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Nutrient distribution within and release from the contaminated sediment of Haihe River

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Abstract

We assessed nutrient characteristics, distributions and fractions within the disturbed and undisturbed sediments at four sampling sites within the mainstream of Haihe River. The river sediments contained mostly sand (> 60%). The fraction of clay was < 3%. Total nitrogen (TN) and total phosphorus (TP) concentrations ranged from 729 to 1922 mg/kg and from 692 to 1388 mg/kg, respectively. Nutrient concentrations within the sediments usually decreased with increasing depth. The TN and TP concentrations within the fine sand were higher than for that within silt. Sediment phosphorus fractions were between 2.99% and 3.37% Ex-P (exchangeable phosphorus), 7.89% and 13.71% Fe/Al-P (Fe, Al oxides bound phosphorus), 61.32% and 70.14% Ca-P (calcium-bound phosphorus), and 17.03% and 22.04% Org-P (organic phosphorus). Nitrogen and phosphorus release from sediment could lead to the presence of 21.02 mg N/L and 3.10 mg P/L within the water column. A river restoration project should address the sediment nutrient stock.

Key words: total nitrogen and phosphorus; calcium-bound phosphorus; organic phosphorus; undisturbed aquatic sediment; disturbed aquatic sediment; river restoration

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Introduction

Haihe River is the largest river in Tianjin, China, with a mainstream length of 73 km. This river originates in Sanchakou (confluence of three primary tributaries), flows through the metropolitan region of Tianjin City and discharges into Bohai Sea. The river serves as an important source for drinking, agricultural, industrial, and aquaculture waters, and it is also important as a key tourist attraction for more than 10 million people. With the rapid development of urbanization and the intensive use of water resources, the river is now subject to water shortages and water quality deterioration. Relatively low heavy metal and toxic organic compound concentrations have been recorded at previous studies. However, measured water concentrations of ammonium-nitrogen (NH_4^+-N), total nitrogen (TN) and total phosphorus (TP) were in the ranges between 0.5 and 1.5 mg/L, 2.1 and 5.38 mg/L, and 0.4 and 1.2 mg/L, respectively (Wen et al., 2008). These nutrient data indicate that Haihe River may be subject to eutrophication.

The sustainable water management of rivers, lakes and other watercourses has become an increasingly difficult task due to the threat of eutrophication (McDowell et al., 2003). Considering the economic and environmental importance of Haihe River to Tianjin, much effort has been spent to control the pollution loads by a series of environmental protection programs such as the domestic wastewater treatment and enforcement of the water pollution control law in China, but eutrophication still remains one of the most serious water quality problems of Haihe River.

Studies have shown that sediment acts not only as a sink of nutrients but also as a source (Aigars and Carman, 2001). The nutrient release process has a significant impact on the water quality and may result in continuous eutrophication of lakes and rivers, especially when external nutrient sources are under control (Abrams and Jarrell, 1995; Tian and Zhou, 2007; Xie et al., 2003).

To control eutrophication, it is necessary to reduce

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nutrient sources within the upstream tributaries and the corresponding release from the sediments. However, nitrogen control is more difficult than phosphorus control in many natural water systems, because nitrogen originates from a greater number of sources (Kim et al., 2003). It is, therefore, believed that controlling phosphorus is the best way to reduce eutrophication assuming that phosphorus is the limiting nutrient for excess algal growth (Dahl et al., 1993; Kim et al., 2003). Phosphorus is present in sediments in several chemical forms (Gonsiorczyk et al., 1998; Reitzel and Hansen, 2005). Thus, the prediction of future internal phosphorus loads requires more than the knowledge of the total concentration of phosphorus (Ribeiro et al., 2008). In several studies, sequential extraction schemes made it possible to characterize the diverse forms in which phosphorus is distributed within sediments, classified as water soluble P (phosphorus), readily desorbable P, algal available P and ecologically important P (Pettersson et al., 1988; Zhou et al., 2001).

However, for Haihe River, it is still an open question where and in which amount and form phosphorus is present within the sediment. Furthermore, the correlations between sediment phosphorus concentrations, organic matter and nitrogen concentrations are still not fully understood. Therefore, this study investigates the levels of nitrogen, phosphorus and organic matter, and defined phosphorus fractions and profile within the sediments of Haihe River. The main objectives were: (1) to examine the sediment characteristics of Haihe River including grain size, total nitrogen, organic matter, and total phosphorus and forms of phosphorus; (2) to quantify and evaluate the extent of sediment pollution with sediment depth and along a reach of the river; (3) to assess the relationships between phosphorus, including its various forms, and total nitrogen and organic matter contents; and (4) to provide the baseline data for the management and conservation of Haihe River.

