Characteristics, distribution and ecological risk assessment of phosphorus in surface sediments from different ecosystems in Eastern China: A ^{31}P -nuclear magnetic resonance study

Wenqiang Zhang^a, Baoqing Shan^{a,*}, Jie Li^{a,b}, Wenzhong Tang^a, Xin Jin^c, Hong Zhang^a, Yuekui Ding^{a,b}, Yuanyue Wang^{b,d}, Xiaolei Zhu^{a,b}

^a State Key Laboratory on Environmental Aquatic Chemistry, Research Center for Eco-Environmental Science, Chinese Academy of Science, Beijing, 100085, PR China

^b University of Chinese Academy of Science, Beijing, PR China

^c Hebei University of Engineering, Hebei Handan 056038, PR China

^d Department of Water Pollution Control Technology, Chinese Academy of Science, Beijing 100085, PR China

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ABSTRACT

Surface sediments in different ecosystems (lake, river, reservoir, estuary and wetland) in Eastern China were extracted with NaOH–EDTA, and the extracts were analyzed by ^{31}P -NMR to reveal the phosphorus (P) species distribution. The P release risk was also assessed by sorption experiments. The river sediments accumulated significant amounts of P compared with other sediments. The organic phosphorus (Po) concentration in the estuarine sediment was lower than that in other sediments. Two P compounds classes (phon-P and mono-P) and five P compounds were detected in the sediments. Ortho-P (83.3–97.6%) was the dominant P compounds and mono-P (1.1–18.0%) were the dominant Po compounds classes, while smaller amounts of DNA-P (0–4.1%), pyro-P (0–4.0%) and lipid-P (0–0.8%) were found in the surface sediment. Poly-P and phon-P were detected only in site 11 (wetland), site 10 (wetland) and 11, respectively. The ERI values, as a measure of eutrophication risk, were different in the various sediments, being greater than 25% in sites 1 (river), 3 (estuary) and 4 (estuary), and with values of 26, 59 and 83%, respectively. The X_m and ERI values fitted a power function ($R_{X_m-ERI} = 0.89$, $p < 0.01$) and a positive correlation between X_m and OM in the sediment ($R_{X_m-OM} = 0.84$, $p < 0.01$) indicated that the chemical–physical conditions play a vital role in controlling P sorption and desorption.

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1. Introduction

Phosphorus (P) is a vital element to all life and aquatic ecosystems. Excessive P inflow in the water column will accelerate primary productivity in the water leading to eutrophication (Wetzel, 2001; Paytan and McLaughlin, 2010). Eutrophication of aquatic ecosystems has become one of the most severe environmental problems, especially in developing countries, and is driven by the amount of nutrient inputs from untreated sewage and agricultural wastewater (Xu et al., 2010; Pernet-Coudrier et al., 2012). The consequences of eutrophication include algal blooms, oxygen depletion, fish kills, aquatic ecosystem deterioration and increasing water treatment costs to ensure freshwater is suitable for human use (Nyenje et al., 2010; Vörösmarty et al., 2010).

Within the last two decades, China has become one of the fastest growing economies, with a GDP growth rate of nearly 10% (Liu and Raven, 2010). Meanwhile, the generation and consumption of P-containing compounds has dramatically increased. In particular, human activities associated with agriculture and industry has greatly accelerated the production of bioactive nutrients containing P (Qu and Kroeze, 2010). Currently, the population density in Eastern China is over 400 people per square kilometer. The rapid population growth, industrial development and increased agricultural production have led to an increased inflow of untreated sewage and waste into the environment. As a result, anthropogenically mobilized P in watersheds enters rivers, lakes and marine systems, which increase the risk of surface water eutrophication (Pernet-Coudrier et al., 2012). Research has shown that the total P (TP) load in the Songhuajiang watershed was $4.05 \times 10^4 \text{ t}$ in 2008, which was caused mainly by man-made non-point source pollution and the load of P was $3.40 \times 10^4 \text{ t}$, accounting for 83.94% of the TP load (Ma et al., 2011). High P

* Corresponding author. Tel.: +86 10 62849817; fax: +86 10 62849817.
E-mail address: bqshan@rcees.ac.cn (B. Shan).

concentrations were also found in the Zhujiang (Pearl) river estuary wetland, ranging from 648.9 to 1064.0 mg kg⁻¹ in the surface sediment. These results showed that the potential risk of eutrophication in the wetland sediment was high (Wang et al., 2013a,b). The average concentration of TP in Taihu lake sediment (18 sites) was 648 mg kg⁻¹, and the concentration of TP in Meiliang bay exceeded 1800 mg kg⁻¹, which means that the sediment was a potential source of P for overlying water leading to likely eutrophication (Bai et al., 2009). The Haihe watershed, which includes many large cities such as Beijing and Tianjin, provides 30% of China's wheat and 20% of its corn, and the nutrient concentrations (N and P) in their rivers have drastically increased in the past 40 years (Hong and Luan, 1998; Shi et al., 2008).

