



Characteristics of phosphorus fractionated from the sediment resuspension in abrupt expansion flow experiments

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Received 30 November 2009; revised 04 May 2010; accepted 26 May 2010

Abstract

Phosphorous (P) fraction characteristics in sediment resuspension were investigated under adequately hydrodynamic conditions. Four forms of P in overlying water, including dissolved inorganic P, dissolved total P, total P, and particulate P, and six fractions of P in suspended particulate matter (SPM), including loosely sorbed P (NH₄Cl-P), redox-sensitive P (BD-P), aluminum-bound P (Al-P), organic P (NaOH-nrP), calcium-bound P (Ca-P) and residual P (Res-P), were quantified, respectively. Different hydrodynamic conditions resulted in different P form changes. Four states could be ascribed: (1) P desorption by sediment and SPM, and P adsorption by overlying water; (2) P desorption by SPM, and P adsorption by overlying water; (3) P adsorption by SPM, and P desorption by overlying water; and (4) P equilibrium between SPM and overlying water. The contents of P in overlying water acquired peak values in the middle position of the vertical P distribution due to the combined actions of SPM and sediment. P fractions in SPM were in the following order: BD-P > NaOH-nrP > Ca-P > Al-P > Res-P > NH₄Cl-P. BD-P in SPM frequently exchanged with P forms in overlying water. Resuspension was favorable to forming Ca-P in SPM.

Key words: phosphorus fractions; hydrodynamic conditions; suspended particulate matter; abrupt expansion flow

DOI: 10.1016/S1001-0742(09)60283-7

Introduction

Suspended particulate matter (SPM), whether delivered from external sources or caused by riverine autochthonous production, discharge, or sediment resuspension, has a major impact on the ecological function of a river system (Kleeberg et al., 2008). The amount, composition and temporal variation of SPM and fluxes of phosphorus (P) with lakes are strongly regulated by retention and release processes (Hupfer et al., 1995; Haggard et al., 2004). It is important to understand these mechanisms because the transport of sediment associated P in shallow lakes often constitutes a high percentage (23%–61%) of the total annual P flux (Svendsen et al., 1995; Wang et al., 2006). Entrainment of P from the sediment and its subsequent dislocation may stimulate riverine, latching, and marine phytoplankton production, contributing to the displacement of eutrophication potential (Ruban et al., 1999; Rydin, 2000; Kleeberg et al., 2007).

Sorption and desorption of P in lake sediment have been well investigated, because of their importance in regulating P concentration in stream water (Wang et al., 2006, 2009; Li et al., 2007; Derrick and Kin, 2008; Sun et al., 2009). In

contrast, less is known about P fluxes caused by resuspension events associated with changing flow conditions (Ku and Lin, 2008; Roos et al., 2008). Consequently, the impact of hydrodynamic conditions on the extent of P fractions is poorly documented both in terms of in magnitude and source strength from the sediment.

The importance of P fractions has been observed in many laboratory studies (Zhou et al., 2001; Xie et al., 2003; Jin et al., 2006; Li et al., 2007; Jiang et al., 2008; Bai et al., 2009). However, these experimental approaches do not adequately consider hydrodynamic conditions. Most of these studies use full stirring of water using plungers, stirrers, or oscillating grids, which do not occur in nature. Consequently, the rates of P entrainment are likely overestimated and restricted.

Annular flume systems have been extensively used to investigate sediment transport (Amos et al., 1992; Maa et al., 1993; Widdows and Brinsley, 1998a). Annular flumes enable control over experimental conditions, and readily allow the measurement of experimental parameters (velocity profiles, turbulence, and suspended sediment). Unlike common circulating flumes, annular flumes convert the length of straight flumes into a time criterion that satisfies lead-time and long distance during sediment particle flocculation and sedimentation. In addition, they

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do not disrupt flocculation state because of the recovery tank (Bale et al., 2006; Manning et al., 2007; Bowes et al., 2008).

Most existing studies on wall-bounded flows focus on pipe, or rectangle or wedge-shaped channels (Lin et al., 2002; You et al., 2003; Recking et al., 2008). Sediment resuspension flowing with abrupt expansion has received limited attention, although this phenomenon is common in nature, such as in estuaries. P release from sediments in this region is more active due to the change in hydrodynamic condition.

The objectives of this study were (1) to estimate the amount and forms of P in SPM using a sequential extraction procedure; and (2) to evaluate the P exchange processes in sediment, SPM, and overlying water, in order to reveal their inner relationship.

