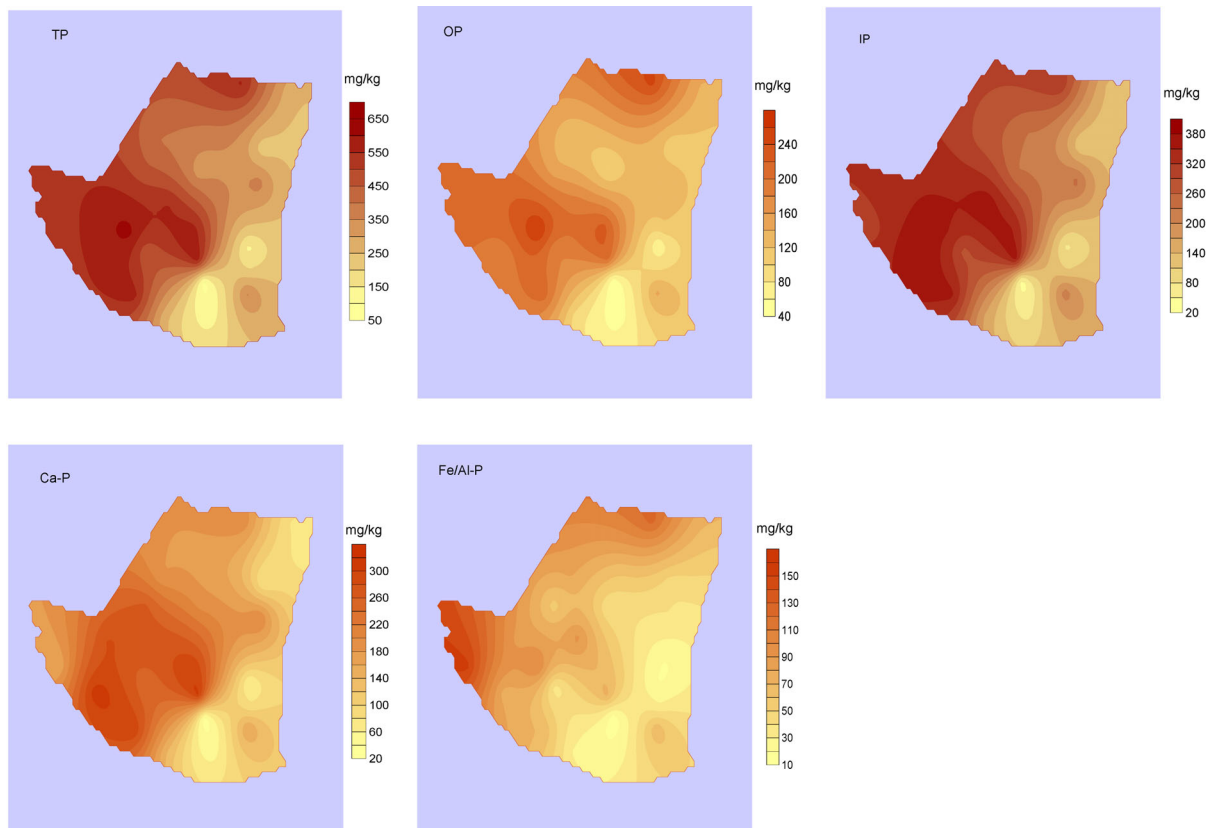


Figure 2. Spatial distribution of TP and various P forms (OP, IP, Ca-P and Fe/Al-P) in surface sediments.

Table 2. Descriptive analysis on TP and various P forms in surface sediments from Swan Lake ($n = 25$)

	TP	IP	OP	Fe/Al-P	Ca-P	AAP	Olsen-P	WSP	RDP
Min (mg/kg)	79	33	46	13	26	9	10	0.7	0.06
Max (mg/kg)	616	377	263	153	310	120	38	6	2
Mean (mg/kg)	396	244	153	64	185	41	21	3	0.7
CV (%)	41.64	44.92	39.79	55.31	47.59	65.43	33.17	48.52	87.47

Pearson Correlation. The differences in PSI, DPS, and ERI of the sediments among six sites were tested by one-way analysis of variance (ANOVA) followed by Duncan's test post hoc analysis when appropriate.

3 Results

3.1 Spatial distribution of TP and various P forms

There were great spatial differences in TP concentrations in sediments from Swan Lake (Fig. 2, Tab. 2). Highest concentrations were observed at the NW corner and central area, followed by those sites at the western tip, and the lowest at the SE corner. Throughout the lake, TP concentrations were significantly higher in NW region than those in SE region ($t = 3.45, p < 0.01$), whose mean values were 493 and 307 mg/kg, respectively (Fig. 3).

