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Sequential fractionation of reactive phosphorus in the sediment of a shallow eutrophic lake—Donghu Lake, China

FU Yong-qing, ZHOU Yi-yong* , LI Jian-qiu

(Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, China)

Abstract: The bioavailability of phosphorus in lake sediment mainly depends on its forms. Therefore, reactive phosphorus (RP) pool of the sediment in a shallow eutrophic lake (Donghu Lake) was determined seasonally and spatially by sequential chemical extraction according to the scheme proposed by Psenner *et al.* (Psenner, 1985) and its modified version respectively. The ammonium chloride extracted 3%—7% of the total reactive phosphorus (Tot-RP), while the distilled water extracted less (<3%). These two forms of P were significantly higher at the most eutrophic stations (I and IV). The sum of BD-RP (reductant soluble P) and NaOH-RP extracted accounted for 57%—81% of Tot-RP, which could play significant roles in P cycling. The percentages of HCl-extractable RP in the sediments of station III, however, were usually much more than those of other stations, which could reflect the original geochemical characteristics and trophic status of the sediments. It was noted that the sediment RP in different fractions varied in different months studied.

Key words: Donghu Lake; sediment reactive phosphorus; sequential fractionation

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Introduction

Sediment phosphorus has been the focus of a number of studies due to its role in the eutrophication of lakes. Phosphorus fractions in sediments are characterized by their differential solubilities in various chemical extractants. The early fractionation schemes (Chang, 1957; Petersen, 1966) grouped soil P into four pools (Williams, 1971): orthophosphorus ions (*o*-P) sorbed onto the surface of P-retaining components (non-occluded P), P present within the matrices of P-retaining components (occluded P), P present in phosphate minerals such as apatite, and organic P. Of the above-mentioned P, the non-occluded P (*o*-P) can be directly utilized by phytoplankton, while for apatite P (mainly calcium-bound P), it is more difficult than the iron-bound P to be used (Golterman, 1976).

For calcareous sediments, however, these fractionation schemes have been proved to be unsatisfactory and therefore Hieltjes and Lijklema (Hieltjes, 1980) introduced an analytical extraction scheme. Later Psenner *et al.* (Psenner, 1985) presented a fractionation procedure which was also tested on calcareous sediment. The sequential extraction procedure involved a series of solvents as follows: H₂O, 0.11 mol/L bicarbonate-dithionite, 1 mol/L NaOH, 0.5 mol/L HCl and 1 mol/L NaOH (85°C). Each suggested fractional composition extracted is presented in Table 1.

Although considerable reported extraction schemes were used by many authors (Chen, 1993; Olila, 1995; Golterman, 1996; Baldwin, 1996; Fabre, 1996), none of the schemes was based on

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stoichiometrical or structural study of sediment P, but on the expediences of operation. Thus, what is achieved is actually a rough estimation of several fractions (Pettersen, 1988).

Table 1 Fractional compositions extracted in the Psenner scheme

Extractant	Extractable fraction	Mainly species
H ₂ O	H ₂ O-RP	Orthophosphorus, o-P
BD	BD-RP	Reductant soluble P, RSP(iron-bound)
NaOH	NaOH-RP	Iron-bound P(Fe-P)
HCl	HCl-RP	Calcium, magnesium-bound P(Ca, Mg-P)
NaOH(85°C)	NaOH-RP(85°C)	Refractory P, inorganic or organic poly-P

Since the amount of phosphorus release from sediment is called internal phosphorus loading, which can enhance the lake's eutrophication, the fractionation of sediment P can be conducive to the understanding of P cycling in the aquatic ecosystem. Phosphorus release is a function of the quantity and distribution of phosphorus fraction within the sediments, the degree of saturation of exchangeable phosphorus, the intensity of biological process in sediment and lake water and of hydrological conditions (Jansson, 1988).

Although the relevant studies have been carried out to some extent abroad, the performances in China are almost scarce, especially in shallow eutrophic lakes. In this paper we present an investigation of the calcareous sediment of Donghu Lake, a shallow eutrophic lake.

1 Site description

Donghu Lake is a shallow eutrophic lake on the alluvial plain of the Changjiang (Yangtze) River and on the northern outskirts of Wuhan, China. It has a total surface area of 32 km² and consists of several basins separated by artificial dykes. The sampling sites are stations of I, II and III, which is located within the Shuiguohu, Guozhehu and Tanglinhu districts respectively. Another sampling site, station IV is near station I, where once the cage culture of fish was located. The lake is usually 3–4 m in depth with a maximum of 4.5m. The temperature stratification is usually obscure because of strong wind action and the convection of water in the shallow basin. The lake itself is components of a large drainage system with a total catchment area of 187 km². Successive observations were carried out at station I, II, III and IV (Fig.1) in April, May and June, 1998. The physicochemical characteristics of the lake /sampling sites are given in Table 2.

