

# Impact of aeration disturbances on endogenous phosphorus fractions and their algae growth potential from malodorous river sediment

Jin Zhu<sup>1</sup> · Yan He<sup>1</sup> · Jianhua Wang<sup>1</sup> · Zhaochao Qiao<sup>1</sup> · Yi Wang<sup>1</sup> · Zhihong Li<sup>1</sup> · Minsheng Huang<sup>1</sup>

Received: 19 April 2016 / Accepted: 16 January 2017 / Published online: 30 January 2017  
© Springer-Verlag Berlin Heidelberg 2017

**Abstract** The present work assessed the impact of aeration disturbances on sediment-bound phosphorus fractions and their algae growth potential from a typical malodorous river. Phosphorus was sequentially extracted by a modified version of Hedley fractionation method. It was found that the mean contents of TP was  $1476.1 \pm 60.3$  mg/kg, consisting mainly of dilute HCl-extractable P (52.6%) and NaOH-P (19.2%). The algae growth potential tests demonstrated that algae growth had varied P-level requirements for different P speciation and NaOH-P promoted algae growth remarkably and its promoting effect was positively related to its concentration. Additionally, intermittent

overlying water aeration modes were recommended, and run 1 (7.0 mg/L, 12 h) was deemed as the optimized aerated mode in terms of its relatively low ecological risk and high P retention. It was noted that NaOH-P was most affected by aeration disturbance and exhibited marked increase with the elevated dissolved oxygen (DO) level whether for intermittent overlying water or sediment aeration. This research helps to gain improved understanding of the ecological risk on sediment P, and NaOH-P is recognized as one ecologically important P fraction in the sediments considering its relatively high proportion and bioavailability.

**Keywords** Endogenous phosphorus · Fractionation · Algae growth potential · Aeration disturbances · NaOH-P · Malodorous river sediment

Responsible editor: Vitor Manuel Oliveira Vasconcelos

✉ Yan He  
yhe@des.ecnu.edu.cn

Jin Zhu  
zhujin90s@126.com

Jianhua Wang  
18801737840@163.com

Zhaochao Qiao  
675264908@qq.com

Yi Wang  
1037873102@qq.com

Zhihong Li  
ecnulzh@163.com

Minsheng Huang  
abcecnu@126.com

<sup>1</sup> Shanghai Key Laboratory for Urban Ecological Processes and Eco-Restoration, School of Ecological and Environmental Sciences, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China

## Introduction

Phosphorus (P) has long been considered as an essential nutrient limiting the primary production for aquatic ecology (Rydin 2000; Jiang et al. 2006; Jin et al. 2006; Katsaounos et al. 2007; Zhu et al. 2013; Tang et al. 2014). Eutrophication is driven by anthropogenic P inputs from phosphorus fertilization practices in agricultural areas and discharges from urban wastewater treatment plants (Martins et al. 2014). Sediments of malodorous river act as a sink of intense anthropogenic P inputs and thus will become a major source of phosphorus after the effective interception of pollutants discharged into the river systems (He et al. 2013; Cao et al. 2015a). Although sulfur is widely recognized as the crucial element directly related to the “malodor” of rivers, the phosphorus control has become a big challenge even after malodor is effectively reduced. It is well recognized that phosphorus release from the sediments can exert a significant impact on the quality of overlying water and accelerate the eutrophication (Wang et al. 2006a; Katsaounos et al. 2007; Gao et al. 2015).

A striking phenomenon associated with eutrophication is algal blooms. Algae growth potential (AGP) can be considered excellent indicators of eutrophication risk. However, P in sediments exists in many complex chemical forms, which differ markedly in their behavior, mobility, and bioavailability. And not all the forms of P can be utilized by algae growth. Knowledge about the quantity and characteristics of P as well as the availability of P fractions are of high importance for the prediction of P behavior and the estimation of the potential risk of eutrophication.

Previous related studies are mainly centered on the distribution of different P forms in lake or wetland sediment (Rydin 2000; Jin et al. 2006; Wang et al. 2006b; Zhang et al. 2007; Zan et al. 2011; Leote et al. 2014; Gao et al. 2015), and little information is available regarding the bioavailability of P fractions especially for the intensely anthropogenic perturbed malodorous river sediments.

As one of the most effective technologies in treating malodorous rivers, artificial aeration can regulate resuspension of sediments and anaerobic-anoxic-oxic distribution, which are critical for phosphorus fate at sediment-water interface (Lu et al. 2010; He et al. 2013). Some related investigations have been conducted mainly focusing on the effects of aeration on different P fractions without considering the availability of each P fraction to algae growth (Lin et al. 2005; Peng et al. 2004; Sun et al. 2012), and most of these studies were done in a monotonous aeration mode and failed to allow a more precise description of P dynamics in response to various aeration (Li and Huang 2012; Wang and Li 2014).

The objectives of this study were (1) to investigate concentrations and proportions of P forms in the malodorous river sediments by a modified Hedley fractionation scheme, (2) differentiate various phosphorus fractions for their potential as nutrients for algae growth, and (3) establish general differences in P forms influenced by aeration disturbances.

## Materials and methods

### Sediment sampling

All samples in this study were collected from a typical malodorous river Gongye, a small broken-ends streamlet with a length of 864 m and depth of 1–2 m, located in Taopu Town of Shanghai, in which the water quality was worse than the Class V of National Surface Water Quality Standard.

Surface sediments (0–5 cm) were sampled using a prismatic sampler from the river in May 2014. All the sediment samples were taken to the laboratory in air-sealed plastic bags and stored at 4 °C. The main physicochemical properties of sediments are as follows: pH, 7.92; total phosphorus (TP), 1.49 g/kg; and moisture content, 87.23%.

### Phosphorus fractionation

P fractions in the sediments were analyzed using a modified Hedley fractionation method (Tiessen and Moir 1993; Fu and Zhou 1999; Wang et al. 2006a; He et al. 2008; Qu et al. 2012). The sediment-derived phosphorus was sequentially extracted and classified into six fractions including resin-P,  $\text{NaHCO}_3$ -P,  $\text{NaOH}$ -P, dilute HCl-extractable P (D.HCl-P), concentrated HCl-extractable P (C.HCl-P), and residual-P, respectively.