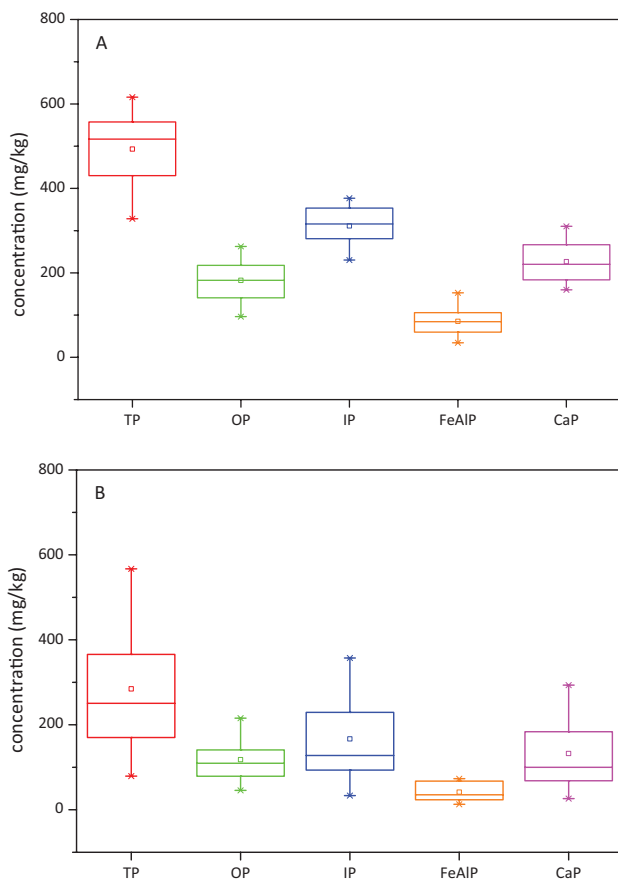


Figure 3. The concentrations of TP and various P forms in surface sediments from the northwestern (A) and southeastern (B) lake.

Highest OP concentrations were observed at the NW corner and the western tip, followed by those sites in the center (Fig. 2). While for the Ca-P, higher concentrations were observed in the central area, the lowest at the SE corner. Compared with other P forms, Fe/Al-P had a greater spatial variation (Tab. 2), with highest concentrations occurring at the western tip. Various P forms showed significant concentration differences between the NW region and SE region (Fig. 3). At most sites, the rank order of P fractions was Ca-P > OP > Fe/Al-P, while in the northern region and western tip, OP concentrations were higher than Ca-P.

TP showed significant correlations with various P forms, and the highest correlation was found with IP (Tab. 3), indicating the great contribution of IP to TP in surface sediments from Swan Lake. Ca-P was significantly correlated with IP ($p < 0.01$). However, Fe/Al-P had relatively weak correlation with other P fractions, especially with Ca-P.

3.2 Spatial distribution of bioavailable P

In Swan Lake, the concentrations of four BAP forms all varied greatly among different lake regions (Fig. 4). Compared with other fractions, AAP showed greater spatial difference, whose concentrations in NW region were significantly higher than those in SE region ($t = 3.79, p < 0.01$). While for WSP and RDP, the high concentrations were both observed at the SE corner. Different BAP showed the mean concentrations as follows: AAP > Olsen-P > WSP > RDP.

AAP had significant correlations with TP, OP, IP, and Fe/Al-P, but not with Ca-P (Tab. 3). Olsen-P was well correlated with TP, SMT fractions and other BAP ($p < 0.01$). Significant relationship was observed between RDP and WSP ($p < 0.01$), but the two forms had no significant correlation with TP and SMT fractions. Compared with other P forms, Fe/Al-P had stronger positive correlations with BAP forms.

3.3 The P sorption kinetics on sediments

The similar adsorption processes were observed at the six studied sites (Fig. 5). P adsorption amount increased rapidly within the initial 10 h; after that, it changed slightly with time, and reached equilibrium approximately at 24 h. For the six sites, P adsorption amount within 2 h accounted for 50–67% of the total amount at equilibrium, while within 10 h that accounted for approximately 80% of the total. Adsorption rates at different sites all declined gradually with time, the maximum occurring at the initial 0–0.25 h (Tab. 4). This indicates that a fast adsorption process mainly occurred within 2 h, and after 10 h P sorption reached to a slow reaction stage.

3.4 The P adsorption isotherms on sediments

At lower initial P condition (< 0.02 mg/L), sorption amount was very low, and negative adsorption occurred at S1 and S5 (Fig. 6A). While at high concentrations, the sorption amount increased rapidly when P

Table 3. Correlation coefficients between TP, P fractions and bioavailable P in sediments ($n=25$)

	TP	IP	OP	Fe/Al-P	Ca-P	AAP	Olsen-P	WSP	RDP
TP	1.00								
IP	0.98**	1.00							
OP	0.95**	0.87**	1.00						
Fe/Al-P	0.76**	0.70**	0.79**	1.00					
Ca-P	0.92**	0.95**	0.77**	0.46*	1.00				
AAP	0.55**	0.50*	0.59**	0.87**	0.25	1.00			
Olsen-P	0.61**	0.59**	0.60**	0.76**	0.42*	0.52**	1.00		
WSP	-0.15	-0.20	-0.05	0.22	-0.33	0.16	0.57**	1.00	
RDP	0.06	0.03	0.10	0.27	-0.08	0.31	0.60**	0.80**	1.00

* $p < 0.05$.
** $p < 0.01$.