1 Materials and methods

1.1 Sampling and pretreatment

Sediment samples were collected in May 2009. Due to water diversion from the Yangtze River to Taihu Lake, the Wangyu Estuary formed an abrupt expansion flow, resulting in a higher P exchange process. The sample sites were located in Gonghu Bay, in the northeast basin of Taihu Lake in China (31°37'N, 120°33'E) (Fig. 1).

Sediment samples were collected using a cylinder sample device (inner diameter 60 mm, pipe length 0.5 m) from the top 5 cm layer. The samples were taken to the laboratory in air-sealed boxes. To exclude the effects of biological activity on P release, sterilization was conducted under air-dried, homogenized conditions, after which the samples were passed through a 150 μm sieve. Water samples were collected 0.5 m below the water surface. The sediment samples were analyzed for total P (TP) using SMT protocol (Ruban et al., 1999). Water content and loss on ignition measurements were based on weight losses after drying and combustion of sediments at 105 and 550°C. Total organic carbon in the sediments was determined after treating the sample with $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (Hupfer, 1995). Particle sizes were analyzed using a laser particle analyzer (Mastersizer2000, Malvern, British). All samples were analyzed in triplicates, and the data were

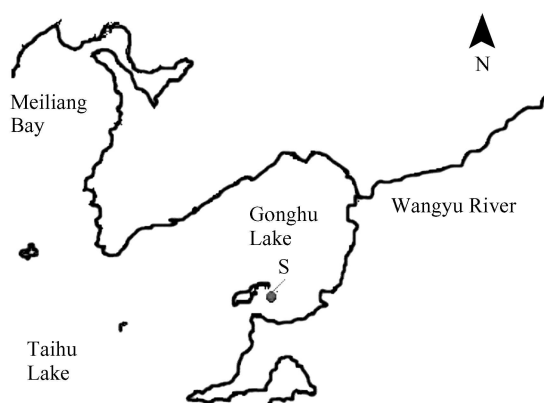


Fig. 1 Map of Taihu Lake showing sampling sites. S: sampling site.

expressed as the average (Tables 1 and 2).

Table 1 Physical and chemical characteristics of the sediment

	pH	W (%)	LOI (%)	TP (mg/kg)
Minimum	7.39	47.36	2.90	504.04
Maximum	7.40	53.66	3.28	524.15
Mean	7.40	50.51	3.09	514.10

W: water capacity; LOI: loss on ignition; TP: total phosphorus.

Table 2 Grain diameter distribution characteristics of the sediment

Grain diameter (D) (μm)	Percentage (%)
$D(0.5)^*$	10.48 ± 0.136
$D < 4$	18.457 ± 0.227
$4 < D < 16$	52.599 ± 0.143
$16 < D < 32$	22.879 ± 0.155
$32 < D < 64$	5.766 ± 0.251
$D > 64$	0.299 ± 0.203

* Median particle diameter.

1.2 Annular flume system

The laboratory flume system consisted of two independent annular flumes, each with a 0.56 m inner diameter and 0.3 m outer diameter, creating a 0.13 m-wide annular channel and a 0.21 m wide abrupt expansion area. Each had a continuous bed with a total area of 0.3 m^2 , a working depth of 0.25 m, and a maximum volume of 70 L. Water flow was induced by rotating an annular driver cylinder with two or four paddles. The flumes were programmed to generate free-stream current velocities ranging from 5 to 50 cm/sec with 5 cm/sec step-wise increments controlled by the gearbox.

Current velocities in the flume were measured using 3D Sontek Acoustic Doppler Velocimeter (ADV, Sontek, USA), including upward and downward velocities.

1.3 Experimental methods

To study the effects of hydraulic conditions on P release, four sample sites (Sites #1, #2, #3, and #4) for P fraction of SPM were compared (Fig. 2b). Sediments were paved approximately 5 cm deep. Water samples were filled in an annular flume on a 22 cm scale. Velocity characteristics were measured in the flume system.

Experiments were carried out as follows: (1) the device was started, and four samples were collected at intervals 0, 5, 30, and 90 min ($H = 14$ cm); (2) samples from Sites #1 and #3 were collected at 30 min ($H = 7, 11, 15, 18,$ and 22 cm); (3) samples from Site #1 and #3 were collected at 4, 6, 9, 13, 19, 24, 30, 48, 72, 96, and 120 hr; (4) the device was turned off, and samples from Site #1 were collected in 0, 5, and 30 min, then at 1.5, 4, 6, 9, 13, 19, and 24 hr ($H = 14$ cm).

The 300 mL sample was divided into two equal parts. One was used to determine concentration of SPM by gravimetric method (GB11901-89), while the other (150 mL) was used to analyze P fraction in SPM and water after centrifuge.

