Vertical variation of phosphorus forms in surface sediments from Wuli Bay, Taihu Lake, China*

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Abstract In order to investigate the cycling of phosphorus in the Taihu Lake, a sequential extraction technique was used to separate different phosphorus forms in surficial sediments from the Wuli Bay of the Taihu Lake. The concentrations of total P are high in the sediments, with an average of 2.80 mg · g^{-1}, and a variation range between 4.02 and 2.05 mg · g^{-1}. Total P is composed mainly of inorganic P (70% –90%), a large portion (75% –85%) of which lies in the CDB-extractable iron oxide phase. The low Fe/P atomic ratios (2.0 – 5.3) indicate that the Fe compounds extracted with CDB have a lower proportion of relatively crystalline phases in all samples, and that the absorption between iron and phosphorus has probably reached certain equilibrium. Organic C/N atomic ratios (8.8 – 10.6) for most of the samples are lower, which suggests a lacustrine authigenic source of organic matter in the sediments. Moreover, organic C/P atomic ratios (135 – 320) are usually higher than the Redfield ratio (106 : 1), showing that the organic phosphorus had been preferentially released via organic matter degradation during the early diagenesis process.

Key words sequential extraction; phosphorus; forms; sediment; Taihu Lake

1 Introduction

Phosphorus, an essential nutrient for the primary productivity in freshwater systems, is an important factor controlling lacustrine eutrophication. Although external input of phosphorus has been assumed as the vital responsibility for the eutrophication of lakes (Zhu Jun et al., 2005), the remobilization of phosphorus in sediments has a distinct influence on it as well (Boström et al., 1982). The concentrations of total phosphorus (P_{total}) in the sediments are often related to the trophic state or to the trophic development of lakes. The P_{total} is composed of different forms, which can undergo a release and transformation during the early diagenesis process, resulting in the formation of orthophosphates. Orthophosphates can be incorporated into lacustrine organisms and also bonded rapidly with Ca, Fe, Mg and Al ions to form insoluble phosphates, which can be released again by dissolution when the physical and chemical conditions change, e. g. redox and pH conditions. Moreover, orthophosphates in pore water released by sediments can be absorbed or bonded on particles, as discrete minerals or organic compounds. They can also be released into the overlying water via the sediment-water interface by advection, diffusion, ionic exchange and biological disturbance, thereby changing the trophic status of lakes (Föllmi, 1996). Therefore, the composition and distribution of phosphorus forms in sediments are of great significance both in the study on the cycle of phosphorus in lakes and the practical control of eutrophication.

There are many shallow lakes on the East Plain of China, which are critical to the regional society and economy, since they have been exploited for water supply, recreation, fishing, shipping, agriculture and industry. Since the 1980s, the water quality, particularly the trophic state of these lakes has been gradually worsened due to the growth of population and economic development. So research on the eutrophication mechanisms of shallow lakes is of increasing impendence (Fan Chengxin et al., 2000). Previous studies were mainly focused on the loads and behaviors of phosphorus in water and sediments, however, the forms of phosphorus in sediments have been rather poorly documented. Since the forms of phosphorus in sediments are helpful to understand the cycling of phosphorus in shal-

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** Correspondence to Li Jun, E-mail: junli5931@hotmail.com low lakes, we carried out research on the distribution of different forms of phosphorus in surficial sediments from the Wuli Bay of the Taihu Lake using a sequential extraction technique — the SEDEX method (Ruttenberg, 1992). In addition, the present authors also used the extraction techniques published by Aspila et al. (1976).

2 Materials and methods

The Taihu Lake is the third largest freshwater lake in China, with the maximum and average depths of 2.9 and 1.9 m, respectively. It is located in the middle-lower reaches of the Yangtze River, covering an area of 2350 km^2. Phosphorus is not only an important limiting factor for the algae bloom, but also a primary factor controlling the eutrophication of water in the Taihu Lake. Based on the hydrological characteristics and the extents of eutrophication of different locations, a few representative sites were selected for the study of eutrophication mechanism of the Taihu Lake. This paper presents preliminary results of the phosphorus forms in surficial sediments at one site from the Wuli Bay of the Taihu Lake (S, Fig. 1). The Wuli Bay abuts against Wuxi City, which is not only an industrialized city, but also an impacted area. So considerable amounts of industrial and urban pollutants are input into the Taihu Lake via the Wuli Bay, resulting in the worsening water quality and the increasingly severe eutrophication.

