

# Phosphorus adsorption and sedimentation by suspended sediments from Zhushan Bay, Taihu Lake

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**Abstract** The process of phosphorus (P) transformation in particulate matter during sediment resuspension and sedimentation was studied. The P-binding forms in resuspended particles (RP) and settled particles (SP) were analyzed by sequential fractionation (modified Psenner method) and an extended extraction with ammonium oxalate. Water quality data and P fractions were used to estimate P release and uptake by the resuspended and settling sediment particles. Results of 8-h resuspension experiments showed increases of dissolved oxygen, pH, total phosphorus, and particulate phosphorus in overlying water, but no change in soluble reactive phosphorus (SRP). P fractions extracted with common sequential fractionation showed that the increase of total P in RP was mainly due to increases of redox-sensitive bound P BD (BD-SRP) and P bound to Al and Fe oxides (NaOH-SRP) (36–52 % and 30–36 % of total increased P, respectively). Comparisons between two sequential fractionations indicated that inorganic P extracted with ammonium oxalate consisted of P bound to amorphous Fe/Al oxy-hydroxides and partially of carbonate-bound P (HCl-SRP) and that increased P in RP was mainly caused by increases in P bound to amorphous oxides. It is concluded that the formation of amorphous oxides and subsequent adsorption of P

lead to the increase of P in RP. However, P adsorbed by amorphous oxy-hydroxides in RP is unstable and may be released under sedimentation conditions. Meanwhile, increases in HCl-SRP, refractory P, and crystalline Fe-P were found in SP compared with RP. NaOH-SRP in SP increased gradually under sedimentation conditions. It is suggested that, during sedimentation, mobile P can be transformed to non-mobile P forms that provide long-term P retention. The findings contribute to the understanding of P cycling in particulate matter during sediment resuspension and sedimentation.

**Keywords** Sediment resuspension · Adsorption · Amorphous oxides · Sedimentation · Retention · Phosphorus

## Introduction

The release of internal phosphorus from sediments in water systems has been studied most extensively under certain environmental conditions, particularly sediment resuspension (Qin et al. 2004; Wang et al. 2006; Cyr et al. 2009). Sediment resuspension can accelerate diffusion of pore water and remobilization of particulate matter, resulting in the increase of particulate and soluble phosphorus (P) in the water column. However, most prior studies focus only on sediment resuspension processes; by comparison, P transformations in relation to sedimentation processes are still poorly understood (You et al. 2007; Li et al. 2011). Once the driving force for sediment resuspension is removed, much of the P associated with resuspended particles (RP) will settle back to the bottom, and oxygenation of overlying water will cease. Rychła et al. (2014) suggested that P in settled particles (SP) undergoes microbial and chemical transformation processes during or after

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sedimentation and that these processes depend on the proportion of different P-binding forms within SP and on chemical conditions. Hupfer and Lewandowski (2005) found that at least 50 % of settled particulate P was released rapidly, either during or after sedimentation. However, SP may also adsorb P through flocculation, precipitation, and co-precipitation. Li et al. (2011) reported that mobile P can be transformed to non-mobile P, such as P bound to calcium compounds and refractory P.

Moreover, many studies have reported increases in total phosphorus (TP) following natural or experimental sediment resuspension in lakes but have shown no—or only weak—evidence for an increase in soluble reactive phosphorus (SRP) (Lenzi et al. 2005; You et al. 2007; Cyr et al. 2009; Schallenberg and Burns 2004). Cyr et al. (2009) suggested that increases in TP were due to the increase of suspended sediments, and the lack of change in SRP was generally attributed to rapid P uptake by bacteria and algae. It has been clearly demonstrated that sediment can also function as a sink for P. Fe/Al oxy-hydroxides, especially amorphous metal oxy-hydroxides, play a key role in determining P sorption capacity as a result of their high specific surface (Makris et al. 2005). Sediment resuspension may influence the physicochemical properties of the water column, such as dissolved oxygen (DO), pH, and turbidity, and then influence the transformation of P (Qin et al. 2004; Peng et al. 2007). However, much experimental researches on P adsorption or release focus on P kinetics (Zhou et al. 2005; Wang et al. 2009; Fan et al. 2013), and the release or sorption of P during sediment resuspension is mainly judged by the variation of P concentration in overlying water (Lenzi et al. 2005; You et al. 2007). The release or sorption of P, based on the forms of P in particles, remains poorly understood.

The various forms of P show marked differences in mobility and can be fractionated via several methods. The sequential scheme of Psenner et al. (1984) has been widely used for sediments. Individual ammonium oxalate was widely used for extraction of amorphous Fe, Al, and P (Jan et al. 2013; Li and Huang 2013; Arai et al. 2005). Jan et al. (2013) showed that sequential extraction (via the Psenner method) combined with ammonium oxalate was selective and efficient for extraction of amorphous P in non-calcareous sediments. Therefore, the objective of the present study was to investigate the P fractions in particulate matter in order to estimate phosphorus release and uptake by sediment particles under conditions of sediment resuspension and sedimentation. RP and SP were collected at different times and then analyzed for P forms. P fractions were determined via common sequential fractionation method (Rydin 2000) and by fractionation combined with ammonium oxalate.

## Material and methods

### Experimental instruments and materials

The pneumatic racetrack-style flume used for our experiment is a patented product of Hohai University, which has proven very effective in simulating sediment resuspension caused by wind–wave disturbance (Qian et al. 2011). The total height of the flume was 0.7 m, and the width of flow channel was 0.205 m. According to our previous studies, the experimental overlying water and sediment thickness were designed to 0.4 and 0.1 m, respectively, giving a water to sediment ratio of 4:1 (Qian et al. 2011).

