



Phosphorus fractions and its release in the sediments of Haihe River, China

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Abstract

The amounts and forms of phosphorus (P) in surface sediments of Haihe River, Tianjin, North China, were examined using a sequential chemical extraction procedure. Five fractions of sedimentary P, including loosely sorbed P (NH₄Cl-P), redox-sensitive P (BD-P), metal oxide bound P (NaOH-P), calcium bound P (HCl-P), and residual P (Res-P) (organic and refractory P), were separately quantified. The results indicated that the contents of different P fractions in the sediments varied greatly. The total P (TP) contents ranged from 968 to 2017 mg/kg. Phosphorus contents in NH₄Cl-P, BD-P, NaOH-P, and HCl-P ranged from 6.7 to 26.6 mg/kg, 54.5 to 90.2 mg/kg, 185.2 to 382.5 mg/kg, and 252.3 to 425.5 mg/kg, respectively, which represented 1.2%–3.2%, 7.7%–13%, 33.3%–48.9%, and 36.2%–54.2% of the sedimentary inorganic P, respectively. For all the sediment samples, the rank order of P-fractions was Res-P > HCl-P > NaOH-P > BD-P > NH₄Cl-P. The highly positive relationship between the amounts of P released from the sediments and those in the NH₄Cl-P and BD-P fractions, indicated that NH₄Cl-P and BD-P were the main fractions that can release P easily.

Key words: phosphorus fractions; sequential extraction; phosphorus release; sediments; Haihe River

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Introduction

Various pollutants may be adsorbed to the sediments accumulated on the bottom of the rivers or lakes. These sediments may accumulate over long periods and can act as new pollutant sources to the overlying water after the water quality has improved (Lijklema *et al.*, 1993; Masunaga *et al.*, 1993; Abrams and Jarrell, 1995; Søndergaard *et al.*, 1996). As a major nutrient for aquatic ecology, phosphorus (P) has been recognized as the most critical nutrient limiting rivers or lakes productivity (Dorich *et al.*, 1984). P can be transferred from water to sediment through biochemical and physical reactions, such as ion exchange, adsorption, and precipitation (Stumm and Morgan, 1996), and also could be released from sediments as the overlying water quality changing (Furumai *et al.*, 1989). Physical and chemical characterizations of sediments are important for evaluating the P exchange processes between sediments and overlying waters (Gonsiorezyk *et al.*, 1998). Solubility of phosphate in the interstitial water of sediment is significantly controlled by its chemical composition and the interactions with other minerals or amorphous materials (Maine *et al.*, 1992). The association of phosphate with iron, aluminum, and calcium, and the adsorptive properties of carbonates and clays are of special interest (Jensen *et al.*, 1992). Because the amount of P release from sediments, called internal P loading, can result in the eutrophication,

the sediment P separation can enhance the understanding of P cycling in the aquatic ecosystem. Several extraction schemes have been developed to elucidate the chemical nature of sediment phosphates (Barbanti and Sighinolfi, 1988; Hupfer *et al.*, 1995) and sequential extraction of P is a useful tool for characterization of various P compounds (Pardo *et al.*, 1998; Psenner *et al.*, 1988; Zhou *et al.*, 2001).

Haihe River, the largest water system in North China, flows through Tianjin City and empties into the Bohai Sea. Its mainstream in Tianjin City is 72 km long with a watershed area of 2066 km². Along with the rapid economic growth, industrialization, and urbanization, accompanied by inadequate infrastructure investment and management capacity, water shortage limited the further development of the economy and crop production. Serious pollution and environmental degradation have aggravated the water scarcity by reducing the availability of usable fresh water. Eutrophication is the main problem of the Haihe River. To improve water quality, it will be necessary to further reduce the nutrients sources including sediment release. Nitrogen is hard to be controlled in many natural water systems, because the nitrogen originates from a greater number of sources. Therefore, it is believed that controlling P is the best approach for reducing eutrophication (Dahl *et al.*, 1993).

The objective of the present study was to estimate the amount and forms of P in the sediments of Haihe River, using a sequential extraction procedure, and to evaluate

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their possible contributions to the P-loadings of the river systems.