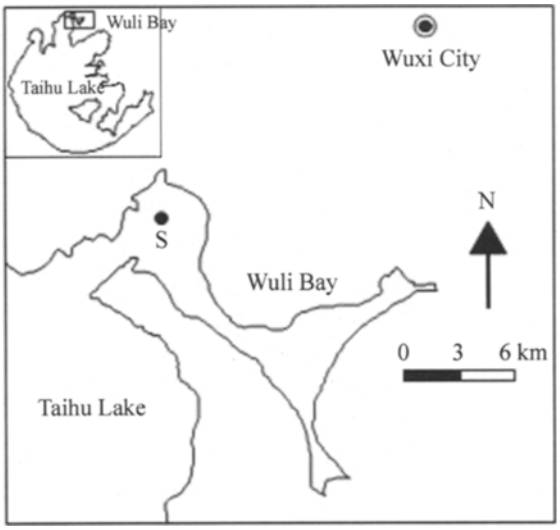

Fig. 1. Map showing the location of the Taihu Lake and sampling sites.

Surficial sediment cores were collected from northern Taihu Lake at the site of the Wuli Bay using a columned corer in October, 2002. The cores were immediately sliced into 1-cm sized sections using a plastic slicer *in-situ*. The sections were kept in the polythene centrifuging tubes, which had been washed with diluted acid and deionized water in turn. The sediment samples were stored at 4℃ for solid-phase analysis at the IGCAS laboratory.

Sediment samples were freeze-dried by means of a freeze-dryer and then ground as fine as to be < 125 μm in an agate mortar. An extraction procedure based mainly on the methods of Aspila et al. (1976) and Ruttenberg (1992) was used for separating different forms of phosphorus in the sediments, but modified at our laboratory. In this procedure the original sample was divided into four subsamples. One was oven-ashed at 550℃ for 2 hours and then extracted with 1 M HCl for 16 hours in order to determine total phosphorus. Another subsample, which is designated to determine inorganic phosphorus (P_{inorg}), was extracted as above without ashing. The difference between the results of the two extractions is assumed to be organic phosphorus (P_{org}). The third subsample was analyzed for different forms of phosphorus using the SEDEX method, which involves 4 extraction steps: (1) exchangeable + loosely bound phosphorus (P_{ex}); (2) iron-bound phosphorus (P_{Fe}); (3) authigenic + biogenic apatite + calcium carbonate-bound phosphorus (P_{aut}) and (4) detrital apatite + other remaining inorganic phosphorus phases (P_{det}). In order to avoid the efflux of phosphorus, additional water washing procedures were conducted in any step if the HCl is used as an extractant.

The concentrations of phosphorus and associated elements in the sediments, such as C, N and Fe, were also analyzed. The fourth subsample was used to determine organic carbon and nitrogen by combustion using the Element Analyzer (PE2400-Ⅱ). Firstly, the subsample was acidified with 3 M HCl for 24 hours to remove inorganic carbon, and then washed to remove excess acid, followed by freeze-drying in a freeze-dryer. The iron concentrations in CDB solutions (the extractant for iron-bound phosphorus) were determined by Flame-AAS (PE5100-Ⅱ) after acidified with ultra-pure concentrated HNO_3. Phosphorus of all solutions was analyzed using the standard spectrophotometric techniques, and the concentrations were expressed in mg · g^{-1} of dry mass of sediments.

3 Results and discussion

Figure 2 shows the vertical distribution of the different phosphorus forms throughout the core according to the SEDEX method. The concentrations of P_{total} are very high in the sediments, with an average value of 2.80 mg · g^{-1} and a variation range between 2.05 and