1 Experiments

1.1 Sample site description

The climate of Haihe River basin is transitional between semi-wet and semi-arid with a mean annual precipitation between 500 and 550 mm. The distribution of precipitation is uneven, for instance the precipatation in 1964 was 798 mm while 358 in 1965; most of the rainfall (80%) occurs in summer (between June and September). In recent decades, the discharge of Haihe River decreased sharply. For example, the annual mean runoff was 44 m^3/sec during the time period between 1965 and 1980. In contrast, the corresponding value between 1980 and 2004 was only 7.05 m^3/sec, due to the construction of Erdao Gate and the decresing receiving water from upriver (Zheng et al., 2005). The declines of both the inflow and flow velocity resulted in the rapid accumulation of sediment in the river and an acceleration of eutrophication of the corresponding water column.

As shown in Fig. 1, there are two gates on the mainstream of Haihe River. One is the Erdao Gate (used for flood control) and the other one is the Haihe Gate (constructed for preventing sea water inflow). The river reach between Erdao Gate and Haihe Gate was mainly used for flood control and navigation, while the Erdao Gate upstream of the river was exploited as an important source for drinking water, agricultural irrigation water, industrial water, aquaculture water sources.

1.2 Sediment sampling and grain size determination

Disturbed and undisturbed sediment samples were both collected from the four sampling sites 1 (Zhangjiazui), 2 (Zhaobeidu), 3 (Xingjiajuan) and 4 (Dazheng), which were all located upstream of the Erdao Gate. The corresponding detailed sampling positions are given in Table 1.

The disturbed samples were collected with a grab style sampler and the undisturbed samples were obtained with a self-made gravity corer equipped with two parallel acrylic liners with an inside diameter of 10 cm on 7 July 2007. The undisturbed sediments were immediately cut on a ferry used for sampling in 10 to 15-cm sections, and each section was fully blended. All sediment samples were immediately transported to the laboratory within sealed plastic bags that were put in iceboxes, and all samples were freeze-dried before analysis.

Sediment size distributions of undisturbed samples were measured using the sieve analysis method. In the present study, five different sieves with 20, 60, 100, 200 and 400

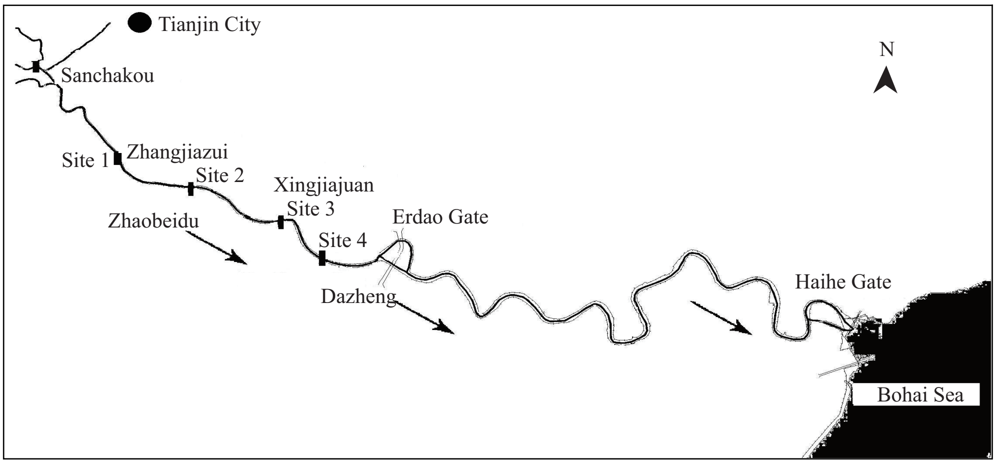

Fig. 1 Map of Haihe River showing the sampling sites of the sediment.

Table 1 Parameters concerning different undisturbed sediments collected from Haihe River

Parameter	Sampling site			
	Site 1	Site 2	Site 3	Site 4
Position	39°03′06″N 117°22′21″E	39°01′24″N 117°24′09″E	39°03′03″N 117°21′30″E	39°01′07″N 117°26′18″E
Water depth (m)	1.80	1.27	1.90	1.83
Sediment depth (cm)	125	90	75	105
Grain size (%)*				
< 0.0385 mm (clay)	1.22 ± 1.96	2.32 ± 2.28	2.50 ± 2.04	0.82 ± 0.71
0.0385–0.074 mm (silt)**	33.93 ± 9.83 ab	35.47 ± 10.58 b	36.57 ± 5.80 b	26.19 ± 10.63 a
0.074–0.147 mm (very fine sand)	22.36 ± 10.63	22.23 ± 17.72	15.69 ± 7.33	25.93 ± 11.08
0.147–0.246 mm (fine sand)	11.64 ± 1.90	9.92 ± 2.84	11.55 ± 2.29	11.79 ± 2.20
> 0.246 mm (medium sand)	30.84 ± 7.52	30.05 ± 8.97	33.69 ± 6.05	35.26 ± 4.68