1 Materials and methods

1.1 Sediment sampling and pretreatment

Twenty four sediment samples in 8 sites along the Haihe River were collected in October, 2005. Figure 1 shows the study area and sampling locations. The sediment samples were collected using an Eckman sampling device from the top 10 cm layer. The samples were taken to the laboratory in air-sealed plastic bags and kept at 4°C. Three samples from the same site were mixed. Stones and plant fragments were removed by passing the samples through a 1-mm sieve. The samples were air dried, homogenized, passed through a 150- μ m sieve and stored in glass bottles.

1.2 Sediment analysis and phosphorus fractions

The sediment samples were analyzed for total nitrogen (TN) (Institute of Soil Science, Chinese Academy of Sciences, 1978) and total P (TP) (SMT protocol by Ruban *et al.*, 1999). Water content and loss on ignition

measurements were based on weight losses after drying and combustion of the sediments at 105 and 550°C, respectively. Total organic carbon (TOC) in the sediments was determined after treatment of the sample with $K_2Cr_2O_7/H_2SO_4$ according to the Walkey-Black method (Tan, 1995). All samples were analyzed in triplicates and the data were expressed as the average.

Chemical fractionation, involving sequential extraction procedures, is based on differences in reactivity of solid phases to different extractant solutions. The contents of different P fractions were determined using the sequential extraction scheme suggested by Psenner *et al.* (1984) with the modifications of Hupfner *et al.* (1995) (Fig. 2).

The extracts were centrifuged and the supernatants were filtered through a 0.45- μ m GF/C filter membrane. The soluble reactive P (SRP) in each sample was determined by the molybdenum blue/stannous chloride method (APHA, AWWA, WEF, 1995). This extraction procedure divided inorganic P (IP) fractions into loosely sorbed P (NH_4Cl -P), redox-sensitive P (BD-P), metal oxide bound P (NaOH-P) and calcium bound P (HCl-P). The difference between TP and IP is the residual P (Res-P) fraction, which contains organic P and refractory P compounds. For each fraction, four replicates were performed and all the data were expressed as the average.

1.3 Phosphorus release experiments

The P release experiments were performed with batch experiments in Pyrex screw cap centrifuge tubes. Dried sediment sample 0.50 g was put into 100 mL tube, and 50 mL of deionized water was added into each tube to maintain a solid/water ratio at 1:100 (W/W). The tubes were capped and incubated at $(25 \pm 1)^\circ C$ in an orbital shaker at 200 r/min for 24 h. The sample solution was immediately centrifuged at 5000 r/min for 10 min, and then filtered through a 0.45- μ m GF/C filter membrane. The filtrate was taken for the SRP analysis. For all samples, triplicates analysis were performed and the data were expressed as the average.

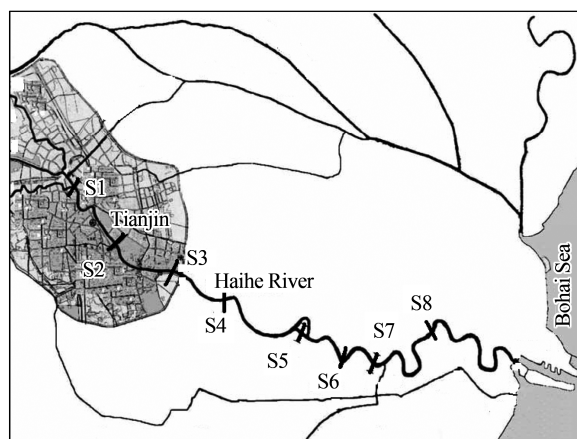


Fig. 1 Map of the study area and sampling sites.

