Original Research Phosphorus Distribution in Lake Sediments and Interstitial Water in Different Ecological Function Zones

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Abstract

For shallow lakes, phosphorus released from sediments becomes a major reason for eutrophication. To learn about the distribution characteristics of sedimentary phosphorous in Nansi Lake, China, the vertical distributions of sedimentary phosphorus at 5 representative sites were analyzed. The results showed that the sedimentary total phosphorus (TP) concentrations varied greatly, ranging from 313.50 to 963.48 mg·kg⁻¹. As a typical macrophyte-dominated lake, organic phosphorus (Org-P) in Nansi Lake was the major phosphorus accounting for 41.56-52.60% of TP in sediment. Detrital apatite phosphorus (De-P) and authigenic calcium-bound phosphorus (ACa-P) also represented a large proportion of TP in sediments, accounting for 14.77-35.24% and 1.4-32.09% of TP, respectively. The vertical phosphorus distribution demonstrated a trend that Ex-P, Fe-P, Oc-P Org-P, and TP values decreased gradually with depth, Al-P and ACa-P decreased first and then increased with depth, and De-P had no obvious trend with depth. The results also indicated that the concentrations of PO₄³-P in interstitial water and the concentrations of Ex-P in sediments had a remarkable positive correlation.

Keywords: phosphorus fractions, sediments, interstitial water, Nansi Lake

Introduction

Phosphorus is regarded as a key factor responsible for eutrophication in shallow freshwater lakes. External phosphorus can be accumulated in sediments in shallow lakes. When conditions (temperature, pH, redox potential etc.) at the sediment-water interface are changed, phosphorus would be released into the overlying water [1, 2]. As to the sedimentary phosphorous release, phosphorus species are key factors that play a great role [3]. PO_4^3 -P diffuses into interstitial water first and then into the overlying water by phosphorus concentration gradient [4, 5]. Therefore, to reveal the mechanism of internal phosphorus release, it is important to study the relationship between phosphorus species in lake sediment and PO_4^3 -P in interstitial water.

Nansi Lake (116°34'-117°21'N, 34°27'-35°20'E), the sixth largest freshwater lake in China, is located in Shandong Province. The lake has a total surface area of 1,266 km² and is the largest and important freshwater lake in northern China for the South-North Water Transfer Project (eastern route). According to "Water Pollution Prevention Planning of the South-to-North Water Diversion Project of Shandong Section," the water quality in Nansi Lake should meet grade III of the "China surface water

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quality standard (GB3838-2002)." However, due to industrial wastewater discharge in the 1990s, considerable amounts of nutrients were deposited and accumulated in Nansi sediments. In recent years, external pollution sources have been controlled in a way that all influent water should meet grade III requirements. However, phosphorous released from polluted sediments still adversely affect the water quality of the overlying water (e.g., causing constant eutrophication).

So far, only a few studies have investigated the sedimentary phosphorus characteristics of Nansi [6-11]. In the projects carried out by Li et al. [6], Cao et al. [7], and An and Li [11], only sediments of the estuary in Nansi were sampled and tested. Thus, the results could not comprehensively reflect the situation of the entire lake. Yang et al. [8], Zhou et al. [9], and Liu et al. [10] only studied the nutrient distribution characters in the upstream sediment of Nansi. As a typical shallow and macrophyte-dominated lake, little is known about its PO_4^3 -P in sedimentary interstitial water, which is important to further understanding its sedimentary phosphorous release potential.

In this paper we aimed to characterize vertical phosphorous fraction distributions in sediments and their correlation with PO_4^{3} -P in interstitial water in Nansi Lake.

Material and Methods

Study Sites

Nansi Lake was divided into an upper lake and a lower lake after the building of a dam in 1960. The upper lake takes 80% inflow water, so investigation was focused on it. Five sampling sites were selected in upper Nansi Lake (Fig. 1). Sampling sites were located in different ecological function zones, open water area (OW), waterway (WW), aquaculture (AC), and estuaries of the Guangfu River (GF) and Baima River (BM). Physical and chemical characteristics were different at each site (Table 1). Linear-regression analysis was applied to reveal the correlations between different phosphorus fractions in sediments and PO_4^{3} -P in interstitial water, so that we could understand the potential mobility of P from sediments to the overlying water.