Phosphorous forms in overlying water were divided

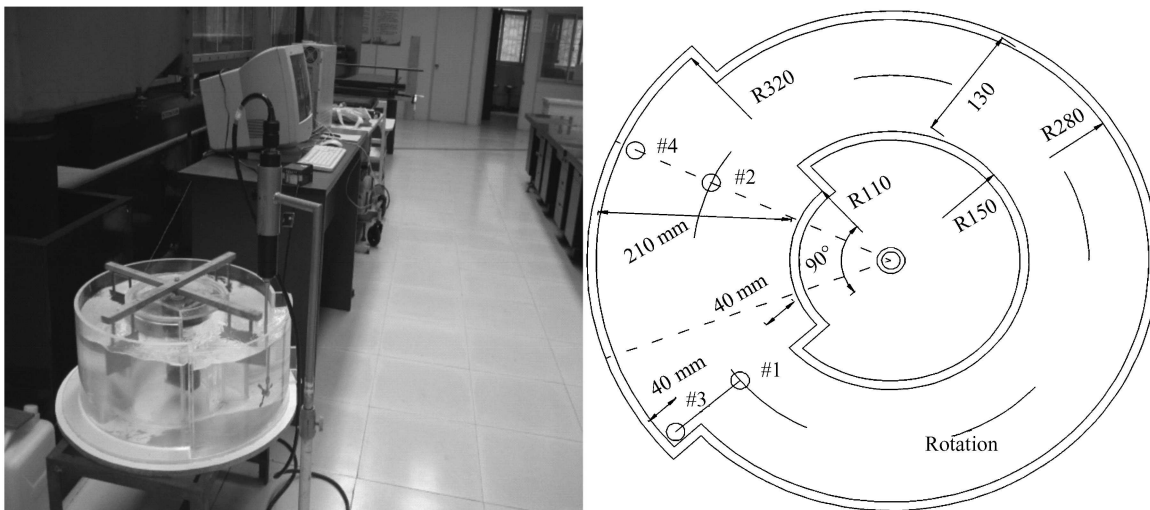


Fig. 2 Photograph of annular flume system (a) and size chart of annular flume system (b). R (mm): radius.

into dissolved inorganic phosphorus (DIP), dissolved total phosphorus (DTP), TP, and particulate phosphorus (PP). DIP in each sample was filtered through a 0.45 μm filter membrane and directly analyzed by the molybdenum blue method. DTP was filtered through a 0.45 μm filter membrane and analyzed by ammonium molybdate spectrophotometric method (GB11893-89) to determine TP. PP was calculated using the value of TP minus DTP.

Phosphorous fraction in SPM, involving sequential extraction, is based on the difference in reactivity of solid phases to different extractant solutions. The contents of different P fractions were determined using the sequential extraction scheme suggested by Rydin (2000) (Fig. 3). The extracts were centrifuged, and the supernatants were filtrated through 0.45 μm filter membrane. SRP in each sample was determined by the molybdenum blue method. This extraction procedure divided inorganic P (IP) fractions into loosely sorbed P (NH₄Cl-P), redox-sensitive P (BD-P), Al-P (NaOH-rp), organic-P (NaOH-nrp), and calcium-bound P (HCl-P). The difference between TP and IP is the Res-P fraction, which contains organic P and refractory

P compounds. For each fraction, three replicates were performed, and all data were expressed as the average.

2 Results and discussion

2.1 Velocity distribution

Vertical velocity distributions were compared at different locations (Sites #1, #2, #3, #4). Flows in annular flume were not satisfied with log-law, which were different from classic flows. Four flows were greatly varied (Fig. 4). However, the flows at Sites #1 and #2 were more similar to the log-law than flows at Sites #3 and #4. These flows could be considered as turbulent flows. Little variation was the characteristic of vertical velocity in flows at Site #3 due to eddy current. Velocity distributions in flows at Site #4 had great variations, similar to wind-driven current.

2.2 Phosphorus forms in overlying water

Concentration changes of P forms in Sites #1 and #3 are shown in Fig. 5. The changes were similar in TP and PP.