* Mass percentage content within grain size ranges was calculated as the mean value of each divided sediment interval. Nutrient concentrations are the mean values for fine sand, very fine sand and silt samples. All measurements were conducted in triplicates.
** Values with different letters indicate significant differences at $p \leqslant 0.05$ based on the Duncan's multiple range tests.

mm-diameter meshes were used to determine the mass fractions with the corresponding grain sizes: bigger than 0.247 mm, 0.147–0.246 mm, 0.074–0.147 mm, 0.0385–0.074 mm, and smaller than 0.0385 mm. These ranges can be categorized into medium sand, fine sand, very fine sand, silt and clay, respectively, according to the China Soil Partition method (Wang and Kang, 1991). According to Table 1, the sand fraction (0.06–0.5 mm, sum of the medium sand, fine sand and very fine sand) dominated the sediment fractions for all the undisturbed sediment samples (60.93%–72.98%), while the clay fraction was minor, accounting for less than 3% of the total. Except for sample site 4, silt fractions gradually increased from the upstream to the downstream of Haihe River. Like sediments collected from other Chinese natural lakes or rivers (Jin et al., 2006), silt was the major sediment component for Haihe River and contributed to 26.19%–36.57% of the total (Table 1).

1.3 Sediment and data analysis

The following measurements were carried out for the fractions of the disturbed and undisturbed sediments with particle sizes of between 0.147 and 0.246 mm (fine sand), 0.074 and 0.147 mm (very fine sand), and less than 0.074 mm (silt and clay). Sequential extraction of phosphorus was undertaken to determine the phosphorus species. The Standards, Measurements and Testing (SMT) protocol for sequential extraction, which is a modified version of a European standard, was followed (Ruban et al., 1999, 2001).

Exactly 20 mL of 1 mol/L NH_4Cl were added to 500 mg sediment (dry weight equivalent), and the suspension was shaken for 2 hr. After shaking, the suspension was centrifuged at 3000 r/min for 10 min, and the supernatant was decanted. This process was repeated with 1 mol/L NaOH (shaken for 12 hr) and then with 1 mol/L HCl (shaken for 12 hr). These fractions represent exchangeable P (Ex-P), P bound by Fe, Al oxides (Fe/Al-P) and calcium bound P (Ca-P), respectively. The total phosphorus concentration within the sediments was determined by treating the sub-sample at 450°C, followed by HCl extraction (Ruban et al., 1999, 2001). Organic phosphorus (Org-P) was approximately evaluated as the difference between total phosphorus and the sum of Ex-P, Fe/Al-P and Ca-P.

Concentrations of total nitrogen and organic matter within the sediments were analyzed using the soil physical and chemical standard method introduced by Bao (2000). For each nutrient, phosphorus fraction, total nitrogen and organic matter concentration, three independent replicates were conducted and all the data were expressed as mean values.

The self organizing map (SOM), which is based on an unsupervised learning algorithm, was applied as a pattern analysis and clustering tool to provide visualization of relationships between variables (Kohonen et al., 1996). The SOM toolbox (version 2) for Matlab 7.0 developed by the Laboratory of Computer and Information Science at Helsinki University of Technology was used in this study. (http://www.cis.hut.fi/projects/somtoolbox).

2 Results and discussion

2.1 Nutrient concentrations in disturbed sediment

Nutrients including organic matter, nitrogen and phosphorus were analyzed to evaluate the extent of disturbed sediment pollution of Haihe River. The maximum and minimum nitrogen and phosphorus concentrations were determined for sampling sites 1 and 3 (Table 2). Previous works indicate that nutrient and organic matter concentrations decreased from upstream to downstream river stretches, which is counter-intuitive (Ruban et al., 1999; Tian and Zhou, 2007). This unusual pattern can be explained by the slow flow velocity (less than 0.3 m/sec) resulting in rapid sediment accumulation of nutrients at the upper reach of Haihe River. This can be partly confirmed by the rank order of the corresponding undisturbed sediment depths (Table 1).

Table 2 shows the results for nutrient data determined at different locations. Most samples had organic matter fractions within the range of 3.22% and 5.92%. An exception was sampling site 4, where the organic matter fraction exceeded 10% because of the presence of the Erdao Gate, which encouraged nutrient accumulation in this area. The total nitrogen values for the monitored sediments varied considerably from 728.20 to 1922.03 mg/kg.