Sediment/Water Sampling and Treatment

Sediment samples (0-25 cm) and corresponding overlying water were collected in May 2008. Sediment samplings were collected with a core plexiglass sampler and divided into five sections (0-2 cm, 2-5 cm, 5-10 cm, 10-15 cm, 15-25 cm) to study sediment characters at different depths. The sediment samples were dried at room temperature (25°C), ground in an agate mortar and screened through a 100 mesh sieve, finally sealed and conserved in air-sealed plastic bags for analysis [5, 12]. Two liters overlying water was collected for each site.

Analysis Methods

The sequential extraction method of phosphorus in sediments was divided into 7 steps.

- Step 1: The Ex-P is extracted by 0.3 g sediment added 30 ml MgCl₂ (1 mol/L) at pH 8 with the conditions of centrifugation (5,000 r/min) and washing
- Step 2: Al-P is extracted by 30 ml NH₄F (0.5 mol/L) based on the residues of step 1
- Step 3: Based on the residues of step 2, Fe-P is extracted by adding Na₂CO₃ (0.5 mol/L) and NaOH (0.1 mol/L) at the conditions of washing and filtering
- Step 4: Is for Oc-P extraction; sodium citrate (0.1 mol/L) and NaHCO₃ (0.1 mol/L), and Na₂S₂O₄ (0.675 g) are added to the residues of step 3
- Step 5: Is for the extraction of De-P, the residues of the above step is added the buffer of NaAc-HAc (pH 4),



Fig. 1. Map showing sampling sites in Nansi Lake.

GF - Guangfu River estuaries, AAC - aquaculture, BM - Baima River estuarie, WW - waterway, OW - open water area

Site	Ex-P/mg·kg ⁻¹	Al-P/mg·kg ⁻¹	Fe-P/mg·kg-1	Oc-P/mg·kg ⁻¹	Ca-P/mg·kg ⁻¹	De-P/mg·kg-1	Org-P/mg·kg ⁻¹	TP ¹ /mg·kg ⁻¹
OW	8.33±1.15*	4.45±0.53	9.06±2.82	11.70±2.87	111.08±18.87	229.69±35.93	377.91±16.73	752.20±20.28
WW	5.24±1.02	3.47±0.82	14.70±3.36	14.94±2.08	125.57±28.86	209.39±20.91	301.56±60.70	674.87±25.22
ACAC	9.89±1.62	3.61±0.70	15.04±2.01	17.16±2.23	132.05±15.27	216.70±28.07	280.73±19.86	675.19±29.28
GF	33.98±5.88	2.98±0.69	4.73±1.32	4.02±0.70	164.58±11.03	6.59±1.36	250.29±10.67	475.81±72.07
BM	27.48±2.98	2.23±0.23	2.81±0.44	1.98±0.95	95.60±7.60	15.52±2.67	125.70±12.17	271.32±42.18

Table 1. Phosphorus species in sediments of different locations in Nansi Lake.

GF – Guangfu River estuaries, AC – aquaculture, BM – Baima River estuaries, WW – waterway, OW – open water area ¹/TP=Ex-P + Al-P + Fe-P + Oc-P + Ca-P + De-P + Org-P

*means \pm standard deviations

then the liquids from the centrifuge are extracted by adding $MgCl_2$ (0.1 mol/L)

- Step 6: The residues of step 5 are centrifuged at the condition of adding 30 ml HCl (0.1 mol/L), then the Ca-P in the extraction liquids is determined
- Step 7: The residues of step 6 are heated at 550°C for 2 hours, then the residues are extracted for 16 hours after cooling, finally Org-P in the extraction liquid is measured

The detailed procedures can be seen in the research of Zhu et al. [13]. At present, this extraction method was applied extensively [14]. After each extraction step, samples were centrifuged at 5,000 rpm for 20 min and the supernatant was filtrated through a 0.45 μ m membrane. The solutions were analyzed for P according to the molybde-num blue/ascorbic acid method [15]. Interstitial water in sediments was centrifuged in centrifuge tubes at 5,000 rpm for 20 min and the supernatant was filtered through a 0.45 μ m membrane. The concentration of PO₄³-P was measured immediately according to the methods above.