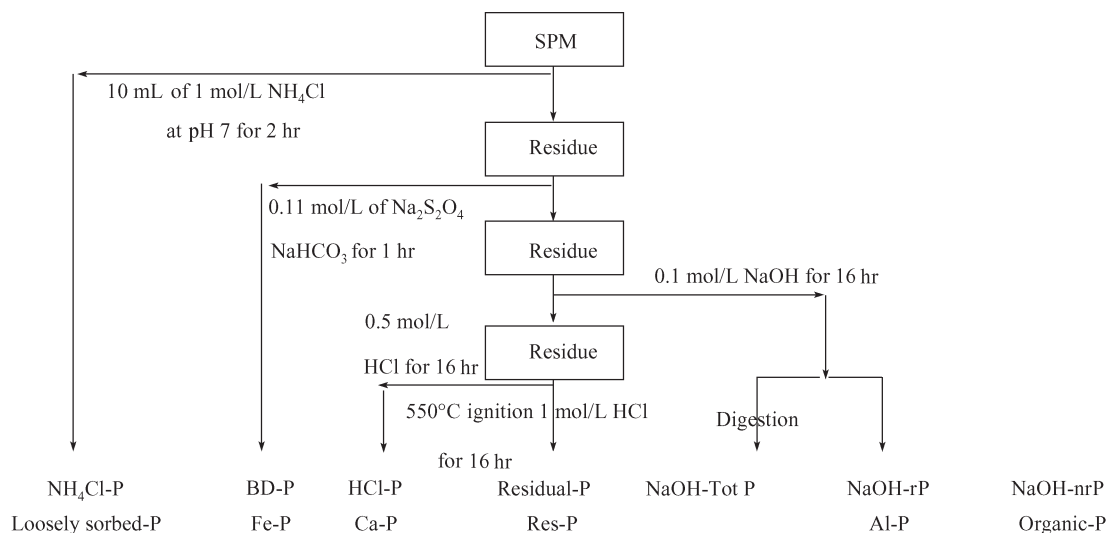


Fig. 3 Sequential extraction of SPM (suspended particulate matter).

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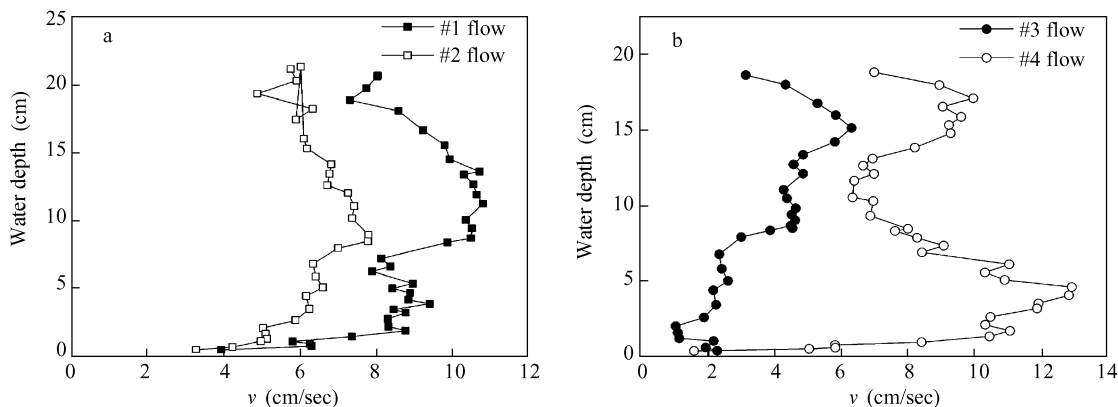


Fig. 4 Velocity distribution in Sites #1 and #2 (#1 abrupt expansion section, #2 eddy current region) (a) and Sites #3 and #4 (after abrupt expansion)(b).