Resin-P was considered as the most labile and freely exchangeable inorganic phosphorus.  $\text{NaHCO}_3$ -P represented inorganic and organic P forms which loosely sorbed on the surfaces of Fe and Al oxides as well as some microbial P.  $\text{NaOH}$ -P included secondary inorganic phosphorus bound to Fe and Al compounds and organic phosphorus associated with fulvic and humic acids (Wang et al. 2006b). D.HCl-P was deemed as inorganic P associated with Ca. C.HCl-P represented very stable residual inorganic P. Residual-P was occluded phosphorus in the residue.

### Algal source and inoculation

The strains of *Chlorella* were obtained from freshwater algal species pool, wildlife species quality library, Chinese Academy of Sciences. *Chlorella* was precultured with sterilized selenite enrichment (SE) medium for a week (Ni et al. 2015). Subsequently, algal samples were washed with 15 mg/L of  $\text{NaHCO}_3$  after centrifugation at 5000 rpm. Algae were diluted with sterile water and prepared for inoculation.

### Determination of algae growth potential of different P fractions

In order to examine various phosphorous fractions for their potential as nutrients for the cultivation of algae, the algae growth profiles with each P fraction of 0.05 mg/L and the algal kinetic growth characteristics under different P fraction concentrations (0.02, 0.05, 0.10, and 0.20 mg/L) were investigated. A 100 mL volume of the modified SE medium was put into 250-mL flasks and inoculated with algae. Immediately after this, algae were separately exposed to different P fractions, control 1 (pure water), and control 2 (the diluted river water of 0.20 mg/L TP, for the TP level is the legislative threshold of Class V of National Surface Water Quality Standard). A ratio of nitrogen to phosphorus (N/P > 80:1) was controlled to maximize the function of P as the limiting nutrient contributing to algae bloom (Feng et al. 2008a), and  $\text{NaNO}_3$  was added as an additional nitrogen source (Yu and Wang 2005; Vidal et al. 2015). The cultivation was carried out at 26 °C and pH 7–7.5 with a light intensity of 2000 lx on a 14:10 h (light/dark) light cycle.

Residual-P was not involved in the AGP assays, in view that it was recognized as occluded P with no bioavailability by many researchers (Wang et al. 2006b; Qu et al. 2012; Wang et al. 2015)

as well as only a minimal portion among the extracted P speciation. In addition, resin-P was replaced with  $K_2HPO_4$  in the cultivation, considering that resin-P was defined as freely exchangeable inorganic P (Zhang et al. 2009) and its content in the extraction was very low.

Algal samples were taken from the culture media every day for measurement of absorbance as the indicator of biomass for algae (Wang et al. 2010; Jena et al. 2011). Algae growth curve was plotted based on the absorbance. The average specific growth rate ( $\mu$ ) was calculated by fitting the absorbance to an exponential function (Chen et al. 2011; Bährs and Steinberg 2012; Cao et al. 2015b):

$$\mu = \frac{\ln(X_{t_2} - X_{t_1})}{t_2 - t_1}$$

where  $X_t$  = absorbance at time  $t$ ,  $t_1$  = the start of the experiment, and  $t_2$  = the end of the experiment.

The Monod equation was applied to characterize the algae growth potential with different P fractions (Feng et al. 2011),

$$\mu = \mu_{\max} \frac{S}{K_s + S}$$

where  $\mu_{\max}$  = the maximum growth rate for algae,  $S$  = the limiting substrate concentration for algal proliferation, and  $K_s$  = the constant that characterizes the effectiveness of substrate to algae growth.  $\mu_{\max}$  and  $K_s$  are two key kinetic parameters derived from this model that quantify algae growth responses to different P fractions.

### Aeration experimental setup

Experiments were performed in homemade organic glass reactors with dimensions 0.14 m long, 1 m high, and a volume of 15.39 L. The bottom of the reactors was laid sand and fresh sediments with the thickness of 0.05 and 0.30 m, respectively. Additionally, the overlying water from the river was siphoned into the reactors to avoid disturbance to the sediments as much as possible. The outer flank of the column reactor was covered with a gabo in order to prevent light penetration. The microporous aerators were positioned 0.02 m above the water-sediment

interface for overlying water-aerated modes and 0.02 m below the interface for sediment-aerated modes, respectively.

All the aeration experiments were operated at ambient temperature, and the operational conditions throughout the study are shown in Table 1. Runs 1, 2, 3, and 4 and runs 5, 6, 7, and 8 separately represented the overlying water-aerated and sediment-aerated modes, whereas run 0 was unaerated condition and acted as the control. Runs 1, 2, 3, 5, 6, and 7 were operating intermittently (12 h), while runs 4 and 8 were continuously (24 h) operated. The time-controlling switches and the glass rotor flow meters were used to control aeration time and flow. Dissolved oxygen in the overlying water was measured by dissolved oxygen (DO) meter. Enough time was allowed to achieve a stable operation at each run. The variation rates of each P fractions were defined as  $VR = \frac{C_t - C_i}{C_i} \times 100\%$ , where VR is the variation rates of P fractions and  $C_t$  and  $C_i$  are the contents of each P fraction at time  $t$  and the initial stage, respectively.

Additionally, velocity gradient value ( $G$ ) was used to characterize fluid turbulence and is shown in Table 1. To be more specific, the difference in velocity between adjacent layers of the fluid is known as a velocity gradient and is given by the ratio of the velocity difference to the distance between the fluid layers. A greater  $G$  is often referred to as stronger disturbance.  $G$  is calculated as  $G = \sqrt{\frac{P}{\mu V}}$  where  $G$  = velocity gradient value,  $P$  = power consumption of fluid flow,  $\mu$  = kinetic viscosity, and  $V$  = fluid volume.

### Statistical analysis

Each of the measured parameters was used for statistical analysis via ANOVA, and the results in this study are expressed as means  $\pm$  standard deviation. The precision for all analysis was within 5% by relative standard deviation of duplicates by repeated measurements.