Surface sediments were collected by Peterson grab sampler from Zhushan Bay, Lake Taihu (31° 24.895 N, 120° 02.573 E) in July 2013. Lake Taihu, one of the third biggest freshwater lakes in China, is a high eutrophic lake. Zhushan Bay is a heavily polluted, semi-enclosed bay in the northern part of Taihu Lake with a water area of 66 km<sup>2</sup> and water depth of 1.2–2 m. Collected sediments were placed carefully into the flume and tap water was injected slowly to avoid disturbing the sediment. The experimental instrument was allowed to stand undisturbed for 2 weeks in order to approach field conditions.

### Sediment resuspension experiment

The disturbance intensity and duration were designed for a RP concentration of approximately 500 mg/L and 8 h respectively, following our previous studies (Zheng et al. 2013). Afterwards, the wind effect was removed and the flume was allowed to stand for 24 h. The 32-h experiment simulated a strong wind–wave disturbance process including resuspension and following sedimentation.

During sediment resuspension, water samples were collected at 0, 1, 2, 4, 6, and 8 h. Samples (4 L) of overlying water were collected using simultaneous-layered sampling equipment at a distance of 0.02 m (lower) and 0.25 m (upper), respectively, from the surface of the sediment. From each collected water sample, 100 mL was analyzed for the concentration of resuspended particles, 100 mL was used for phosphorus analysis, and the remainder of each sample was centrifuged to collect the resuspended particles.

After the 8-h resuspension experiment, ten autonomous quadrat settlement vats were placed in the same position as the water sampling in order to trap settling particles during the 24-h incubation period. Two settlement vats were taken back at 1, 3, 6, 15, and 24 h after the beginning of settlement. Samples were also centrifuged to collect SP. Collected RP and SP were frozen and stored for further P fractionation experiments. Water samples were also collected during sedimentation for phosphorus analysis.

## Analytical methods

### *Water and sediment*

The pH and DO of overlying water were immediately analyzed by HACH portable automatic monitors (HACH Sension 5). Water samples of 100 mL were filtered through a 0.45- $\mu\text{m}$  glass fiber membrane, and the membranes were dried at 105 °C for 4 h. RP concentration was determined from an aliquot of overlying water that was filtered by a 0.45- $\mu\text{m}$  glass fiber membrane. Water content was calculated based on the weight loss by drying at 105 °C for 4 h, and loss on ignition (LOI) was estimated based on the weight loss by igniting at 550 °C for 2 h. The grain size of resuspended particles was calculated by a laser particle analyzer.

For TP, unfiltered water samples were digested by potassium persulfate; for total dissolved phosphorus (TDP), filtered water samples through 0.45- $\mu\text{m}$  membranes were digested by potassium persulfate. TP and TDP concentrations were determined photometrically as SRP, after neutralization, by the molybdenum blue method. The particulate phosphorus (PP) concentration was the difference between TP and TDP. SRP was determined directly by a molybdenum blue colorimetric assay of filtered water samples.

### *Phosphorus forms*

The common phosphorus fractionation method used in this study was the Psenner scheme as modified by Rydin (2000). The P forms separated in this sequential fractionation include loosely adsorbed P (extracted with 1 M  $\text{NH}_4\text{Cl}$  for 1 h, pH=7.0), redox-sensitive bound P (extracted with 0.11 M bicarbonate dithionite for 2 h, pH=7.0), P bound to hydrated oxides of aluminum and non-reducible Fe (SRP extracted with 0.1 M NaOH for 16 h), organic P (dissolved non-reactive P extracted with 0.1 M NaOH for 16 h), carbonate-bound P (extracted with 0.5 M HCl for 16 h), and refractory P (extracted with 1 M HCl after ignition for 16 h). The P binding forms were studied using 0.2 g of freeze-dried particles mixed with 20 mL extraction solution (solution to solid ratio 100:1) (Lukkari et al. 2007). After each step, the samples were centrifuged at 5000 rpm for 10 min, and then the supernatant liquor was filtered through a 0.45- $\mu\text{m}$  filter. Filtered samples were analyzed with a spectrophotometer for TP and SRP. Dissolved non-reactive P (NRP) was subsequently determined by subtracting SRP from TP and was assumed to predominantly represent organically bound P.

Additionally, common sequential phosphorus fractionation combined with ammonium oxalate extraction was also performed in this study to determine the amount of P bound to amorphous Fe/Al oxy-hydroxides. Following Jan et al. (2013), an oxalate extraction step was inserted between the  $\text{NH}_4\text{Cl}$  and BD steps. The ammonium oxalate extraction

solution was prepared by dissolving 16.2 g of ammonium oxalate monohydrate and 10.8 g oxalic acid dihydrate in 1 L of pure water. The pH of this solution was 3.0 (Schoumans 2000). The extraction procedure was the same as for sequential fractionation extraction, but lasted for 2 h, and samples were protected from light to prevent dissolution of more crystalline Fe-P forms. Extracted P was analyzed for TP and SRP after oxalate decomposition with hot, concentrated  $\text{HNO}_3$  to avoid the influence of oxalate (Peltovuori et al. 2002). One-milliliter subsamples of BD and ammonium oxalate extractions were transferred into Teflon crucibles, evaporated to near dryness, and then diluted to 25 mL with 5 %  $\text{HNO}_3$ . After pretreatment, the Fe content was analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7700).

Concentrations of SRP and NRP extracted by sequential fractionation were referred to using abbreviations, for example, SRP extracted by  $\text{NH}_4\text{Cl}$ , ammonium oxalate, BD, NaOH, and HCl are abbreviated as  $\text{NH}_4\text{Cl}$ -SRP, Ox-SRP, BD-SRP, NaOH-SRP, and HCl-SRP, respectively, and the refractory P as Ref-P.