There is significant diversity in the water ecosystems in Eastern China, as reflected in the rivers, wetlands, lakes, reservoirs and estuaries. Different water ecosystems have various P compounds which exhibit diverse P retention mechanism (Wang and Pant, 2010a,b). Lakes and reservoirs are considered a “sink” for such chemical species in the watershed, so appreciable P compounds are retained in the sediments of lakes and reservoirs (Zhang et al., 2009). Rivers are often considered the “corridor” of the watershed, which means that P might input to lake or ocean via river transportation. However, P is largely contained within the river sediment because of dams and the smooth grain particles in the flood plain, as in the Haihe river basin. There is, however, a lack of research on the occurrence and nature of P species within such sediments and also little information on the associated ecological risk assessment at the regional scale.

To this end, different P compounds in the sediments were measured by ³¹P-nuclear magnetic resonance spectroscopy (³¹P-NMR), a powerful, non-destructive and non-invasive technique for identifying chemical forms of P. The technique enables multiple P compounds with distinct binding properties to be characterized simultaneously (Cade-Menun, 2005; Cade-Menun et al., 2006). Since the first application of ³¹P-NMR in soil analysis (Newman and Tate, 1980), many researches have been carried out for soil, manure and sediment (Cade-Menun and Liu, 2013; Toor et al., 2005; Ahlgren et al., 2006).

Several P compounds have been studied by ³¹P-NMR, including phosphonate, orthophosphate, orthophosphate monoesters, orthophosphate diesters (lipids-P and DNA-P), pyrophosphate and polyphosphate (Cade-Menun, 2005). ³¹P-NMR spectroscopy can provide detailed information pertaining to P compounds and concentrations, which can contribute to a better understanding of P transformation and recycling in the environment.

To date, many studies have focused only on P in rivers or lakes sediment; there is a lack of research at the regional scale including studies on wetlands, lakes, rivers and reservoirs. Thus, this study aims to provide a basis for understanding the characteristics and distribution of P compounds in surface sediments of Eastern China using ³¹P-NMR. Experiments have also been performed to evaluate the ecological risk of P in surface sediments of the different ecosystems.

2. Materials and methods

2.1. Site description

Twelve surface sediments were collected from rivers (Songhuajiang River-site 1, Haihe River-sites 5, 6 and Zhujiang River-site 12), lakes (Chaohu Lake-site 8 and Poyanghu Lake-site 9), reservoir (Miyun Reservoir-site 2), wetlands (Shijiuyang Wetlands-sites 10, 11 and Baiyangdian Wetland-site 7) and estuaries (Haihe estuary-sites 3 and 4) (Fig. 1). The trophic status of the water bodies ranged from mesotrophic to hypereutrophic. The concentrations of TP ranged from 0.04 to 6.80 mg L⁻¹ and water pH ranged from 6.8 to

Fig. 1. Location of the 12 sample sites in Eastern China. The sites were in Heilongjiang Province, Hebei Province, Beijing Municipality, Tianjin Municipality, Zhejiang Province, Anhui Province, Jiangxi Province, Guangdong Province. Sampling sites consisted of rivers, estuaries, reservoirs, wetlands and lakes.

8.5. The longitudes for the sampling area were from 113°15'31.08" to 126°30'52.43", and the latitudes ranged from 23°50'26.85" to 45°46'18.01. The sites represented typical water ecosystems of Eastern China.

2.2. Sediment sampling and analyses

Three surface sediments (about 5 cm) were collected by a Peterson grab sampler. Samples at the same site were pooled and homogenized to obtain representative samples. All the samples were frozen and stored at -20 °C immediately on return from the field. The sediment samples were freeze drying by freezer dryer. The samples were homogenized before removing impurities. Representative sample were obtained for grinding with quartering methods (Zhang et al., 2013).

