In: Phosphorus: Properties, Health Effects and the Environment ISBN: 978-1-62081-399-7
Editors: Ming Yue Chen and Da-Xia Yang © 2012 Nova Science Publishers, Inc.

Chapter 6

APPLICATION OF THE STANDARDS, MEASUREMENTS AND TESTING PROGRAMME AND X-RAY POWDER DIFFRACTION TO STUDY PHOSPHORUS SPECIATION IN SEDIMENTS FROM BAIHUA LAKE, CHINA

Mei Jin[1,2,*], Jiwei Hu[1], Liya Fu[1] and Miao Jia[1]

[1]Guizhou Provincial Key Laboratory for Information System of Mountainous Areas and Protection of Ecological Environment, Guizhou Normal University, Guiyang City, Guizhou Province, China

[2]School of Chemistry and Materials Science, Guizhou Normal University, Guiyang City, Guizhou Province, China

ABSTRACT

The distribution characteristics of phosphorus speciation in 17 surface sediment samples collected from Baihua Lake, one of the five drinking water sources for Guiyang City in southwest China, were investigated using the Standards, Measurements and Testing (SMT) programme and X-ray powder diffraction (XRD). In the study area, the total phosphorus (TP) concentrations varied from 591.57 to 2374.80 mg/kg with the mean concentration of 1604.02 mg/kg (dry weight), and it was evident that the phosphorus level in the sediments was generally higher than in other eutrophic lakes such as Chaohu Lake and Xihu Lake. The results of the two methods, the SMT and XRD, demonstrated the presence of different phosphorus species in the lake sediments. The results of the SMT protocol indicated that the average percentages of inorganic phosphorus (IP), organic phosphorus (OP), iron/aluminum-bound phosphorus (Fe/Al-P) and calcium-bound phosphorus (Ca-P) were 67.33%, 30.53%, 39.38% and 27.41%, respectively. Notably, the concentrations of inorganic phosphorus (IP) were higher than that of OP, and the IP consisted mainly of Fe/Al-P. The high concentrations of Fe/Al-P, a major and direct source of phosphorus release, might play an important part in accelerating eutrophication of water bodies. The present XRD analysis showed that AlPO4 was found in all sediment samples among phosphorus species. Further statistical analyses of the

* E-Mail: jwhu@gznu.edu.cn (J.H.), E-Mail: jinmeimei1985102@163.com (M.J.).

results revealed significant and positive correlations between phosphorus species in sediments, and the four cluster levels were obtained. Additionally, remediation measures were briefly evaluated for the lake considering its pollution conditions and distinctive environmental features.

1. INTRODUCTION

Baihua Lake (E 106º27′- 106º34′, N 26º35′- 26º 42′), a man-made reservoir built in the 1960s, is located in Qingzhen County and only 16 km west of Guiyang City, the capital of Guizhou Province in southwest China [1-3]. Baihua is a deep lake lying between mountains in an area with typical carbonate rock (Karst) terrain in Yungui Plateau. The mean depth of the lake is approximately 12 meters, with the greatest depth up to 45 meters [4]. The lake covers a surface area of 14.5 km^2 and holds 1.82×10^8 m^3 of water. Baihua Lake is one of the five drinking-water sources for approximately 3 million people in Guiyang, and it is a multi-functional water body that is also used for flood control, shipping, and fishery [5, 6].

Phosphorus, a mineral nutrient, often limits primary production in many freshwater ecosystems [7-9], and it is generally regarded as one of the most important limiting nutrients for accelerated eutrophication [10-13]. Lake sediment, an important part of water environment, can act as either a sink or a source for phosphorus [14-16]. Under normal conditions, sedimentation of phosphorus via particulates exceeds the amount released by sediments, causing a net accumulation over time. However, under certain conditions, release of phosphorus from sediments may be large enough to cause, or at least perpetuate, the eutrophication process [17]. Bengtsson demonstrated that although 98% of the external phosphorus load had been diverted from Lake Sodra Bergundasjon in Sweden, it remained eutrophic due to the high rate of phosphorus regeneration from its sediments [18]. Consequently, sediment phosphorus most obviously plays an important role in accelerating eutrophication of water bodies.

With the development of various industries and agricultures in the surrounding areas, Baihua Lake has been polluted seriously by phosphorus, nitrogen, organic matter and heavy metals. At present, the lake is already in a eutrophic state, and phosphorus has been one of the main factors [19]. The eutrophication has sometimes caused algal blooms, fish suffocation and other undesired effects [20]. Some algae can produce toxins that have been associated with human health problems [21]. Therefore, it is necessary to analyze sediment phosphorus, especially the role of which should be considered. However, not all phosphorus is bio-available. The total phosphorus (TP) concentration is not enough to indicate the potential risk. Thus, in this investigation, phosphorus forms were studied based on the Standards, Measurements and Testing (SMT) programme proposed by the European Commission [22]. The SMT protocol leads to obtaining five phosphorus fractions: iron/aluminum-bound phosphorus (Fe/Al-P) bound to Al, Fe and Mn oxyhydrates; calcium-bound phosphorus (Ca-P); inorganic phosphorus (IP); organic phosphorus (OP) and TP. The concentration of the Fe/Al-P fraction can be used for the estimation of both short-term and long-term available phosphorus in sediments and it is a measure of available algal phosphorus [23]. Conversely, Ca-P is a relatively stable, inter and non-bioavailable phosphorus fraction [24]. The most important inorganic phosphorus pools seem to be Fe/Al-P and Ca-P [25]. Most methods of phosphorus determination are based on the reaction of phosphorus with an acidified molybdate reagent to yield a phosphomolybdate heteropolyacid, which is then reduced to an intensely coloured blue compound and determined spectrophotometrically [26, 27].

At present, eutrophication problem of Baihua Lake has received much attention from governments and environmental researchers. Hitherto, Jiang et al. [19] and Wang et al. [28] have investigated the chemical species of phosphorus in sediments from Baihua Lake, using a sequential extraction technique reported by Jin et al.. However, to the best of our knowledge, few of studies on the chemical species of phosphorus in sediments from Baihua Lake have been conducted employing SMT programme and X-ray powder diffraction (XRD), a non-destructive and rapid analytical technique primarily used for phase identification of crystalline materials that can provide information regarding unit cell dimensions [29]. The objectives of this research were to study the distribution characteristics of phosphorus speciation using the SMT programme and XRD, to make a statistical analysis on test data for interpretation of possible origins of the phosphorus loadings and transformation mechanism of the phosphorus species, and finally to provide relevant data for the management of the lake. Additionally, remediation measures were briefly evaluated for the lake considering its pollution conditions and distinctive environmental features.