### Quality control

For quality control, all experimental equipment was steeped with acids and rinsed with ultrapure water, and all reagents were of analytical grade. Samples were analyzed using a blank and three replicates in order to estimate the precision of analytical work. Mean values are presented in all figures and tables, and variations in results are reported as the standard error of the mean ( $\pm\text{SEM}$ ) ( $n=3$ ). Coefficients of variation are generally less than 10 (CV%<10 %).

## Results

### Properties of overlying water and sediments

The total P content in sediment was 948 mg/kg dry weight (DW) (Table 1). The major P forms in sediment were BD-SRP and NaOH-SRP. The sediment had high mean concentration of Fe extracted by ammonium oxalate (Ox-Fe, 5125 mg/kg DW). During sediment resuspension, the average median particle size ( $d_{50}$ ) of RP was 14.7  $\mu\text{m}$ , and the proportions of clay and silt grains of the sediment were almost 10.5 and 84 %, respectively.

RP concentration increased sharply from 4 to almost 550 mg/L within the first hour and then remained relatively constant during sediment resuspension (Fig. 1). However, during sedimentation, RP concentration decreased, especially within the first hour. After a 24-h settlement, RP concentration declined to 10 mg/L, which was similar to that of the initial

**Table 1** Physicochemical properties of sediments and grain size of resuspended particles (mean value)

Characteristics	Value
Water content (%)	58
LOI (%)	4.5
pH	7.3
TP (mg/kg)	948
BD-SRP (mg/kg)	349
NaOH-SRP (mg/kg)	205
Ox-Fe (mg/kg)	5125
$d_{50}$ ( $\mu\text{m}$ )	14.7
Clay (<3.9 $\mu\text{m}$ )	10.5 %
Silt (3.9–63 $\mu\text{m}$ )	84 %
Sand (63–2000 $\mu\text{m}$ )	5.5 %

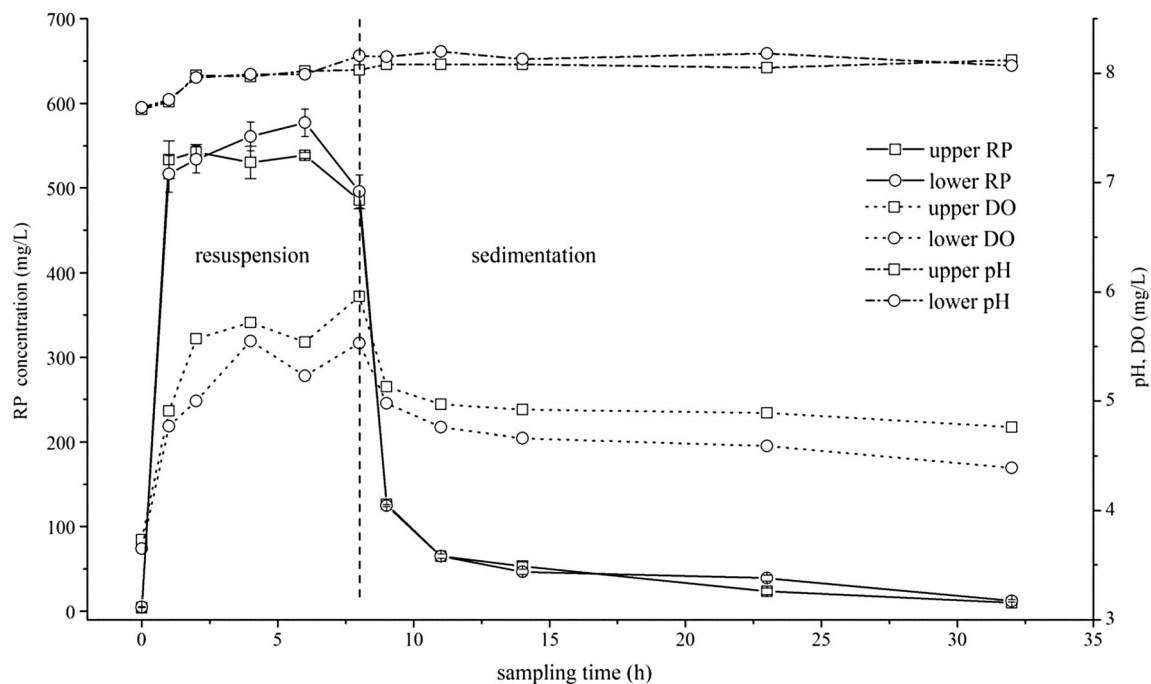
water. No obvious differences in RP concentrations were found between the upper and lower water columns except during resuspension when concentrations of RP directly above the sediment were slightly higher. The wind–wave disturbance promoted remarkable oxygenation of the water column, especially within the initial 2 h (Fig. 1). When the disturbance was stopped, DO concentrations decreased sharply in the first hour and then smoothly in the following 23 h. The DO concentration in the overlying water during resuspension was generally higher than that during sedimentation. The DO concentration in the lower overlying water was perceptibly less than that in the upper sampling zone. The pH values in the overlying water were greater than 7, meaning that the overlying water was weakly alkaline. Along with the increase

of oxygen concentration, pH values also increased during sediment resuspension; pH values remained relatively constant under sedimentation conditions and were higher than those under resuspension conditions.