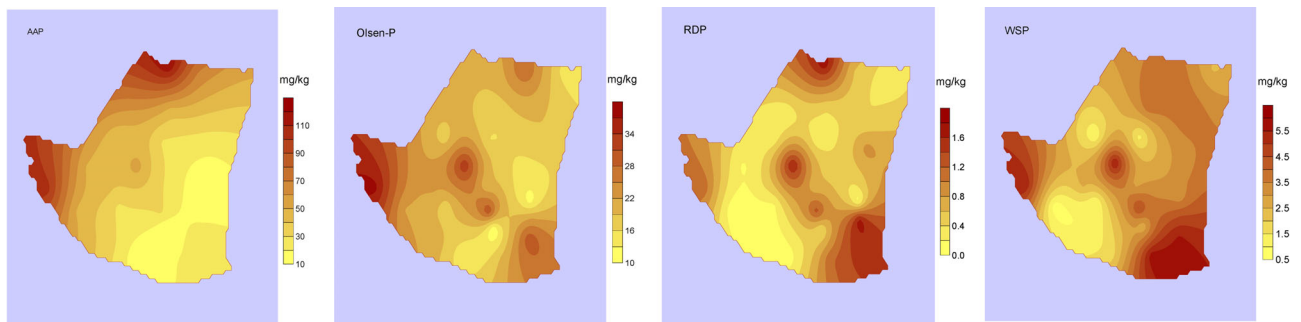


Figure 4. Spatial distribution of various bioavailable P forms (AAP, Olsen-P, RDP, and WSP) in surface sediments.

concentration at equilibrium was <10 mg/L, and then increased slowly until to a stable sorption state (Fig. 6B). Similar trends were observed at the studied sites except for S1. However, the sorption ratio decreased as the increase of added P concentration. When 0.05 mg/L of P solutions were added to sediment samples, $>80\%$ of the added P was adsorbed (except at S5), while at the initial P concentration of 50 mg/L the mean sorption ratio decreased to 9%. The results suggest that long-term external P inputs into the wetland may result in the decrease of P retention capacity of the sediments.

The sorption isotherms at low P concentrations were well fitted by the linear equation (Tab. 5). At the NW corner (S1) and SE corner (S5),

the EPC_0 of the sediments were higher than soluble reactive P (SRP) concentration in overlying water (Tab. 1), indicating sediment P in these regions had higher release risk [17, 18]. At high P concentrations, R^2 value for the Langmuir equation was higher, indicating that Langmuir equation can effectively describe P sorption isotherms in Swan Lake. The Q_m of the sediments estimated by Langmuir equation followed the order: $S1 > S3 > S2, S4 > S5 > S6$. This indicates that the sediments along the NW shore (S1 and S3) had relatively high sorption capacity for P, while at SE corner (S5 and S6) the sediments had low buffering ability.

3.5 The eutrophication risk of lake sediments

In Swan Lake, PSI of the sediments was significantly high at S1, relatively low at S5 and S6 (Tab. 6). PSI showed significant correlations with OM, Al_{ox} and clay concentration of the sediments, respectively ($p < 0.01$). In addition, PSI was well related with the Q_m , and the linear equation was as follows:

$$Q_m = 38.26 \text{ PSI} + 15.40 \quad (p < 0.01) \quad (5)$$

suggesting that PSI can effectively reflect P adsorption ability of the sediments from Swan Lake.

Sediments with high DPS values were suggested to have a high susceptibility to P release [20]. The DPS was significantly low at S1, while the highest at S5 with low Fe_{ox} and Al_{ox} concentration (Tab. 6). ERI varied greatly among different sites, which followed the order: $S5 > S6 > S3 > S2 > S4 > S1$. ERI value at S5 was 20 times higher compared to S1. In general, the sediments in northern lake had higher P sorption capacity, while in southern lake that had higher release risk.