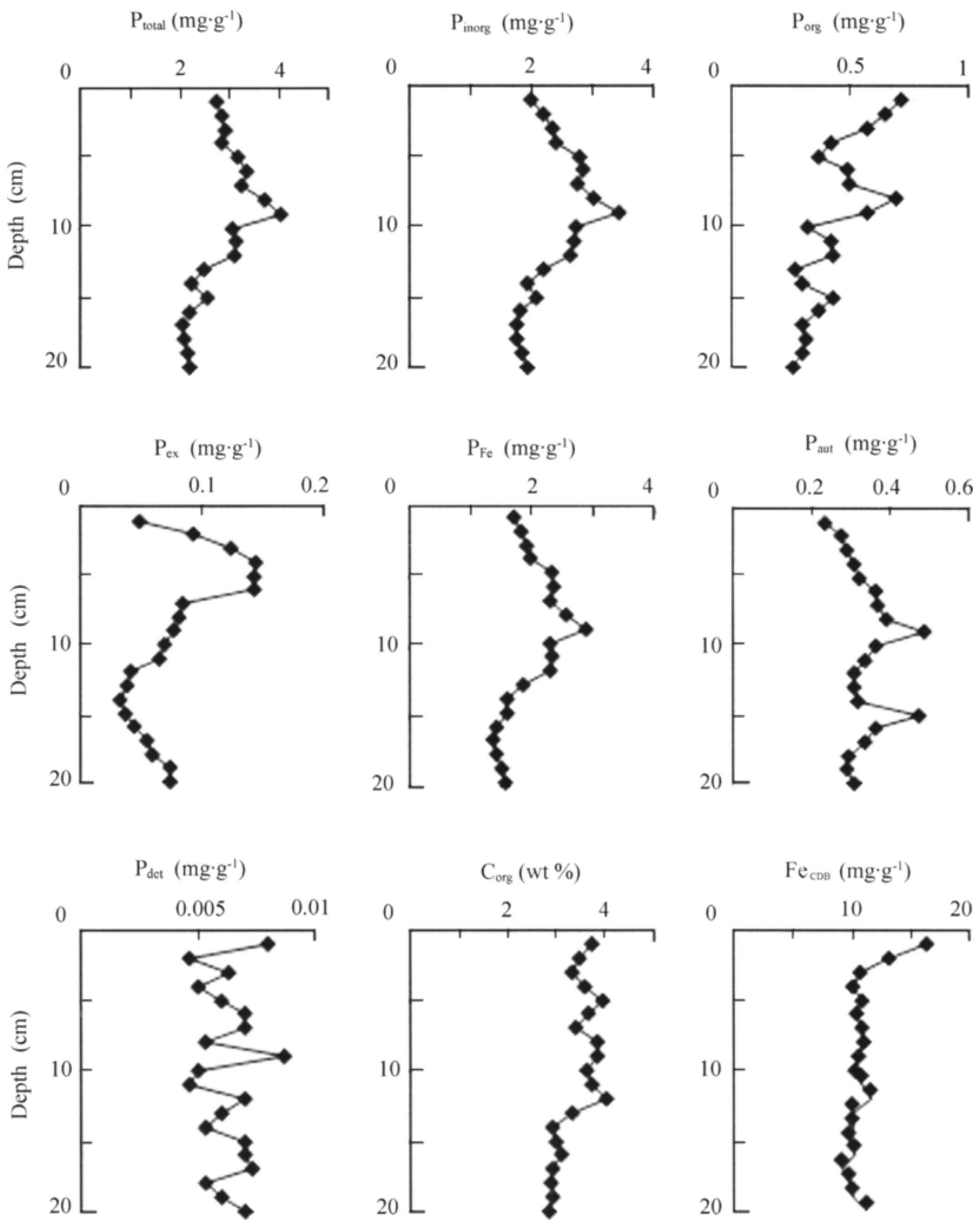

Fig. 2. Vertical variations of P_{total}, P_{inorg}, P_{org}, P_{ex}, P_{Fe}, P_{aut}, P_{det}, C_{org} and Fe_{CDB} in the sediment core.