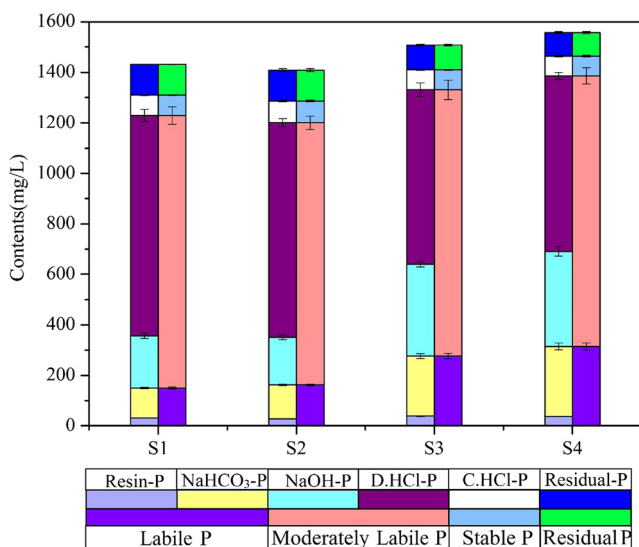
## Results and discussion

### Characteristics of malodorous river sediment-derived P fractions

Figure 1 demonstrates the averaged levels of different P speciation from the malodorous river sediments. Each value is the mean

**Table 1** Operation conditions for overlying water and sediment aerations in this study (average value)

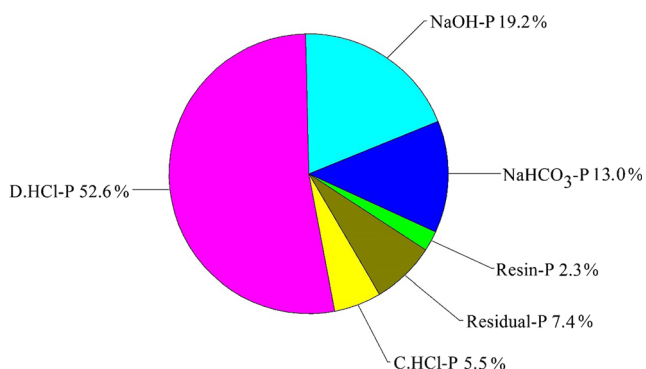
	Control	Overlying water aerations				Sediment aerations			
Run	0	1	2	3	4	5	6	7	8
Time (h)	0	12.0	12.0	12.0	24.0	12.0	12.0	12.0	24.0
DO (mg/L)	0.2	7.00	1.00	4.00	4.00	–	–	–	–
Flow (L/min)	–	–	–	–	–	1.10	2.10	0.10	1.10
$G$ ( $s^{-1}$ )	0	218.08	120.55	192.33	218.08	427.06	592.91	354.33	427.06



**Fig. 1** Distribution of different P fractions in four sediment samples. Error bars represent average  $\pm$  SD

of four randomly selected sediment samples, and there are no significant differences among four samples in P fraction distribution ( $P > 0.01$ ). The mean contents of TP for the four sediment samples was  $1476.1 \pm 60.3$  mg/kg, whereas resin-P,  $\text{NaHCO}_3\text{-P}$ ,  $\text{NaOH-P}$ ,  $\text{D.HCl-P}$ ,  $\text{C.HCl-P}$ , and residual-P was  $34.4 \pm 1.4$ ,  $191.6 \pm 5.2$ ,  $283.6 \pm 8.2$ ,  $777.0 \pm 12.5$ ,  $80.7 \pm 2.4$ , and  $108.8 \pm 4.3$  mg/kg, respectively. Accordingly, their respective proportions in TP are 2.3, 13.0, 19.2, 52.6, 5.5, and 7.4% (Fig. 2). The P speciation distribution in the sediments was ranked as follows:  $\text{D.HCl-P} > \text{NaOH-P} > \text{NaHCO}_3\text{-P} > \text{residual-P} > \text{C.HCl-P} > \text{resin-P}$  and moderately labile P > labile P > residual P > stable P.

Knowledge of total P concentration is not always adequate to assess the risk associated with its presence in natural waters. The distribution of P species in sediments is drawing more attention. In the literature, fairly similar observations are found concerning distribution characteristics of freshwater sediment P speciation. Zan et al. (2011) found that  $\text{HCl-P}$  dominated among the extracted sediment P fractions from Lake Chaohu, while Zhang’s (2007) work demonstrated that  $\text{NaOH-P}$  and  $\text{D.HCl-P}$  were the main



**Fig. 2** The average percentage of different P fractions in TP of the sediments

fractions in sediment-derived P speciation of Lake Taihu. Wang’s (2008) experiments indicated that dilute  $\text{HCl}$ -extractable inorganic P was the predominant form in wetland sediment-bound P fractions. Our research showed that moderately labile P including  $\text{D.HCl-P}$  and  $\text{NaOH-P}$  predominated in the sediment-derived P from a malodorous river Gongye, which could be crucial in regulating endogenous P behaviors.

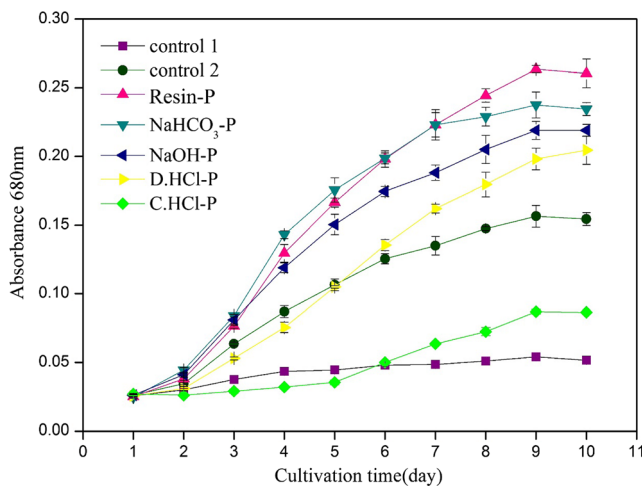
$\text{D.HCl-P}$  is defined as apatite or Ca-bound P and mainly represents the co-precipitation of phosphate with Ca. This P speciation is dominant in the calcareous sediment-derived P, and a neutral or alkaline environment (pH 7–8) favored its formation.  $\text{NaOH-P}$  is deemed as P associated with Fe and Al through physical and chemical adsorption to the surface of Fe and Al oxides, hydroxides, as well as humic compounds (Norton et al. 2008; Jan et al. 2013). The sediment from river Gongye was relatively abundant in Fe, Ca, and humic substances, and phosphate was more labile to be bound with them and act as sink of P. The alkaline condition (pH 7.6–8.2) also promotes the formation of  $\text{D.HCl-P}$  and  $\text{NaOH-P}$ . These geochemical backgrounds could explain the predominated role of  $\text{D.HCl-P}$  and  $\text{NaOH-P}$  in the sediment-associated P fractions. Additionally, the reason for this speciation profiles is also related to the sources of P or the anerobic/anoxic P release mechanisms occurring in the sediment as a function of the redox conditions.