The total nitrogen data recorded for Tianjin were much lower than those (up to 21,750 mg/kg) reported for similar-

Table 2 Nitrogen, phosphorus and organic matter concentrations (mean within disturbed sediments)

Sampling site	TN (mg/kg)	TP (mg/kg)	Ex-P (mg/kg)	Ca-P (mg/kg)	Fe/Al-P (mg/kg)	Org-P (mg/kg)	OM (%)
1	1922.03	1388.43	55.37	648.33	374.97	309.77	13.05
	(209.88)	(202.81)	(8.56)	(126.72)	(95.15)	(68.51)	(4.62)
2	1088.40	810.77	29.63	528.67	76.73	175.73	5.92
	(299.91)	(60.93)	(2.17)	(46.66)	(37.90)	(31.54)	(1.21)
3	728.20	691.73	24.87	497.37	52.97	116.53	3.22
	(123.69)	(54.36)	(1.21)	(11.94)	(12.56)	(46.15)	(0.76)
4	821.17	741.10	22.37	537.77	35.43	145.53	3.93
	(174.50)	(41.62)	(2.22)	(54.85)	(9.09)	(42.07)	(0.88)

TN: total nitrogen; TP: total phosphorus; Ex-P: exchangeable phosphorus; Ca-P: calcium-bound phosphorus; Fe/Al-P: iron/aluminum-bound phosphorus; Org-P: organic phosphorus; OM: organic matter.
Concentrations are the mean values for fine sand, very fine sand and silt samples. Data are expressed as mean (standard deviation) (n = 3).

ly disturbed sediment collected from the eutrophic Taihu Lake, China (Jiang et al., 2006). Kim et al. (2003) found that the concentration of total nitrogen varied overall from 310 to 2600 mg/kg within the Han River, Korea. Total nitrogen concentrations ranged from 300 to 5200 mg/kg for shallow lakes located between the middle and lower reaches of the Yangze River region, China (Wang et al., 2005). The range for total phosphorus concentrations of all sediment samples was between 691.73 and 1388.43 mg/kg.

Different species of phosphorus within the sediments of the study areas are summarized in Table 2. For the sampling sites 1 to 4, Ex-P, Ca-P, Fe/Al-P and Org-P varied from 22.37 to 55.37 mg/kg, 497.37 to 648.33 mg/kg, 35.43 to 374.97 mg/kg and 116.53 to 309.77 mg/kg, respectively. Inorganic phosphorus (sum of Ex-P, Ca-P and Fe/Al-P) was higher than Org-P within the disturbed sediments. The rank order for inorganic phosphorus species within the sediments was Ca-P > Fe/Al-P > Ex-P.

Similar results were also obtained for the Han River sediments, where Ca-P was invariably the dominant form of phosphorus. Most values exceeded 83% of total phosphorus (Tian and Zhou, 2007). Ca-P was also reported to be the abundant fraction within sediments of some estuaries and mesotrophic lakes (Kaiserli et al., 2002; Zhou et al., 1996).

2.2 Nutrient distribution of undisturbed sediment

Table 3 shows the spatial distribution of organic matter, nitrogen and phosphorus for the undisturbed sediments. It can be seen that nutrient enrichment variations were apparent at different sampling sites. In general, undisturbed sediment had a similar nutrient distribution compared to disturbed sediment. Nutrient-enriched sediment dominated sampling site 1. Nutrient concentrations within the undisturbed sediment tended to decrease from the upstream to the downstream river stretches. These findings confirmed the facts that water flow conditions, pollution duration, composition and sediment structure could greatly change the nutrient accumulation process (Ferreira et al., 1996).

The general vertical distribution pattern for the four sample sites was that the concentrations of organic matter, nitrogen and phosphorus including specific fractions decreased with increasing depth. However, at the sampling sites 1, 3 and 4 (Table 3), this general pattern was interrupted by an increasing concentration trend for the depth ranges (from top to bottom) 70–80 cm (site 1), 60–75 cm (site 3) and 70–80 cm (site 4). This vertical concentration pattern is due to historic water pollution patterns, reflecting the industrial past (Kim et al., 2003). The reason for the unexpected increase of nutrient concentrations within the top sediment may reflect the age of the sediment and temporal changes in nutrient inputs.

Figure 2 shows mean nutrient concentrations for fine sand, very fine sand and silt, respectively. Sediment particle size information is important because smaller particles have greater specific surface areas for pollutant adsorption (Xu et al., 2006). In contrast to the disturbed sediment (Table 2), organic matter, nitrogen and phosphorus concentrations were slightly lower within the undisturbed sediment. It can be concluded that undisturbed sediments had lesser sediment pollution levels when compared to disturbed surface sediment. Similar results were also found for other river or lake sediments (Edlund and Carman, 2001; Ruban et al., 1999).