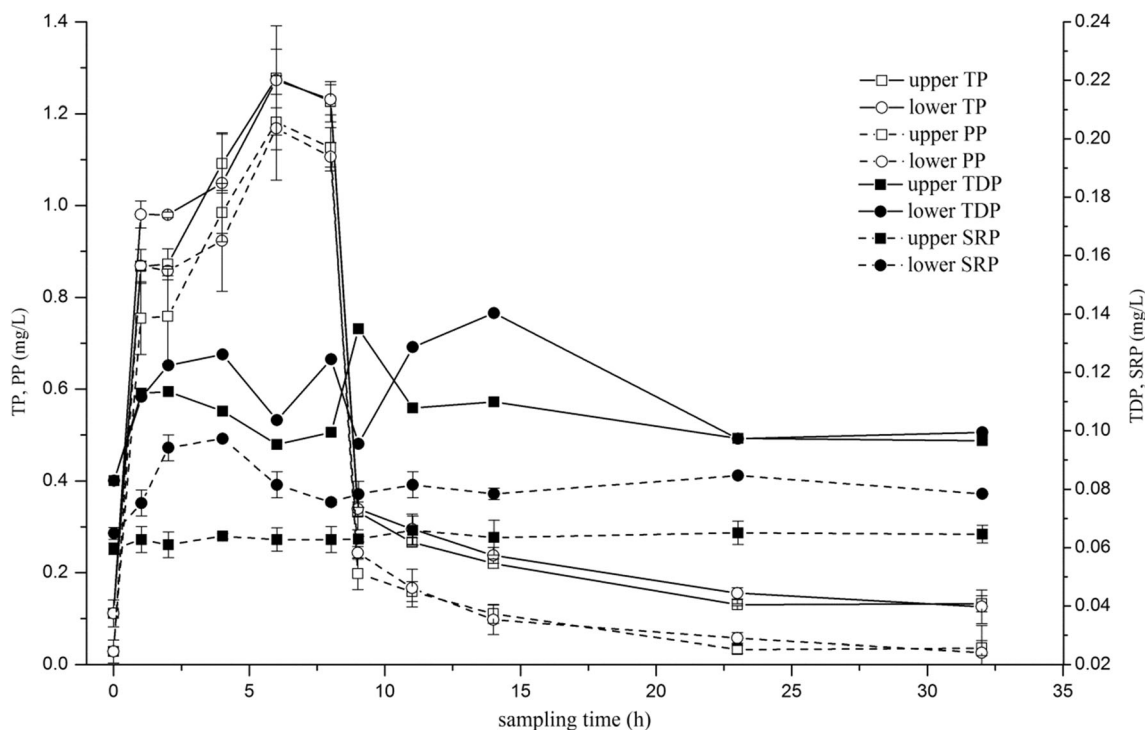
#### Distribution of phosphorus in water

Phosphorus (both particulate and soluble) in sediment can be released into the overlying water during sediment resuspension (Fig. 2). TP and PP concentrations in the overlying water increased gradually during sediment resuspension. Increases in TP and PP were mainly caused by increased RP. TDP concentration in overlying water showed a decrease after initial increase during resuspension. Meanwhile, SRP in the lower overlying water increased and peaked after 4-h resuspension and then decreased during the remaining resuspension time. However, SRP in the upper overlying water showed no obvious variations during sediment resuspension and was much less than that observed in the lower water column (Fig. 2).

Most of the P, associated with resuspended particles, settled out from water during sedimentation, resulting in a sharp decrease of TP and PP (Fig. 2). A slight increase in SRP was found at the beginning of the sedimentation period, which might be attributed to desorption of P from the settling particles. SRP in the lower water column was greater than that in the upper water throughout the experimental period.



**Fig. 1** Characteristic of the upper (square) and lower (circle) overlying water during both resuspension and sedimentation. The dashed line is the boundary between different experiment conditions: resuspension (left) and sedimentation (right)



**Fig. 2** Changes in P concentrations in the upper (*square*) and lower (*circle*) overlying water

**Common sequential P fractionation**

TP in particles (both RP and SP) ranged from 912 to 1038 mg/kg (Fig. 3). In both RP and SP, most of the extracted P was present as soluble reactive phosphorus (TSRP, 83–88 % of TP), and extracted organic phosphorus forms (total non-reactive phosphorus, TNRP) contributed only 12–17 % of TP. The dominant binding form of inorganic phosphorus was BD-SRP, which contributed almost 40 % of TP. NaOH-SRP was the second most abundant form (21 % of TP). Organic phosphorus forms were mainly extracted by NaOH (NaOH-NRP), followed by BD (BD-NRP). Organic phosphorus extracted by NH<sub>4</sub>Cl or HCl was negligible (<10 mg/kg, data not given).