It should be noted that the TP level (Fig. 1) in the sediment was about twofold greater than the critical level of 0.6 mg/g for polluted sediments described by Katsaounos et al. (2007), which indicated that the river was intensely disturbed by human activities and heavily contaminated. Additionally,  $\text{NaOH-P}$  was sensitive to redox conditions of the sediment-water interface and easily causes release from sediment to overlying water under anoxic environment (Zan et al. 2011). However, little information was available to differentiate the contributions of  $\text{NaOH-P}$  and other P forms to algal bloom.

### Kinetic analysis of algae growth

In order to gain improved understanding of the ecological risk of sediment-derived P, the comparisons of algae growth potential were done among different P forms in the sediments. The profiles of algae growth exposed to different P speciation are shown in Fig. 3. No lag phases were presented in the growth curves for resin-P,  $\text{NaHCO}_3\text{-P}$ , and  $\text{NaOH-P}$ , which illustrated that algae could adapt themselves well to these three P fractions as nutrients. Similar growth patterns were observed for resin-P,  $\text{NaHCO}_3\text{-P}$ , and  $\text{NaOH-P}$ , with exponential phases in the initial 9 days followed by stationary phases. The average specific growth rates ( $\mu$ ) in the exponential phases were 0.335, 0.318, and  $0.242 \text{ day}^{-1}$  for resin-P,  $\text{NaHCO}_3\text{-P}$ , and  $\text{NaOH-P}$ , respectively.

Comparatively, algae growth was minimal or relatively slow for control 1 and  $\text{C.HCl-P}$  ( $\mu 0.056 \text{ day}^{-1}$ ), which is far below the growth from control 2 ( $\mu 0.104 \text{ day}^{-1}$ ). Additionally, a lag phase was observed in the initial 5 days and then an exponential phase



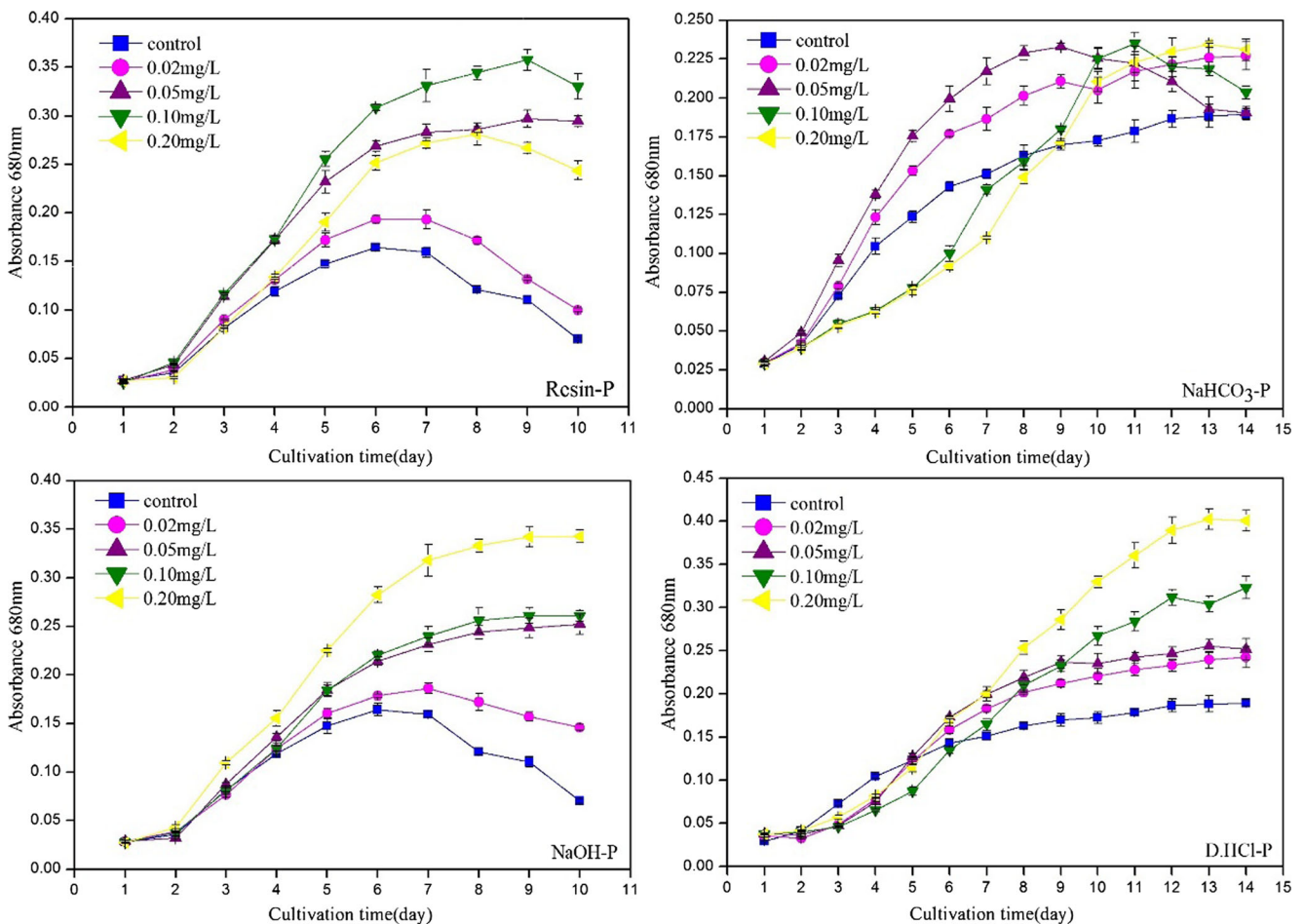
**Fig. 3** Profiles of algae growth with different P form at 0.05 mg/L. Pure water (*control 1*); diluted river water (*control 2*). Error bars represent average  $\pm$  SD

followed by a stationary phase in the growth pattern for C.HCl-P. Different from resin-P, NaHCO<sub>3</sub>-P, and NaOH-P, the algae growth was slower than that of control 2 initially and then increased sharply close to that of NaOH-P. The average specific

growth rate ( $\mu$ ) for D.HCl-P was 0.145 day<sup>-1</sup>, which was obviously higher than that of control 2 and C.HCl-P ( $P < 0.05$ ).