Sample pH was determined in sediment suspension in deionized water with ratio of sediment to water being 1:2.5 (Bai et al., 2009). Organic matter (OM) was measured by combustion at 550 °C for 4 h (Heiri et al., 2001). Samples (0.1 g, dry weight basis) were digested with HNO₃-HCl-HF (MARSXpress, CEM, USA) and measured using ICP-OES/MS for total Fe, Al, Mg, Mn, Ca (Duzgoren-Aydin et al., 2011). Measurement of TP in sediment was based on treatment at 500 °C (2 h), followed by HCl (1 mol L⁻¹) extraction (16 h). For inorganic P (Pi), samples were extracted (16 h) with HCl (1 mol L⁻¹). Organic P (Po) concentrations in the sediments were calculated as the difference between TP and Pi (Aspila et al., 1976). The P in the respective extracts was measured by molybdate colorimetry (Murphy and Riley, 1962).

For solution ³¹P-NMR analysis, sediment sample (3.0 g) was extracted with 30 ml of 0.05 mol L⁻¹ EDTA + 0.25 mol L⁻¹ NaOH for 16 h at room temperature (Cade-Menun and Preston, 1996). An aliquot of the extracts was used to measure Pi (Pi in NaOH-EDTA) and TP (TP in NaOH-EDTA). Pi was determined in diluted extracts by molybdate colorimetry (Murphy and Riley, 1962). The Pi fraction is mainly ortho-P but can include acid-labile organic and condensed P compounds (Dick and Tabatabai, 1977). TP was measured by a similar procedure after acid-persulphate digestion of the samples (Rowland and Haygarth, 1997). Po was calculated as the difference between TP and Pi. Thus, the Po were overestimated,

because the poly-P and pyro-P were not react with color reagent (Cade-Menun and Liu, 2013; Shand et al., 2000). So the P in the sediment may be divided into molybdate-reactive P (MRP) and molybdate-unreactive P (MUP) (Cade-Menun and Liu, 2013; Haygarth and Sharpley, 2000). However, we use the terms Pi and Po for clarity as in Turner et al. (2003a). The remaining solutions were frozen and lyophilized for subsequent ^{31}P -NMR analysis. Freezing the extracts has been shown not to alter the P components composition (Hupfer et al., 1995, 2004; Shinohara et al., 2012).

The lyophilized NaOH–EDTA extracts (300 mg) were re-dissolved in 0.6 ml D_2O and 0.1 ml 10 mol L^{-1} NaOH, and ultrasonicated for 30 min and then equilibrated for 5 min. A 2% (v/v) solution of BD ($0.11\text{ M NaHCO}_3 + 0.11\text{ M Na}_2\text{S}_2\text{O}_4$) was added to the extracts for reducing paramagnetic ion (Fe^{3+} , Mn^{2+}) interference (Zhang et al., 2013). The supernatants were centrifuged for 15 min at 14,000 rpm and transferred to 5 mm NMR tubes. Solution ^{31}P -NMR spectra were obtained using a Bruker 400 MHz spectrometer (Bruker, Billerica, MA, USA) operating at 129.53 MHz at 25°C . Measurement parameters included a 90° observation pulse, a relaxation delay of 3.6 s and an acquisition time of 0.6 s. Spectra were acquired based on about 20,000 scans (Beijing NMR center). Chemical shifts were recorded relative to 85% H_3PO_4 standard ($\delta = 0\text{ ppm}$). Signals were assigned to P components based on the literatures (Cade-Menun, 2005b; Turner et al., 2003a,b). The peak area responses for samples were calculated based on visual inspection and an automated peak analysis routine. Based on the differing peak area responses for each P components, the contribution of each components (phosphonate: phon-P, orthophosphate: ortho-P, orthophosphate monoesters (inositol phosphates, sugar phosphates and phosphoproteins): mono-P, orthophosphate diesters (lipids-P and DNA-P): diester-P, pyrophosphate: pyro-P and polyphosphates: ploy-P) was calculated relative to the TP in the NaOH–EDTA extraction, as determined by the molybdenum blue method (Turner et al., 2005; Cade-Menun et al., 2005).