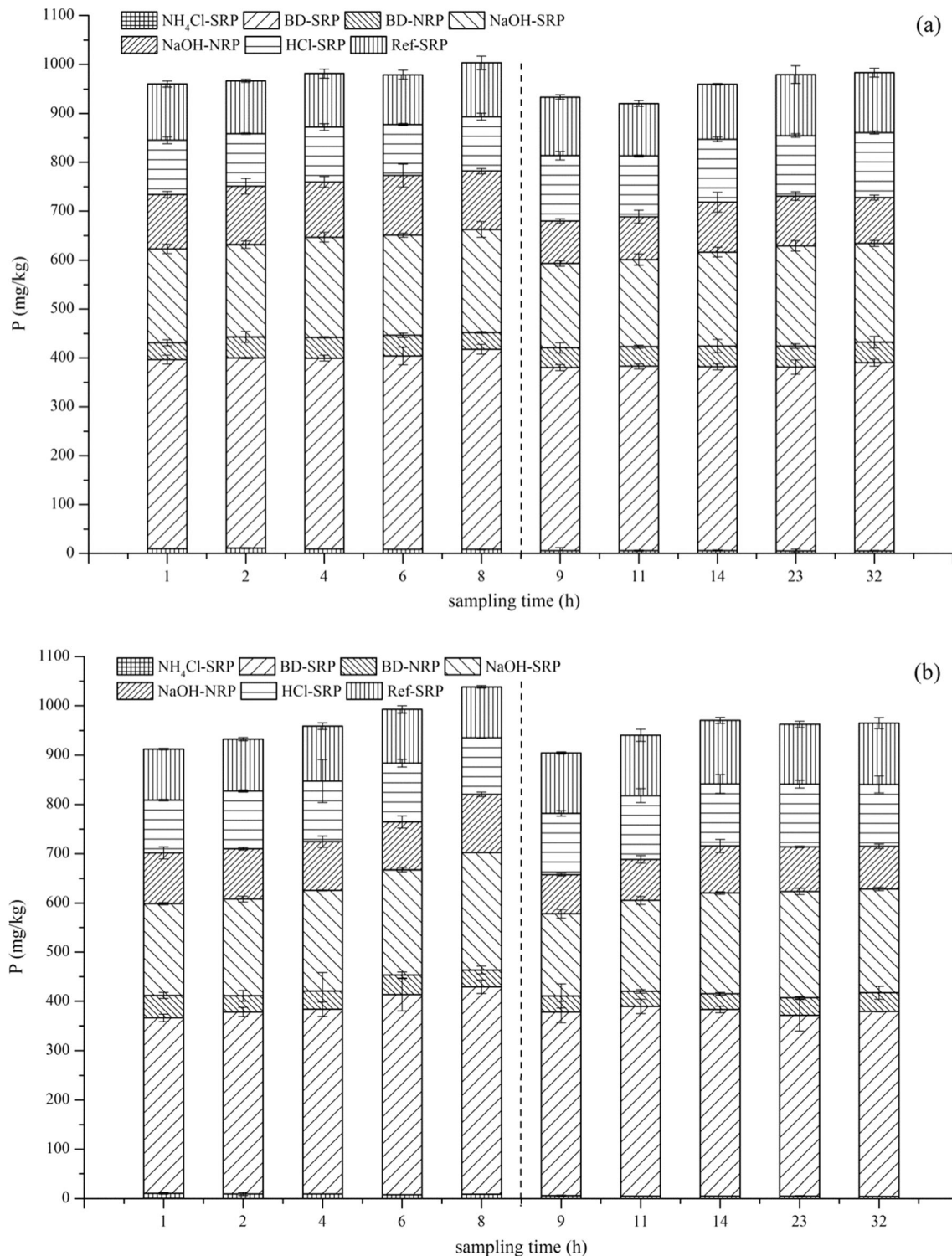
NH<sub>4</sub>Cl-SRP, HCl-SRP, and Ref-P content in RP maintained relatively constant concentrations during sediment resuspension. Gradual increases in both BD-SRP and NaOH-SRP in RP were shown during sediment resuspension (Fig. 3). NaOH-SRP and BD-SRP in RP collected from the upper overlying water increased by 18 and 22 mg/kg, respectively. TP increased from 960 to 1021 mg/kg. Therefore, increased BD-SRP and NaOH-SRP in RP of the upper overlying water contributed to 36 and 30 % of increased TP, respectively. Similarly, increased BD-SRP and NaOH-SRP in RP of the lower overlying water contributed to 52 and 36 % of increased TP, respectively. Together, BD-SRP and NaOH-SRP in RP contributed to 66 and 88 % of increased TP in the upper and lower overlying water, respectively.

Compared with P forms in RP, the NH<sub>4</sub>Cl-SRP, BD-SRP, and NaOH-NRP in SP decreased during the first hour of sedimentation and then remained constant. The TP decrease in RP, compared to SP, was mainly caused by the decrease of BD-SRP and NaOH-NRP. NaOH-SRP decreased to 167 mg/kg in the first hour and then increased to 216 mg/kg. Concentrations of HCl-SRP and Ref-P in SP were larger than those in RP and increased by 20 and 15 mg/kg respectively. BD-NRP in SP, similar to RP, remained at 40 mg/kg. There were no obvious differences in P forms between the upper and lower SP, except that there was greater concentration of NaOH-NRP in the upper.

**Combined sequential P fractionations**

TP concentrations extracted by combined P fractionations ranged from 914 to 1031 mg/kg (Fig. 4). Inorganic phosphorus extracted by ammonium oxalate (Ox-SRP), considered as amorphous P, was the predominant form, which constituted 57–60 % of TP: in RP of the upper overlying water, it gradually increased from 563 to 604 mg/kg; in SP of the lower overlying water, it increased from 531 mg/kg and then remained at approximately 572 mg/kg. The mean BD-SRP concentration was almost 85 mg/kg. It remained constant at 81 mg/kg in RP of the upper overlying water and gradually increased from 83 to 104 mg/kg in SP of the lower

