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RELATIONSHIPS OFPHOSPHORUSFORMS INSEDIMENTS OF FUBAO GULF, LAKE DIANCHI, CHINA

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ABSTRACT

Phosphorus (P) forms found in lake sediments provide information that is important for eutrophication control. Contents of nine kinds of phosphorus forms in five top-layer (0–10 cm) sediment samples collected from Lake Dianchi, China were investigated. Inorganic phosphorus (I-P) comprised 62.3–78.2% of TP in these samples, owing to the low level of aquatic life caused by the high content of external pollutant sources and the low water exchange rate of once annually. Algae significantly deplete sedimentary P, resulting in low BAP forms in the sediment. Aluminum (Al) and manganese (Mn) oxides and iron hydroxides (Fe-P), organic phosphorus (Org-P),and calcium-bound P (Ca-P) were significantly correlated with TP content in the top sediment layers. The correlation between I-P and Fe-P content was also significant in these layers. All BAPs showed low correlation with Org-P. It was concluded that the bioavailability of TP in sediment is affected by inflow and anthropogenic activities. The P species and contents in the sediments are useful for the cognition of environmental geochemical behavior of P in the sediment of Dianchi Lake, and this is of great importance for the pollutant load, especially the internal load, control and environmental restoration of Lake Dianchi.

Key words: Bioavailable phosphorus,Correlation, Lake Dianchi, Phosphorus forms, Sediment

INTRODUCTION

Phosphorus (P) is an essential element in lake ecosystems and plays a dominant role in cellular energetics as ATP and as an important part of many structural and biochemically functional components of the cell growth of hydrophytes, including algae (Amano *et al*., 2010; Jia *et al*., 2013; Hao *et al*., 2012). Algae absorb the dissolved phosphorus. Evaluations of eutrophication and the selection of methods to prevent and treat it are more feasible when based on knowledge of P forms rather than solely on total phosphorus (TP).

In general, two main sources contribute to the nutrient status of lake estuaries: (a) loading from point and nonpoint sources and (b) internal loading originating from sediments (Cai *et al*., 2013; Liang *et al*., 2008; Ding *et al*., 2014; Ma *et al*., 2012). Many cities throughout the world are located on estuaries, which are highly productive ecosystems and also function as nurseries for various fish, crustacean, and mollusk species of commercial interest (Kon *et al*., 2012; Vinagre *et al*., 2010). Therefore, estuarine sediment research is of great interest from geochemical, recreational, environmental, economic, and ecological perspectives.

Internal loading by sediment release plays an important role in the P status of some lakes, and thus evaluating the potential for P release is important. As P enrichment of lake sediments increasing, P forms and potential bioavailability in lake sediments have been increasingly investigated (Zhang, 2011; Meng *et al*., 2014; Li and Brett, 2013).Excessive growth of algae and bacteria in freshwater systems has been linked to the content of bioavailable phosphorus (BAP) in the system (Baken *et al*., 2014; Gao *et al*., 2012).

Usually, the BAP was divided into various P forms, such as algae available P (AAP) and water-soluble P (WSP), according to different extracting agents (Zhu *et al*., 2013; Gao *et al*., 2014). Gao *et al*. (2014) found that AAP was the major form of BAP, followed by $NaHCO_3$-extraction P (Olsen-P). Furthermore, AAP and Olsen-P showed significant correlations with P extracted by NaOH and HCl. Zhu *et al*. (2013) reported that the BAP accounted for only 12.1-27.2% of total organic P in sediments while Zhou *et al*. (2013) stated that BAP accounted for 26.8-71.8 % of the contents of total phosphorus (TP) in the top 5 cm sediment. Both the results mentioned above indicated that the sediments were a potential source of P for algae blooms in lake. The BAP might play an important role in maintaining the eutrophic status of lakes. However, the contents of various P forms varied greatly because the investigation sites were different and the extraction methods were also not the same (Gao *et al*., 2014; Wang *et al*., 2010; Xiang *et al*., 2011; Zhu *et al*., 2013). Moreover, the anthropogenic activities can also affect the distribution of phosphorus fractions in a lake and caused a great variation of phosphorus content in various sampling sites of a lake (Wang *et al*., 2010).