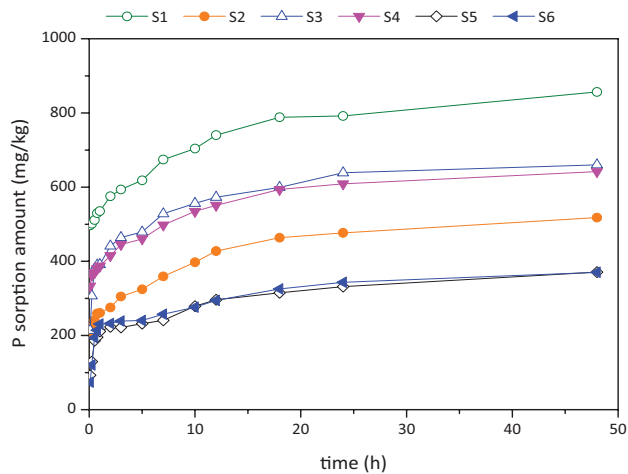


Figure 5. Adsorption kinetic process of P on the sediments from six sampling sites.

Table 4. Adsorption rates of P on sediments at different sampling intervals (mg/kg/h)

Site	Sampling intervals (h)							
	0–0.25	0.25–0.5	0.5–1	1–2	2–5	5–10	10–24	24–48
S1	2004.2	40.4	48.4	40.0	14.3	17.1	6.3	2.7
S2	889.2	75.1	38.9	14.8	16.3	14.6	5.7	1.7
S3	1227.8	292.2	22.4	50.0	12.6	15.5	5.9	0.9
S4	1450.9	25.5	35.9	28.1	15.1	14.8	5.3	1.4
S5	517.8	225.1	50.6	12.3	2.9	9.4	3.8	1.6
S6	481.4	295.6	73.2	1.7	2.6	7.2	4.8	1.1

4 Discussions

4.1 Quantity and distribution of TP and P fractions in sediments from Swan Lake

In Swan Lake, TP concentrations in surface sediments were not high, ranging at 79–616 mg/kg, which were similar to the margin sediments in Yellow Sea [29], but lower than other estuarine and coastal sediments of China, such as the wetland of Yellow River Delta [17, 30], and the estuarine sediments of Daliao River [31]. The

spatial distribution of sediment P is mainly related to anthropogenic inputs, sediment texture, hydrodynamic conditions, and the distribution of aquatic organisms [15, 32–34]. In Swan Lake, highest TP concentrations were observed at the NW corner and central area, the lowest at SE corner. Along the NW shore, some rivers are distributed, through which large amounts of domestic sewage from Chengshan Town comes into the lake, therefore long-time external inputs resulted in high P accumulation in the nearby sediments. While in the central area, there were abundant submerged macrophytes, and particle size was finer (clay range: 20–37%). The lowest concentrations at SE corner, close to the inlet where the lagoon was connected to Yellow Sea, may be attributed to coarser grain size in sediments (sand range: 58–93%).

P fractions in sediments depend on the origin of sediments, biological activity, geochemical compositions, and so on [22, 32, 35]. In Swan Lake, IP concentration was higher than that of OP, and Ca-P was the important fractions in the IP. This was in disagreement with the results in Lake Dianchi and Lake Taihu in Southern China [12, 35], where Fe/Al-P was the dominant P fractions. The high concentration of Ca-P in the studied region might be interpreted in following reasons: in Swan Lake catchments, the soil type was coastal saline soil, whose Ca-P concentration was higher than Fe/Al-P. Due to the connection with the Yellow Sea, Ca-P is likely from marine origin [21, 31]. In addition, large amounts of shellfish live in southern lake, where apatite can be formed at the surface of shell fragments (Tab. 7) [23, 34]. Fe/Al-P had a large spatial variation, with higher concentrations at NW corner and the western tip where external pollution from the discharge of wastewater is serious. Some researchers reported that Fe/Al-P concentration in sediments was closely related to the pollution degree [12, 27], which was also confirmed in this study.

In Swan Lake, TP and P fractions showed significant positive correlations with clay and silt fractions, respectively (Tab. 7), suggesting that grain size was an important factor influencing the spatial distribution [21, 34]. In addition, TP was significantly correlated to total Fe and Mn ($p < 0.01$), and Fe/Al-P was positively correlated to Fe, Mn ($p < 0.01$), and Al ($p < 0.05$). However, Ca had no significant correlation with any of P fractions, which also indicates that Ca-P was mainly likely from authigenic marine origin [23, 31]. As a whole, sediment grain size and external inputs were the main factors affecting the distribution of P in surface sediments from Swan Lake.