2 Materials and Methods

2.1. Sampling

The sediment samples used in this study were collected during June 2011 in Baihua Lake with a grab-sampler. Superficial sediment samples were taken at Dachong (DC), Yueliangwan (YLW), Meituwan (MTW), Pingpu (PP), Guanyinshanzhuang (GYSZ), Laojiutu (LJT), Jiangjiapu (JJP), Yapengzhai (YPZ), Tishuizhan (TSZ), Longtan (LT), Jinyinshan (JYS), Dahewan (DHW), Pijiangou (PJG), Baifan (BF), Chafanzai (CFZ), Tangchong (TC) and Maixihekou (MXHK), which were selected based on the size, shape, and water flowing direction of the lake (Figure 1). The precise collection sites were located in situ using a global positioning system (GPS). Each sediment sample was obtained by mixing three to four sediments collected near the sampling locations. Samples were put in the glass bottles (1000 cm^3 volume) that were cleaned with 5% HCl (v/v) and 5% HNO_3 (v/v), and immediately transported to the laboratory. In our laboratory, the sediments were centrifuged and the supernatant were discarded. After air-dried at room temperature, the sediment samples were ground to < 100 mesh for analysis.

2.2. Instruments and Reagents

The following instruments were used in this research: (1) GPS-72 from American Garmin Corporation made in Taiwan, (2) UV-Visible spectrophotometer (Cary 100 Bio) by Varian Corporation from USA, (3) X-ray diffractometer (X’pert PRO) produced by PANalytical Corporation in Holland, (4) Immersion oscillator (SHZ-C) by Shanghai Medical Instruments Corporation from China, (5) Water purification system (Nex Power 2000) from Human Corporation in Korea. All reagents used in this research were made in China. The hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were guaranteed reagent (GR) grade. All of the other reagents used were analytical reagent (AR) grade. Deionized water was prepared by the water purification system presented above.

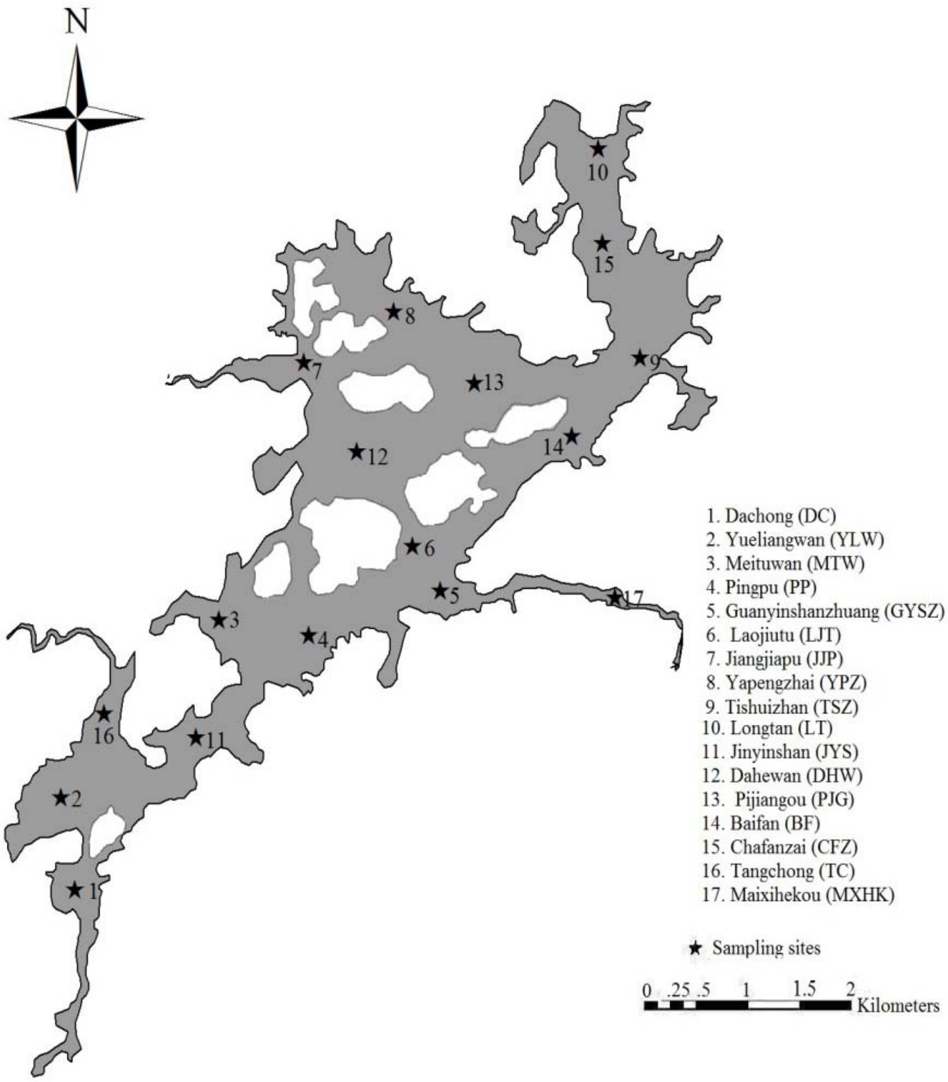

Figure.1: Distribution of sampling sites in Baihua Lake.

2.3. Analytical Procedures of TP and Phosphorus Forms

In this investigation, TP and phosphorus forms were studied based on SMT protocol, the process of which was shown in Figure 2.

