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Release characteristics of sediment P in all fractions of Donghu Lake, Wuhan, China

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ABSTRACT

The aim of the study was to understand the releasing characteristics of sediment phosphorus (P) in all fractions under varying environmental conditions and the relationship between sediment P and eutrophication in shallow city lake, Donghu Lake of Wuhan in China. Effects of P concentration in overlying water, oxygen, light, pH, temperature, and agitation intensity on release processes of sediment P in all fractions in Donghu Lake, China, were investigated. The release quantity and release rate of sediment P in the distilled water were significantly higher than those of lake water, and under anaerobic condition, they were higher than those of aerobic treatment. The concentrations of each P form decreased obviously in both dark and irradiated systems. Both high and low pH promoted the release of Fe/Al-P, IP, and TP, but Ca-P decreased sharply with decreasing pH, while the difference of OP was not obvious. The release rate of each P form accelerated drastically when water temperature rose from 5 to 30°C. The magnitude of the each P form released increased with the increase in the agitation intensity at the first 6 d, while it showed no significant difference after 8 d in different agitation intensities (100-200 rpm). The results showed that the extent of P in all fractions released from Donghu Lake sediment was affected variously by the environmental factors, and the sediment was unstable, at risk of releasing P to Donghu Lake.

Keywords: Environmental factors; Sediment; Phosphorus fractions; Phosphorus release; Donghu Lake

1. Introduction

As a major nutrient for aquatic ecology, phosphorus (P) has been identified as the probable limiting nutrient in lakes [1–3]. Sediments in lakes are considered as a sink of nutrients, and the supply of P from

sediments can play a vital role in the eutrophication of water bodies [4–7]. P can be transferred from lake to sediment through biochemical and physical reactions. Also, P could be released from sediments as the overlying water quality changes [8–10]. In many shallow lakes, resuspended materials disturbed by wind, boats, and internal activities are the majority of

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P released from sediments to overlying water, causing the redistribution of P at sediment–water interface [11]. The release processes have a significant impact on the water quality, may lead to continuous eutrophication in eutrophic lakes, especially when external nutrient sources get control along with the controlling of pollutant discharge and management of water ecological restoration [12]. The final trophic level of water bodies depends on this type of adsorption–release balance to a large extent [13,14]. So, the studies about P release characteristics under various environmental conditions can reveal the releasing regularity of each P form from sediments, which helps understand the contribution of each sediment P form to lake eutrophication.

However, many previous studies were usually conducted in the modest environments only considering individual factor [15,16], and they mainly focused on the releasing characteristics of TP in the sediments [17,18]. So far, few studies have investigated the release processes of sediment P in all fractions in Donghu Lake under different conditions. The releasing process of sediment P in all fractions (Ca-P, Fe/Al-P, IP, OP and TP) under varying environmental conditions: overlying water, oxygen, light, pH, temperature, and agitation intensity, especially extreme heat and pH, was firstly studied in the paper, aiming to investigate the releasing characteristics and risks of sediment P in Donghu Lake of Wuhan in China.

2. Materials and methods

2.1. Study sites and sampling

Donghu Lake (30°33′N, 114°23′E) is situated on the northeast of Wuhan city with outlet joining the Yangtze River. As the largest urban lake in China, Donghu Lake is a typical urban shallow lake, with an area of approximately 33 km² and elevation of 20.5 m above sea level. Like many other lakes, it has become hypertrophic due to decades of excessive increase in the input of nutrients, through domestic sewage and agricultural run-off. At present, the external nutrient sources are under control along with completing sewage interception project of Donghu Lake, so the release processes of sediment in Donghu Lake have a more significant impact on the water quality, and lead to continuous eutrophication.

Sampling site is located in Shuiguo Lake (a subarea of Donghu Lake), in the west of the lake, a severe eutrophic region (30°33′04.9′N, 114°21′07.1′E). Surface sediment samples (0–10 cm) were collected using a Peterson sediment collector (model HNM1–2, with a surface area of 0.1 m²). The samples were taken to lab-

oratory in air-sealed plastic bags and kept at 4° C. Then, samples were freeze dried and sieved with a standard 80 mesh to remove big particles for further experiments. Water samples were collected 0.5 m below the water surface and were immediately filtered through 0.45 mm cellulose acetate membranes.