Sediment grain sizes can effect nutrient concentrations. The rank order for total nitrogen, total phosphorus, Ca-P and Org-P concentrations of the undisturbed sediments was as follows: very fine sand > fine sand > silt. These findings compared well with that reported in the literature. Wang et al. (2004) assessed the nutrient concentrations of undisturbed Wuli Lake and Gonghu Lake sediment. Their results indicate that the total nitrogen and total phosphorus contents of fine sand are higher than for silt. However, the rank order of Ex-P concentrations for the examined sediments was as follows: silt > very fine sand > fine sand. Silt had the smallest grain size distribution, and therefore the highest surface area, indicating a high potential for direct reaction with phosphorus (Drizo et al., 1999). In contrast to nutrients, organic matter and Fe/Al-P concentrations showed different distribution patterns; their values were higher for fine sand compared to very fine sand and silt (Fig. 2). In general, organic matter, nitrogen, and phosphorus increased with an increase in the accumulation of detritus and decreased with increasing particle sizes.

Phosphorus factions, total nitrogen, total phosphorus and organic matter distributions determined in this study only partly fitted these trends. This can be explained by the complexity of the water flow conditions and sedimentation processes. Moreover, environmental conditions may affect the sediment particle size distribution (Wang et al., 2004).

A correlation analysis was undertaken to further test the relationships between each nutrient. The fine sand

Fig. 2 Abstract visualization of the overall distributions of Ex-P, Ca-P, Fe/Al-P, Org-P, TP, TN, OM within the different undisturbed sediment fractions using a self-organizing map model.

sediment was selected as an example, because the very fine sand, fine sand and silt had a similar nutrient distribution pattern (Fig. 2). The coefficients of the corresponding correlation matrix for all variables are shown in Table 4.

The total nitrogen concentrations were positively correlated with Ex-P, Ca-P, Fe/Al-P, Org-P, total phosphorus and organic matter concentrations. Furthermore, total phosphorus concentrations were also positively correlated with organic matter concentrations (Table 4).

These findings confirm the strong linear correlations between organic matter, total nitrogen and total phosphorus within the sediment as observed by Clarke and Wharton (2001). This relationship reflects the common origin of nitrogen and phosphorus, which was released from organic material during decomposition processes. There were inter-correlations among various phosphorus fractions (Table 4). Total phosphorus and Ca-P concentrations had the most significant correlations. The relationships between total phosphorus and Ex-P, Fe/Al-P, Org-P were also significant. Close correlations between total phosphorus and its fractions have also been reported for river delta and reservoir sediments (Martinova, 1993; Wang et al., 2005; Watts, 2000).

2.3 Phosphorus fractions of disturbed sediment

The contributions of each phosphorus fraction relative to total phosphorus within the disturbed sediments are shown in Fig. 3. The Ex-P content contributed to less than 5% of total phosphorus. The Fe/Al-P proportions related to total phosphorus were roughly between 8% and 14%, and indicated a decline from the upstream to the downstream river stretch. The Ca-P fraction was invariably the dominant form of phosphorus, with most values exceeding 70%. The Org-P/TP ratios fell into the range of between 17% and 23%. There was more Ex-P and Fe/Al-P content within the sediment sample 1, because more sediment was allowed to settle in this area (Table 1), where the water velocity was low due to a broader water course (Zheng et al., 2005). The

Table 3 Nitrogen, phosphorus and organic matter concentrations at different depths for the four sites within undisturbed sediment