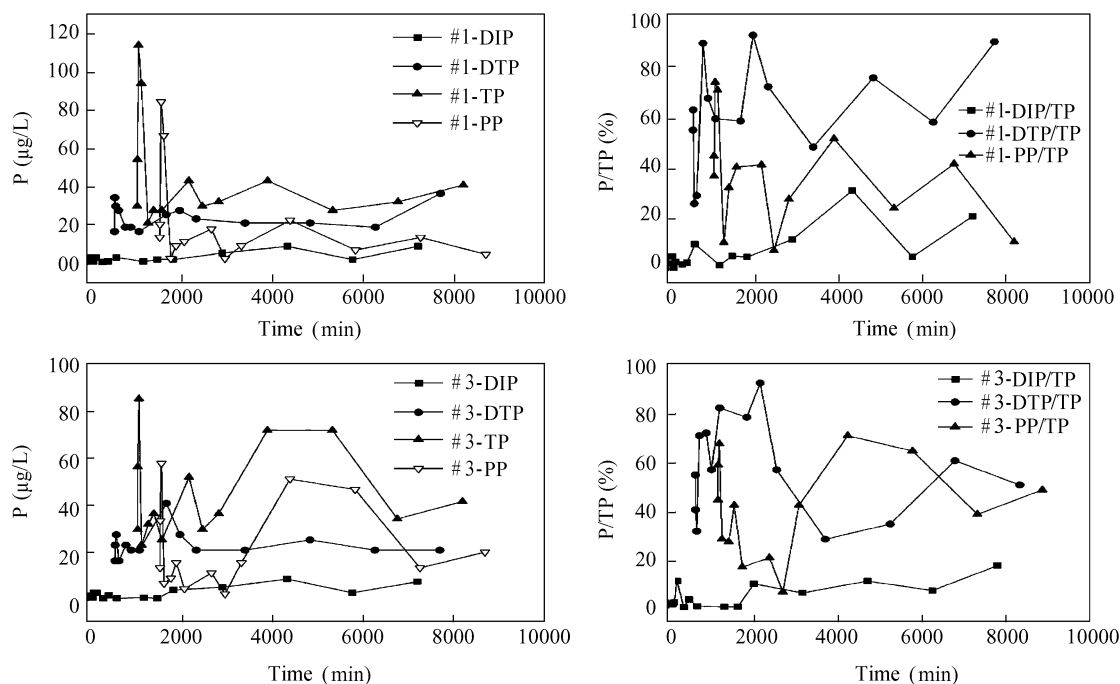


Fig. 5 Variation of different P forms in Sites #1 and #3 under the conditions of sediment resuspension.

The changes of DTP were consistent with that of DIP. DIP in Sites #1 and #3 showed slight variation from 0.7 to 8.6 $\mu\text{g/L}$, and from 0.7 to 7.4 $\mu\text{g/L}$, respectively. TP in Site #1 increased from 29.6 to 40.7 $\mu\text{g/L}$. TP in Site #3 increased from 29.6 to 41.5 $\mu\text{g/L}$. DTP in Sites #1 and #3 increased from 16.3 to 36.3 $\mu\text{g/L}$, and from 16.3 to 20.8 $\mu\text{g/L}$. PP in Site #1 decreased from 13.3 to 4.4 $\mu\text{g/L}$, while PP in Site #3 increased from 13.3 to 20.8 $\mu\text{g/L}$, which explains why PP in Site #1 was partly converted into DTP. PP in Site #3 did not exhibit this conversion. Different hydrodynamic conditions resulted in different P form changes.

To facilitate the observation and analysis (Figs. 5 and 6), each curve of the abscissa was followed by an additional 100. DTP in Site #1 had a great proportion in TP (Fig. 5b). However, DTP in Site #3 did not have a significant proportion (Fig. 5d). Changes of DIP/TP in Site #1 were not apparent to DIP/TP in Site #3, which was gradually increased.

Figure 6 shows that the concentration of TP, DTP, and PP first increased then decreased after approximately 90 min. The peak values of TP, DTP, and PP were 94, 34.1, and 84.3 $\mu\text{g/L}$ in Site #1; 91.8, 34.5, and 66.6 $\mu\text{g/L}$, in Site #2; 85.1, 27.4, and 57.7 $\mu\text{g/L}$, in Site #3; and 131.5, 34.1, and 99.7 $\mu\text{g/L}$ in Site #4. Slight changes of DIP concentration were observed. The values of DIP were approximate 3 $\mu\text{g/L}$.

The complicated P release process in overlying water was observed (Figs. 5 and 6). First, sediment was eroded to suspension due to that a flow velocity was greater than activated velocity. Concentration of P in overlying water increased due to P released by sediment. In this process, P was absorbed by overlying water. Then, all activated SPM entered into the water body. The peak value of P in overlying water was acquired when P was released by SPM. The bigger sediment particles were not suspended in the absence of a greater flow rate. Due to