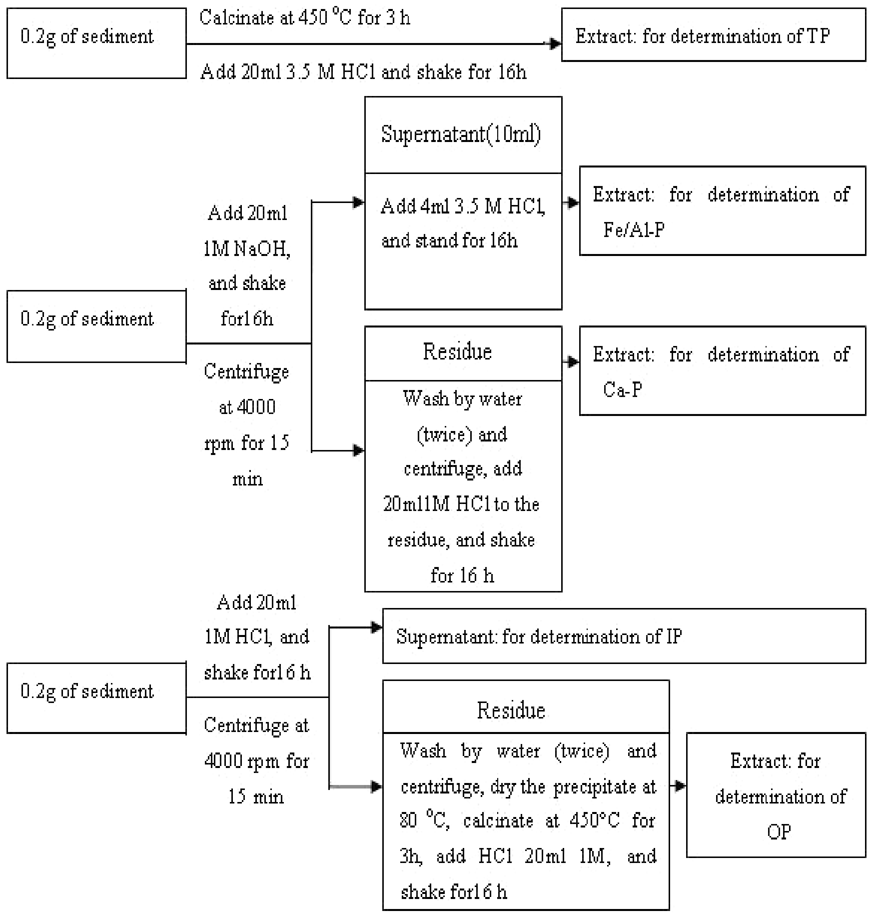

Figure 2. SMT protocol for phosphorus forms in freshwater sediment.

At the end of each extraction, the extract was separated from the solid residue by centrifugation at 4000 rpm (round per minute) for 15 min. Then, the supernatant was decanted and collected for analysis, and the residue was discarded. Meanwhile, a blank was prepared and replicate samples were analyzed in a similar way.

2.4. Study of Phosphorus Forms in Sediments from Baihua Lake by XRD

In this study, XRD was also used to analyze phosphorus forms in sediments from Baihua Lake. Briefly, each sediment sample described above was pressed into a 1.3-cm-diameter sample plexiglass holder well of 1 mm thickness. The analysis of XRD adopted a multifunctional sample stage MPSS (vertical system), with the scan speed of 32°/min, the tension of 40 kV, the current of 40 mA and the step size of 0.0167°. The original data were rectified based on the Jade program to eliminate Kα, and then obtain the XRD patterns of the whole samples. In combination with the database, the major chemical compositions were obtained.

3 Results and Discussion

3.1. Distribution of TP and Phosphorus Forms in Sediments from Baihua Lake

According to the SMT protocol, TP could be represented by the sum of OP and IP, and IP could be divided into Fe/Al-P and Ca-P. These relations could be described by the following formula: TP = OP + IP, and IP = Fe/Al-P + Ca-P. Generally, the recovery rate was 97.2%-103.2% for TP, and 95.5%-104.7% for IP in most cases in the present work, and this recovery rate was reasonable [30]. The TP concentrations and phosphorus forms in sediments from Baihua Lake were shown in Table 1. In this study, it is obvious that there were notably high recovery rates for TP and IP, and most recovery rates were within the range described above.

In the study area, the TP concentrations varied from 591.57 to 2374.80 mg/kg (Table 1), with the mean concentration of 1604.02 mg/kg, whereas the TP concentrations in sediments from Chaohu Lake in Anhui Province and Xihu Lake in Fujian Province, China, ranged from 450 to 560 mg/kg and from 750 to 900 mg/kg, respectively [31, 32]. Obviously, it was evident that the phosphorus level in the sediments from Baihua Lake was generally higher than those from Chaohu Lake and Xihu Lake, which are both eutrophic lakes. In order to make pollution condition of the whole lake more intuitive, the kriging interpolation was conducted by ArcGIS software (Figure 3). It can be found in Table 1 and Figure 3 that the largest value of TP turned up at the TC sampling site, followed by the TSZ sampling site. While, at site of MTW, the TP had the lowest content. This is probably attributable to the fact that near the site of TC, there was a pig farm. Its effects on phosphorus loading are relatively significant. At the TSZ sampling site, domestic sewage from the Baiyun area might be the main reason leading to the high concentration of TP.

In all sediment samples, the concentration of IP ranged from 355.74 mg/kg to 1863.75 mg/kg, with the highest concentration observed at TC, and the lowest observed at MTW. Fe/Al-P (bio-available fraction of phosphorus), a major and direct source of phosphorus release, might play an important part in accelerating eutrophication of water bodies. It was considered to be primarily from industrial wastewater and urban swage discharges. As shown in Table 1, the concentration of Fe/Al-P ranged from 184.40 mg/kg to 1243.60 mg/kg, with the highest and the lowest concentration observed at TC and MTW, respectively. The highest concentration is approximate 7 times the lowest. This wide concentration range showed that the influence of human activity on different regions were different. Ca-P (non-bioavailable phosphorus fraction) was considered to be related to the local geology. The highest concentration of Ca-P was observed at CFZ, and the lowest was observed at JJP. In comparison with Fe/Al-P, the narrow concentration range of Ca-P exhibited that Ca-P was relatively stable, which was agreed with its source. OP (bio-available fraction of phosphorus), considered to be primarily from rural agricultural cultivation and fertilization, is an important phosphorus fraction buried in the sediment. It might be released to the overlying water, and thus directly affects the availability levels of dissolved phosphorus for primary production [33]. For OP, the concentration varied from 231.54 mg/kg to 571.40 mg/kg. The highest and the lowest concentration were also observed at TC and MTW, respectively.