4.2 P adsorption characteristics of the sediments from Swan Lake

P sorption capacity of sediments has close relationship with sediment properties, which varies greatly in different types of coastal sediments, such as the sandy, clay and organic rich sediments [13, 16, 36]. In Swan

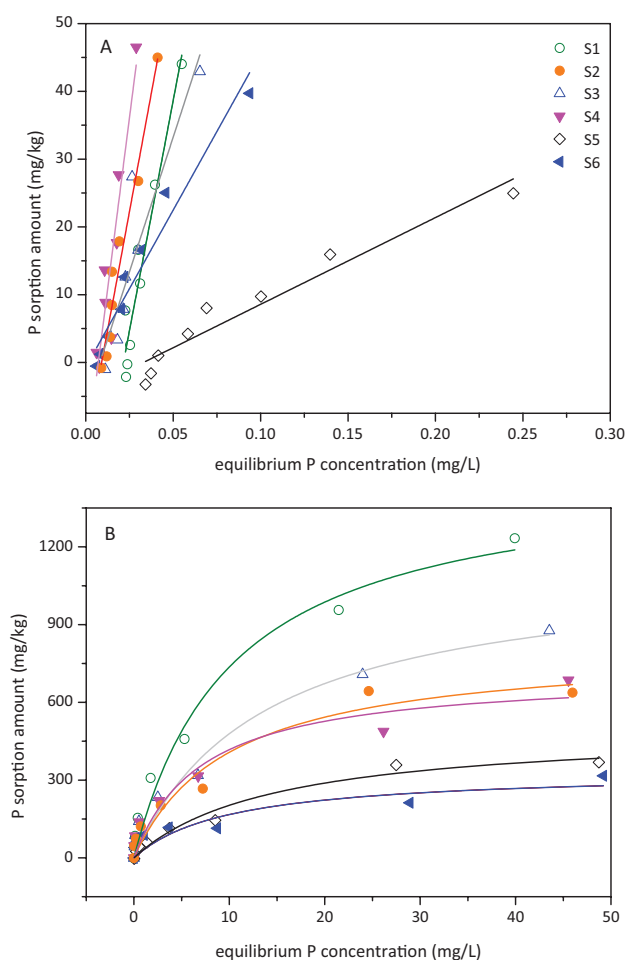


Figure 6. The measured and simulated sorption isotherms of P on different sediments. (A) the sorption isotherms simulated by linear equation at low P concentration; (B) the sorption isotherms simulated by Langmuir equation at high P concentration.

Table 5. Fitting results for the adsorption isotherm data and the relevant parameters

Site	Linear equation			Langmuir equation			Freundlich equation	
	EPC ₀ (mg/L)	NAP (mg/kg)	R ²	Q _m (mg/kg)	k _L (L/mg)	R ²	k _F (L/kg)	R ²
S1	0.022	29.2	0.94**	1111	0.90	0.84**	141.16	0.78**
S2	0.009	12.7	0.96**	667	0.47	0.91**	96.34	0.83**
S3	0.008	6.5	0.86**	833	0.41	0.87**	104.71	0.86**
S4	0.007	14.5	0.87**	6250	0.64	0.91**	111.35	0.78**
S5	0.033	4.2	0.94**	400	0.18	0.91**	35.22	0.90**
S6	0.002	0.7	0.95**	294	0.29	0.89**	55.99	0.79**

**p* < 0.05.
***p* < 0.01.

Table 6. Values of PSI, DPS and ERI at the studied sediments

Site	STP (mg/kg)	PSI (mg/100 g)/(μmol/L)	DPS (%)	ERI (%)
S1	9.5 ^d	28.9 ^a	0.85 ^e	2.93 ^e
S2	15.2 ^c	15.1 ^c	2.23 ^c	14.76 ^c
S3	26.7 ^a	18.9 ^b	3.11 ^b	16.41 ^c
S4	11.5 ^d	18.8 ^b	1.80 ^d	9.55 ^d
S5	21.0 ^b	11.1 ^d	4.99 ^a	44.96 ^a
S6	7.6 ^e	7.4 ^e	2.51 ^c	33.76 ^b

Different letters represent the significance at *p* < 0.05.

Lake, the Q_m of the sediments ranged at 294–1111 mg/kg, which was similar to the Yellow River Delta [17], much higher than the Yangtze Estuary and Hangzhou Bay in China [14], and the estuary in the State of Florida in USA [16], but significantly lower than two coastal areas (Minorca and Majorca) in the Balearic Islands [36].

In different aquatic systems, the sediments have different P sorption characteristics due to the difference in sediment properties [13, 17, 36, 37]. In Swan Lake, P adsorption capacity varied greatly among different lake regions, and the high sorption capacity was observed in the northern and central sediments. Correlation analysis showed that the Q_m had close relationship with Al_{ox}, OM, TN, silt, OP, and Fe/Al-P (in the order of correlation coefficient) (Tab. 8). k_L, a constant reflecting the binding energy, was significantly correlated with OM, clay, TN, silt, and Al_{ox}. In addition, the average adsorption rate within 48 h also showed strong correlation with OM and Al_{ox}. This indicates that Al_{ox}, OM and fine particles were the important factors influencing P adsorption in coastal sediments from Swan Lake. For the whole lake, OM concentrations were much higher in the northern and central lake than those in southern lake. On the other hand, fine fraction concentrations were relatively high in northern

and central sediments, while in southern lake sand was the dominant fraction. All that would lead to higher P adsorption capacity for the sediments in the northern and central lake.