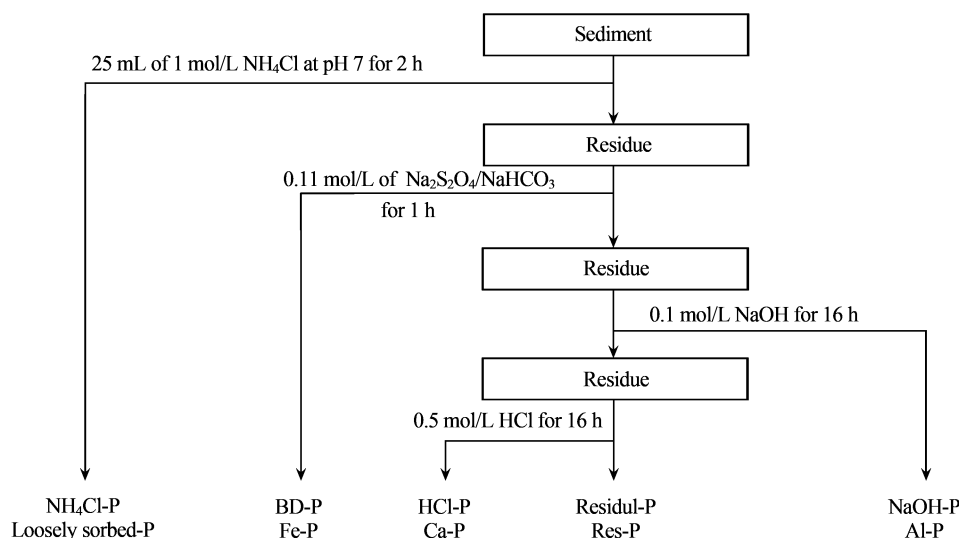


Fig. 2 Sequential extraction method

2 Results and discussion

2.1 Sediment characteristics and comparison to other water body

The selected physical and chemical characteristics of the sediment sample varied greatly (SPSS 11.0, ANOVA, $P < 0.01$) (Table 1).

The amount of TP in the surface sediments of Haihe River is similar to that of Lake Erken and Lake Koronia, which both are mesotrophic lakes. It implies that Haihe River may be mesotrophic (Table 2).

2.2 Phosphorus fraction composition

As shown in Fig. 3, the amounts of TP and different P fractions ranged greatly. For all the sediment samples P-fractions was in the order: Res-P > HCl-P > NaOH-P > BD-P > $\text{NH}_4\text{Cl-P}$, except S4 with sequence of Res-P > NaOH-P > HCl-P > BD-P > $\text{NH}_4\text{Cl-P}$. This distribution pattern was similar to that in Mexico Estuaries (Zhou *et al.*, 1996) and Lake Volvi and Lake Koronia (Kaiserli *et al.*, 2002; Fytianos and Kotzakioti, 2005). It was reported that in heavily polluted lakes, the rank order of NaOH-P > HCl-P was found (Lijklema *et al.*, 1993), while it was

the opposite order of HCl-P > NaOH-P in mesotrophic lakes (Kaiserli *et al.*, 2002). The rank order of P fraction suggests that Haihe River is mostly mesotrophic (except for site 4), which was consistent with the TP results.

The $\text{NH}_4\text{Cl-P}$ represents the loosely sorbed P in the sediments, may include dissolved P in pore water (Kaiserli *et al.*, 2002), and is also a seasonally variable pool of P compounds (Rydin, 2000). In Haihe River, the mean $\text{NH}_4\text{Cl-P}$ amounts in sediments were the lowest among the four P fractions, and exhibited high variability in various sample sites. The highest $\text{NH}_4\text{Cl-P}$ amount was observed in S4 (26.6 mg/kg), which was almost three times higher than that in sample S2 (6.7 mg/kg). The TP contents of S4 and S2 were 1469 and 1072 mg/kg, respectively, and the TP content of S4 was not the highest in the sediments. These results indicated that $\text{NH}_4\text{Cl-P}$ content was not strongly positively related with TP. The percentage of $\text{NH}_4\text{Cl-P}$ contributing to inorganic P (IP) is in the range of 1.2%–3.4% for all sample sites (Fig. 3b).

The BD-P represents the redox-sensitive P fraction, mainly including P bound to Fe-hydroxides and Mn compounds (Kozerski and Kleeberg, 1998). This fraction was considered as a potentially mobile pool of P (Rydin, 2000). In occasional dissolved oxygen (DO) depletion environments, the BD-P fraction was released from anaerobic sediments and acted as an internal P source to the overlying water (Kleeberg and Kozerski, 1997). The BD-P amounts in the sediments ranged from 54.5 mg/kg (S8) to 90.2 mg/kg (S4), which contributed 7.7%–13% of the total IP (Fig. 3b). The percentages are relatively lower than in Lake Muggelsee (23%–31%) (Kleeberg and Kozerski, 1997), and are higher than that in Volvi Lack and Koronia Lakes (Kaiserli *et al.*, 2002; Fytianos and Kotzakioti, 2005). DO, pH, bacterial activity, and organic content may affect the content of BD-P in sediments (Kaiserli *et al.*, 2002). DO depletion, high pH level or bacterial activity enhanced contribution of the BD-P fraction, while high organic content may result in the low BD-P due to the competition from binding sites (Maine *et al.*, 1992; Balchand and Nair, 1994; Ting and Appan, 1996; Perkins and Underwood, 2001).