Table 1. The TP concentrations and phosphorus forms in sediments (dry weight) and recovery rates

Sample number	Fe/Al-P		Ca-P		IP		OP		TP	(Fe/Al-P+ Ca-P)/IP	(IP+OP)/TP
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	%
1	671.18	43.82	409.04	26.71	1083.83	70.77	434.95	28.40	1531.54	99.67	99.17
2	947.67	49.34	483.80	25.19	1379.68	71.83	494.77	25.76	1920.76	103.80	97.60
3	184.40	31.17	156.63	26.48	355.74	60.13	231.54	39.14	591.57	95.86	99.27
4	362.08	32.43	260.82	23.36	636.59	57.01	425.22	38.08	1116.60	97.80	95.10
5	677.19	38.24	471.07	26.60	1166.57	65.88	561.63	31.72	1770.85	98.40	97.60
6	694.48	36.16	727.15	37.86	1390.98	72.42	475.30	24.75	1920.76	102.20	97.16
7	285.53	38.97	144.50	19.72	444.21	60.63	271.46	37.05	732.66	96.80	97.68
8	777.51	41.21	546.97	29.00	1317.75	69.85	547.33	29.01	1886.63	100.51	98.86
9	941.61	42.08	732.81	32.75	1650.57	73.76	544.57	24.34	2237.77	101.44	98.09
10	538.36	37.49	302.61	21.07	823.38	57.34	496.42	34.57	1436.05	102.10	96.08
11	852.43	45.39	424.79	22.62	1319.84	70.28	514.79	27.41	1878.04	96.80	97.70
12	963.32	50.54	422.70	22.18	1370.28	71.90	491.23	25.77	1905.88	101.10	97.70
13	700.82	42.47	432.52	26.21	1114.42	67.53	509.77	30.89	1650.30	101.70	98.40
14	338.43	33.39	303.21	29.91	657.92	64.90	358.22	35.34	1013.63	97.50	100.20
15	787.17	37.76	848.41	40.70	1668.11	80.02	474.08	22.74	2084.68	98.05	102.76
16	1243.60	52.37	548.73	23.11	1863.75	78.48	571.40	24.06	2374.80	96.20	102.5
17	202.30	16.64	395.33	32.52	630.82	51.89	485.69	39.95	1215.73	94.74	91.80
Mean	656.95	39.38	447.71	27.41	1110.26	67.33	464.02	30.53	1604.02	99.10	98.10

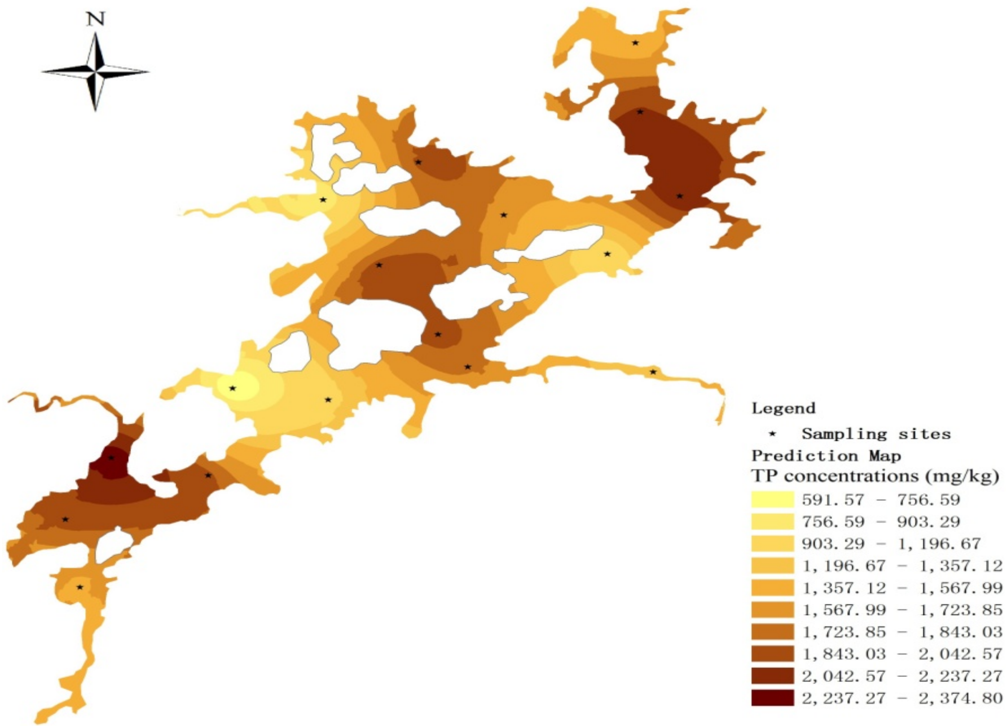

Figure 3. Kriging map of distribution of TP in sediments from Baihua Lake.

As shown in Table 1, it was clear that the average percentages of IP, OP, Fe/Al-P and Ca-P were 67.33%, 30.53%, 39.38% and 27.41%, respectively. Notably, the concentrations of IP were higher than that of OP, and the IP consisted mainly of Fe/Al-P. The high concentrations of Fe/Al-P might be related to the environmental conditions of Baihua Lake. The lake has a relatively short history (45 years), and is still in the stage of the accumulation of sediments [28]. Iron oxide or hydroxide minerals, abundant in sediment, can easily adsorb phosphatic ions (PO_4^{3-}). Therefore, although in calcareous regions with high concentration of Ca, the concentrations of Fe/Al-P in Baihua Lake are found to be still high compared with those of Ca-P. Additionally, human activities might be another reason leading to the high concentrations of Fe/Al-P. In order to obtain the specific reason, further studies are needed to be done.

Table 2. Correlation coefficients between Fe/Al-P, Ca-P, IP, OP and TP in sediments from Baihua Lake

	TP	IP	Fe/Al-P	Ca-P	OP
TP	1				
IP	0.983**	1			
Fe/Al-P	0.932**	0.944**	1		
Ca-P	0.845**	0.858**	0.649**	1	
OP	0.870**	0.772**	0.739**	0.652**	1