4.02 mg · g^{-1}, and tend to increase gradually with depth, till a peak at 9 cm, and then decrease gradually downward (Fig. 2). P_{total} is mainly composed of P_{inorg}, which accounts for 70% – 90% of P_{total} (Fig. 2). The variation trend of P_{inorg} is consistent with that of P_{total}, with an excellently positive correlation ($R = 0.97$), which suggests the concentrations of phosphorus in the sediments are mostly controlled by the concentrations of P_{inorg}. In spite that the concentrations of P_{org} vary greatly, P_{org} shows a gradual decrease with depth, which indicates that the degradation extent of organic matter increases gradually downward (Fig. 2). Generally, phosphorus in the top 10-cm sediments is considered to take part in the whole-lake metabolism, then the release of phosphorus occurred continuously, resulting in a decrease in phosphorus concentrations in the top sediments with time (Søndergaard et al., 1999). The Taihu Lake, with very high water dynamical conditions, is a shallow lake, so the re-suspending effect of sediments is very notable. Thus, the release of phosphorus due to the decomposition of organic matter and the hydrolization of particle matter has a very important influence on the quality of overlying water. The highest concentrations of phosphorus present at 9-cm depth could suggest the release of phosphorus occurred in the top sediments. Even so, the overall higher concentrations of P_{total} above 9 cm than 9 cm downward indicate the input of phosphorus from the anthropogenic sources has been accreted, leading to the accumulation of phosphorus in the sediments.

3.1 Forms of inorganic phosphorus

P_{ex}, which can diffuse into overlying water when the physical and chemical conditions change, e. g. temperature, pH, water dynamics and biological disturbs, is composed mainly of the phosphorus absorbed or bonded on the particle surface of oxides, hydroxides and clay minerals. P_{org} degradation and P_{Fe} dissolution can give rise to the increase of P_{ex} concentrations (Krom and Berner, 1981). P_{ex} increases with depth up to a peak at 5 cm below the water-sediment interface, followed by a general decrease down to 14 cm, and then begins to increase with depth again. Because of the dilution of pore water, the concentrations of P_{ex} gradually decrease from 5-cm depth to the top with increasing pore water.

P_{aut} is composed mainly of apatite due to authigenesis and biogenesis, and the phosphorus followed the autogenous carbonate precipitation. This form of phosphorus has been generally suggested to represent a permanent sink of reactive phosphorus, and can undergo certain release no other than in weakly acidic condition. P_{aut} formation in sediments is of great importance for a permanent sink of reactive phosphorus, whereas P_{org} and P_{Fe} can still be released after burial. The two prerequisites for P_{aut} formation are the high enough concentrations of phosphorus for precipitation and nucleation sites (Van Cappellen and Berner, 1988). The necessary intensity of subsurface phosphate production cannot be produced solely by the decomposition of organic matter. Additional sources, such as the release from P_{Fe} dissolution are needed. The evolution trend of P_{aut} is similar to that of P_{Fe}, indicating the phosphorus release due to P_{Fe} dissolution could be a most important factor leading to P_{aut} formation.

As a permanent sink of reactive phosphorus, P_{det} originates from terrigenous sources such as apatite in metamorphic and igneous rocks, the phosphorus bound by clay minerals, and the phosphorus existing in other mineral phases. It does not dissolve in weakly acidic solutions and can indicate the change of drainage weathering. In the present study, P_{det} concentrations keep constant with depth, being the lowest in all phosphorus forms analyzed.

P_{Fe}, composed mainly of phosphorus absorbed by Fe oxides and hydrous oxides, has been suggested to represent a temporary sink of reactive phosphorus in an anoxic environment, and yet a permanent sink of reactive phosphorus in an oxic environment. P_{Fe} concentrations, constituting the main proportion of P_{inorg} (75% – 85%), and P_{total} (55% – 75%) as well, are very high in this sedimentary profile. The variation trend of P_{Fe} is consistent with that of P_{inorg} and P_{total}, and P_{Fe} has an excellent positive correlation with P_{inorg} and P_{total} ($R = 0.97, 0.99$, respectively). Iron oxides and hydrous oxides have a high affinity to phosphate and consequently, can act as a trap for upward diffusing phosphate in the oxic layer of the sediments. When Fe (Ⅲ) is reduced to Fe (Ⅱ) in the anoxic sediment layer, the absorbed phosphate will be preferentially remobilized into surrounding waters (Krom and Berner, 1981; Van Cappellen and Berner, 1988). In contrast to relatively crystalline Fe phases, poorly crystalline Fe phases have larger surface areas and consequently, they have a higher phosphorus sorption capacity, as is reflected by Fe/P atomic ratios in the CDB solution (Borggaard, 1983). Iron extracted by the CDB solution is composed mainly of Fe oxides and oxyhydroxides, and probably contains little Fe sulfide and Fe absorbed by clay mineral particles. Iron concentrations are very high in the CDB solution with an average value of 10.9 $mg \cdot g^{-1}$, and a variation range between 9.7 and 16.3 $mg \cdot g^{-1}$, indicating that the CDB solution has a high extracting capacity for Fe compounds. The concentrations of Fe_{CDB} rapidly decrease with depth, leading to a lowest value at 3-cm depth, and then begin to stabilize downward (Fig. 2). Iron (Ⅱ) diffusing upward into the oxic layer can be oxidized to form Fe (Ⅲ) oxides and hydrous oxides, leading to the accumulation of Fe in the top 3-cm depth (5). The low Fe/P atomic ratios (2.0 – 5.3) could indicate that the Fe compounds extracted with CDB have a lower proportion of relatively crystalline phases in all samples, and the absorption between iron and phosphorus has probably reached certain equilibrium (Fig. 3). P_{Fe} is the main form of phosphorus in the sediments of the Taihu Lake. It can be remobilized and finds its way into the overlying water through the sediment-water interface, followed by changes in redox conditions in the sediments. Consequently, the release of phosphorus due to P_{Fe} dissolution could exert a significant impact on the water quality and trophic condition of the lake.