2.2. Effects of environmental factors on P release

Release experiments were performed in vessels, containing 250 mL 0.02 M KCl solution (to maintain certain ion concentration) and 5 g of sediment samples, and the detailed processes are as follows:

Effects of light and temperature on P release were studied on a thermostat oscillator (Wuhan scientific instruments plant of Chinese Academy of Sciences, China). Five grams of sediment sample was evenly added into a beaker, to which 250 mL 0.02 M KCl solution was slowly added, and the height of the water column was recorded. The dark/light cycle was 16:8 h. Under the dark condition, the temperature was set at 5–70 °C to consider the impacts of normal and extreme high temperature. In the lighted scenario, a 125 W high-pressure mercury lamp was used as the optical source, and the illumination of sediment–water interface was 400–500 lux.

Experiments for DO effects were conducted under aerobic and anoxic conditions without the presence of light at $20 \pm 2^{\circ}$ C (under dark condition), which were controlled by the circulation of air and of nitrogen (99%) after daily sampling.

Effects of P concentration of overlying water on P release were studied with distilled water and lake water as overlying water (under dark condition). Experiments for pH effects were conducted on the initial pH ranges of the solution controlled to between 2.0 and 12.0 by adding HCl and NaOH (1 mol/L) (under dark condition). Effects of hydrodynamic conditions on P release were studied by static and stirring releasing experiments (at 100–200 rpm) for various time intervals (under dark condition). The detailed experimental procedures were similar to the experiments of light and temperature effects.

All the beakers were covered with plastic film to minimize splashing and evaporation. The concentration of sediment P in all fractions was determined after the release process.

2.3. Analytical methods

The water level in these experiments was noted in order to keep the same water quantity after sampling and supplementation, and an appropriate amount of sterilized water was added to compensate for the loss of water and evaporation.

P fractions in the sediments were determined using the SMT harmonized protocol [19]. The operationally defined scheme was composed of five P forms: Fe/Al-P (NaOH-extractable P, P bound to Al, Fe and Mn oxides and hydroxides), Ca-P (HCl-extractable P, P associated with Ca), OP (organic P), IP (inorganic P), and TP (total P). For each P fraction, three independent replicates were analyzed in three different laboratories, and all the data were expressed as the average.

Each P fraction was measured using the ammonium molybdate spectrophotometric method with UV-visible spectrophotometer (DR4000/U, HACH company, USA). The pH of the sediment was measured in 1:10 (w/v) solid/water suspensions with a pH meter (PHS-3C, Shanghai LeiCi instrument plant, China). The grain sizes were measured using a Mastersizer 2000 Laser Size Analyzer (Malvern Co., UK). The percentages of grain size groups including clay (0.02-4 mm), silt (4-63 mm), and sand fractions (63-500 mm) were determined. Total organic carbon (TOC) in the sediment was analyzed with an Apollo 9000 TOC Analyzer (Tekmar Dohrmann Co., USA). The compositions of sediment were measured with the full spectrum of direct-reading inductively coupled plasma emission spectrometer (Optima 4300DV, Perkin Elmer Ltd, USA).

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted HCl solution for 12 h, then washed and rinsed three times with deionized water. Deionized water was also used for the preparation of solutions. All experiments were conducted in duplicate, and the average values were used for data analysis.

3. Results and discussion

3.1. Sediment characteristics

The general features and chemical component concentrations in Donghu Lake sediments were presented in Table 1. The sediment was siliceous, and total proportions of SiO₂, Al₂O₃, Fe₂O₃, Na₂O, and CaO were more than 80%. The grain size of the sediment was almost less than 63 mm, the silt fraction (4–63 mm) dominated in the fractions of the sediment (79.76%). TOC content of the sediment was 5.22%. The content of Ca-P was relatively low, only 13.6% of TP, Fe/Al-P was about 59.9% of TP, the sum of Ca-P and Fe/Al-P amounted to 73.5% of TP in the sediment, and OP accounted for about 22.4%. Thus, it can be seen that the sediment was unstable, at risk of releasing P to lake.