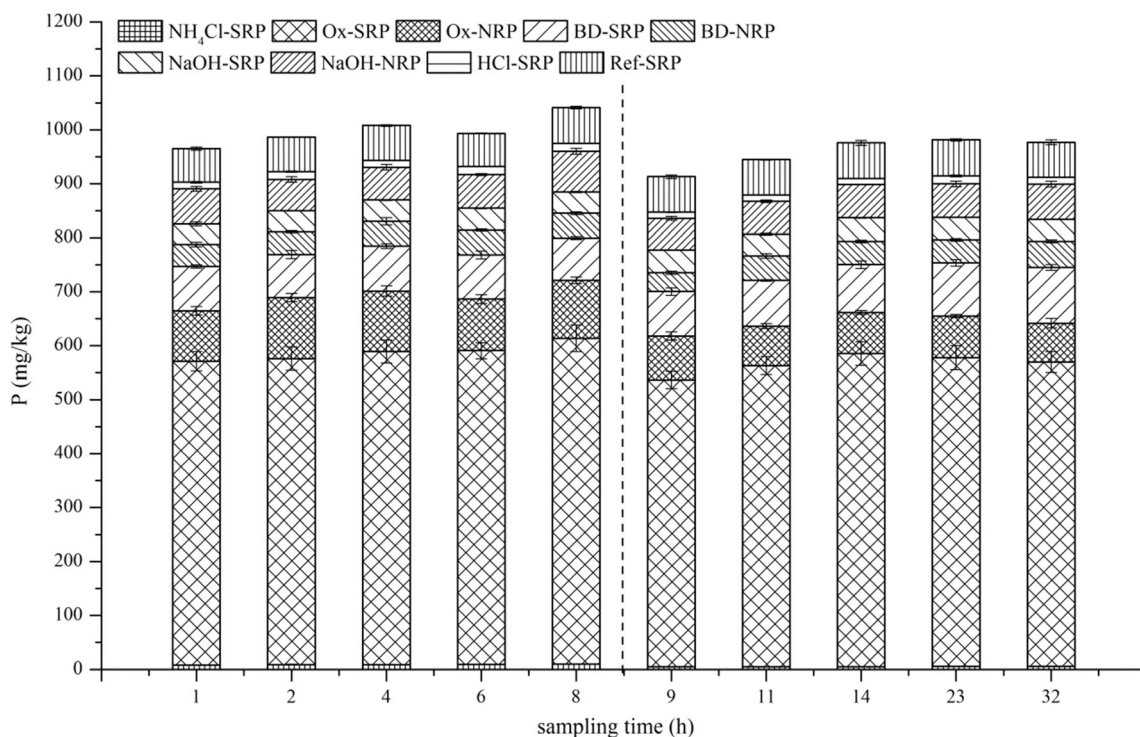




**Fig. 3** P fractions extracted with common sequential fractionation in RP (*left of dashed line*) and SP (*right of dashed line*) collected from the upper overlying water (**a**) and lower overlying water (**b**)

overlying water. NaOH-SRP remained at 40 mg/kg. Oxalate was also effective in extracting organic phosphorus. Ox-NRP concentration ranged from 72 to 113 mg/kg, representing approximately 39–51 % of

TNRP. BD-NRP concentration was almost 40 mg/kg. NH<sub>4</sub>Cl-SRP remained at 9 and 5 mg/kg in RP and SP, respectively. NaOH-NRP, HCl-SRP, and Ref-P in RP and SP were 63, 12, and 64 mg/kg, respectively.



**Fig. 4** P forms extracted with combined sequential P fractionations in the upper RP and the lower SP. Ammonium oxalate extraction step was inserted between the  $\text{NH}_4\text{Cl}$  and BD steps according to Jan et al.

(2013). The dashed line is the boundary between different types of particles: upper RP (left) and lower SP (right)

**Discussion**

P forms extracted by two sequential fractionations

The results clearly indicated that P forms extracted via common sequential fractionation differed from those obtained via extraction combined with ammonium oxalate (Table 2). Oxalate has been shown to be very efficient in dissolving the amorphous and less-crystalline iron and aluminum oxides, but ineffective in dissolving the crystalline forms (Jan et al. 2013). Therefore, inorganic phosphorus extracted with BD and NaOH (BD-SRP and NaOH-SRP) following ammonium oxalate was considered as P bound to crystalline Fe and Al oxides, representing approximately 80 and 41 mg/kg, respectively (Fig. 4). Accordingly, the difference in BD-SRP and NaOH-SRP between the two phosphorus fractionation methods (Table 2) could be considered as P bound to amorphous Fe/Al oxides. No obvious differences in BD-NRP were found between two sequential fractionations, which suggested that organic P extracted with BD was mainly bound to crystalline iron oxides. On the other hand, ammonium oxalate is also non-selective and some P forms can be dissolved due to its low pH. NaOH-NRP generally consists of fulvic acid organic P (FA-P) and humic acid organic P (HA-P) (Xu et al. 2013; Lukkari et al. 2007). FA-P represents a fraction soluble in both alkali and acid, whereas HA-P is soluble in alkali but

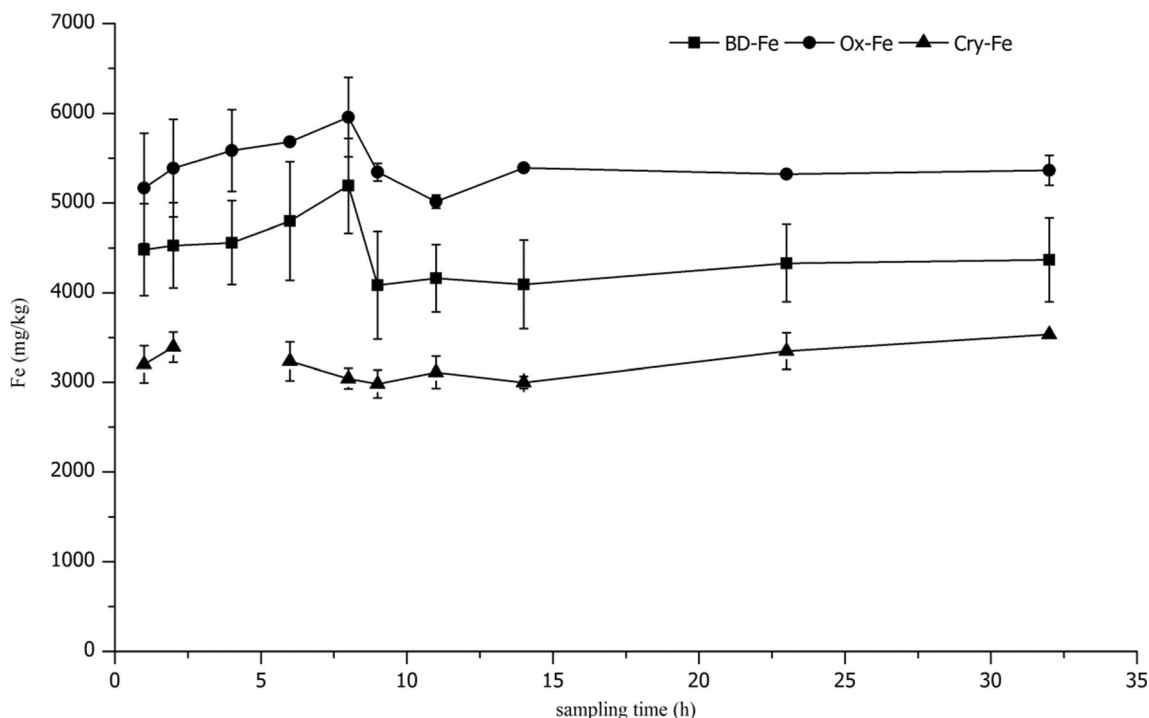
insoluble in acid. Xu et al. (2013) reported the presence of FA-P (approximately 61 mg/kg) in Taihu Lake sediments. We assumed that the dissolution of FA-P resulted in the differences in NaOH-NRP observed between the two sequential extraction methods (pH=3.0). HA-P, considered as non-labile organic phosphorus, remained at almost 63 mg/kg (Table 2), which was similar to that reported by Xu et al. (2013). Moreover, the reduction of HCl-SRP and Ref-P in extraction combined with oxalate is a result of the dissolution of P bound to calcium compounds by acid ammonium oxalate and mobilization of stable organic phosphorus (e.g., refractory P) by oxalate (Yang et al. 2012). The content of organic P extracted by ammonium oxalate was similar to the sum of the reduction of NaOH-NRP and Ref-P between two extraction methods, and the Ox-SRP content was in a similar range to the sum of reduced BD-SRP, NaOH-SRP, and HCl-SRP (Table 2). It is concluded that Ox-SRP is composed of P bound to amorphous Fe/Al oxides and the majority of Ca-P and that NRP extracted with oxalate (Ox-NRP) mainly consists of FA-P and partially Ref-P. The combined sequential phosphorus fractionations with ammonium oxalate seem to be convenient to distinguish P bound to amorphous or crystalline metal oxides.