** Correlation is significant at the 0.01 level (two-tailed).

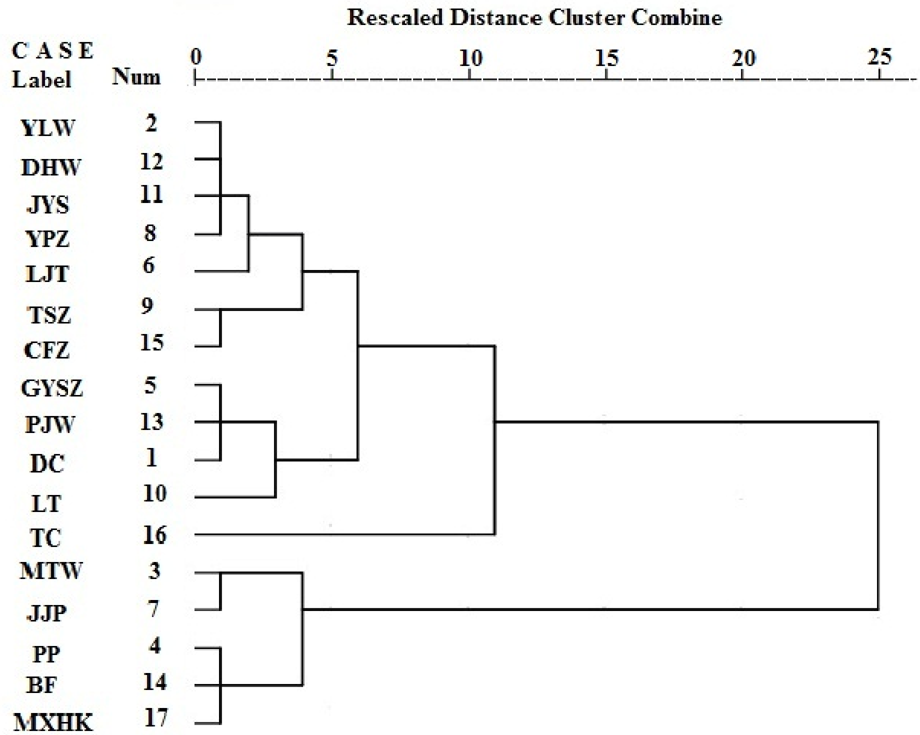

Figure 4. Dendrogram plot of HCA for phosphorus and its species in sediments from Baihua Lake.

Table 3. Major compositions of sediment from Baihua Lake

Sampling sites	Major compositions
DC	SiO2, CaCO3
YLW	SiO2, CaCO3
MTW	SiO2, CaCO3
PP	SiO2, CaCO3
GYSZ	SiO2, CaCO3, [Mg0.03Ca0.97][CO3]
LJT	SiO2, CaCO3, [Mg0.03Ca0.97][CO3]
JJP	SiO2, CaCO3, C15H11ClN2O2
YPZ	SiO2, CaCO3
TSZ	SiO2, CaCO3, [Mg0.03Ca0.97][CO3]
LT	SiO2, CaCO3
JYS	SiO2, CaCO3
DHW	SiO2, CaCO3
PJG	SiO2, CaCO3
BF	SiO2, CaCO3
CFZ	SiO2, CaCO3
TC	SiO2, CaCO3
MXHK	SiO2, CaCO3