	Depth (cm)											
	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100	100–110	110–125
Site 1												
Ex-P	42.13	33.53	23.57	26.20	24.63	23.50	24.87	28.07	25.70	18.97	16.17	16.10
(mg/kg)	(6.43)	(3.54)	(1.97)	(0.00)	(2.26)	(1.32)	(1.81)	(2.89)	(3.32)	(1.29)	(1.74)	(0.69)
Ca-P	763.37	479.13	549.53	478.13	474.07	460.83	446.33	469.67	434.80	431.77	413.13	394.87
(mg/kg)	(179.37)	(13.90)	(83.59)	(29.85)	(41.06)	(55.89)	(80.35)	(46.20)	(66.28)	(56.66)	(45.01)	(58.85)
Fe/Al-P	399.63	140.70	78.17	69.53	76.10	89.20	76.37	99.20	90.87	61.87	61.87	60.90
(mg/kg)	(119.58)	(37.49)	(22.71)	(10.51)	(13.95)	(5.99)	(0.81)	(16.99)	(4.56)	(7.87)	(7.13)	(9.51)
Org-P	258.33	200.47	153.07	151.40	154.40	148.47	154.00	173.83	169.90	139.33	159.67	139.70
(mg/kg)	(11.02)	(46.00)	(33.92)	(21.37)	(21.22)	(33.51)	(22.46)	(44.85)	(29.23)	(18.80)	(23.12)	(16.84)
TP	1463.47	853.83	804.33	725.27	729.20	722.43	701.57	770.77	721.27	651.93	650.83	611.57
(mg/kg)	(168.87)	(38.87)	(85.04)	(28.18)	(48.30)	(83.36)	(98.90)	(72.04)	(72.43)	(71.29)	(58.68)	(72.15)
TN	2003.87	1104.87	1150.50	842.37	810.03	674.73	618.63	778.37	640.07	471.23	542.90	713.63
(mg/kg)	(350.01)	(265.49)	(34.43)	(106.99)	(175.68)	(90.05)	(227.45)	(23.14)	(130.22)	(111.13)	(43.84)	(120.16)
OM	15.32	8.44	6.01	4.13	4.25	3.90	3.15	3.51	2.89	2.28	2.51	2.72
(%)	(2.95)	(1.74)	(1.03)	(0.78)	(0.69)	(0.92)	(0.88)	(0.21)	(0.43)	(0.86)	(0.42)	(0.76)
Site 2												
Ex-P	22.52	20.07	23.83	22.17	18.83	18.67	17.57	15.80	13.00	–	–	–
(mg/kg)	(3.89)	(2.50)	(3.04)	(2.33)	(2.83)	(0.84)	(0.46)	(1.01)	(2.36)			
Ca-P	461.49	456.13	446.77	440.00	429.17	424.43	437.20	470.67	449.83	–	–	–
(mg/kg)	(4.22)	(44.50)	(55.56)	(54.33)	(58.60)	(47.15)	(55.12)	(96.35)	(160.72)			
Fe/Al-P	64.74	66.33	74.67	70.87	61.17	69.40	59.40	49.73	41.97	–	–	–
(mg/kg)	(1.22)	(18.70)	(19.63)	(16.61)	(13.89)	(6.27)	(14.60)	(14.68)	(8.05)			
Org-P	124.62	122.87	116.80	117.43	105.77	123.93	99.87	74.80	52.10	–	–	–
(mg/kg)	(8.89)	(43.12)	(18.66)	(8.35)	(20.36)	(14.45)	(51.65)	(59.51)	(29.73)			
TP	673.35	665.40	662.07	650.47	614.93	636.43	614.03	611.00	556.90	–	–	–
(mg/kg)	(15.77)	(60.35)	(35.56)	(54.71)	(26.60)	(46.84)	(100.51)	(98.39)	(176.17)			
TN	889.22	617.17	707.10	578.53	648.47	569.83	513.53	452.23	335.27	–	–	–
(mg/kg)	(36.89)	(109.82)	(197.05)	(176.40)	(127.28)	(112.35)	(178.04)	(256.51)	(202.99)			
OM	4.49	3.58	3.81	3.07	2.90	3.21	2..51	2.22	1.59	–	–	–
(%)	(0.12)	(0.69)	(1.14)	(0.69)	(0.69)	(0.65)	(1.01)	(1.43)	(1.48)			
Site 3												
Ex-P	24.15	26.60	29.23	23.83	19.30	16.13	14.93	–	–	–	–	–
(mg/kg)	(1.02)	(1.64)	(1.83)	(1.93)	(1.06)	(0.35)	(1.03)					
Ca-P	480.29	486.90	483.87	454.43	430.40	404.67	421.93	–	–	–	–	–
(mg/kg)	(24.16)	(7.88)	(24.35)	(46.82)	(76.82)	(72.51)	(31.02)					
Fe/Al-P	55.59	69.27	80.80	69.37	46.90	43.23	52.30	–	–	–	–	–
(mg/kg)	(3.70)	(14.27)	(13.75)	(10.75)	(4.06)	(4.08)	(7.55)					
Org-P	118.23	162.10	148.70	112.43	99.80	91.17	88.67	–	–	–	–	–
(mg/kg)	(2.40)	(11.07)	(36.84)	(70.84)	(31.95)	(4.75)	(43.52)					
TP	678.25	744.87	742.60	660.07	596.40	555.20	577.83	–	–	–	–	–
(mg/kg)	(19.06)	(16.61)	(46.15)	(60.65)	(67.05)	(65.68)	(37.61)					
TN	791.10	634.90	724.93	811.93	532.13	401.17	479.23	–	–	–	–	–
(mg/kg)	(88.95)	(83.25)	(98.82)	(44.58)	(66.27)	(89.67)	(245.25)					
OM	3.30	3.51	3.72	3.08	2.34	2.12	2.64	–	–	–	–	–
(%)	(0.11)	(0.39)	(0.20)	(0.49)	(0.46)	(0.65)	(1.03)					
Site 4												
Ex-P	20.45	19.17	22.70	21.57	18.83	17.57	15.90	22.67	26.47	30.73	–	–
(mg/kg)	(0.88)	(0.95)	(1.47)	(1.29)	(2.21)	(1.01)	(1.61)	(1.91)	(2.73)	(4.93)		
Ca-P	486.35	461.53	493.57	462.47	443.03	412.83	463.37	462.93	509.37	531.93	–	–
(mg/kg)	(45.93)	(61.16)	(41.15)	(25.08)	(49.84)	(24.85)	(57.50)	(27.64)	(14.45)	(2.31)		
Fe/Al-P	44.32	49.97	49.20	48.40	43.13	53.87	57.57	83.50	80.67	94.57	–	–
(mg/kg)	(1.72)	(8.29)	(8.22)	(8.14)	(9.14)	(13.26)	(20.12)	(18.30)	(10.80)	(1.01)		
Org-P	157.72	103.23	154.77	164.40	145.73	152.73	149.47	191.37	171.33	205.57	–	–
(mg/kg)	(6.20)	(73.46)	(53.16)	(51.94)	(48.31)	(21.51)	(32.52)	(33.30)	(17.22)	(28.50)		
TP	708.84	633.90	720.23	696.83	650.73	637.00	686.30	760.47	787.83	862.80	–	–
(mg/kg)	(51.29)	(73.78)	(32.28)	(66.61)	(55.18)	(46.26)	(43.25)	(29.18)	(16.74)	(26.79)		
TN	688.30	580.10	616.73	628.93	545.17	666.90	532.43	638.17	727.37	1230.63	–	–
(mg/kg)	(136.90)	(145.23)	(149.86)	(83.48)	(126.97)	(143.48)	(177.49)	(106.75)	(122.81)	(208.44)		
OM	3.80	3.74	3.41	3.08	2.52	2.72	2.94	3.88	4.01	8.04	–	–
(%)	(0.13)	(0.80)	(0.64)	(0.34)	(0.59)	(0.62)	(1.14)	(0.46)	(0.39)	(1.45)		