NaOH-P is exchangeable and P bound to metal oxides (mainly Al and Fe) (Kaiserli *et al.*, 2002). NaOH-P was

Table 1 Physical and chemical characteristics of the sediments

Sample	TP (mg/kg)	TN (mg/kg)	TOC (%)
S1	2017	4581	10.49
S2	1072	2833	5.07
S3	1039	2754	5.21
S4	1469	3199	7.63
S5	1195	3858	7.33
S6	1207	3576	7.21
S7	968	3027	7.67
S8	1531	4590	9.92

Table 2 Comparison of TP in different surface sediments and water bodies

Sediment source	TP (mg/kg)	Reference
Lake Erken, Sweden	1814	Rydin, 2000
Thames, UK	53–20119	House and Denison, 2002
Han River, Korea	580–1450	Kim <i>et al.</i> , 2004
Lake Koronia, Greece	1305	Fytianos and Kotzakioti, 2005
Taihu Lake, China	420–3408	Jin <i>et al.</i> , 2006
Haihe River, China	968–2017	The present study

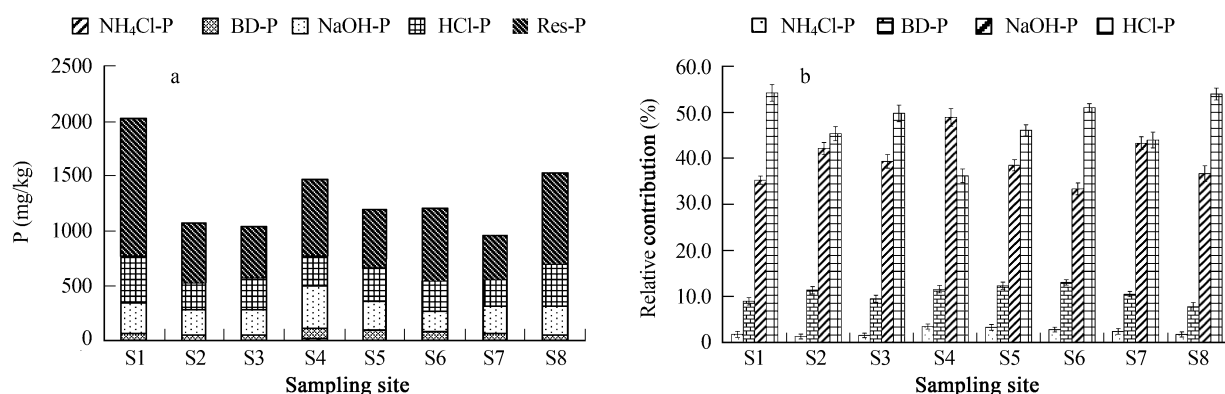


Fig. 3 Contents of different P fractions (a) and their relative contribution to inorganic P (IP) (b) in different sediments.

used for the estimation of available P in the sediments and was an indicator of algal available P (Zhou *et al.*, 2001). This fraction can be released for the growth of phytoplankton when anoxic conditions prevail at the sediment-water interface (Ting and Appan, 1996). A 33.3%–48.9% sedimentary IP in the studied samples was NaOH-P, which ranged from 185.2 to 382.5 mg/kg. The highest amount was detected in S4 (382.5 mg/kg), which are two times of that in S6 (185.2 mg/kg) (Fig. 3a). The relative contribution of NaOH-P to IP in the sediments was similar in various sites. This result is consistent with the previous reports that the contribution of NaOH-P to IP was in the range of 5%–70% (Kaiserli *et al.*, 2002).

The HCl-P represents the P fraction sensitive to low pH and was assumed to mainly consist of apatite P (natural and detritus), including P bound to carbonates and traces of hydrolysable organic P (Kaiserli *et al.*, 2002). This P fraction was deemed as a relatively stable fraction of IP in the sediments (Gonsiorczyk *et al.*, 1998; Kaiserli *et al.*, 2002). Similar to other P fractions, the HCl-P contents also varied greatly. The relative contribution of HCl-P to IP in the sediments ranged from 36.2% to 56.7% with the average of 47.6% (Fig. 3a). The high HCl-P content was owing to the calcareous terrain of the recharge area. High portions of calcium mineral P were also observed in lakes with varying trophic status.