2.3. Laboratory Experiments

2.3.1. Phosphorus sorption capacity of sediment

Six subsamples of dry sediment (1.0 g) were well mixed with 40 ml of KH_2PO_4 solution containing 0, 5, 10, 20, 30, 50 mg P L^{-1} , respectively, by magnetic stirring for 24 h at 25°C (Liu et al., 2009). The slurry was filtered and the P in the supernatant was measured by molybdate colorimetry. The difference between P concentrations before and after the procedure was assumed to have been

sorbed. The sorption data were fitted to the Langmuir equation to calculate the X_m value. Sediment P saturation (SPS) was calculated as the $\text{TP}/(\text{X}_m + \text{TP})$ ratio (Kopáček et al., 2005; Liu et al., 2009), where

$$\text{SPS} = \text{TP}/(\text{X}_m + \text{TP}) \times 100\%$$

2.3.2. Eutrophication risk index (ERI)

The ERI was used to assess the risk of eutrophication. In this study, the ERI was calculated as the ratio of SPS to X_m , where

$$\text{ERI} = \text{SPS}/\text{X}_m \times 100\%$$

Huang et al. (2004) showed that the ERI can be classified into four grades: $\text{ERI} > 25$ (highest risk), $25 > \text{ERI} > 20$ (higher risk), $20 > \text{ERI} > 10$ (moderate risk), $\text{ERI} < 10$ (low risk).

2.4. Statistical analysis

The experimental data were analyzed using SPSS 19.0 for Windows. Spearman's correlation was used to assess the relationship between the phosphorus and sediment properties. The Biplot was analyzed by SAS for windows 9.2 (SAS Institute, Inc., Cary, NC, USA). The vector length in Biplot shows the measure ability of variable for distinguishing the environmental factors. The angle between two environment vectors indicated the relationship between two vectors. All analysis was performed using standard procedure in Microsoft Excel.

3. Results

3.1. Sediment properties

The pH, OM, and the concentrations of TP, Po, Al, Ca, Fe, Mg and Mn are shown in Table 1. The pH was higher in estuary samples than other samples, which were 8.10 and 8.35. The OM changed dramatically, which ranged from $3.0 \pm 0.0\%$ to $14.4 \pm 1.1\%$. The average concentration of TP was 1207.1 mg kg^{-1} . The high concentrations of TP were in river sediments, which were $3837.2 \pm 46.5\text{ mg kg}^{-1}$ and $5127.3 \pm 81.6\text{ mg kg}^{-1}$ in sites 5 and 12, respectively. The average concentration of Po was 182.7 mg kg^{-1} . The high concentrations of Po were in river sediments, which were $909.6 \pm 15.4\text{ mg kg}^{-1}$ in site 5.

The Po accounted for 3.0%–35.5% of TP for all the sediment samples. The concentrations of Ca, Mg Mn were much lower than Al and Fe, the concentrations of which were 7.4, 4.0, 0.8, 45.0 and 36.4 g kg^{-1} .

Table 1
Characteristics of the sediments used in this study.

Site	pH	OM %	TP ^a mg kg^{-1}	Po (%) ^b	Al g kg^{-1}	Ca	Fe	Mg	Mn	X_m mP kg^{-1}	SPS %
1	7.27	4.4 ± 0.2^c	567.6 ± 11.2	$46.4 \pm 1.2(8.2)$	60.0 ± 1.9	2.7 ± 0.1	31.1 ± 0.6	3.4 ± 0.3	0.73 ± 0.01	259.4	68.6
2	6.92	11.6 ± 1.1	630.7 ± 22.5	$224.0 \pm 10.7(35.5)$	4.3 ± 0.7	19.1 ± 1.2	40.2 ± 1.1	2.4 ± 0.3	1.89 ± 0.07	997.5	38.7
3	8.10	3.1 ± 0.1	554.6 ± 12.7	$50.7 \pm 2.1(9.2)$	27.6 ± 2.3	8.0 ± 1.8	29.2 ± 0.4	4.2 ± 1.0	0.59 ± 0.01	135.0	80.4
4	8.35	3.0 ± 0.0	515.0 ± 21.7	$56.3 \pm 4.8(9.9)$	19.1 ± 0.7	8.6 ± 1.1	30.7 ± 0.5	3.2 ± 0.2	0.58 ± 0.01	100.4	83.7
5	7.25	14.4 ± 1.1	3837.2 ± 46.5	$909.6 \pm 15.4(19.2)$	30.2 ± 0.5	5.1 ± 0.3	51.7 ± 1.2	3.7 ± 0.2	0.51 ± 0.01	1000.0	79.3
6	7.65	7.5 ± 1.1	938.2 ± 12.5	$225.9 \pm 21.1(19.4)$	2.2 ± 0.6	22.3 ± 1.6	21.9 ± 1.4	2.5 ± 0.3	0.34 ± 0.01	305.1	75.5
7	8.51	5.6 ± 0.3	463.6 ± 22.2	$133.0 \pm 1.1(22.3)$	31.2 ± 0.3	7.1 ± 0.4	29.3 ± 1.4	4.2 ± 0.1	0.42 ± 0.02	297.2	60.9
8	6.87	5.8 ± 0.1	311.4 ± 11.1	$130.6 \pm 6.5(29.5)$	69.4 ± 1.5	3.1 ± 0.0	36.5 ± 0.8	6.0 ± 0.1	1.34 ± 0.02	517.5	37.5
9	6.86	7.5 ± 1.0	240.9 ± 7.7	$70.5 \pm 3.9(22.7)$	102.2 ± 1.2	1.3 ± 0.2	44.2 ± 0.5	5.5 ± 0.5	0.80 ± 0.01	318.5	43.0
10	7.27	4.5 ± 0.8	903.0 ± 10.7	$27.8 \pm 2.2(3.0)$	57.1 ± 2.4	4.0 ± 0.1	39.5 ± 1.2	5.1 ± 0.2	0.73 ± 0.03	401.2	69.2
11	6.81	4.5 ± 0.3	395.6 ± 5.5	$107.7 \pm 6.1(21.4)$	56.8 ± 1.5	4.0 ± 0.1	44.9 ± 1.5	4.7 ± 0.1	1.16 ± 0.05	319.0	55.3
12	7.24	10.4 ± 0.6	5127.3 ± 81.6	$210.4 \pm 3.6(3.9)$	80.2 ± 2.6	3.5 ± 0.2	37.5 ± 1.1	3.2 ± 0.2	0.48 ± 0.03	934.6	84.6