To further differentiate the sediment P pool and allow a more precise description of the potential for P bioavailability, different contents of P fractions (resin-P, NaHCO<sub>3</sub>-P, NaOH-P, D.HCl-P) were correlated with algae growth potential (Fig. 4). C.HCl-P was ignored in this test due to its unavailability for algae. Algae growth was evidently promoted with the increased contents of resin-P from 0.02 to 0.10 mg/L and then decreased with resin-P of 0.20 mg/L. Similarly, algae growth for NaHCO<sub>3</sub>-P was not positively related to the increased concentration, and 0.05 mg/L was deemed as the relatively optimal level. On the contrary, algae growth for NaOH-P and D.HCl-P exhibited a gradual increased tendency within the contents from 0.02 to 0.20 mg/L. These results indicated that algae growth had varied P-level requirements for different P speciation, which confirmed the necessity to differentiate the sediment P pool.

The Monod equation was applied to provide more valuable information for the kinetic algae growth of different P forms. Based on the non-linear least squares method, the kinetic parameters for different P fractions were estimated (Table 2).  $K_s$  in the Monod equation is often referred to as the affinity constant of



**Fig. 4** Comparisons of algae growth with varied P levels (0, 0.02, 0.05, 0.10, and 0.20 mg/L) of different P fractions (*Resin-P*, *NaHCO<sub>3</sub>-P*, *NaOH-P*, and *D.HCl-P*). Error bars represent average  $\pm$  SD

**Table 2** Characteristic parameters of the algae growth with different P fractions

P fractions	Monod equation	$\mu_{\max}$ (day <sup>-1</sup> )	$K_s$ (mg/L)	$R^2$
Resin-P	$\mu = 0.343c/(c + 0.0007)$	0.343	0.0007	0.993
NaHCO <sub>3</sub> -P	$\mu = 0.205c/(c + 0.0004)$	0.205	0.0004	0.999
NaOH-P	$\mu = 0.299c/(c + 0.014)$	0.299	0.0140	0.997
D.HCl-P	$\mu = 0.190c/(c + 0.0111)$	0.190	0.0111	0.996

The maximum specific growth rate ( $\mu_{\max}$ ) and the half saturation constant ( $K_s$ ) for each P fraction were calculated according to the Monod model

substrate. In contrast, the half saturation constants ( $K_s$ ) were lower for algae growing on resin-P (0.0007) and NaHCO<sub>3</sub>-P (0.0009) and were two order of magnitude higher for algae growth on NaOH-P (0.0140) and D.HCl-P (0.0111), suggesting a higher affinity of algae for resin-P and NaHCO<sub>3</sub>-P. Additionally, the algae also exhibited comparable maximum specific growth rates (0.343 or 0.205 day<sup>-1</sup>), when supplied resin-P or NaHCO<sub>3</sub>-P as a sole source of P. It was thus concluded that resin-P and NaHCO<sub>3</sub>-P were highly available to algae, which was consistent with the studies of Fan et al. (2014) and Xie et al. (2010).

It was worth noting that NaOH-P exhibited a high maximum specific growth rate of algae ( $\mu_{\max}$  0.299 day<sup>-1</sup>) despite its relatively low half saturation constant. As for D.HCl-P, both growth kinetic parameters ( $K_s$  and  $\mu_{\max}$ ) showed that it was of relatively low availability for algae, which supported the results of previous studies by Peng et al. (2007) and Tang et al. (2014). Hence, D.HCl-P was deemed as potential P source for algae. To sum up, availability of different P speciation for algae was ranked according to the order resin-P > NaHCO<sub>3</sub>-P > NaOH-P > D.HCl-P.

Phosphorus with high bioavailability was recognized to stimulate algae growth significantly within short time (Cross and Schlesinger 1995). Resin-P and NaHCO<sub>3</sub>-P could be grouped into highly bioavailable P and might act as an important role in initiating algae growth despite their relatively low percentage among the six fractions (2.3 and 13.0% for resin-P and NaHCO<sub>3</sub>-P, respectively). Although D.HCl-P was regarded as potential bioavailable P source for algae, it was likely available to algae during bloom maintenance when resin-P and NaHCO<sub>3</sub>-P were exhausted. Hence, the contribution of D.HCl-P to algae bloom cannot be neglected especially in the context of its largest proportion (52.6%) among the sediment-associated P fractions.

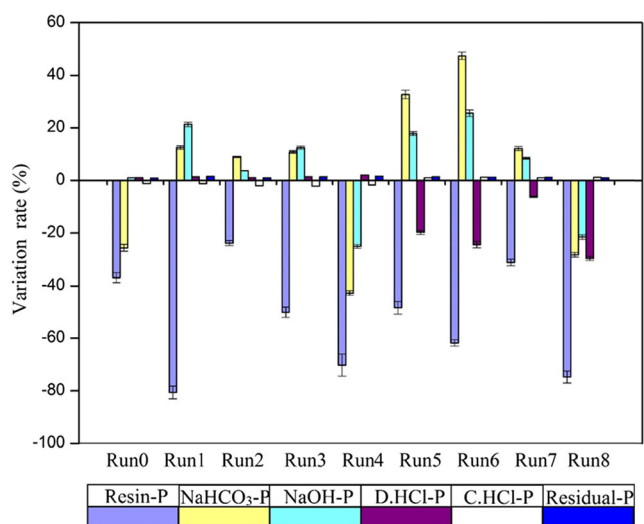
Importantly, as a secondly largest P speciation among all the extracted P forms, NaOH-P promoted algae growth remarkably and its promoting effect was positively related to its concentration. Similar results had been reported that NaOH-P was available for algae in a short time and a significant contributor to algae bloom (Jiang et al. 2006; Jin et al. 2013). Taken together, NaOH-

P was a crucial P fraction in the sediments due to its relatively high proportion and bioavailability.