Results and Discussion

Phosphorus Fraction in Sediments

The concentration of TP and phosphorus fractions in sediments varied greatly in different ecological function zones (Table 1). TP concentration changed from 313.50 to 963.48 mg·kg⁻¹. Org-P was the major phosphorus fraction accounting for 41.56-52.60% of TP in sediment. Ca-P and De-P also represented a large proportion of TP, accounting for 14.77-35.24% and 1.40-32.09% of TP, respectively. Other phosphorus fractions were so small that their total value only accounted for 4.46-12.72% of TP in sediments. Although the concentration of TP at GF and BM sites were much lower than that at the other three sites, the Ex-P at GF and BM sites were higher than that at other three sites. This was because of a much lower redox potential and higher pH (Table 1) at GF and BM sites.

The Fe-P fraction was small, accounting for 0.99-2.22% of TP in sediments, although Fe is the major metal element in sediments, with a mean concentration of 3,4481 mg·kg⁻¹ [11]. In most algae-dominated lakes in China, Fe-P ratios

were detected in a range of 22-67% (Taihu Lake), 29-32% (Taihu Lake) and 19.9-41.9% (Dianchi Lake) of TP in sediment [16, 17]. These three lakes are representative algaedominated lakes in China. In addition, the results also showed that Org-P was the major P source for the sediments in different ecological function zones in Nansi. In open water areas abundant submerged plants die in winter and are deposited in sediments as the main source of Org-P. In fish culture zones, the high density of cage fish culture and excessive feeding lead to massive Org-P in sediments. At the other three sites, external pollution was probably the main source of Org-P.

Vertical Distribution of Different Phosphorous Fractions in Sediment

Ex-P, Fe-P, Oc-P, Org-P, and TP decreased with depth in sediments, while the concentrations of Ca-P and Al-P increased initially and then decreased with depth, and De-P had no obvious change at different depths (Fig. 2).

As an unstable phosphorus fraction which can be easily released from sediment, Fe-P is assumed to be associated with Fe oxide hydroxides. Previous research showed that low redox potential would induce Fe(III) from Fe(OOH) to Fe(II), leading to Fe-P release from sediments [18, 19]. The decease of Fe-P might be ascribed to the fact that redox potential reduces with depth in sediments, and more Fe(III) were reduced into Fe(II) in deeper sediments.

Oc-P is considered as phosphorus occluded by iron hydroxide/aluminum hydroxide in sediments and is difficult to be available by organism, so its changing trend matches the Fe-P trend. But this result is contrary to Uwe Selig's finding [20]. Therefore it is necessary to do further research on the mechanism of Oc-P transformation in lake sediments.

Ca-P in sediments is a very important parameter to evaluate the pollution history of a lake. In the 1990s numerous factories were established in the catchments area of Nansi Lake and massive wastewater was discharged into it. In recent years, a large amount of work was done to control severe external nutrient load and the water quality has been improved from grade V to grade III based on Chinese surface water quality standard (GB 3838-2002). This is the major reason why the maximum Ca-P concentration appears at 5 cm depth rather than the top layer. The De-P has no obvious changes in different depths, implying the stable velocity of natural erosion in the catchment area of Nansi. De-P is from apatite in igneous rock and metamorphic rock. It is also an important parameter to evaluate the degree and velocity of natural erosion.

Org-P is usually combined with organic matters and its concentration mainly depends on the degree of mineralization in sediments. Most researches also showed that the mineralization of organic matters is enhanced with depth, leading to more Org-P transformed into other phosphorous and a decrease of Org-P with depth in sediments [21].