Furthermore, during resuspension, Ox-SRP showed an increase of 41 mg/kg, which was similar to the combined

**Table 2** P fractions extracted with two sequential extraction methods in the upper RP and the lower SP (mean concentrations, mg/kg)

Method	Time (h)	NH <sub>4</sub> Cl-SRP	Ox-SRP	Ox-NRP	BD-SRP	BD-NRP	NaOH-SRP	NaOH-NRP	HCl-SRP	Ref-SRP	TSRP	TP	
Combined sequential phosphorus fractionation	Upper RP												
	1	8	563	94	82	41	38	65	12	62	765	965	
	2	10	567	113	80	42	39	68	15	64	774	998	
	4	9	580	112	83	46	40	61	12	65	789	1008	
	6	10	581	96	82	46	40	62	15	61	790	994	
	8	9	604	108	78	46	39	65	15	67	812	1031	
	Lower SP												
	9	5	531	81	83	35	42	59	11	66	739	914	
	11	5	558	73	85	45	40	61	12	65	766	945	
	14	4	580	76	89	43	44	62	11	67	794	975	
	23	6	572	77	98	43	41	62	15	67	799	982	
32	5	564	72	104	48	41	65	13	65	792	977		
Common sequential phosphorus fractionation	Upper RP												
	1	10	–	–	387	35	192	121	91	115	814	960	
	2	11	–	–	389	43	189	109	108	108	804	967	
	4	9	–	–	390	42	205	113	123	109	826	1000	
	6	8	–	–	396	43	204	122	105	101	814	987	
	8	8	–	–	409	34	210	120	121	110	850	1021	
	Lower SP												
	9	6	–	–	372	33	167	80	124	123	792	911	
	11	5	–	–	384	31	185	83	130	123	827	945	
	14	5	–	–	378	32	185	95	131	129	829	961	
	23	5	–	–	367	35	216	90	122	122	831	962	
32	4	–	–	375	38	211	86	126	125	841	970		





**Fig. 5** Fe contents in the upper RP and the lower SP. *BD-Fe* represents Fe extracted with BD in common extractions, and *Ox-Fe* and *Cry-Fe* represent Fe extracted with oxalate and BD in the combined method, respectively. The missing data result in the breaking off of *Cry-Fe*

increase of BD-SRP and NaOH-SRP (40 mg/kg, common method) in RP of the upper overlying water, while P bound to crystalline Fe/Al oxides (BD-SRP in the combined method) showed no change during resuspension (Table 2). It indicated that during resuspension, increases in P are primarily due to the increase of P bound to amorphous Fe/Al oxides. The stable HA-P concentration in both RP and SP indicated that the decrease of Ox-NRP and NaOH-NRP in RP, compared to SP, may result from the reduction of FA-P during sedimentation (Table 2).

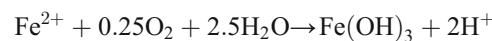
Phosphorus adsorption by RP

The absent change of SRP in the water column and increased P in RP during sediment resuspension indicated that P released from sediment can be adsorbed by RP. As expected, wind disturbance at the surface caused higher oxygenation of overlying water (Fig. 2). The diffusion of oxygen into the water column can initiate a process of autocatalytic Fe oxidation, as represented by the general reaction pathway (Kraal et al. 2009):



where  $Fe^{3+}$  is thought to be the principal oxidant of  $Fe^{2+}$ . Meanwhile, ferric Fe will in part precipitate as Fe oxy-hydroxides. The formation of oxy-hydroxides can be enhanced in a slightly alkaline water column, where hydrogen ion can be

buffered with hydroxyl ions. Under such conditions, the ferrous iron will react to form iron oxy-hydroxides via the following reaction (Kraal et al. 2009):



Furthermore, amorphous Fe oxy-hydroxides formed more readily than crystalline oxides, due to lower thermodynamic stability in the natural environment (Fahlman 2011). The gradual increases in BD-Fe and Ox-Fe confirmed our hypothesis that fresh amorphous Fe oxy-hydroxides were formed during sediment resuspension (Fig. 5). Ferric compounds can adsorb a large quantity of phosphorus by forming  $Fe(OOH)-P$  complexes or precipitates (Peng et al. 2007). Increased BD-SRP in RP of the upper overlying water contributed 36 % of total increased P during resuspension. It is concluded that the formation of amorphous oxy-hydroxides and subsequent adsorption of P lead to the increase in P in RP.