**Variations of P fractions with different aeration disturbances**

To elucidate how different P fractions respond to aeration disturbances, variations of P fractions with different aeration disturbances including overlying water-aerated and sediment-aerated modes were investigated in this study. As shown in Table 1, stronger aeration turbulence was presented for sediment-aerated than overlying water-aerated conditions ( $G$  from 354.33 to 592.91 s<sup>-1</sup> and 120.55 to 218.08 s<sup>-1</sup> correspondingly). Figure 5 illustrates the variation rates of different sediment-derived P speciation with different aeration modes. Each column is the mean of the steady operation for each condition. As for run 0, resin-P and NaHCO<sub>3</sub>-P presented release tendency with the corresponding variation rates of -36.90 and -25.60%, while the other P forms altered little. This observation was mainly due to resin-P and NaHCO<sub>3</sub>-P as labile fractions prone to release from the sediments in anoxic environment (Tiessen and Moir 1993; Qu et al. 2012).

By comparison of overlying water-aerated conditions (runs 1, 2, 3), NaOH-P exhibited a marked increase (VR from 3.62 to 21.30%) with the elevated level of aeration disturbances ( $G$  from 120.55 to 218.08 s<sup>-1</sup>). One exception was observed that NaOH-P was reduced by 25.1% with DO of 4 mg/L and continuous aeration of 24 h (run 4), which is mainly due to relatively high and constant aeration disturbance provoking more transformation and release of the strongly bound chemisorbed P. Although the variation of NaHCO<sub>3</sub>-P was similar to that of NaOH-P, its fluctuation was smaller (VR from 8.87 to 12.54%). Notably, for all the overlying water-aerated conditions, resin-P was markedly reduced up to 80.6% and the variation rates were positively related to the DO level and aeration time. However, the



**Fig. 5** Variation rates of P fractions with different aerated conditions. Error bars represent average  $\pm$  SD

fluctuations of D.HCl-P, C.HCl-P, and residual-P were within a narrow range and could be ignored.

As for sediment-aerated conditions (runs 5, 6, 7), NaHCO<sub>3</sub>-P and NaOH-P presented obvious increase (maximum VR 47.40 and 25.70%, respectively) with the enhanced aeration turbulence ( $G$  from 354.33 to 592.91 s<sup>-1</sup>), whereas resin-P was cut down significantly (maximum VR -61.8%). Different from those of overlying water aerations, D.HCl-P was reduced for all the sediment-aerated modes. The variations of C.HCl-P and residual-P could still be neglected. Specifically, for the continuous sediment aeration (run 8), a large pool of P fractions, i.e., resin-P, NaHCO<sub>3</sub>-P, NaOH-P, and D.HCl-P, decreased drastically with the corresponding variation rates of -74.80, -28.30, -21.54, and -29.64%. The observation further showed that continuous aeration could promote the release of sediment-derived P, which corresponded to the increase of TP in overlying water.

In order to further evaluate the behavior of sediment-derived P, the total P differences were compared before and after aeration for each run (Fig. 6). As shown in Fig. 6, the contents of TP in the sediment decreased notably at run 4 and run 8, indicating that continuous aeration modes were adverse to controlling sediment P release. Additionally, it was observed that the levels of TP in the sediment increased for intermittent overlying water aeration, whereas the TP variations of the sediment could be ignored for intermittent sediment aeration. This observation showed a clear transformation of D.HCl-P to highly bioavailable NaHCO<sub>3</sub>-P and NaOH-P occurred for intermittent sediment aerations and thus increased the ecological risk of algal bloom. Taken together, intermittent overlying water aeration modes were recommended, and run 1 (7.0 mg/L, 12 h) was regarded as the relatively optimized aeration condition in terms of its relatively low ecological risk and high P retention.

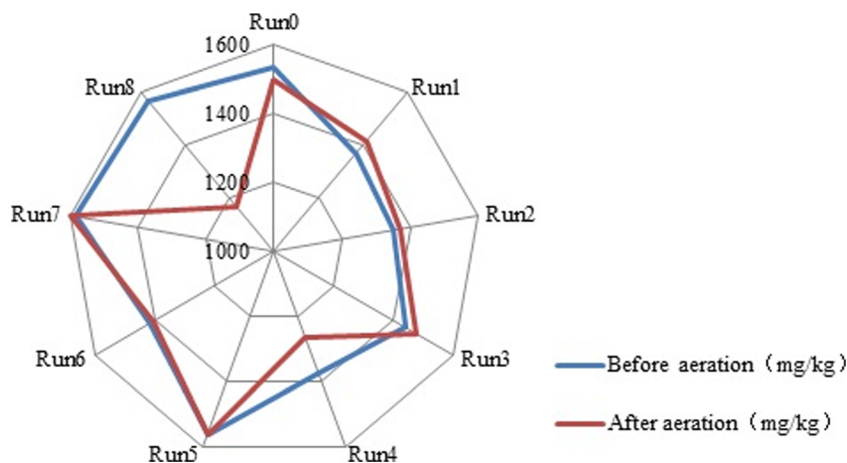
The behavior of sediment-bound P is involved in an integration of complicated physical, chemical, and biological processes. As an important river in situ remediation technology, artificial aeration has dual effects on the endogenous P behavior. On one side, oxygenation via aeration facilitates

transformation of different P forms. For example, increasing DO level promotes more production of NaOH-P and NaHCO<sub>3</sub>-P, and thus alters the fate and bioavailability of sediment-associated P; on the other side, disturbance via aeration can provoke resuspension of sediments in localized environments and thus facilitate release of endogenous phosphorus. Additionally, aeration disturbance can increase the depth of DO penetration and then manipulate the P transformation pathway.

Some studies have been conducted to explore the effects of aeration on the endogenous P behavior. Li et al.'s (2007) work indicates that phosphorus adsorption by sediments can be promoted greatly by aerating to the sediments rather than to the overlying water. Our research shows that overlying water-aerated modes were better than sediment aerations in terms of its low risk of P release and relatively high P retention. This disparity can be mainly attributed to the difference in aeration modes as well as their disregard for the differences of bioavailability among P forms. For example, the transformation of P to more bioavailable forms, e.g., NaHCO<sub>3</sub>-P and NaOH, will promote algal bloom potential for intermittent sediment-aerated modes. Hence, it is necessary to differentiate the sediment P pool for assessing the risk associated with its presence in natural waters.