In this study, five sediment samples were collected from the Fubao Gulf, Lake Dianchi, and theobjectives of this study were investigate the relationships of BAP and other P forms in the samples,and analyzed the effect of anthropogenic activities on the spatial distribution and relationships of various P forms. The understanding of the anthropogenic activities associated with sedimentary P can guide the selection of eutrophication prevention and treatment methods.

MATERIALS AND METHODS

Study Site: This study examined Fubao Gulf, Lake Dianchi, which experiences severe algae blooms. One of the important factors of algae blooms is the phosphorus in the water. The released phosphorus from the sediment is one important source of phosphorus in the lake water (Hu *et al*., 2006; Zhou *et al*., 2013; Liu *et al*., 2009; Chen *et al*., 2010).

The drainage area of Lake Dianchi is situated in the central part of the Yunnan-Guizhou Plateau, along the watersheds of three Yangtze River systems, plus the Zhujiang and Honghe rivers at 102°29'–103°01' E, 24°29'–25°28' N (Figure 1). Lake Dianchi is one of the six largest freshwater lakes in China, with an average depth of 4.4 m and a surface area of 300 km^2. The elevation of the area is 1900 m above sea level, as measured from the Huanghai (Yellow) Sea. The city of Kunming is located in the drainage area and caused greatest influence on the water environment of Lake Dianchi.

Lake Dianchi is divided into two parts: Caohai and Waihai. Caohai is north of Waihai, and Fubao Gulf is in the northern part of Waihai. According to the environmental bulletin of Yunnan Province (2010), Caohai is in a hyper-eutrophication state, and Waihai has moderate eutrophication. According to the environmental bulletin of China (2013), Caohai and Waihaiare in moderate eutrophication. The Daqinghe and Haihe are two important rivers that enter Fubao Gulf from the north. Table 1 shows water quality and quantity measurements of the Daqinghe and Haihe rivers from January to May 2004 (Kunming Municipal Drainage Monitor Station, 2004). Phosphorus is one of the main contaminants from the rivers and more than 165 tons of phosphorus was brought into Fubao Gulf.Contaminated sediments from the Daqinghe and Haihe estuaries are the major internal pollutant sources of the northern part of Waihai.Thus, the most representative study area isFubao Gulf (area 0.2 km^2; Figure 1), which between these two river estuaries.

The investigated area has almost no submerged vegetation except some *Antenoronneofiliforme*(Nakai) Hara, with maximum length of more than 3 m. The substrata in areas between the eastern lake bank and 30 m west of the bank were almost hard.

Sampling: Sediment samples were collected on 14 October 2005 in Fubao Gulf (Figure 1). To illustrate anthropogenic effects on P in the sediment, five sediment samples (i.e., FB1, FB2, FB3, FB4, FB5, Figure 1)were collected from the top 0–10 cm using a Petersen sediment sampler (Table 2). Samples were stored below 4℃ prior to analyses.

The latitude and longitude of sampling positions were recorded by a GPS posting meter (GM-101; Holux, Irvine, CA, USA).

Sample Pretreatment: Firstly, the fresh sediment samples were riddled to remove sundries such as plant residues and seashells and then ground and mixed to homogeneity. Then the sediment samples were divided into three groups after vacuum freeze drying. After vacuum freeze drying, the dry samples were grinded and screened with a sieve (100 Order). The prepared samples were sealed and stored under room temperature.

Analytical Methods

Water Depth, Sediment Depth, Sediment Color, and Sediment Properties: Water depth, sediment depth, sediment color, and sediment properties were measured *in situ*. Sediment samples were placed in plastic bags and stored in an incubator with ice bag.

Contents of Organic Matter (OM) and Water Content (WC): Contents of organic matter (OM) and water content (WC) in the sediments were analyzed using standard soil physical and chemical methods (Bao, 2000).