Concentrations are mean values for fine sand, very fine sand and silt samples. Data are expressed as mean (standard deviation) (n = 3).

disturbed sediments within Haihe River have a relatively high Ca-P content. However, phosphorus concentrations were lower compared to the Hanjiang River and Yangtze River, China (Tian and Zhou, 2007).

The immediately available phosphorus within sediments corresponded mostly to the soluble exchangeable phosphorus, which was predominantly *ortho*-phosphate-phosphorus (Ribeiro et al., 2008). Therefore, Ex-P was the best parameter for the assessment of the bioavailability of phosphorus. Analytical results suggested that the Ex-P concentration within Haihe River was between 13.00 and 42.13 mg/kg. This compares well with reported values

Table 4 Correlation matrix for the undisturbed sediment[a]

Variable	TN	TP	Ex-P	Ca-P	Fe/Al-P	Org-P	OM
TN	1.000						
TP	0.923*	1.000					
Ex-P	0.729*	0.835*	1.000				
Ca-P	0.920*	0.925*	0.773*	1.000			
Fe/Al-P	0.813*	0.892*	0.727*	0.744*	1.000		
Org-P	0.661*	0.820*	0.670*	0.600*	0.668*	1.000	
OM	0.934*	0.940*	0.762*	0.894*	0.912*	0.663*	1.000

* Significance at $p < 0.001$.
[a] Taking silt fraction as representative example.

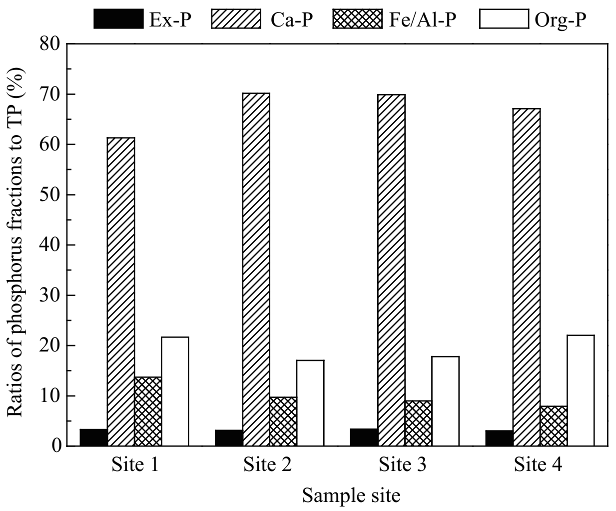

Fig. 3 Mean ratio of individual phosphorus fractions to total phosphorus (TP) within the disturbed sediments of Haihe River.

between 13 and 59 mg/kg for lake sediments (Ribeiro et al., 2008). In comparison with the other three sample sites, site 1 had a high concentration value for Ex-P. This means that loosely exchangeable phosphorus will be easily available to algae, consequently promoting blooms in this area.

Fe/Al-P represents phosphorus bond to metal oxides (mainly Fe and Al) and is exchangeable with OH^- and other inorganic phosphorus compounds, which are soluble in bases (Kozerski and Kleeberg, 1998). Furthermore, Fe/Al-P can also be used for the evaluation of algal available phosphorus (Zhou et al., 2001), because it supports the growth of phytoplankton (Ting and Appan, 1996). However, Fe/Al-P is the minor component of total phosphorus (less than 15%) for Haihe River sediment. Previous studies found that the proportion of Fe/Al-P was between 5% and 70% of the total phosphorus. Particularly high values were recorded for eutrophic and non-calcareous environments (Penn et al., 1995). Furthermore, Ca-P was a relatively stable fraction, and was attributed to the permanent burial of phosphorus within sediments (Gonsiorczyk et al., 1998; Kleeberg and Kozerski, 1998).