Additionally, our research supports the results of previous studies in which high DO level is helpful for controlling endogenous P release from the sediments (Feng et al. 2008b; Li and Huang 2013). The phenomenon indicates that high-level DO in the overlying water is essential to control the P release from sediments. Specifically, among the six fractions, NaOH-P is most affected by aeration disturbance and increases markedly with the increased DO level whether for the intermittent overlying water or sediment aerations. One explanation is that increased DO concentrations will stimulate transformation of Fe<sup>2+</sup> into Fe<sup>3+</sup>, and Fe<sup>3+</sup> can bind with phosphate to form Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> precipitating to the sediments. Moreover, dissolved P in the overlying water can be absorbed by oxides and hydroxides of Fe and Al in the sediments to further form Fe(OH)-P or Al(OH)-P

**Fig. 6** Comparisons of sediment-derived TP contents before and after aeration at each run



complexes that are classified into NaOH-P (Jiang et al. 2008; Sun et al. 2012; Jin et al. 2013). However, under anaerobic conditions, Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> to S<sup>2-</sup>, which will result in the liberation of endogenous phosphate due to the decomposition of Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and the formation of more stable FeS<sub>2</sub>. To sum up, NaOH-P is recognized as one ecologically important P fraction in the sediments.

### Conclusions

These results presented in this study showed that D.HCl-P and NaOH-P predominated in the sediment-derived P from a malodorous river Gongye. Resin-P and NaHCO<sub>3</sub>-P might act as an important role in initiating algae growth and D.HCl-P was likely available to algae during bloom maintenance. NaOH-P was a major contributor to algal bloom considering its relatively high percentage and bioavailability. High-level DO in the overlying water was essential to control the P release from sediments, and a clear transformation of D.HCl-P to highly bioavailable NaHCO<sub>3</sub>-P and NaOH-P was observed for intermittent sediment-aerated modes. Specifically, NaOH-P exhibited a marked increase with the elevated DO level for intermittent overlying water and sediment aeration. Taken together, intermittent overlying water aeration modes were recommended, and run 1 (7.0 mg/L, 12 h) was regarded as the optimized aeration condition in terms of its relatively low ecological risk and high P retention. NaOH-P was also recognized as one ecologically important P fraction in the sediments.

**Acknowledgements** This work was carried out with the financial support from Shanghai Natural Science Foundation (no. 16ZR1408800), Shanghai Pujiang Talent Program (16PJD023), the National Science and Technology Special Project (no. 2013ZX07310001; 2014ZX07101012), and the research funds from China Scholarship Council (no. 201406145031).

### References

Bährs H, Steinberg CEW (2012) Impact of two different humic substances on selected coccal green algae and cyanobacteria—changes in growth and photosynthetic performance. *Environ Sci Pollut Res* 19:335–346

Cao CJ, Chen ZL, Huang MS (2015a) Study on transformation mechanism and control and preventive measures of eutrophication secondary disasters in urban malodorous-back river. *J East China Normal Univ (Nat Sci)* 3(2):9–12 (in Chinese)

Cao DJ, Xie PP, Deng JW, Zhang HM, Ma RX, Liu C, Liu RJ, Liang YG, Li H, Shi XD (2015b) Effects of Cu<sup>2+</sup> and Zn<sup>2+</sup> on growth and physiological characteristics of green algae, *Cladophora*. *Environ Sci Pollut Res* 22:16535–16541

Chen M, Tang HY, Ma HZ, Holland TC, Ng KYS, Salley SO (2011) Effect of nutrients on growth and lipid accumulation in the green alga *Dunaliella tertiolecta*. *Bioresour Technol* 102:1649–1655

Cross AF, Schlesinger WH (1995) A literature review and evaluation of the Hedley fractionation: application to the biochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* 64:197–214

Fan YB, Li XX, Gong YW (2014) A research of improved Hedley phosphate fractionation in different reclamation mode. *J Capital Normal Univ (Nat Sci Ed)* 35(3):50–56 (in Chinese)

Feng HY, Li WX, Yang ZF, Ruan XH (2008a) Influence of dissolved oxygen in overlying water on releasing/absorption of phosphorus from sediments from Suzhou river, East China. *Earth Sci Front* 15(5):227–234 (in Chinese)

Feng MW, Wu YH, Feng SX, Wu YY (2008b) Effect of different N/P ratios on algal growth. *Ecol Environ* 17(5):1759–1763 (in Chinese)

Feng L, Zhang J, Mu B, Liu M (2011) Dynamic studies on the effect of nutrients on the growth of *Chlorella vulgaris*. *Environ Ecol in the Three Gorges* 33(5):6–9 (in Chinese)

Fu YQ, Zhou YY (1999) Speciation and fractionation of phosphorus in sediments and their ecological significance. *J Lake Sci* 11(4):376–381 (in Chinese)

Gao X, Li Y, He Y (2015) Phosphorus release and phosphorus form change in lake sediments. *Chin J Environ Eng* 9(7):3350–3354 (in Chinese)

He Y, Zhao YC, Chai XL, Guo CX, Zhou GM (2008) Phosphorus fractions and activation in aged refuse from mineral solid waste dumping site and landfill. *Environ Chem* 27(1):77–80 (in Chinese)

He Y, Chen YX, Zhang YF, Huang MS (2013) Role of aerated turbulence in the fate of endogenous nitrogen from malodorous river sediments. *Environ Eng Sci* 30(1):11–16

Jan J, Borovec J, Kopacek J, Hejzlar J (2013) What do results of common sequential fractionation and single-step extractions tell us about P binding with Fe and Al compounds in non-calcareous sediments. *Water Res* 47:547–557

Jena U, Vaidyanathan N, Chinnasamy S, Das KC (2011) Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass. *Bioresour Technol* 102:3380–3387

Jin XC, Jiang X, Yao Y, Li LH, Wu FC (2006) Effects of light and oxygen on the uptake and distribution of phosphorus at the sediment–water interface. *Sci Total Environ* 357:231–236

Jiang X, Jin XC, Yao Y, Li LH, Wu FC (2006) Effects of oxygen on the release and distribution of phosphorus in the sediments under the light condition. *Environ Pollut* 141:482–487

Jiang X, Jin XC, Yao Y, Li LH, Wu FC (2008) Effects of biological activity, light, temperature and oxygen on phosphorus release processes at the sediment and water interface of Taihu Lake, China. *Water Res* 42:2251–2259

Jin XD, He YL, Kirumba G, Hassan Y, Li JB (2013) Phosphorus fractions and phosphate sorption-release characteristics of the sediment in the Yangtze River estuary reservoir. *Ecol Eng* 55:62–66