Sequential Extraction Procedures: The particle sizes of sediments were measured using a Mastersizer Analysis Instrument (Malvern Instruments Ltd, Malvern, U.K.). The Standards, Measurements and Testing Programme (SMT; Ruban *et al*., 1999) was used to analyze the following contents of P fractions in the sediments: NaOH-extractable P (NaOH-P), HCl-extractable P (HCl-P), inorganic P (IP), organic P (Org-P), and TP. NaOH-P and HCl-P mainly represented iron-bound P, including P bound to Fe, Al, and Mn oxides and hydroxides (Fe-P), and calcium-bound P (Ca-P).

BAP Extraction Methods: The bioavailable P forms in fresh sediments can be divided by chemical methods into the following four groups (Andrieux and Aminot, 1997): algae-available P (AAP), water-soluble P (WSP), ready-desorptive P (RDP), and $NaHCO_3$-extraction P (Olsen-P).

Fresh sediment samples were used for the analysis of sedimentary BAP, so as to determine the BAP content of sediments under near-natural conditions. Different digestion agents indicated potential BAP content under various environmental conditions. Olsen-P was measured using digestion agent, i.e.,0.5mol/L $NaHCO_3$,and Olsen-Pwas mostly upper-activity calcium

P were extracted (Bu and Magdoff, 2003). Deionized water and 0.01 mol/L $CaCl_2$ were used to extract sediments with high WSP content and low P fixed capability (Bu and Magdoff, 2003). Using NaOH (0.1 mol/L) as the digestion agent, P as AAP, which represented algae-available parts in the photosynthetic layer under aerobic conditions in the lake was extracted(Bu and Magdoff, 2003).

The measured sediment wet-weight contents were converted to sediment dry-weight content via equation 1:$C_{dw}=100^{*}C_{ww}/(100\text{-}WC)$ (1)

Where,$C_{dw}$is the dry-weight content of P in sediment (mg/kg);$C_{ww}$is the wet-weight content of P in sediment (mg/kg); andWC is the water content of sediment (% dry weight).

RESULTS AND DISCUSSION

Particle-size Distribution of The Samples: Table 3 shows the particle size of sediments. According to the U.S. soil texture classification standard, FB1, FB2, and FB5 (Fig. 1) are classified in the silt loam subclass of loam, whereas FB4 is in the sand loam subclass of loam. FB4 has a larger volume and larger weighted mean diameter (D) than those of FB2, FB1, and FB5.

Distribution of P Forms: Inorganic phosphorus comprised the major part of TP, totaling about 62.3–78.2%. The high proportion of IP was probably due to 1) the low aquatic life content resulting from the high content of external pollutant sources and 2) water exchange of only once per year.

Fe-P accounted for 42.8–84.3% and Ca-P represented 19.7–63.9% of IP. Aquatic life consisted mainly of algae, as well as some *Antenoronneofiliforme* (Nakai) Hara, but there were few other emergent, submerged, or floating macrophytes (Dong *et al*., 2014). Lake Dianchi exchanges its water once annually, owing to water use by peripheral agriculture, industry, recreation, and residents. For FB4 sediment, which had a low degree of contamination, the Org-P/TP ratio was greater than that of highly contaminated sediment.

Distribution of BAP: Figure 3 shows BAP contents in the sediments. The ratio of BAP to TP in sediment is shown in Table 5. The rank order of the different P extracts was the same in all cases. AAP account for mostpart ofTP content of the sediment, and then was the Olsen-P, WSP, and RDP.

Among the four BAP forms, AAP represented 14.0–47.9% of TP, with Olsen-P accounting for 2.5–4.3%, WSP comprising 0.1–1.8%, and RDP representing less than 0.1% of TP. For the five sediment samples, the ratios of BAP to TP from lesser to greater were FB4, FB1, FB5, FB2, and FB3, constituting about 17.9%, 30.4%, 31.9%, 32.3%, and 54.0% of TP, respectively. Sandy sediment has less bioavailable matter than sludgy sediment. The difference in sediment specific surface area(Table 3) accounted for the variance in surface adsorption of P between them. Sediment sample at FB4 showed the lowest BAP among the five sampling points, which was probably due to the low specific surface area of the sediment (Zhu *et al*., 2013). Another reason for the low BAP at FB4 was that FB4 was the nearest of the five sampling sites to the bank. Hence, it was most strongly affected by rudimental flotsam resulting from the construction of a reinforced concrete bank. This kind of material contains no phosphorus and resulted in a low BAP content of FB4. Point FB5 was nearest to the Haihe, and point FB1 was the nearest point to the Daqinghe. Similar BAP to TP ratios were found in the FB5 and FB1 samples, because the scouring function of water flowing from the estuary downstream, with both rivers having similar contaminant sources, mainly from resident and agricultural. Point FB3 had a high ratio of BAP to TP, showing that sediments at this point had high potential bioavailability. This was an important finding, as this point was far from estuaries and banks, and helophytes were protected from the impact of estuary inflow and anthropogenic activities. Thus, it was concluded that the bioavailability of TP in sediment is affected by the impacts of inflow and anthropogenic activities.