Table 2 Physicochemical characteristics of sampling sites*

Station	Sediment				Porewater, mg/L				
	Depth, cm	pH	Eh, mV	State	SiO ₂	Ca	Mg	Fe	Ca/Mg
I/IV	0–4	7.8	135	Blue soil	14.0	51.6	10.4	5.01	3.02 [#]
II	0–14	8.1	288	Soft yellow soil	12.0	49.3	8.0	2.07	3.72 [#]
III	0–6	8.1	272	Soft yellow soil	12.4	52.3	8.1	1.81	3.93 [#]

* From Yang(1992); # molar ratio

2 Materials and methods

Surficial sediments (0–10 cm) were collected by Peterson dredge from the sampling sites

(Fig.1) once a month. Within 3h samples were homogenized, placed into acid washed polypropylene tubes and then centrifuged for 20 min at 3000 r/min to remove porewater. For each sample, three subsamples of approximately 250 mg of centrifuged sediments were placed into individual 40 ml acid-washed centrifuge tubes, and extracted with 25 ml of different solution according to the original scheme (Ps) suggested by Psenner (Psenner, 1985) and its modified version (Ps-N) by a replacement of the initial water extraction with two ammonium chloride extractions as in the Hieltjes and Lijklema scheme (Hieltjes, 1980). The original procedure consists of a very quick (10 min) extraction with distilled deoxygenized water, followed by the treatment with 0.11 mol/L buffered sodium dithionite solution (30 min at temperature 40°C), a subsequent extraction with 1.0 mol/L sodium hydroxide at room temperature for 16 h, a 0.5 mol/L hydrochloric acid extraction and a hot (85°C) extraction with 1.0 mol/L NaOH for 24 h. The supernatants of each extraction after centrifugation for 10 min at 3000 r/min were analyzed for molybdate reactive phosphorus (MRP) according to Murphy and Riley (Murphy, 1962). All analysis were run in triplicates, and the MRP content was based on dry weight(dw.).

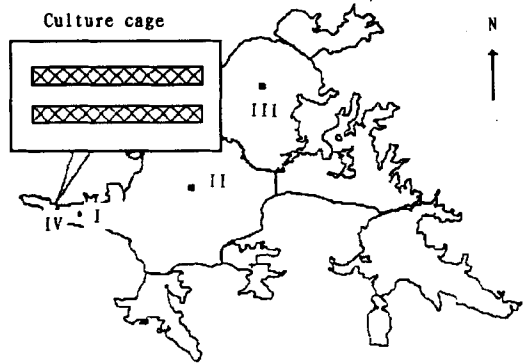


Fig.1 Map of Donghu Lake, showing sampling sites used in the study

3 Results and discussion

The results from the fractionation of the sediment phosphorus according to the Ps and Ps-N schemes are given as Fig.2 and Fig.3. The ratios of varied RP to total reactive phosphorus (TRP) are presented in Table 3.

In the Ps scheme (Fig.2), small amounts of phosphorus (H_2O -RP) were extracted with distilled water. In April, from station I to IV, 4 to 18 $\mu\text{g P/g dw.}$ was extracted, or 0.5%—2.5% of total reactive phosphorus (Tot-RP) respectively. Reductant soluble phosphorus (BD-RP), however, increased from 455 $\mu\text{g P/g}$ at station II to 552 $\mu\text{g P/g}$ at station I and the NaOH-RP was in the range 93 to 461 $\mu\text{g P/g}$ or 10.5%—36.4% of Tot-RP. The amounts of HCl-RP at each station fluctuated a little, as in the Ps-N scheme. The refractory reactive phosphorus extracted with hot sodium hydroxide ($NaOH_{85}$ -RP) varied from 83 to 112 $\mu\text{g P/g}$.

For the Ps-N scheme, in April, however, the first two consecutive extractions with ammonium chloride are efficient in the removal of carbonates and loosely bound calcium ions, thus it extracted much more phosphorus than water, varying from 43 to 81 $\mu\text{g P/g}$. This fraction is often termed labile (desorbed, hydrolyzed), loosely bound or adsorbed phosphorus. It gives the estimate of the immediately available phosphorus (Hieltjes, 1980) which could directly and immediately be utilized by phytoplankton. Pretreated with NH_4Cl , the subsequent fractions showed effects in the Ps-N scheme as shown in Fig.3, i. e. in most cases, more Tot-RP was extracted.

Similar results were recorded in May and June in both schemes for each station, except that in May the BD-RP extracted from the four stations each was about half of those in April or June.