Vertical Distribution of PO₄³⁻P in Interstitial Water

Fig. 3 shows that at BM and GF sites, the concentrations of interstitial water PO_4^3 -P were distinctly higher than that of the other three sites. This might be owing to the large amount of external pollutant from influent deposits at BM and GF sites, which resulted in an anaerobic condition and induced phosphorus release from sediments to interstitial water.

Analysis of Correlations between Different Phosphorus Fractions in Sediments and PO₄³⁻-P in Its Interstitial Water

Correlations between different phosphorus fractions in sediments and $PO_4^{3-}P$ in its interstitial water are shown in Table 2.

Concentration of $PO_4^{3-}P$ in interstitial water was remarkably positively correlated with Ex-P (P<0.05, n=25) in sediments, but no obvious correlation with other phos-



Fig. 2. Vertical distribution of sediment phosphorus fractions in Nansi Lake. GF – Guangfu River estuaries, AC – fish culture zone, BM – Baima Tiver estuaries, WW – waterway, OW – open water area

		Equation	R ²
	Ex-P	$y = 0.0947x_1 - 0.8767$	0.4915*
	Al-P	$y = -0.0975x_2 + 1.0559$	0.0136
	Fe-P	$y = -0.0247x_3 + 0.9584$	0.0280
I in our more reasion	Oc-P	$y = -0.0285x_4 + 1.014$	0.0342
Linear regression	ACa-P	$y = 0.0101x_5 - 0.5404$	0.0675
	De-P	$y = -0.006x_6 + 1.5537$	0.1144
	Org-P	$y = 0.0006x_7 + 0.5574$	0.0032
	TP ¹⁾	$y = -0.0003x_8 + 0.8782$	0.0012
Multiple regression	$y = 0.149x_1 + 0.038x_2 - 0.007x_3 - 0.034x_4 - 0.002x_5 + 0.009x_6 - 0.003x_7 + 0.01x_8 - 2.5680$		

Table 2. Correlations between phosphorus fractions in sediments and PO₄³-P in its interstitial water.

*P<0.05, n=25;

 $^{1)}TP = Ex-P + Al-P + Fe-P + Oc-P + Ca-P + De-P + Org-P$

phorus fractions (Table 2), which suggested that Ex-P was closely related to the concentration of interstitial water PO_4^{3} -P, coincident with the conclusion of Li [3].

At the same time, some research showed that the Fe/Al-P in sediments also had an important influence on PO_4^3 -P in interstitial water [22]. However, in our study the relationship between the Fe-P in sediment and the PO_4^3 -P in interstitial water was weak. This was probably due to the fact that the concentration of Fe/Al-P in sediments was too small to affect the concentration of PO_4^3 -P in interstitial water in Nansi. Although Org-P was the major phosphorus fraction in sediments, the mineralization of Org-P was very slow. So there was a weak relationship between Org-P in sediments and PO_4^3 -P in interstitial water. The characters of other phosphorus fractions such as De-P, Oc-P, and Ca-P were very stable, so the correlations between them and PO_4^3 -P in interstitial water were weak.



Fig. 3. Vertical distribution of $PO_4^{3-}P$ in interstitial water in Nansi Lake.

GF – Guangfu River estuaries, AC – fish culture zone, BM – Baima River estuaries, WW – waterway, OW – open water area

Conclusions

Concentrations of TP in sediments ranged from 313.50 to 963.48 mg·kg⁻¹, and Org-P was the major phosphorus in all sediments. Ca-P and De-P also represented a large proportion of TP, accounting for 14.77-35.24% and 1.40-32.09% of TP respectively. The concentrations of Ex-P, Fe-P, Oc-P, Org-P, and TP in sediments deceased with sediment depth, while the concentrations of ACa-P and Al-P increased with depth at first and then decreased with sediment depth. The concentration of De-P had no obvious change at different depths.

Concentrations of PO_4^{3} -P in interstitial water decreased with sediment depth at the sites of BM and GF, while the maximum PO_4^{3} -P concentration appeared in the sediments at 5-10 cm from the top for the other three sites in interstitial water. Concentrations of PO_4^{3} -P in interstitial water had a significant correlation with Ex-P in sediments, and no significant correlation was presented with other phosphorus fractions.

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