2.3 Phosphorous release

The concentrations of P in the overlying water ranged from 0.17 to 0.63 mg/L after 24 h release experiment. The corresponding amounts of P released from the sediments are in the range 17.3–63.2 mg/kg, which was 1.5%–4.3% of TP contents. However, the amounts of P released from the sediments were not coincident with the amounts of TP. The relationships between released P and different P fractions in the sediments are shown in Fig. 4. It can be concluded that the amounts of P released was strongly in positive correlations with $\text{NH}_4\text{Cl-P}$ ($R^2 = 0.9936$, $P <$

0.01) and BD-P ($R^2 = 0.8386$, $P < 0.01$), while was not correlated with TP ($R^2 = 0.0717$, $P < 0.01$) and HCl-P ($R^2 = 0.0019$, $P < 0.01$). This indicates that $\text{NH}_4\text{Cl-P}$ and BD-P may be easily released from the sediments, and they were main contributors of the release P source in the sediments and of the sources for the overlying water. That is in agreement with the situation of Lake Erken (Rydin, 2000), where the $\text{NH}_4\text{Cl-P}$ and BD-P after P release experiments decreased 50% and 71%, respectively.

3 Conclusions

The contents of TP and different P fractions in the sediments varied greatly in the sampling sites of Haihe River. The total P contents ranged from 968 to 2017 mg/kg with the mean value of 1312 mg/kg, where the mean value of $\text{NH}_4\text{Cl-P}$, BD-P, NaOH-P, HCl-P, and Res-P contents was 15, 68, 258, 309, 663 mg/kg, respectively. The rank order of P-fractions was: Res-P > HCl-P > NaOH-P > BD-P > $\text{NH}_4\text{Cl-P}$, which was similar to Lake Volvi and Lack Koronia. Both the TP contents and the rank order of P-fractions indicated that Haihe River is mesotrophic.

The amounts of P released from the sediments have positive correlations with $\text{NH}_4\text{Cl-P}$ and BD-P. This indicated that $\text{NH}_4\text{Cl-P}$ and BD-P may be easily released from the sediments, and they contributed the most to the release P source in the sediments and of the sources for the overlying water.

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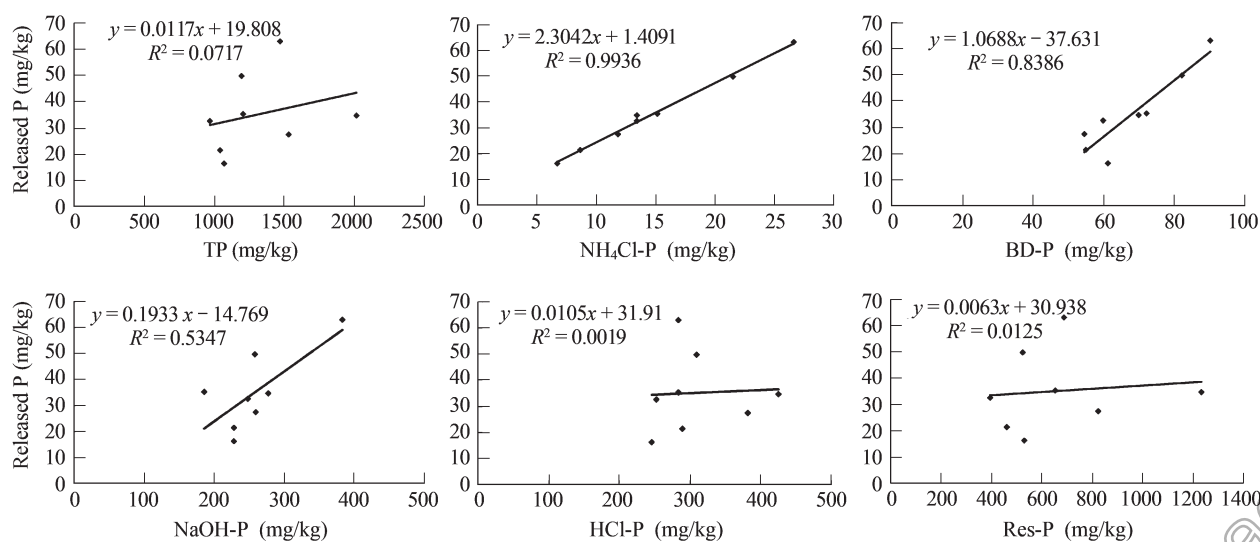


Fig. 4 Relationship between the amounts of P released and different P fractions.

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