4.3 The potential release risk of sediment P in Swan Lake

P fractions in sediments can be used to evaluate P bioavailability and release risk for the overlying water at a certain degree [9, 10, 12]. In Swan Lake, different bioavailable P followed the order: AAP > Olsen-P > WSP > RDP, which was in agreement with the results in other water bodies in China [10, 27]. Higher concentrations of WSP, RDP, and Olsen-P were found at the western tip, the SE corner and central area, suggesting that the sediments at these areas had higher P availability for algal growth at present. OP and Fe/Al-P were also usually considered to be mobile and potential bioavailable [9, 12, 23]. In the present study, Fe/Al-P, OP, and AAP showed significant correlations with each other, thus similar trends were observed according to the BAP and SMT fractions. As a whole, the sediments at

Table 7. Correlation coefficients between P fractions and sediment properties

	TN	OM	Fe	Al	Ca	Mn	Clay	Silt	Sand
TP	0.82**	0.71**	0.85**	0.59**	0.21	0.87**	0.84**	0.91**	-0.91**
IP	0.78**	0.66**	0.82**	0.59**	0.27	0.86**	0.79**	0.92**	-0.90**
OP	0.81**	0.73**	0.82**	0.53*	0.07	0.81**	0.85**	0.79**	-0.85**
Fe/Al-P	0.76**	0.66**	0.78**	0.53*	0.06	0.71**	0.62**	0.67**	-0.67**
Ca-P	0.63**	0.53*	0.68**	0.49*	0.31	0.77**	0.72**	0.85**	-0.82**

**p* < 0.05.
***p* < 0.01.

Table 8. Correlation coefficients between P adsorption parameters and sediment properties

	EPC ₀	NAP	m	k _L	Q _m	Adsorption rate
TP	-0.35	0.62	0.80	0.78	0.75	0.87*
OP	-0.18	0.68	0.75	0.79	0.83*	0.92*
Ca-P	-0.50	0.46	0.93**	0.66	0.33	0.55
Fe/Al-P	-0.13	0.41	0.28	0.48	0.81*	0.77
TN	0.01	0.87*	0.80	0.91*	0.88*	0.95**
OM	0.06	0.94**	0.70	0.98**	0.89*	0.97**
Clay	0.09	0.93**	0.79	0.96**	0.76	0.88*
Silt	-0.23	0.81	0.88*	0.88*	0.84*	0.90*
Sand	0.07	-0.91*	-0.86*	-0.96**	-0.83*	-0.93**
Al _{ox}	0.18	0.96**	0.61	0.93**	0.97**	0.96**
Fe _{ox}	-0.34	0.64	0.87*	0.74	0.75	0.79

p* < 0.05.*p* < 0.01.

the NW corner and western tip of Swan Lake had high potential risk of P release.

5 Concluding remarks

Similar to other lagoons, Ca-P, mainly likely from marine origin, was the important fractions in the sediments from Swan Lake. Fe/Al-P was closely related to the external pollution from inflow rivers, and showed significant correlation with bioavailable P (AAP and Olsen-P). This indicates that Fe/Al-P may be used as a reliable indicator for reflecting external P load as well as predicting bioavailable P level in coastal sediments. In Swan Lake Wetland, Al_{ox} was dominant factor influencing P retention capacity. These findings would be helpful to further understand P cycle at the sediment-water interface in the lagoon.

Compared with other coastal wetlands, TP level in surface sediments were not high in Swan Lake Wetland. However, high potentially mobile P pool was observed at the NW corner and western tip of the lake as a consequence of external nutrients inputs and high sorption capacity by the sediments. At the western tip of Swan Lake, sediment P had high bioavailability and high release risk, moreover large scale of *C. linum* are blooming at present. Sediment P in this area may be easily released into the water column as the environmental condition changes resulting from the growth or decomposition of massive macroalgae, which in turn contributes to the formation of algal bloom. Therefore, sediment internal loading must be taken into consideration in water eutrophication control and future restoration projects in coastal wetlands.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (41273130; 40801084; 41171216), the Promotive Research Fund for Young and Middle-aged Scientists of Shandong Province, China (2007BS08017), the Major National Basic Research Program of China (2013CB430403), One Hundred-Talent Plan of Chinese Academy of Sciences (CAS), the CAS/SAFEA International Partnership Program for Creative Research Teams, the Science & Technology Development Plan of Shandong Province (2010GSF10208), the Science & Technology Development Plan of Yantai City (2011016; 20102450), Yantai Double-hundred High-end Talent Plan (No. XY-003-02) and 135 Development Plan of YIC-CAS.

The authors have declared no conflict of interest.