Table 4. Phosphorus species in 17 sediment samples from Baihua Lake by XRD

Sample number	Phosphorus species
1	$AlPO_4$, $Fe(PO_4)$, $C_2H_8NO_4P$, $Li[Fe_{0.06}Mn_{0.94}][PO_4]$, $LiMnPO_4$, $NaHPO_3NH_2$, $KNaCa_2(PO_4)_2$, $Cs_4P_2O_7$, PON, $MgSiP_2$, CeP_2O_7, $Na_3Mn(PO_4)(CO_3)$, $Ga_6Na_4(PO_3F)_6O_2$, $Hf(HPO_4)_2$, $Zn_2P_2O_7$, $Nd_2Ni_7P_4$
2	$AlPO_4$, $Fe(PO_4)$, PON, $NaHPO_3NH_2$, $KNaCa_2(PO_4)_2$, $LiMnPO_4$, $BaCrP_2O_7$, $[Br_3P(OH)](AsF_6)$, $H_3PW_{12}O_{40}.29H_2O$, $SrIr_2P_2$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $Hf(HPO_4)_2$, $Rb_3Nd(PO_4)_2$, $LiMgPO_4$, $Ga(PO_4)$, $CrPO_4$
3	$AlPO_4$, $Fe(PO_4)$, $Fe_{1.176}(PO_4)(OH)_{0.57}(H2O)_{0.43}$, $CaH_2NO_3PO_4.H_2O$, $MgAlPO_5$, $Be(PO_3)_2$, $Fe_{1.21}(PO_4)[F_{0.45}(OH)_{0.18}(H2O)_{0.37}]$, $Cs_7Ti_3P_7O_{27}$, $Fe_5(PO_4)_4(OH)_3.2H_2O$, $C_4H_{12}O_6P_2$, $C_4H_{12}O_5P_2$
4	$AlPO_4$, $Fe(PO_4)$, $LiMnPO_4$, $Hf(HPO_4)_2$, $PbHPO_4$, $Nd_2Ni_7P_4$, ErPdP, $RbTh_2(PO_4)_3$, $Pb_4BiO_4PO_4$, $SrIr_2P_2$, $[Br_3P(OH)](AsF_6)$, $BaCrP_2O_7$
5	$AlPO_4$, $Fe(PO_4)$, $K_2Na(AlP_2)$, $Zn_2P_2O_7$, (Ca, Ce, La)PO_4.H2O, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $Rb_3Eu(PO_4)_2$, $Ca_6Na_4(PO_3F)_6O_2$, $NaCuPO_4$, $KBaPO_4$, $CuAlP_2Se_6$, $Pb_4BiO_4PO_4$, $NaPO_3NH_3$, $PbHPO_4$, $K_2Na(AlP_2)$
6	$AlPO_4$, $Fe(PO_4)$, $Li[Fe_{0.06}Mn_{0.94}][PO_4]$, $C_2H_8NO_4P$, $LiMgPO_4$, $Cu(H_2PO_2)_2$, $Hf(HPO_4)_2$, $NaHPO_3NH_2$, $Rb_3Nd(PO_4)_2$, $[Br_3P(OH)](AsF_6)$, $LiMnPO_4$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $PbHPO_4$, $NaPO_3NH_3$, $BiSb_3(PO_4)_6$
7	$AlPO_4$, $Fe(PO_4)$, $C_4H_{12}O_6P_2$, $C_2H_8NO_4P$, $C_{12}H_{33}N_2O_4P.H_2O$, $(Fe, Mn)_2(PO_4)F$, CeP_2O_7, UP_2O_7, $Ag(ZnPO_4)$, $Fe_5(PO_4)_4(OH)_3.2H_2O$, Ce_2NiP_4, $Zn_2P_2O_7$, $Nd_2Ni_7P_4$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $Hf(HPO_4)_2$, $BiSb_3(PO_4)_6$
8	$AlPO_4$, $Fe(PO_4)$, $Fe_{1.176}(PO_4)(OH)_{0.57}(H2O)_{0.43}$, $LiMnPO_4$, $Zn_2P_2O_7$, $NaCuPO_4$, $K_2Ni(P_2O_7)$, Li_3PO_4, CsMnP, $BiSb_3(PO_4)_6$, $Rb_3Eu(PO_4)_2$, $[Br_3P(OH)](AsF_6)$, $PbHPO_4$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $BiSb_3(PO_4)_6$, $Be(HPO_4)(H_2O)$
9	$AlPO_4$, $Fe(PO_4)$, $[Li_{0.834}Fe_{0.055}]MgPO_4$, $CH_6O_5P_2$, $(Zn, Ca)Al_2P_2H_6O_{12}.3H_2O$, Na_3PO_4, $PbHPO_4$, $Mo_3Ni_2P_{1.167}$, $LiMgPO_4$, Li_3PO_4, $Zn_2P_2O_7$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $BiSb_3(PO_4)_6$, $Rb_3Nd(PO_4)_2$
10	$AlPO_4$, $Fe(PO_4)$, $LiMnPO_4$, $CaDPO_4(D_2O)_2$, $[Li_{0.834}Fe_{0.055}]MgPO_4$, $Li[Fe_{0.06}Mn_{0.94}][PO_4]$, CaP, $CH_6O_6P_2$, $CH_6O_5P_2$, $KNaCa_2(PO_4)_2$, $Zn_4(P_2N_4)_3S$, $Hf(HPO_4)_2$, $SrIr_2P_2$, $LiMgPO_4$, $PbHPO_4$, $Rb_3Nd(PO_4)_2$
11	$AlPO_4$, $LiMnPO_4$, PON, $CrPO_4$, $Li[Fe_{0.06}Mn_{0.94}][PO_4]$, $(Al_{0.29}Ga_{0.71})(PO_4)$, $Zn_4(P_2N_4)_3S$, $Ga(PO_4)$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $Rb_3Nd(PO_4)_2$, $Hf(HPO_4)_2$, $BiSb_3(PO_4)_6$
12	$AlPO_4$, $Fe(PO_4)$, $CaDPO_4(D_2O)_2$, $(Al_{0.29}Ga_{0.71})(PO_4)$, $NaPO_3NH_3$, $Ba_{10}(PO_4)_6S$, $BiSb_3(PO_4)_6$, $LiMgPO_4$, $Hf(HPO_4)_2$, $LiMnPO_4$, $Cr(NH_4)HP_3O_{10}$, $Hf(HPO_4)_2$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $BiSb_3(PO_4)_6$, $Rb_3Nd(PO_4)_2$
13	$AlPO_4$, $CaDPO_4(D_2O)_2$, $Ba_5(PO_4)_3Cl$, $CsAl_3(P_3O_{10})_2$, $BaCr(P_2O_7)$, $NaAl(P_2O_7)$, $Li[Fe_{0.06}Mn_{0.94}][PO_4]$, $Ba_{10}(PO_4)_6S$, $Ba_5(PO_4)_3(OH)$, $LiMnPO_4$, $CrPO_4$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $BiSb_3(PO_4)_6$
14	$AlPO_4$, $Fe(PO_4)$, $C_4H_{12}O_5P_2$, $C_4H_{12}O_6P_2$, YbPtP, LuPtP, $KNaCa_2(PO_4)_2$, $LiMgPO_4$, $Hf(HPO_4)_2$, $Cu(H_2PO_2)_2$, $NaPO_3NH_3$, Zn_2P_207, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $BiSb_3(PO_4)_6$, $NaPO_3NH_3$, $NaHPO_3NH_2$, $Nd_2Ni_7P_4$
15	$AlPO_4$, $Fe(PO_4)$, Li_3PO_4, $Rb_3Nd(PO_4)_2$, $Hf(HPO_4)_2$, $KNaCa_2(PO_4)_2$, $Li[Fe_{0.06}Mn_{0.94}][PO_4]$, $LiMnPO_4$, $NaPO_3NH_3$, $LiMgPO_4$, $NaHPO_3NH_2$, $PbHPO_4$
16	$AlPO_4$, $Fe(PO_4)$, $CaDPO_4(D_2O)_2$, $Nd_2Ni_7P_4$, $Pb_4BiO_4PO_4$, $SrIrP_2$, $C_2H_8NO_4P$, $Bi_{0.5}Sb_{1.5}(PO_4)_3$, $NaPO_3NH_3$, $NaHPO_3NH_2$, $Rb_3Nd(PO_4)_2$, $BiSb_3(PO_4)_6$, $Zn_2P_2O_7$, $LiMgPO_4$, $Hf(HPO_4)_2$
17	$AlPO_4$, $Fe(PO_4)$, $Fe_3(PO_4)_2$, $Ca_4Ir_8P_7$, $Ca_6Na_4(PO_3F)_6O_2$, $CuAlP_2Se_6$, $SrMn_2(PO_4)_2$, $Rb_3Eu(PO_4)_2$, $GaPO_4$, $KBaPO_4$, $Zn_2(P_2Se_6)$, $RbPO_3$, $PbHPO_4$, $Zn_2P_2O_7$, $(Al_{0.29}Ga_{0.71})(PO_4)$, $Hf(HPO_4)_2$

Correlations between phosphorus and its species in sediments from Baihua Lake were analyzed, with the results shown in Table 2. The Pearson correlation coefficient between Fe/Al-P, OP, Ca-P and TP were 0.932, 0.870, 0.845 ($P<0.01$), respectively. It was clear that Fe/Al-P, OP and Ca-P all showed significant positive correlations with TP. The results indicated that an increase in the TP concentrations was mainly caused by increased Fe/Al-P, and then OP, which was in accordance with the previous research [34]. However, Ca-P also played an important role in the increase of the TP concentrations. For phosphorus forms, significant positive correlations ($P<0.01$) between OP and Fe/Al-P, as well as Ca-P demonstrated that both Fe/Al-P and Ca-P might be affected by OP. Fe/Al-P also showed significant positive correlations ($P<0.01$) with Ca-P. This might be attributed to the phosphate solubilizing bacteria that could transform insoluble phosphate into the bio-available forms mentioned above. However, owing to the different sources of Fe/Al-P and Ca-P, the Pearson correlation coefficient was relatively small.