Along with iron oxy-hydroxides, Al oxy-hydroxides have a high affinity for phosphorus. Increases in NaOH-SRP were also found in RP during sediment resuspension (Fig. 3). P fractionations indicated that almost all of the increased P comprised BD-SRP and NaOH-SRP. These results support those of previous studies, which found Fe and Al to be the main P-binding elements (Li et al. 2011).

It was observed that the increase in P differed between RP collected from the upper and lower overlying water. The comparison of BD-SRP in RP with initial sediment demonstrated

that BD-SRP in RP of the upper water column mainly increased within 1 h after sediment resuspension, whereas in the lower water column, it principally increased after 4-h resuspension. This phenomenon corresponded to the variations of SRP in overlying water (Fig. 2). It is indicated that the RP in the upper water column were more effective in P sorption than those in the lower water column. Staunton and Nye (1989) postulated that rapid sorption was primarily influenced by the time taken for P to move into contact with particles. Based on our previous study, strong disturbance was associated with higher velocity in the upper water column (Qian et al. 2011). Accordingly, there was a greater probability of collision between P reactants and P, which may promote the sorption of P by RP (Li and Huang 2013). Additionally, the higher DO concentration and more fine-grained RP in the upper water column may also result in more effective P sorption (Fan et al. 2013; Wang et al. 2008). Many studies reported that the adsorption amount and the rate of phosphorus adsorption by sediment increased with higher SRP concentration (Zhou et al. 2005; Wang et al. 2009). Therefore, greater P sorption by RP of the lower overlying water can be explained by the higher SRP concentration in the lower water column during sediment resuspension.

#### P sedimentation by SP

The raw rapid sorption by Fe/Al oxides is assumed to be reversible, and partially adsorbed P can subsequently be released again as a result of environmental changes. Hupfer and Lewandowski (2005) found that rapid loss of P from settling particles takes place either during or immediately after sedimentation. The effect of P leakage was clearly shown by the decrease in  $\text{NH}_4\text{Cl}$ -SRP, BD-SRP, and NaOH-NRP (Fig. 3). Amorphous Fe oxy-hydroxides have low stability and are therefore reduced more readily than crystalline oxides (Jan et al. 2013). BD-Fe and Ox-Fe in particles sharply decreased under sedimentation conditions and Cry-Fe remained relatively constant (Fig. 5). It is indicated that the decrease in BD-Fe mainly results from the decrease in Ox-Fe. The amorphous Fe oxy-hydroxides were reduced during sedimentation and subsequently liberate associated P into water. The decrease of BD-SRP in SP and stable content of P bound to crystalline Fe oxides confirmed with these results (Table 2). Xu et al. (2013) reported that  $\text{NH}_4\text{Cl}$ -SRP and FA-P are respectively considered as labile P and moderate mobile organic P, which can be readily released. Therefore, the decrease of NaOH-NRP and  $\text{NH}_4\text{Cl}$ -SRP may result from the release of FA-P and labile P during sedimentation.

The concentration of BD-SRP in SP was still larger than that in the initial sediment (Table 1), even if partly desorbed during settlement. The Cry-Fe concentration in SP had a slight

increase during sedimentation (Fig. 5). Many studies reported that ferrous iron could catalyze the transformation of amorphous Fe oxy-hydroxides to crystalline forms (Pedersen et al. 2005; Borch and Fendorf 2007; Boland et al. 2013). Pedersen et al. (2005) and Boland et al. (2013) reported that the transformation of amorphous Fe oxy-hydroxides to more stable forms occurred within several hours to days. Gradual increases in P bound to crystalline Fe-P and Cry-Fe in SP indicated that partial amorphous or poorly crystalline P transformed to crystalline P within SP. The decrease of Ox-SRP in SP also confirmed this, while there was no decrease of HCl-SRP and NaOH-SRP. The transformation of P into non-mobile crystalline oxides may reduce the likelihood of P release and therefore represent an important mechanism for retention of P in sediments.

Generally, Al oxy-hydroxides are unaffected by redox conditions, and as such, those bound P are considered to be a permanent sink for P. Al oxy-hydroxides can prevent P release by adsorbing P liberated from Fe oxy-hydroxides. However, a dramatic decrease in NaOH-SRP was found, followed by a gradual increase in SP (Table 2). One explanation for the decrease could be the liberation of P and Al from Al organic complexes (Kopáček et al. 2007). Afterwards, the liberated Al can adsorb P by forming Al oxy-hydroxides within weakly alkaline water and then provide long-term P retention.

#### Conclusions

Under sediment resuspension, DO concentrations and pH in overlying water showed an obvious increase, after which they remained relatively constant. DO concentrations in the upper overlying water column were greater than those in the water above the sediment. Particulate and soluble P were released from sediment to water during sediment resuspension. However, during resuspension, the freshly formed amorphous oxy-hydroxides in particles could adsorb released SRP. On the one hand, effective sorption of P onto RP in the upper water derived from the higher DO concentration and higher collisional probability; on the other hand, the higher SRP in the lower water column promoted sorption of P onto RP. Once the driving force of resuspension was removed, RP settled out from water to sediment, and DO was consumed during the process of sedimentation. P associated with SP may be released during sedimentation through reductive dissolution of P bound to iron oxides and by the mineralization of labile P and FA-P. However, increases in NaOH-SRP and crystalline Fe-P indicated that mobile P may be transformed to non-mobile forms, such that sedimentation conditions may facilitate long-term retention of P.

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