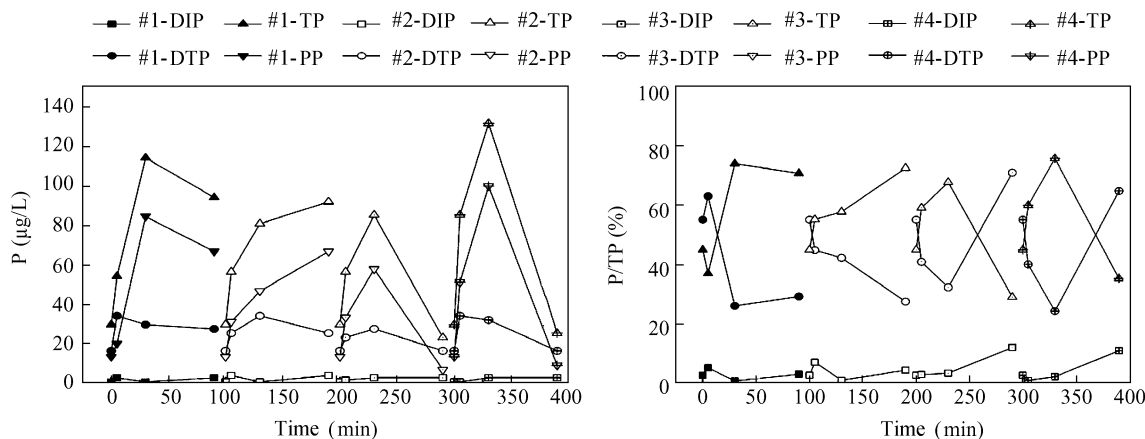


Fig. 6 Variation of different P forms in four positions within 60 min.

SPM adsorbability, concentration of P in overlying water decreased until it reached a fluctuating equilibrium through adsorption and desorption between SPM and overlying water.

In sum, four states could be ascribed as follows: (1) P desorption by sediment and SPM, and P adsorption by overlying water. (2) P desorption by SPM, and P adsorption by overlying water. (3) P adsorption by SPM, and P desorption by overlying water. (4) P equilibrium between SPM and overlying water.

Figure 7 shows changes in P forms in different flow depths after the device was started for 30 min. For Sites #1 and #3, sample P forms were in the following order: TP > PP > DTP > DIP. These P forms acquired peak values in the middle of vertical P distribution. At the bottom of the water, P release was mainly caused by sediment; on the water surface, P release was mainly caused by SPM. Nevertheless, in the middle position of the water body P release was caused by the combined actions of SPM and sediment.

After the flume system device was stopped, SPM gradually reached a static settlement. To facilitate observation and analysis (Fig. 8), each curve of the abscissa was followed by an increase of 200. At 100 min, a sharp decline in the concentration of P forms in Site #1 overlying water was found (Fig. 8). Concentrations of DIP, DTP, TP, and PP decreased from 27.4, 28.3, 76.2, and 47.9 µg/L

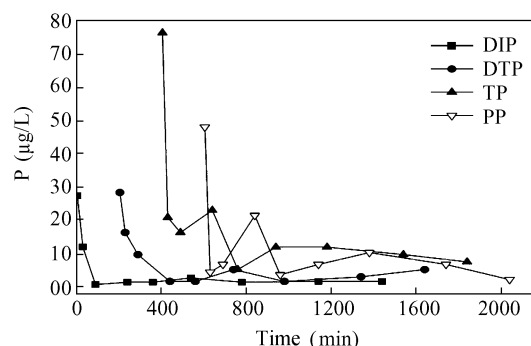


Fig. 8 Variation of different P forms in #1 position in SPM static settlement.

to 1.6, 5.2, 7.5, and 2.2 µg/L respectively. This indicates that the equilibrium concentration of P between SPM and overlying water changed with hydrodynamic conditions. The equilibrium concentration of P in the dynamic flow was bigger than that in the static flow.

2.3 Phosphorus fractions in SPM

As the sequential extraction procedures required a minimum of 0.2 g dry sample, only part of the SPM samples completed sequential extraction procedures in the experiments. SPM samples were collected by centrifuge at 2500 r/min for 10 min, dried using a cabinet dryer, and ground using a pharmaceutical mill. The content of TP in SPM was lower compared with that in sediment. The percentages of $TP_{SPM}/TP_{sediment}$ had a range of 50.04%–72.71% (Fig. 9a). The content of TP in sediment was identified with that in SPM. The increase of TP content in SPM and SS (suspension solid) was not consistent due to the flocculation precipitation reaction in SPM (Fig. 9b). Tiny particles gathered and became bigger, eventually turning into sediment. The amounts of TP in SPM in samples from Site #1 were approximated to that in samples from Site #3.

Figure 10 shows that amount of different P fractions have great variations. For the samples from Sites #1 and #3, P fractions were in the following order: BD-P > NaOH-nrp > Ca-P (HCl-P) > Al-P (NaOH-P) > Res-P > NH₄Cl-P, which differs from that in the sediment (Sun et al., 2009). In heavily polluted lakes, the rank order is Al-P > Ca-P

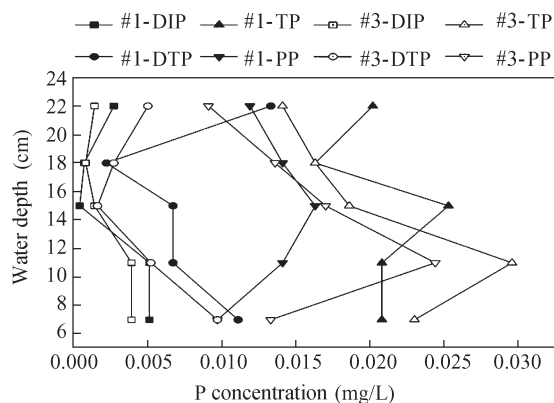


Fig. 7 Variation of different P forms under different water depth at 30 min.