Hierarchical cluster analysis (HCA), a statistical method for identifying relatively homogeneous clusters of cases based on measured characteristics was carried out in the present research as well. The dendrogram of HCA regarding phosphorus and its species in sediments from Baihua Lake was shown in Figure 4. It can be seen that the 17 locations in this survey can be divided into 4 groups. The first group contains 7 locations: YLW, DHW, JYS, YPZ, LJT, TSZ and CFZ; the second group contains 4 locations: GYSZ, PJW, DC and LT; the third group contains 1 location: TC; the fourth group contains 5 location: MTW, JJP, PP, BF and MXHK. It is obvious that the pollution status of all locations belonging to one cluster is similar. The farther the distance between two clusters, the greater the discrepancy of pollution intensity in the sediments. Hence, according to the results of HCA in our investigation, it is inferred that the distribution of phosphorus in sampling sites of one group is affected by the same factors which needs further studies.

3.2. Determination of Phosphorus Forms in Sediments from Baihua Lake by XRD

XRD was used to determine mineralogy of crystalline phases of all samples for which there was adequate crystalline sediment for analysis. The major compositions and phosphorus species of 17 sediment samples from Baihua Lake were presented in Tables 3 and 4, respectively. It seemed from Table 3 that the major compositions of all sediment samples from Baihua Lake included SiO_2 and $CaCO_3$. As shown in Table 4, XRD analysis demonstrated the existence of phosphorus species in sediments from Baihua Lake, including TP, IP, OP, Fe/Al-P and Ca-P, which partly confirmed the results of SMT. Furthermore, AlPO4 was found in all sediment samples among phosphorus species, which was probably related to the discharge of Guizhou Aluminum Company around the lake. However, Ca-P was found only in part of sediment samples. This might be attributable to the ligand competition between PO_4^{3-} and CO_3^{2-} in the sediments, which would decrease the availability of binding sites on calcic complex, because the major compositions of all sediment samples from Baihua Lake included $CaCO_3$.

3.3. Methods of Controlling Phosphorus Release from Sediments

Some remediation measures for controlling the release of phosphorus from the sediment have been put forward, e.g. dredging and sediment capping [35]. Dredging is the removal of accumulated lake sediments. In consideration of the high cost, environmental impact and public acceptance, dredging will not be a feasible method [36]. Furthermore, at the bottom of Baihua Lake, there are probably caves and underground rivers which can transport phosphorus pollutants to other places to cause unknown consequences for a long period of time [4]. Consequently, dredging is not considered to be useful for Baihua Lake. For sediment capping, contaminated sediments remaining in place at the site are covered by stable layers of sediment, gravel, rock, and synthetic materials. Indeed, a research showed that the calcite barrier can control phosphorus release from sediments [37]. With capping approach, the cost is relatively high due to the need for a long term monitoring and maintenance to prevent contaminants from migrating. Thus, a new method should be developed for this drinking-water source.

Conclusion

In summary, the results of the XRD analysis showed that $AlPO_4$ was found in all sediment samples among phosphorus species. The SMT protocol demonstrated that TP consisted mainly of IP, and the IP consisted mainly of Fe/Al-P. The high concentration of Fe/Al-P indicated a significant risk of phosphorus release. Thus, in addition to curtailing external sources of phosphorus, some remediation measures should be taken to control the release of phosphorus from lake sediments, an internal source of phosphorus. As a result of the distinctive environmental features of Baihua Lake, more feasible methods are needed.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 20967003) and by the Government of Guiyang City (Project No. [2010] 5-2).

References

[1] J. Luo, L.Y. Fu, J. W. Hu, Z. W. Yu, C. Liu, S. M. Duan and X. F. Jin, "Estimation of organochlorine pesticides and dioxin-like PCBs in surface sediments from Baihua Lake", *Advanced Materials Research*, vol. 233-235, pp. 2988-2993, 2011.

[2] L.Y Fu., J. Luo, J.W. Hu, Q. Wu, X.F. Huang and L.F. Tian, "Estimation of Organochlorine Pesticides (DDT and HCH) in Surface Sediments from Baihua Lake", Selected Proceedings of the Fifth International Conference on Waste Management and Technology (ICWMT 5), pp. 534-538, 2010.

[3] J. J. Deng, X. F. Huang, J. W. Hu, C. X. Li, Y. Yi and J. Long, "Distribution of several microorganisms and activity of alkaline phosphatase in sediments from Baihua Lake", *Asia-Pacific Journal of Chemical Engineering*, vol. 4, pp. 711-716, 2009.

[4] X. F. Huang, J. W. Hu, J. J. Deng, C. X. Li, J. Long and F. X. Qin, "Heavy-metals pollution and potential ecological risk assessment of sediments from Baihua Lake", *International Journal of Environmental Health Research*, vol. 19, pp. 405-419, 2009.

[5] X. F. Huang, J. W. Hu, J. J. Deng, C. X. Li and F. X. Qin, "Speciation of heavy metals in sediments from Baihua Lake and Aha Lake", *Asia-Pacific Journal of Chemical Engineering*, vol. 4, pp. 635-642, 2009.

[6] W. Shen, J. W. Hu, L. Y. Fu, and M. Jin, "Distribution of several microorganisms in sediments from Baihua Lake", *Advanced Materials Research*, vol. 396-398, p. 1923, 2011.

[7] H. W. Paerl, L. M. Valdes, A. R. Joyner and M. F. Piehler, "Solving problems resulting from solutions: evolution of a dual nutrient management strategy for the eutrophying Neuse River Estuary, North Carolina", *Environmental Science and Technollogy*, vol. 38, pp. 3068-3073, 2004.

[8] W. J. Surridge, A. L. Heathwaite and A. J. Baird, "The release of phosphorus to porewater and surface water from river riparian sediments", *Journal of Environmental Quality*, vol. 36, pp. 1534-1544, 2007.

[9] D. L. Correll, "The role of phosphorus in the eutrophication of receiving waters: A review", *Journal of Environmental Quality*, vol. 27, pp. 261-266, 1998.

[10] D. J. Conley, H. W. Paerl, R. W. Howarth, D. F. Boesch, S. P. Seitzinger, K. E. Havens, C. Lancelot and G. E. Likens, "Controlling eutrophication: nitrogen and phosphorus", *Science*, vol. 323, pp. 1014-1015, 2009.

[11] C. J. Penn and R. B. Bryant, "Phosphorus solubility in response to acidification of dairy manure amended soils", *Soil Science Society of America Journal*, vol. 72, pp. 238-243, 2008.