Similar to the monitoring results of this study (Fig. 3), high proportions of calcium mineral-P were observed within rivers and lakes with various trophic statuses (Jin et al., 2006; Tian and Zhou, 2007). For these studies, Ca-P fractions were dominant, contributing between 35% and 90% of total phosphorus, with calcareous sediments close to the upper limit of this range (Penn et al., 1995; Tian and Zhou, 2007). Org-P represented the phosphorus fraction bound to organic matter, and was quantitatively one of the most important phosphorus phases buried within the sediment. Thus, it directly affected the availability levels of dissolved phosphorus for primary production (Edlund and Carman, 2001). For the disturbed sediment in the heavily eutrophic Haihe River, phosphorus was mainly of detrital origin (Ca-P), whereas Fe/Al-P+Org-P (less than 20%) originated less from detritus but more from anthropogenic sources (Ruban et al., 1999).

2.4 Assessment of the nutrient stock within the sediment

Taking into account the mean length (37 km) and width (120 m) of the examined river reach, it was possible to calculate the sediment stock for Haihe River. The surface area of the sediment was approximately 4.4 km^2. The mean depths of the disturbed and undisturbed sediments were 5 and 95 cm, respectively. The disturbed and undisturbed sediment volumes were 2.2×10^5 and 4.2×10^6 m^3, respectively. The mean water content and density were 86.5% and 1.12 tons/m^3 for the disturbed sediment. The corresponding values for the undisturbed sediment were 38.4% and 2.65 tons/m^3. Thus, the calculated dry disturbed and undisturbed sediment masses were 2.5×10^5 and 11.1×10^6 tons, respectively.

Nitrogen and phosphorus releases mostly occurred within the easily disturbed surface sediment at a depth of 5 cm (Jensen et al., 1992; Xing et al., 2006). Ex-P and Fe/Al-P were usually used for the assessment of the bioavailability of phosphorus (Ribeiro et al., 2008; Zhou et al., 2001), while ammonia-nitrogen was the best parameter for evaluation of bioavailability of nitrogen (Xing et al., 2006). Further nitrogen fraction analysis suggests that ammonia-nitrogen constitutes approximately 70% of the total nitrogen within the disturbed sediment samples. For Haihe River, mean nitrogen (estimated as ammonia-nitrogen) and phosphorus (Ex-P and Fe/Al-P) concentrations within the disturbed sediment were 1139.95±202 mg N/kg and 168.09±42.22 mg P/kg, and the stock of bioavailable nitrogen and phosphorus averaged 283.48 ± 50.26 tons and 41.8±10.5 tons, respectively.

Considering the water volume was 13.3×10^6 m^3 (mean water depth of 3 m) and assuming that the nutrient release only occurred within the disturbed sediment, calculated increments of nitrogen and phosphorus concentrations within Haihe River water column reached 21.02 and 3.10 mg/L, respectively. These data were several hundred times higher than the values for ammonia-nitrogen (0.2 mg/L) and phosphorus (0.02 mg/L), which are the recommended maximum concentrations for flowing water to discourage water blooms (Sawyer et al., 1994).

3 Conclusions

Sand dominated the undisturbed Haihe River sediment samples (60.93%–72.98%), while the clay fraction was low (less than 3%). Except for sampling site 4 (located near the Erdao Gate), disturbed and undisturbed sediment from the upper reach of Haihe River were both much more polluted than those from the lower reach.

For undisturbed sediment, concentrations of organic matter, nitrogen and phosphorus decreased with increasing depth. The sediment grain size impacted on nutrient concentrations, the rank order of the total nitrogen and total phosphorus concentrations of the sediment was as follows: very fine sand > fine sand > silt.

The contents of Ex-P and Fe/Al-P were relatively low, and contributed to < 5% and 8%–14% of total phosphorus, respectively. Their concentrations both decreased from upsteam to downstream. The Ca-P was the dominant form of phosphorus with the content exceeding 70%. The Org-P/TP fraction was between 17% and 23%.

The stock of disturbed and undisturbed sediment was estimated to be 2.5×10^5 and 11.1×10^6 tons for the examined area. Sediment releases could contribute substantially to the eutrophication of the watercourse. Future sediment dredging may result in an unwanted release of nutrients.

It is important to keep in mind that a large stock of easily releasable nitrogen and phosphorus exists within the river, which could delay the recovery of the river even when adaptive measurers to reduce nitrogen and phosphorus inputs are taken.

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