The correlation coefficients between the four BAP forms (WSP, RDP, AAP, and Olsen-P) and TP were 0.0004, 0.0866, 0.7659, and 0.5082 (Table 5), respectively, with AAP having the highest correlation with TP content. This result differs from that of Zhou *et al*. (2001), who found that WSP, RDP, and Olsen-P, but not AAP, correlated significantly with TP. The difference is mainly due to different growth conditions of helophytes (algae, emergent, submerged, and floating plants) in various lakes and different sediment characteristics. The better correlation of AAP among the four BAP forms with TP content may be related to algal blooms in Fubao Gulf in recent years.

Among the various sampling positions, measured BAP content showed the following descending order: FB3>FB1>FB2>FB5>FB4. Four BAP forms in sample FB4 had lower contents than the other samples, perhaps because algae that were present (Figure 4) significantly depleted P in the sediment. The main algal species was *Microcystis aeruginosa*, with some *Scenedesmus quadricauda* also present (see Figure 4).

Correlation Analysis of BAP and Other P Forms: Table 6 shows dependency relationships between TP, Fe-P, Ca-P, Org-P, I-P, WSP, RDP, AAP, and Olsen-P.

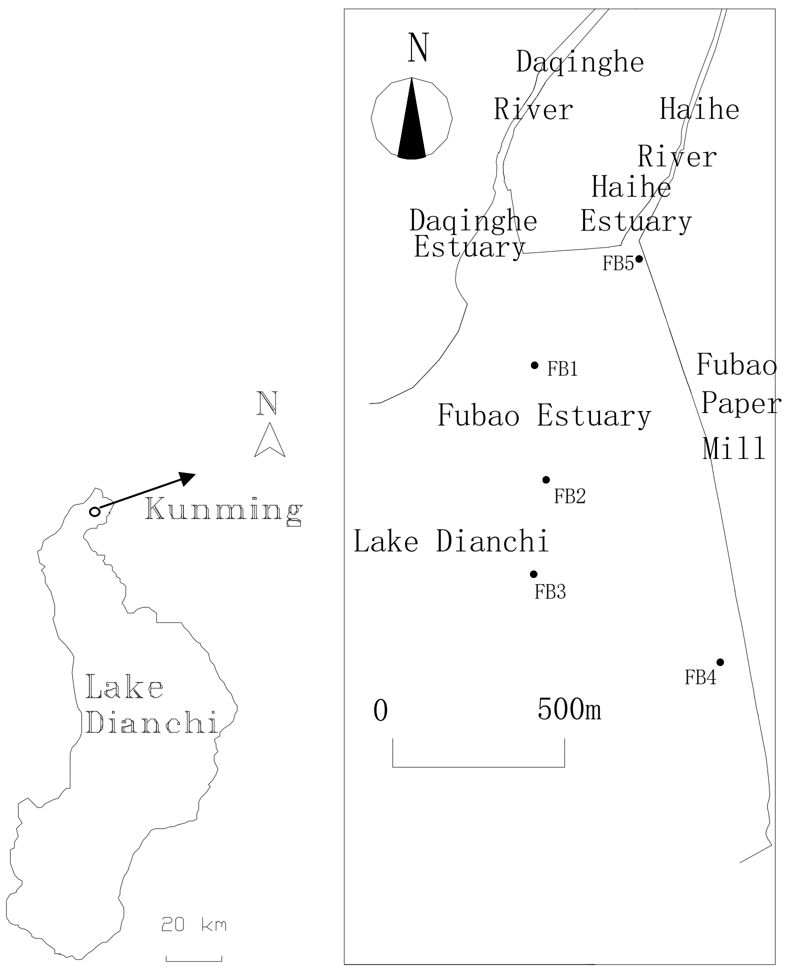
Correlations between TP and other P forms: In the top sediment layers, I-P, Fe-P, Org-P, and Ca-P showed the greatest dependency relationship with TP, with the corresponding correlation coefficients being 0.9982 (α=0.01), 0.988 (α=0.01), 0.8837 (α=0.05), and 0.7517, respectively. Thus, the content of sedimentary I-P, Fe-P, Org-P, and Ca-P was high in this lake with a high TP content in the sediment. In Fubao Gulf, P forms in sediments having various characters all had significant dependency relationships with TP.