Table 1
Properties and chemical compositions of sediment

Properties		Content
Grain size (%)	<4 μm	9.26
	4–63 μm	79.76
	63–400 μm	6.89
Major element (wt%)	SiO_2	49.58
,	Al_2O_3	11.46
	Na ₂ O	23.57
	CaO	12.64
	Fe_2O_3	5.14
рН	2 0	7.39
TOC (%)		5.22
P fractions (mg kg ⁻¹)	Fe/Al-P	462
	Ca-P	105
	IP	553
	OP	173
	TP	771

3.2. Effects of P concentration in overlying water on P release

The concentration changes of each P form of the sediments in the overlying water effect experiment without irradiation were shown in Figs. 1 and 2. The physicochemical properties of lake water were shown in Table 2. The release quantity and release rate of sediment P in the distilled water were significantly higher than those in the lake water. The maximum release quantity of each P form was obtained on the 10th d when distilled water as overlying water, the maximum release quantity of Ca-P, Fe/Al-P, IP, OP, and TP were 1.6, 24.5, 27.1, 5.3, and 38.0 mg/kg, respectively. And the maximum release quantity of

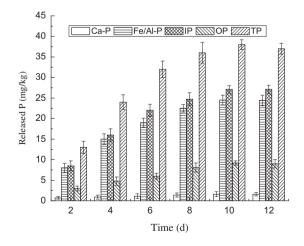


Fig. 1. Release amount of sediment P when distilled water as overlying water.

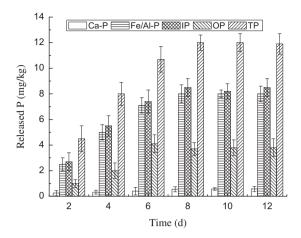


Fig. 2. Release amount of sediment P when lake water as overlying water.

each P form was obtained on the 8th d when lake water as overlying water, the maximum release quantity of Ca-P, Fe/Al-P, IP, OP, and TP were 0.6, 8.1, 8.5, 3.7, and 11.9 mg/kg, respectively. Thus, it can be seen that the P concentration in overlying water had obvious effect on sediment P release, the maximum release amount of each P form in distilled water–sediment system was about three times more than that in lake water–sediment system.

The geochemical behavior of P in sediment-water system should be controlled by threshold values of all kinds of compounds, which manifests as P release and absorption of sediment [20,21]. Adsorption action plays a leading role in the reaction when the concentration of P is higher than the threshold value, whereas the reverse is manifested as release action. While the intensity of the release is associated with P concentration, the higher the P concentration, the less the release amount of sediment P; the release rate constant is negatively related to the P concentration, and almost no P released as the equilibrium in water -sediment phases is achieved. In the study, the concentration of TP in overlying water was 0.29 ± 0.02 mg/L, the higher P concentration reduced the P release from the sediment to some extent. So, the release quantity and release rate of sediment P in the distilled water were significantly higher than that of lake water.

3.3. Effects of oxygen supply levels on P release from sediment

Two treatments were conducted: DO content of anaerobic treatments (aerated by nitrogen) was lower than 1 mg/L, that of aerobic treatments (aerated by oxygen) was higher than 7 mg/L. Sediment P in all fractions in different oxygen supply levels after the release experiments was shown in Figs. 3 and 4. As shown in Figs. 3 and 4, oxygen supply level in the overlying water played an important role in influencing P release from the sediment, after the release experiment, the release rate and amount of sediment P in all fractions under anaerobic condition were significantly more than those in aerobic treatment. Under anaerobic condition, the release quantity of Ca-P, Fe/ Al-P, IP, OP, and TP on the 10th d was 2.5, 36.5, 40.8, 8.1, and 57.0 mg/kg, respectively, the corresponding release rate was 2.4, 7.9, 7.4, 8.1, and 7.4%, respectively. Sediment P in all fractions reached maximum release quantity on the 6th d under the aerobic condition, and the release quantity of Ca-P, Fe/Al-P, IP, OP, and TP was 0.9, 12.3, 13.9, 4.7, and 19.8 mg/kg, respectively; correspondingly, the release rate was 0.8, 2.7, 2.5, 2.7, and 2.6%, respectively.