Katsaounos CZ, Giokas DL, Leonardos ID, Karayannis MI (2007) Speciation of phosphorus fractionation in river sediments by explanatory data analysis. *Water Res* 41:406–418

Leote C, Mulder L, Epping E (2014) A budget of bioavailable inorganic phosphorus in the sediment for the western Wadden Sea. *J Sea Res* 87:79–90

Li DP, Huang Y (2012) Effect of disturbance intensity on phosphorus release and its transformation in the sediment from Taihu Lake. *Environ Sci* 33(8):2614–2620 (in Chinese)

Li DP, Huang Y (2013) Effect of dissolved oxygen on phosphorus removal and immobilization under sediment disturbance conditions. *Chin J Environ Eng* 7(10):3785–3790 (in Chinese)

Li DP, Huang Y, Li WG (2007) Effect of different aeration ways on phosphorus adsorption on sediments. *Technol water treat* 33(11):17–20

Lin JW, Zhu ZL, Zhao JF (2005) Effect of aeration on release of nitrogen and phosphorus from sediments in eutrophic waterbody. *Ecol Environ* 14(6):812–815 (in Chinese)

Lu XM, Zhang Y, Chen JJ (2010) Seasonal variation of water qualities and physical responses of nymphaea tetragonal under continuous aeration. *Chin J Environ Eng* 4(9):1978–1983 (in Chinese)



- Martins G, Peixoto L, Teodorescu S, Parpot P, Nogueira R, Brito AG (2014) Impact of an external electron acceptor on phosphorus mobility between water and sediments. *Bioresour Technol* 151:419–423
- Ni LX, Li DY, Hu SZ, Wang PF, Li SY, Li YP, Li Y, Acharya K (2015) Effects of artemisinin sustained-release granules on mixed alga growth and microcystins production and release. *Environ Sci Pollut Res* 22:18637–18644
- Norton SA, Coolidge K, Amirbahman A, Bouchard R, Kopáček J, Reinhardt R (2008) Speciation of Al, Fe, and P in recent sediment from three lakes in Maine, USA. *Sci Total Environ* 404:276–283
- Peng JP, Pang Y, Li YP, Ding L, Wu ZQ (2004) Change of phosphorus in lake after water dynamical condition and its contribution to eutrophication. *Ecol Environ* 13(4):503–505 (in Chinese)
- Qu FZ, Yu JB, Chen XB, Wang YL (2012) A review on soil phosphorus fractionation scheme on wetlands. *Chin J Soil Sci* 43(1):243–248 (in Chinese)
- Rydin E (2000) Potentially mobile phosphorus in lake Erken sediment. *Water Res* 34(7):2037–2042
- Sun HQ, Wang P, Jiang HL (2012) Behavior of phosphorus in interface of sediment-overlying water in Taihu Lake under different simulative conditions. *Environ Sci Technol* 35(5):141–146 (in Chinese)
- Tang XQ, Wu M, Dai XC, Chai PH (2014) Phosphorus storage dynamics and adsorption characteristics for sediment from a drinking water source reservoir and its relation with sediment compositions. *Ecol Eng* 64:276–284
- Tiessen H, Moir JO (1993) Characterization of available P by sequential extraction. In: Cater, M.R. and Gregorich E.G. (ed) *Soil sampling and methods of analysis*, 2nd edn. Talor and Francis, London, pp 75–86
- Vidal T, Marques C, Abrante N, Pereira JL, Soares AMVM, Gonçalves F (2015) Optimization of growth conditions for laboratory and field assessments using immobilized benthic diatoms. *Environ Sci Pollut Res* 22:5919–5930
- Wang SR, Jin XC, Zhao HC, Wu FC (2006a) Phosphorus fractions and its release in the sediments from the shallow lakes in the middle and lower reaches of Yangtze River area in China. *Colloid Surf A* 273: 109–116
- Wang GP, Liu JS, Wang JD, Yu JB (2006b) Soil phosphorus forms and their variations in depressional and riparian freshwater wetlands (Sanjiang Plain, Northeast China). *Geoderma* 13:259–274
- Wang GP, Zheng LZ, Jing SL, Jin DW (2008) Forms and profile distribution of soil phosphorus in four wetlands across gradients of sand desertification in Northeast China. *Geoderma* 145:50–59
- Wang L, Min M, Li YC, Chen P, Chen YF, Liu YH, Wang YK, Ruan R (2010) Cultivation of green algae *Chlorella* sp. in different wastewaters from municipal wastewater treatment plant. *Appl Biochem Biotechnol* 162:1174–1186
- Wang PF, Hu B, Wang C, Lei Y (2015) Phosphorus adsorption and sedimentation by suspended sediments from Zhushan Bay, Taihu Lake. *Environ Sci Pollut Res* 22:6559–6569
- Wang S, Li DP (2014) Influence of different disturbance intensity on the phosphorus adsorption and immobilization by the sediments from an inner city heavily polluted canal. *Environ Sci* 35(6):2171–2177 (in Chinese)
- Xie YH, Hong JP, Han X, Li TL, Su L, Feng GL, Meng HS, Tian DF (2010) Study on soil bioavailability of the Hedley P forms in calcareous soil with different phosphorus level. *J Soil Water Conserv* 24(6):141–144 (in Chinese)
- Yu Z, Wang CH (2005) Optimization of culture conditions of *Chlorella*. *J Yantai Univ (Nat Sci Eng Ed)* 18(3):206–211 (in Chinese)
- Zan FY, Huo SL, Xi BD, Li QQ, Liao HQ, Zhang JT (2011) Phosphorus distribution in the sediments of a shallow eutrophic lake, Lake Chaohu, China. *Environ Earth Sci* 62:1643–1653
- Zhang L, Wu N, Wu Y, Luo P, Liu L, Chen WN, Hu HY (2009) Soil phosphorus form and fractionation scheme: a review. *J Appl Ecol* 20(7):1775–1782 (in Chinese)
- Zhang TX, Wang XR, Jin XC (2007) Variations of alkaline phosphatase activity and P fractions in sediments of a shallow Chinese eutrophic lake (Lake Taihu). *Environ Pollut* 150:288–294
- Zhu YR, Wu FC, He ZQ, Guo JY, Qu XX, Xie FZ, Giesy JP, Liao HQ, Guo F (2013) Characterization of organic phosphorus in lake sediments by sequential fractionation and enzymatic hydrolysis. *Environ Sci Technol* 47:7679–7687