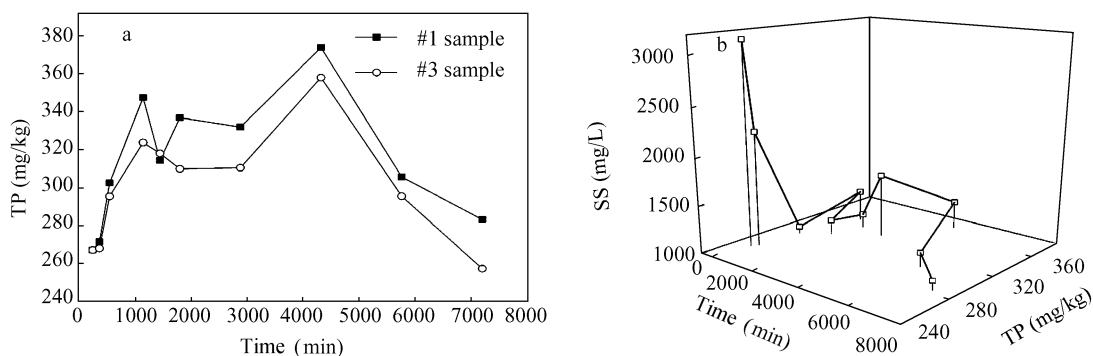


Fig. 9 Comparison of variation of TP between #1 and #3 position (a) and correlation between TP and SS (suspension solid) at #1 position (b).