The released amount of each P form in anaerobic treatment was about three times more than that in aerobic treatment. The potential reasons for this phenomenon may be that: the DO concentration at the sediment and water interface controlled the redox potential. Anaerobic condition results in the occurrence of low redox potential, the low redox potential induced the changes of positive ion (Fe³⁺, Al³⁺) valence, and made the minerals gradually decomposed and P was released into the overlying water in the reductive environment [11]. While under the oxic and aerobic conditions, almost all the metal ions presented as high valence stage; thus, the mineral compounds were stable and difficult to dissolve in the water, and phosphate can bind with these metal ions. Consequently, the oxic and aerobic conditions hindered the interacting and exchanging between sediment and overlying.

3.4. Effects of light on P release from sediment

The concentration changes of sediment P in all fractions in the light effect experiment were shown in

Table 2
Physical and chemical characters of overlying water above sediments

Index	TN (mg/L)	$\mathrm{NH_4^+}\text{-N (mg/L)}$	NO_2^- -N (mg/L)	TP (mg/L)	Transparency (m)	pН
Value	3.52 ± 0.04	1.81 ± 0.02	0.23 ± 0.01	0.29 ± 0.02	0.50	7.1

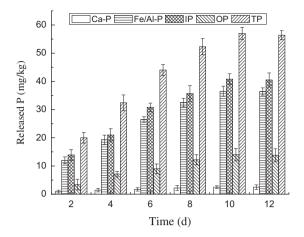


Fig. 3. Release amount of sediment P under anaerobic condition.

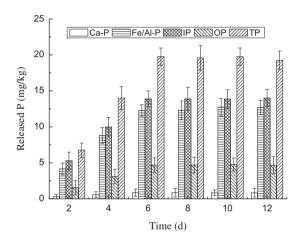


Fig. 4. Release amount of sediment P under aerobic condition.

Fig. 5. The concentrations of each P form decreased obviously in both dark and irradiated systems, while no significant differences for various P fractions were observed in systems with and without irradiation, comparing Fig. 5 to Fig. 1. The maximum release quantity of TP under irradiated conditions was only 7.3 mg/kg lower than that without irradiation. The results indicate that irradiation had no major effect on P release from sediment.

Relevant research results showed that light stimulated the growth of the micro-organisms in the sediment, and the release ability of sediment P could be influenced by life activities of micro-organisms [17,22]. The effect of micro-organisms on sediment P releasing was not obvious in the study, the possible reason was that the release time was relatively short. The changes of sediment P influenced with irradiation were the

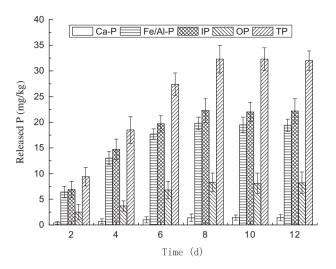


Fig. 5. Release amount of sediment P under illumination condition.

comprehensive reflection of irradiation, life activities of micro-organisms, and sediment properties, while the specific reaction process and effect need further research.

3.5. Effects of pH on P release

Under ordinary conditions, pH of sediment in lakes was between 7.0 and 8.5. However, the pH of sediment sometimes changed, due to the great amount of pollutant or other organic matter deposited in the sediment. Extreme pH may change the sediment properties, thus affecting the P release from lake sediments [23]. The release rate of each P form from sediments as a function of pH was illustrated in Fig. 6. For Fe/ Al-P, IP, and TP, the release rate decreased with the increasing pH under acidic condition. While under alkaline condition, the release rate increased with the increasing pH. The effect of overlying water pH on these three P forms release followed U-shaped curves. At pH 12, the release amount of Fe/Al-P, IP, and TP reached 45.8, 48.6, and 64.7 mg/kg, respectively. Correspondingly, the release rate was up to 9.9, 8.8, and 8.4%, respectively.