Dependency relationships between P forms:I-P and Fe-P contents of the sediment were significantly correlated (α=0.01), with a correlation coefficient of 0.9855. The correlation coefficients between Fe-P and Org-P, I-P and Org-P, I-P and Ca-P, Fe-P and Ca-P, and Ca-P and Org-P, were 0.8644, 0.8607, 0.7692, 0.6623 and 0.6122, respectively.

Thus, at the various sampling points in the Fubao Gulf, I-P and Org-P in the top sediment layers were commonly correlated. This may be related to the interaction between the transformations of I-P and Org-P. Bacteria absorb and transfer is one of the most important mechanisms of transformation of I-P and Org-P. More than 6×10^5 cell/g dry sediment of I-P degrading and Org-P degrading bacteria was found in lake sediment. These kinds of bacteria can transfer the I-P into Org-P or Org-P into I-P (Feng, *et al*., 2008).

Dependency Relationships Between P Forms and BAP: Correlation analysis of the four types of BAP with P forms showed that AAP and I-P had the best dependency relationship (dependency coefficient 0.7978), perhaps due to the high soluble phosphate content of I-P, with the soluble phosphate being easily assimilated by algae. Dependency relationships between AAP, Fe-P, Ca-P and Org-P were also significant, as was the relationship between Olsen-P and Ca-P. All of the BAPs showed a low dependency relationship with Org-P.

Dependency Relationships Between BAPs: Correlation analysis of the four types of BAP showed the best dependency between WSP and ADP content (dependency coefficient 0.8409). The dependency coefficient between AAP and Olsen-P was 0.8143, and that between RDP and Olsen-P was 0.7189.



Note: FB1, FB2, FB3, FB4, FB5 are five sampling sites.

Figure 1. Schematic figure of the research area and sampling points in Fubao Gulf, Lake Dianchi

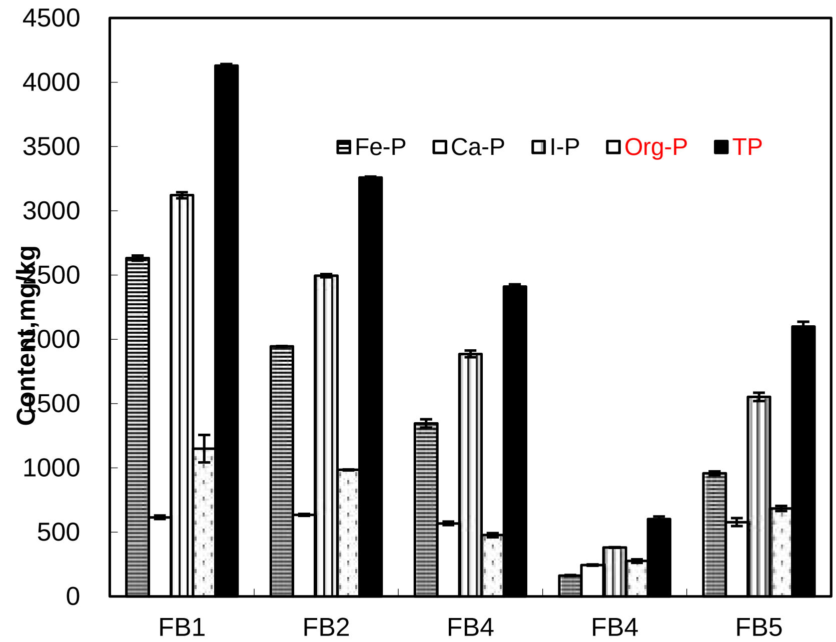


Figure 2.Contents of various P fractions (Fe-P, Ca-P, I-P, Org-P) and TP in sediments (mg/kg)