3.2 Vertical variation of organic phosphorus

Organic carbon, organic C/N and C/P atomic ratios can be used to constrain the source of organic matter, the extent of organic matter degradation and the geochemical behaviors of organic phosphorus in the sediments. The C_{org} concentrations are low and stable (2.8% - 4.0%). The C_{org} concentrations are high and stable at the first 12-cm depth with a small variation range between 3.3% and 4.0%, which may reflect the accumulation of organic matter (Fig. 2). The C_{org} concentrations rapidly decrease from 4.0% to 2.9% at the following 2-cm depth, reflecting rapid degradation of organic matter. The C_{org} concentrations are low and steady from 14-cm depth to the bottom sediments, indicating a stable sedimentary environment. Few bottom samples have very high organic C/N atomic ratios (Fig. 3), which could reflect a relatively high contribution of terrigenous organic matter, or the nitrogen of algae protein is preferentially released during the algae degradation. Organic C/N atomic ratios are low (8.8 - 10.6) in the rest of the samples, suggesting that the organic matter is mainly derived from lacustrine authigenesis (Meyers, 1997). Moreover, organic C/N atomic ratios with slight variation do not show specific variation trends, which could be related to the selective degradation of organic matter during early diagenesis, so organic C/P atomic ratios can actually reflect the productivity of the lake (Emmeis et al., 2000). Organic C/P atomic ratios, covering a range from 135 to 320, are usually higher than the Redfield ratio (106 : 1) in all samples (Fig. 3). In spite of the fluctuation, organic C/P atomic ratios show an overall decrease trend from the bottom to the top of the profile. All those show that the degradation extent of organic matter increases gradually with sedimentary depth, while organic phosphorus was preferentially released via organic matter degradation during the early diagenesis process (Ingall and Van Cappellen, 1990). At the same time, the high organic C/P atomic ratios, probably due to a high productivity in the lake water, could indicate an increase in anthropogenic phosphorus as well (Ruiz-Fernández et al., 2002). Organic C/P atomic ratios are high in top sediments, suggesting part of organic matter was decomposed in the process of organic matter settling from water to sediments. Furthermore, the release of P_{org} occurred in this process as well.