References

- [1] H. B. Shao, B. S. Cui, J. H. Bai, Outlook: Wetland Ecology in China, *Clean – Soil Air Water* **2012**, *40*, 1011–1014.
- [2] H. B. Shao, B. S. Cui, J. H. Bai, Editorial: Wetland Ecology in China, *Clean – Soil Air Water* **2012**, *40*, 1009–1010.
- [3] L. W. Zhang, H. B. Shao, Direct Plant-Plant Facilitation in Coastal Wetlands: A Review, *Estuarine Coastal Shelf Sci.* **2013**, *119*, 1–6.
- [4] M. Søndergaard, J. P. Jensen, E. Jeppesen, Role of Sediment and Internal Loading of Phosphorus in Shallow Lakes, *Hydrobiologia* **2003**, *506–509*, 135–145.
- [5] P. Kelderman, F. Kansime, M. A. Tola, A. van Dam, The Role of Sediments for Phosphorus Retention in the Kirinya Wetland (Uganda), *Wetland Ecol. Manage.* **2007**, *15*, 481–488.
- [6] J. H. Bai, X. F. Ye, Y. Zhi, H. F. Gao, L. B. Huang, R. Xiao, H. B. Shao, Nitrate-Nitrogen Transport in Horizontal Soil Columns of the Yellow River Delta Wetland, China, *Clean – Soil Air Water* **2012**, *40*, 1106–1110.
- [7] M. Hupfer, J. Lewandowski, Oxygen Controls the Phosphorus Release from Lake Sediments – a Long-Lasting Paradigm in Limnology, *Int. Rev. Hydrobiol.* **2008**, *93*, 415–432.
- [8] K. R. Reddy, R. H. Kadlec, E. Flaig, P. M. Gale, Phosphorus Retention in Streams and Wetlands: A Review, *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 83–146.
- [9] E. Rydin, Potentially Mobile Phosphorus in Lake Erken Sediment, *Water Res.* **2000**, *34*, 2037–2042.
- [10] Q. X. Zhou, C. E. Gibson, Y. M. Zhu, Evaluation of Phosphorus Bioavailability in Sediments of Three Contrasting Lakes in China and the UK, *Chemosphere* **2001**, *42*, 221–225.
- [11] T. Mayer, F. Rosa, R. Mayer, M. Charlton, Relationship between the Sediment Geochemistry and Phosphorus Fluxes in a Great Lake Coastal Marsh, Cootes Paradise, ON, Canada, *Water Air Soil Pollut.* **2006**, *6*, 131–139.
- [12] M. Y. Zhu, G. W. Zhu, W. Li, Y. L. Zhang, L. L. Zhao, Z. Gu, Estimation of the Algal-available Phosphorus Pool in Sediments of a Large, Shallow Eutrophic Lake (Taihu, China) Using Profiled SMT Fractional Analysis, *Environ. Pollut.* **2013**, *173*, 216–223.
- [13] G. L. Bruland, G. DeMent, Phosphorus Sorption Dynamics of Hawaii's Coastal Wetlands, *Estuaries Coasts* **2009**, *32*, 844–854.
- [14] M. Li, M. J. Whelan, G. Wang, S. M. White, Phosphorus Sorption and Buffering Mechanisms in Suspended Sediments from the Yangtze Estuary and Hangzhou Bay, China, *Biogeosciences* **2012**, *9*, 17519–17538.
- [15] J. R. Tian, P. J. Zhou, Phosphorus Fractions and Adsorption Characteristics of Floodplain Sediments in the Lower Reaches of the Hanjiang River, China, *Environ. Monit. Assess.* **2008**, *137*, 233–241.
- [16] Q. R. Wang, Y. C. Li, Phosphorus Adsorption and Desorption Behavior on Sediments of Different Origins, *J. Soil Sediment.* **2010**, *10*, 1159–1173.