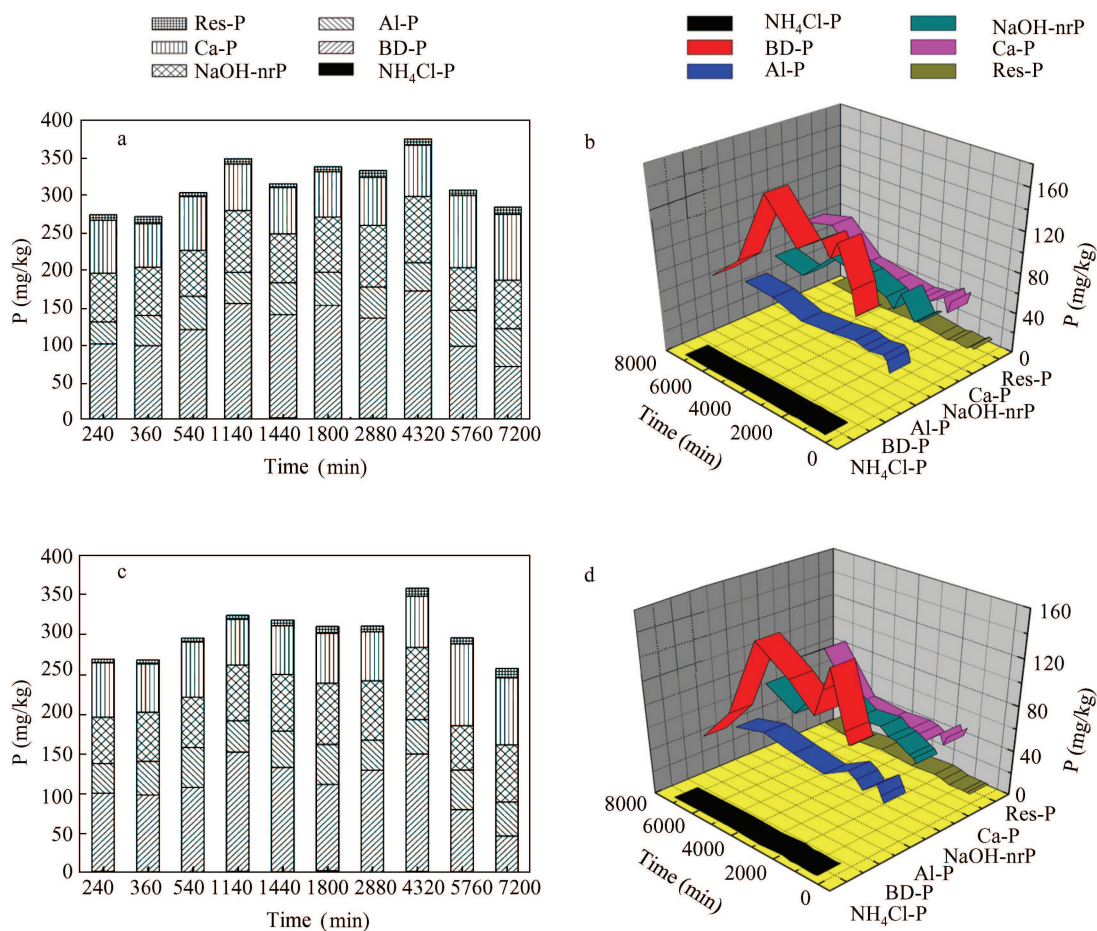


Fig. 10 Different P fractions (a, c) and variation of different P fractions (b, d) at #1 and #3 positions of SPM, respectively.

(Lijkema et al., 1993). However, it is in the opposite order (Ca-P > Al-P) in mesotrophic lakes (Kaiserli et al., 2002). The rank order of the P fraction implies that Gonghu Lake may be mesotrophic.

The amounts of NH₄Cl-P in SPM were the lowest among the six P fractions, consistent with that in the sediment results (Rydin, 2000), and ranged from 1.37 to 3.62 mg/kg. The content of NH₄Cl-P did not have significant positive correlation to the content of TP.

The BD-P represents the redox-sensitive P fraction, mainly including P bound to Fe-hydroxides and Mn compounds (Kleeberg and Gruenberg, 2005). This fraction is considered as a potentially mobile pool of P (Rydin,

2000). The BD-P amounts in SPM ranged from 69.4 to 152.94 mg/kg. BD-P was the most active in SPM due to great variations (Figs. 10b, d), and also had the highest proportion of TP concentration. The content of BD-P first increased, and then decreased after short period. This change coincided with the change of TP in SPM and overlying water. BD-P in SPM frequently exchanged with P forms in overlying water.

The change of Al-P content in SPM was the lowest among the six P fractions (from 37.9 to 50.35 mg/kg). This indicates that Al-P was not much affected by the change in hydrodynamic condition. NaOH-nrP is considered as exchangeable P. NaOH-nrP was used to estimate available

P in the sediment, and as an indicator of algal available P (Zhou et al., 2001). In the experiments, the content of NaOH-nrP ranged from 56.97 to 90.5 mg/kg. Exchange action was observed, and NaOH-nrP in SPM could be converted into the other P fractions. The change in NaOH-nrP was opposite to the change of BD-P. Therefore, partial NaOH-nrP was converted into BD-P.

Ca-P represented the P fraction sensitive to low pH, and was deemed a relatively stable fraction (Kaiserli et al., 2002). However, in the experiments, the Ca-P content in SPM ranged from 61.2 to 102.1 mg/kg, and gradually increased. The change of Ca-P was assumed to be related to the resuspension condition. Partial Ca-P may be released into SPM from sediment, and resuspension was favorable to the formation of Ca-P in SPM.

Res-P is considered a hard-release P. The content of Res-P ranged from 4.7 to 9.04 mg/kg. This could be neglected due to its scant contribution to P forms in the overlying water.

3 Conclusions

The changes had similarities in the TP and PP of overlying water. PP in turbulent flow (Site #1) was partly converted into DTP. PP in eddy current (Site #3) did not exhibit this conversion. Different hydraulic conditions resulted in different P form changes.

According to resuspension experiments, four states could be ascribed: (1) P desorption by sediment and SPM, and P adsorption by overlying water; (2) P desorption by SPM, and P adsorption by overlying water; (3) P adsorption by SPM, and P desorption by overlying water; and (4) P equilibrium between SPM and overlying water. The content of P in overlying water acquired peak values in the middle position of the vertical P distribution due to the combined action of SPM and sediment. The equilibrium concentration of P in dynamic flow was bigger than that in static flow.

The percentages of $T_{\text{SPM}}/T_{\text{sediment}}$ ranged from 50.04% to 72.71% in the experiments. For samples from Sites #1 and #3, the P fractions were in the following order: BD-P > NaOH-nrP > Ca-P > Al-P > Res-P > $\text{NH}_4\text{Cl-P}$.

The contribution of $\text{NH}_4\text{Cl-P}$ to P in overlying water was not observed due to its lowest content. BD-P in SPM was frequently exchanged with P forms in overlying water. Al-P was not much affected by the change of hydraulic condition. Partial NaOH-nrP was converted into BD-P. Resuspension was favorable for forming Ca-P in SPM.

Acknowledgments

This work was supported by the National Basic Research Program (973) of China (No. 2008CB418203).

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