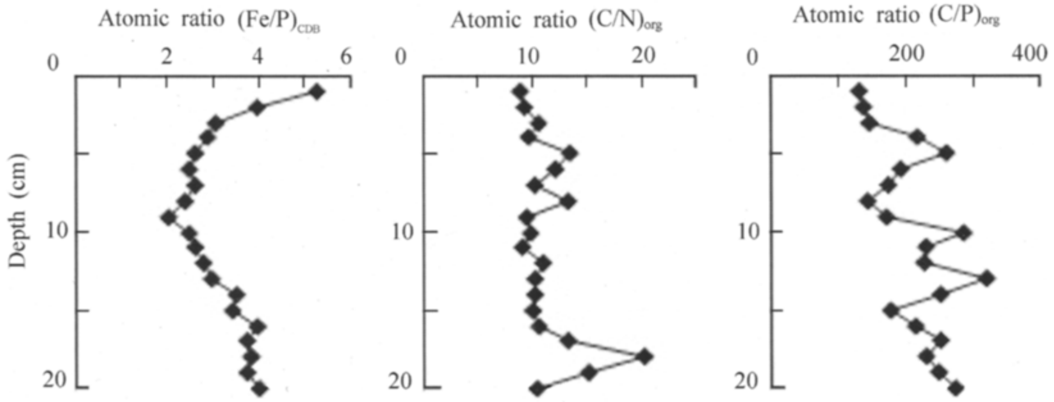

Fig. 3. Vertical variations of Fe/P atomic ratios in CDB solutions, organic C/N and C/P atomic ratios.

C_{org} shows a remarkable positive correlation with P_{total} and P_{inorg} ($R = 0.88$, 0.84, respectively), suggesting that the concentrations of P_{total} and P_{inorg} could be regulated by organic sources (Fig. 4). However, the positive intercept on the TP axis indicates that an amount of unidentified phosphorus may be anthropogenic phosphorus, present in the sediments. Moreover, a preferable positive correlation between C_{org} and P_{org} ($R = 0.62$) shows that organic matter is the main source of P_{org} (Fig. 4). Meanwhile, P_{inorg} and P_{org} have a small positive intercept on the C_{org} axis, i.e., there is still part of organic matter in existence, though no P_{inorg} or P_{org} in the sediment. This indicates organic phosphorus could have been preferentially released in inorganic phosphorus forms via organic matter degradation during the early diagenesis process, and the portion of organic phosphorus could be extracted in the acid extraction process due to the hydrolization of organic phosphorus as well (Eijsink et al., 1997; Liang Xiaobin et al., 2004). On the other hand, some bacteria and protozoa species can assimilate excess P_{inorg} and store them in polyphosphorus forms under favorable conditions, which are the potential energy and can be utilized in the metabolic process when the conditions become less favorable (Khoshmanesh et al., 2002). So the P_{org} can be remobilized in P_{inorg} forms, thus promoting the translation and remobilization among the different forms of phosphorus.

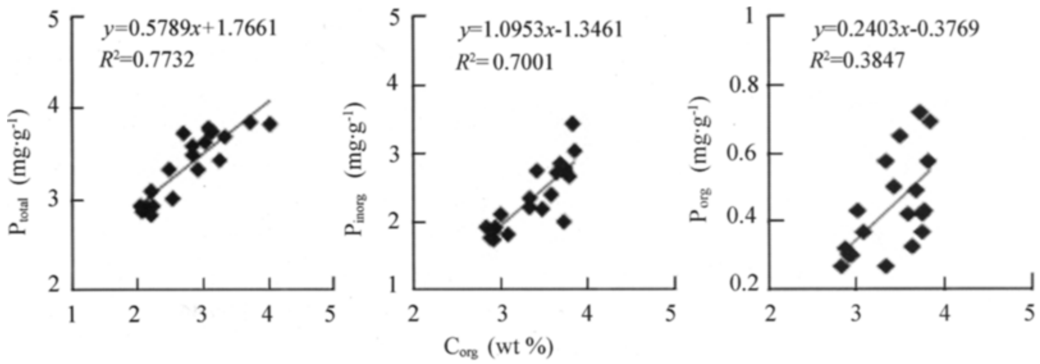

Fig. 4. P_{lots} of C_{org} versus P_{total}, P_{inorg} and P_{org}.

4 Conclusions

The SEDEX method was used to determine the concentrations of phosphorus present in different forms in the surficial sediments from the Wuli Bay of the Taihu Lake. The results show the concentrations of phosphorus are high in the sediments, which could undergo a further release, while the waste input of anthropogenic sources can have a distinct influence on eutrophication of the Taihu Lake. The organic phosphorus has been preferentially released via organic matter degradation in inorganic phosphorus forms during the early diagenesis process. The inorganic phosphorus, especially iron-bonded phosphorus, could be released, following changes in redox conditions in the sediments; consequently it exerts an important impact on the water quality and trophic status of the Taihu Lake. Microorganisms could have a distinct influence on the translation and remobilization among different forms of phosphorus; more research must be carried out on its biogeochemical mechanism.

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