- [17] J. N. Sun, G. Xu, H. B. Shao, S. H. Xu, Potential Retention and Release Capacity of Phosphorus in the Newly Formed Wetland Soils from the Yellow River Delta, China, *Clean – Soil Air Water* **2012**, *40*, 1131–1136.
- [18] W. C. An, X. M. Li, Phosphate Adsorption Characteristics at the Sediment–Water Interface and Phosphorus Fractions in Nansi Lake, China, and Its Main Inflow Rivers, *Environ. Monit. Assess.* **2009**, *148*, 173–184.
- [19] M. L. Machesky, T. R. Holm, J. A. Slowikowski, Phosphorus Speciation in Stream Bed Sediments from an Agricultural Watershed: Solid-phase Associations and Sorption Behavior, *Aquat. Geochem.* **2010**, *16*, 639–662.
- [20] R. Kröger, M. T. Moore, Phosphorus Dynamics within Agricultural Drainage Ditches in the Lower Mississippi Alluvial Valley, *Ecol. Eng.* **2011**, *37*, 1905–1909.
- [21] F. Andrieux-Loyer, A. Aminot, Phosphorus Forms Related to Sediment Grain Size and Geochemical Characteristics in French Coastal Areas, *Estuarine Coastal Shelf Sci.* **2001**, *52*, 617–627.
- [22] L. M. Dong, Z. F. Yang, X. H. Liu, Phosphorus Fractions, Sorption Characteristics, and Its Release in the Sediments of Baiyangdian Lake, China, *Environ. Monit. Assess.* **2011**, *179*, 335–345.
- [23] F. Andrieux-Loyer, X. Philippon, G. Bally, R. Kérouel, A. Youenou, J. Le Grand, Phosphorus Dynamics and Bioavailability in Sediments of the Penzé Estuary (NW France): In Relation to Annual P-Fluxes and Occurrences of *Alexandrium minutum*, *Biogeochemistry* **2008**, *88*, 213–231.
- [24] E. Rydin, J. M. Malmaeus, O. M. Karlsson, P. Jonsson, Phosphorus Release from Coastal Baltic Sea Sediments as Estimated from Sediment Profiles, *Estuarine Coastal Shelf Sci.* **2011**, *92*, 111–117.
- [25] V. Ruban, S. Brigault, D. Demare, An Investigation of the Origin and Mobility of Phosphorus in Freshwater Sediments from Bort-Les-Orgues Reservoir, France, *J. Environ. Monit.* **1999**, *1*, 403–407.
- [26] P. Pardo, J. F. López-Sánchez, G. Rauret, Relationships between Phosphorus Fractionation and Major Components in Sediments Using the SMT Harmonised Extraction Procedure, *Anal. Bioanal. Chem.* **2003**, *376*, 248–254.
- [27] S. R. Wang, X. C. Jin, Q. Y. Bu, H. Q. Liao, F. C. Wu, Evaluation of Phosphorus Bioavailability in Sediments of the Shallow Lakes in the Middle and Lower Reaches of the Yangtze River Region, China, *Environ. Earth Sci.* **2010**, *60*, 1491–1498.
- [28] R. K. Lu, *Soil and Agrochemical Chemistry Analytical Methods*, China Agriculture Science and Technology Press, Beijing **1999** (in Chinese).
- [29] S. M. Liu, J. Zhang, D. J. Li, Phosphorus Cycling in Sediments of the Bohai and Yellow Seas, *Estuarine Coastal Shelf Sci.* **2004**, *59*, 209–218.
- [30] P. P. Liu, J. H. Bai, Q. Y. Ding, H. B. Shao, H. F. Gao, R. Xiao, Effects of Water Level and Salinity on TN and TP Contents in Marsh Soils of the Yellow River Delta, China, *Clean – Soil Air Water* **2012**, *40*, 1118–1124.
- [31] P. Wang, M. C. He, C. Y. Lin, B. Men, R. M. Liu, X. C. Quan, Z. F. Yang, Phosphorus Distribution in the Estuarine Sediments of the Daliao River, China, *Estuarine Coastal Shelf Sci.* **2009**, *84*, 246–252.
- [32] S. Matijević, Z. Kljaković-Gašpić, D. Bogner, A. Gugić, I. Martinović, Vertical Distribution of Phosphorus Species and Iron in Sediment at Open Sea Stations in the Middle Adriatic Region, *Acta Adriat.* **2008**, *49*, 165–184.
- [33] J. H. Bai, J. J. Wang, D. H. Yan, H. F. Gao, R. Xiao, H. B. Shao, Q. Y. Ding, Spatial and Temporal Distributions of Soil Organic Carbon and Total Nitrogen in Two Marsh Wetlands with Different Flooding Frequencies of the Yellow River Delta, China, *Clean – Soil Air Water* **2012**, *40*, 1137–1144.
- [34] K. R. Renjith, N. Chandramohanakumar, M. M. Joseph, Fractionation and Bioavailability of Phosphorus in a Tropical Estuary, Southwest India, *Environ. Monit. Assess.* **2011**, *174*, 299–312.
- [35] L. Gao, J. M. Zhou, H. Yang, J. Chen, Phosphorus Fractions in Sediment Profiles and Their Potential Contribution to Eutrophication in Dianchi Lake, *Environ. Geol.* **2005**, *48*, 835–844.
- [36] P. Lopez, X. Luch, M. Vidal, Adsorption of Phosphorus on Sediments of the Balearic (Spain) Related to Their Composition, *Estuarine Coastal Shelf Sci.* **1996**, *42*, 185–195.
- [37] K. Börling, E. Otabbong, Phosphorus Sorption in Relation to Soil Properties in Some Cultivated Swedish Soils, *Nutr. Cycl. Agroecosyst.* **2001**, *59*, 39–46.