As to the bicarbonate-dithionite reactive phosphorus (BD-RP), the amounts extracted were similar at each station in a certain month. It is assumed that the reductant soluble phosphorus forms are extracted mainly from iron hydroxide surfaces (Zinder, 1985; Psenner, 1988), about half of which appears in a reactive or "inorganic" form that can regulate the dissolved reactive phosphorus (DRP) in the porewater and has a good linear correlation with DRP concentration. Porewater DRP and sediment BD-RP may be the key factors of determining the way and amount of sediment P release (Psenner, 1988). In the Ps and Ps-N schemes the percentages of BD-RP extracted were in the range 18% to about 60% of Tot-RP (Table 3). More BD-RP was usually extracted from the sediment at station I or IV, which could indicate that BD extracts phosphorus bound to iron hydroxides sensitive to low redox potential.

The NaOH-extractable phosphorus at room temperature represents phosphate adsorbed to iron or aluminum oxides and other surfaces, exchangeable against OH^- , and phosphorus compounds soluble in bases. In our studies, this part accounted for 11%—61% of the Tot-RP in the Ps and 14%—57% in the Ps-N scheme (Table 3). Meanwhile, much more NaOH-RP were extracted from the sediments of stations I and IV than from those of stations II and III as shown in Fig. 2 and Fig. 3. The reactive P extracted in this fraction, however, was found to be negatively correlated with the P uptake capacity of the sediment (Psenner, 1984). This suggested that sediments with high percentage of NaOH-RP, such as of stations I and IV, could have low uptake capacity of phosphorus. The non-reactive P in the extract however, were identified as polyphosphate (poly-P) which presented in the sediment bacteria containing P-rich granules, and played as an important transient sink for P in sediments (Hupfer, 1995).

It can be found that the total percentages of BD-RP and NaOH-RP account for 57%—81% of Tot-RP in the Ps schemes and 61%—80% in the Ps-N, and both fractions have larger proportions in Tot-RP at station I/IV than at station II/III (Table 3). Since the two fractions related with iron, iron might be an important factor of determining P release patterns under specific circumstances such as redox potential, pH and temperature. Porewater iron concentration at station I/IV is significantly higher (5.01 mg/L) than that at station II/III (2.07/1.81 mg/L), combining with the surficial sediments' Eh we can see why a larger ratio of H_2O -RP or NH_4 -RP to Tot-RP often appeared for the sediments at station I/IV than at station II/III during our study period. Therefore, both kinds of iron bound phosphorus could play significant roles in P cycling in the ecosystem of Donghu Lake.

Of the reactive phosphorus extracted with HCl (HCl-RP) for each station, the largest ratios of HCl-RP to Tot-RP appeared in the sediment of station III for each month. HCl-extractable phosphorus represents P bound to calcium and magnesium and P released by the dissolution of oxides (not adsorbed to the surface). We assumed that the highest percentage of HCl-RP to Tot-RP in the sediment at station III could to some extent have well reflected the original geochemical characteristics. Sediment in Lake Donghu is very calcareous ($\text{CaCO}_3 > 50\%$) and the sediment at station III originate from calcareous depositions (Yang, 1992). The molar ratio of Ca/Mg was higher at station III (3.93) than at other stations (Table 2). Thus, calcium bound P may be dominant in HCl-RP. The ratio of iron-bound P (Fe-P, including BD-RP and NaOH-RP) to calcium-bound P (Ca-P, mainly HCl-RP) was regarded as an indicator of trophic status, both of which were positive correlated (Weng, 1993). The Fe-P:Ca-P ratio of the sediment at station III was usually lower than those at any other stations. In April for example, in the Ps scheme, the ratios of the four stations were 80:10, 75:11, 75:14, 81:8 respectively. In addition, the water quality of station III was thought to be superior to the other stations, as shown in Fig. 2 or Fig. 3

that the amount of H₂O/NH₄Cl-RP, BD-RP and NaOH-RP were usually the least. This could be caused partly by the relatively small introduction or loading of external P.

The percentages of hot NaOH-extractable phosphorus (termed refractory P) which was regarded mainly as organic P, varied from 8% to 23% in both procedures. This fraction could not be utilized by phytoplankton or algae, but itself, as a P pool, could be hydrolyzed under some specific conditions such as the existence of phosphatase.

It was noted that the sediment RP in different fractions varied in different months studied. This was probably caused by the variation of the environmental conditions such as the redox potential and the populations of aquatics.

The effect of cage-culture of fish on lake eutrophication deserved our attention. Recently Persson (Persson, 1997) found that P released from fish was in a form directly available to phytoplankton, suggesting that P release from fish may be an important nutrient source for algae. In April and June, we get a higher H₂O-RP concentration at station IV than at station I, which could relate with the P release by fish.

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