Ca-P was a relatively stable fraction and attributed to the permanent burial of P in sediments [24]. The results showed that with pH varying, Ca-P mobility changed correspondingly, and higher pH effectively improved Ca-P immobility. It was at pH 2 that Ca-P exhibited the highest release capacity; the release quantity and release rate were 6.5 mg/kg and 6.2%, respectively. Comparatively, only 1.3% of Ca-P was released at pH 12. While the difference in release quantity of OP under acidic and alkaline conditions

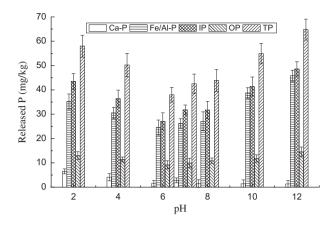


Fig. 6. Effect of overlying water pH on sediment P release.

was not obvious, the release quantity at pH 12 was about 1.5 mg/kg more than that at pH 2.

In order to describe the relationships of release quantity of sediment TP (y) and overlying water pH (x), a curve fitting was applied and found that the release quantity of sediment TP was in parabolic curve relationship with overlying water pH (Fig. 7), the corresponding regression equation: $y = 0.8103x^2 - 10.65x + 77.046$, the correlation coefficient $R^2 = 0.9266$.

Based on the above results of the simulated release experiments and analyzing, we can draw the conclusion that pH value of overlying water has a more significant effect on the sediment P release, the release rate in alkaline solutions was significantly higher than under acidic conditions, and an obvious U-shaped curve relationship existed between the release amount and pH value. The release of sedimentary P mainly depends on surface electric charge of particles and P fractionation, which have a strong relationship with pH values. The potential reasons: the effect of pH on P release was mainly reflected through the P speciation

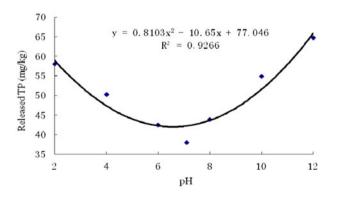


Fig. 7. Fitting curve of effect of overlying water pH on TP release.

in combination with metals such as Fe, Al, and Ca. The P binding capacity of iron and aluminum compounds decreased as pH increased in the overlying water and in the sediment, primarily due to the ligand exchange reactions in which hydroxide ions may replace orthophosphate. The alkaline pH facilitated the competitive adsorption of OH and some anions, and OH may exchange with phosphate in the Fe-P and A1-P complex, thus increased the desorption process of phosphate, subsequently resulting in P liberation from positive adsorption sites; orthophosphate in the water existed as HPO_4^{2-} and $H_2PO_4^{-}$ under the neutral condition, which was easy to combine with metal ions and adsorbed on sediment, thus reduced the release amount; the acidic pH increased the solubility of adsorbed sedimentary P, especially affected the desorption of Ca-P from sediment. While the influence of pH on OP release needs further study.

3.6. Effects of temperature on P release from sediment

Effects of temperature on P fractions in the sediments under dark conditions were shown in Fig. 8. The released amount of each P form increased with the increasing temperature, the release rate accelerated dramatically from 5 to 30°C, the release quantity of Ca-P, Fe/Al-P, IP, OP, and TP reached 2.0, 33.9, 36.5, 12.8, and 49.9 mg/kg, respectively, and the corresponding release rate was 1.9, 7.3, 6.6, 7.4, and 6.5%, respectively. The P release amount of variation had leveled off as the temperature rose up to a extreme high temperature of 70°C from 30°C.