[12] S. L. Chinault and G. A. O'Connor, "Phosphorus release from a biosolids-amended sandy spodosol", *Journal of Environmental Quality,* vol. 37, pp. 937-943, 2008.

[13] K. Ádám, T. Krogstad, F. R. D. Suliman and P. D. Jenssen, "Phosphorous sorption by filtralite P-small scale box experiment", *Journal of Environmental Science Health*, vol. 40, pp. 1239-1250, 2005.

[14] T. Gonsiorczyk, P. Casper, and R. Koschel, "Phosphorus binding forms in the sediments of an oligotrophic and an eutrophic hardwater lake of the Baltic district (Germany)", *Water Science and Technology*, vol. 37, p. 51, 1998.

[15] F. C. Wu, H. R. Qing and G. J. Wan, "Regeneration of N, P and Si near the sediment/water interface of lakes from southwestern China plateau", *Water Research*, vol. 35, p. 1334, 2001.

[16] P. A. Moore, K. R. Reddy and D. A. Graetz, "Phosphorus geochemistry in the sediment-water column of a hypereutrophic lake", *Journal of Environmental Quality,* vol. 20, pp. 869-875, 1991.

[17] L. J. Lennox, "Lough Ennel: Laboratory studies on sediment phosphorus release under varying mixing, aerobic and anaerobic conditions", *Freshwater Biology*, vol. 14, pp. 183-187, 1984.

[18] L. Bengtsson, "Phosphorus release from a highly eutrophic lake sediment", *Verh International Verein Limnology*, vol. 19, pp. 1263-1271, 1975.

[19] C. H. Jiang, J. J. Deng and J. W. Hu, "Phosphorus speciation in sediments from Lakes Baihua and Aha with a typical karstic environment, China", *Advanced Materials Research*, vol. 113-114, pp. 420-424, 2010.

[20] G. J. Wan, "Environmental process of the deep- water lakes and approach to the protection of water resources on the Yunnan-Guizhou Plateau", *Engineering Sciences*, vol. 11, pp. 60-71, 2009. (in Chinese).

[21] K. Kotut, A. Ballot and L. Krienitz, "Toxic cyanobacteria and their toxins in standing waters of Kenya: implications for water resource use", *Journal of Water and Health*, vol. 4, pp. 233-245, 2006.

[22] V. Ruban, J. F. López-Sánchez, P. Pardo, G. Rauret, H. Muntau and P. Quevauviller, "Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments-a synthesis of recent works", *Fresenius' Journal of Analytical Chemistry*, vol. 370, pp. 224-228, 2001.

[23] Q. X. Zhou, C. E. Gibson and Y. M. Zhu, "Evaluation of phosphorus bioavailability in sediment of three contrasting lakes in China and the UK", *Chemosphere*, vol. 42, pp. 221-225, 2001.

[24] C. H. Jiang, J. W. Hu, X. F. Huang, C. X. Li, J. J. Deng, J. Zhang and F. Liu, "Phosphorus speciation in sediments of Lake Hongfeng, China", *Chinese Journal of Oceanolgy and Limnology*, vol. 29, pp. 53-62, 2011.

[25] H. L. Golterman, *The chemistry of phosphate and nitrogen compounds in sediments*: Kluwer Academic Publishers, 2004.

[26] J. Murphy and J. P. Riley, "A modified single solution method for the determination of phosphate in natural waters", *Analytica Chimica Acta*, vol. 27, pp. 31-36, 1962.

[27] I. D. McKelvie, D. M. W. Peat and P. J. Worsfold, "Techniques for the quantification and speciation of phosphorus in natural waters", *Analytical Proceedings including Analalytical Communications*, vol. 32, pp. 437-445, 1995.

[28] Y. C. Wang, G. J. Wan, S. L. Wang, S. H. Li and R. G. Huang, "Forms of phosphorus in sediments of Lake Baihua and Lake Hongfeng, Guizhou", *Acta Mineralogica Sinica*, vol. 20, pp. 273-278, 2000. (in Chinese)

[29] C. H. Jiang, D. Wu, J. W. Hu, F. Liu, X. F. Huang, C. X. Li and M. Jin, "Speciation of phosphorus in sediments from Lake Hongfeng using chemical fractionation and X-ray powder diffraction, China", *Chinese Science Bulletin*, vol. 56, pp. 2098-2108, 2011.

[30] P. Pardo, G. Rauret and J. F. Lopez-sanchez, "Shortened screening method for phosphorus fractionation in sediments: A complementary approach to the standards, measurements and testing harmonised protocol", *Analytica Chimica Acta*, vol. 508, pp. 201-206, 2004.

[31] Q. H. Huang, D. H. Wang, C. X. Wang, M. Ma and Z. J. Wang, "Relation between phosphorus forms in the sediments and lake eutrophication", *China Environmental Science*, vol. 23, pp. 583-586, 2003. (in Chinese).

[32] Y. P. Su, D. X. Zheng, Y. T. Zhuang, G. Li, W. Z. Lin and L. Q. Xue, "Phosphorus fractionations in sediments from eutrophicated lakes in Fujian Province", *Journal of Agro-Environmental Science*, vol. 24, pp. 362-365, 2005. (in Chinese).

[33] G. Edlund, R. Carman, "Distribution and diagenesis of organic and inorganic phosphorus in sediments of the Baltic proper", *Chemosphere*, vol. 45, p. 1053, 2001.

[34] V. Ruban, S. Brigault, D. Demare and A. M. Philippe, “An investigation of the origin and mobility of phosphorus in freshwater sediments from Bort-Les-Orgues Reservoir, France”, *Journal of Environmental Monitoring*, vol. 1, pp. 403- 407, 1999.

[35] K. Siong and T. Asaeda, “Does calcite encrustation in chara provide a phosphorus nutrient sink”, *Journal of Environmental Quality*, vol. 35, pp. 490-494, 2006.

[36] C. Kinaci, B. Inanc, A. F. Aydin, E. Yuksel, M. F. Sevimli, O. Arikan and D. Topacik, “Quality of the bottom sediment prior to dredging in the Golden Horn of Istanbul”, *Journal of Environmental Science Health*, vol. A39, pp. 365-374, 2004.

[37] J. W. Lin, Z. L. Zhu, J. F. Zhao and Y. H. Zhan, “Influencing factors of calcite active barrier system to control phosphorus release from sediments”, *Environmental Science*, vol. 29, pp. 121-126, 2008. (in Chinese).