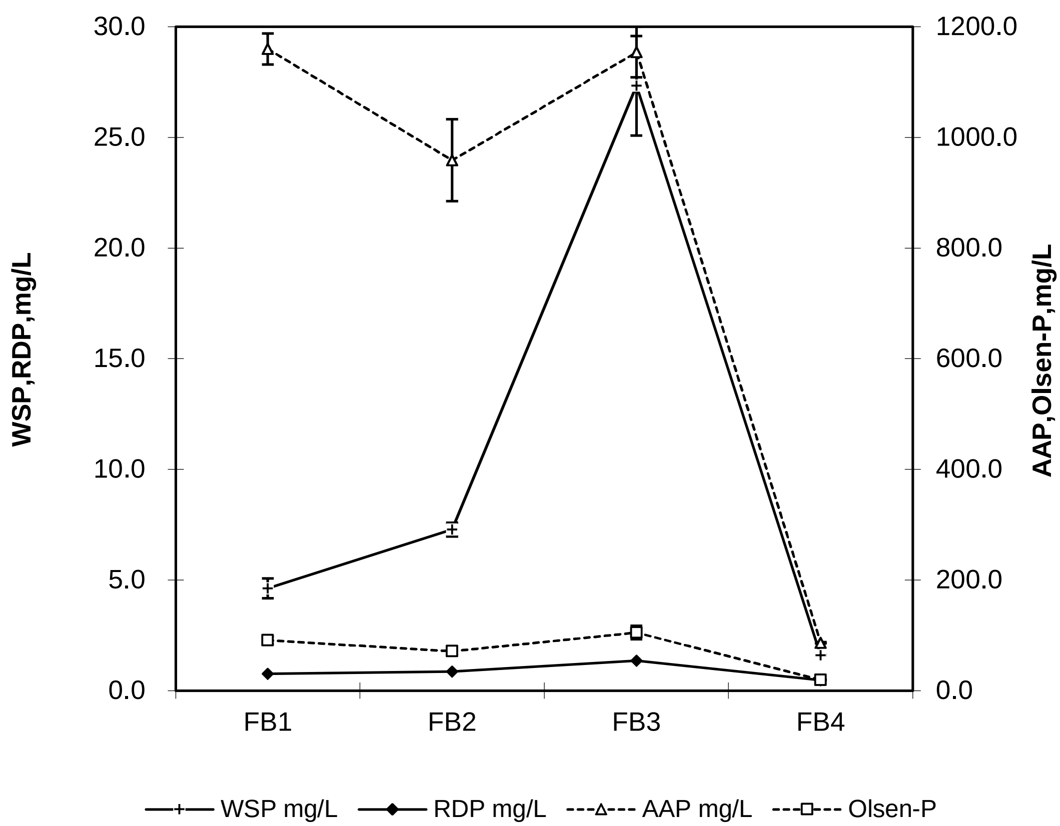


Figure 3. Contents of BAP forms in sediments (mg/kg) RDP- ready desorptive P, WSP- water soluble P, Olsen-P - $NaHCO_3$ extractable P, AAP-algae available P

Conclusions: I-P was the major P form in the five top-layer sediment samples due to the lack of aquatic life resulting from the high content of outside pollutants and the low water exchange rate of only once annually. Algae significantly depleted sedimentary P, resulting in low sedimentary BAP forms. I-P, Fe-P, Org-P,and Ca-P contents showed the highest dependency relationships with TP content in the top sediment layers. I-P and Fe-P content were significantly correlated in these sediment layers. All of the BAP forms had a low dependency relationship with Org-P. The bioavailability of TP in sediment is thus affected by the impacts of inflow and anthropogenic activities, such as bank construction.

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