The possible reasons for the great effects of temperature on the sediment P release were that: temperature obviously affected the biomass and growth of bacteria and autotrophic alga [25]. As temperature

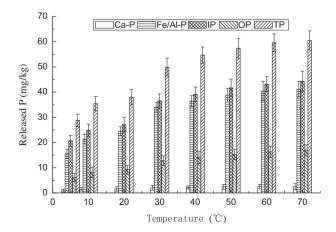


Fig. 8. Effect of temperature on sediment P release.

increased, the activities of bacteria, benthic alga, and phytoplankton were enhanced, thus accelerated the decomposition of organic matter, resulting in the consumption of oxygen and decrease in redox potential; the low redox potential induced the reduction of Fe (III) from Fe(OOH) to Fe(II) and finally resulted in Fe/Al-P release.

Meanwhile, the mineralization of organics was strengthened with increasing temperature, promoted the transformation of OP to IP, accelerated the dynamic balance of adsorption–desorption to the direction of desorption, and consequently, P released from the sediments of orthophosphate and hydroxide.

3.7. Effects of agitation intensity on P release from sediment

The effects of agitation intensity (100–200 rpm) on P release from sediment were shown in Fig. 9. It can be seen from the comparison (Fig. 1) that agitation intensity was an important factor that affected the P release from Donghu Lake sediments. At the beginning of the first 6 d, the stronger the agitation intensity, the higher the sediment P release rate, the magnitude of the each P form released increased with the increase in the agitation intensity. The release quantity of Ca-P, Fe/Al-P, IP, OP, and TP on the 6th d reached 1.9, 32.8, 35.9, 11.9, and 48.2 mg/kg, respectively; the corresponding release rate was 1.8, 7.1, 6.5, 6.9, and 6.3%, respectively, under 200 rpm agitation intensity condition. While the release amount of each

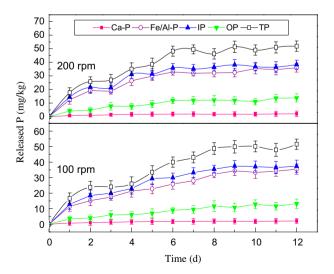


Fig. 9. Effect of different disturbance strengths on sediment P release.

P form under the conditions of different disturbing intensities (100–200 rpm) showed no significant difference after 8 d.

In this study, after the stronger disturbing (200-100 rpm), various P fractions content in Donghu Lake sediment decreased sharply comparing to static conditions (Fig. 1), showing that the sediments could act as a sink for P after the stronger disturbing. And the water was always in dynamic condition, especially for the shallow lakes in China. The P concentration in the overlying water of shallow lakes in China can maintain relatively high level after the disturbing, and this provides necessary nutrition for eutrophication [1,26]. This is one of the reasons that it is difficult to control the shallow lake eutrophication in China and algal bloom often occurs after the high turbulence caused by fish, boating activity, or stronger wind. So, it is of significance to minimize potential disturbance of water bodies to reduce the sediment P release for harnessing eutrophic shallow lakes.

4. Conclusions

- (1) The extent of sediment P in all fractions released from Donghu Lake were affected variously by the environmental factors such as P concentration in overlying water, oxygen, light, pH, temperature, and agitation intensity.
- (2) The P concentration in overlying water had obvious effect on sediment P release, the maximum release amount of each P form in distilled water-sediment system were about three times more than that in lake water-sediment system.
- (3) The release amount of each P form in anaerobic treatment was about three times more than that in aerobic treatment.
- (4) No significant differences for various P fractions were observed in systems with and without irradiation.
- (5) Both high pH and low pH promoted the release of Fe/Al-P, IP, and TP, higher pH could effectively improve Ca-P immobility while the difference of OP release quantity under acidic and alkaline conditions was not distinct. And an obvious U-shaped curve relationship existed between the TP release amount and pH value.
- (6) The released amount of each P form accelerated dramatically from 5 to 30°C and leveled off as the temperature rose up to a extreme high temperature of 70°C from 30°C.

(7) Various P fractions content in the sediment decreased sharply comparing to static conditions after the stronger disturbing (200 and 100 rpm), while the release amount of each P form under the conditions of different disturbing intensities showed no significant difference after 8 d.

Acknowledgments

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