^a The concentration is based on the dry weight.

^b The figures in brackets are the proportions of the Po to the TP concentrations in the sediments.

^c The values are the means and standard deviations for three replicate determinations.

Fig. 2. ^{31}P -NMR spectra for NaOH-EDTA extracts of the sediments in different ecosystems, Eastern China. (A: phon-P; B: ortho-P; C: mono-P; D: diesters-P; E: lipid-P; F: DNA-P; G: pyro-P; H: poly-P).

3.2. Phosphorus ^{31}P -NMR assignments

The NMR spectra for the sediments are shown in Fig. 2, where seven P compounds classes were detected in the NaOH-EDTA extracts. These include: phon-P (20 ppm), ortho-P (6–7 ppm), mono-P (4–6 ppm), lipids-P (1–3 ppm), DNA-P (0 ppm), pyro-P (–3.5 to –4.5 ppm) and poly-P (–17 to –19 ppm) (Cade-Menun, 2005; Cade-Menun et al., 2006,c; Turner et al., 2003b,c), respectively. Phon-P was only detected at sites 10 and 11. Poly-P was only found in site 11.

The concentrations and relative distributions of the various P compounds in the different sediments are presented in Table 2. Po in the NaOH-EDTA fraction ranged from 3.2 to 801.3 mg kg^{-1} , which accounted for 2.4%–20.9% of the TP concentration in NaOH-EDTA extracts. The ortho-P was the dominant form of P in the

NaOH-EDTA extracts of different sediments, and ranged from 119.6 to 4271.9 mg kg^{-1} , accounting for 81.3–97.6% of TP in NaOH-EDTA extracts. The concentration of pyro-P was much less than ortho-P, ranging from 0.3 to 130.0 mg kg^{-1} and accounting for 0.0–4.0% of TP in sediment extracts. Poly-P was only detected in site 11, the concentration of which was 0.3 mg kg^{-1} , and accounting for 0.2% of TP in sediment extracts. Mono-P was the dominant Po in the NaOH-EDTA fraction of sediments, and ranged from 2.0 to 690.0 mg kg^{-1} , accounting for 1.1–18.0% of TP in sediment extracts. DNA-P ranged from 0.6 to 74.0 mg kg^{-1} , with relative contributions of 0.2–4.1% of the extracted P in the different sediments. Lipid-P ranged from 0.5 to 22.0 mg kg^{-1} , with relative contributions being 0.3–0.8% of extracted P in the sediments. Phon-P was only detected at site 10, with concentrations of 2.4 mg kg^{-1} , accounting for 0.4 of TP in the sediments, respectively.

Table 2
Concentrations^a for P compounds in NaOH-EDTA extracts of the sediments by ^{31}P -NMR.

Site	TP	Po	Inorganic-P			Organic-P			
			Ortho-P	Pyro-P	Poly-P	Mono-P	Lipid-P	DNA-P	Phon-P
	mg kg^{-1}								
1	367.5	36.1(9.8) ^b	331.4(90.2) ^c	0.5(0.1)	n.d.	34.4(9.4)	n.d.	1.2(0.3)	n.d.
2	322.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3	126.6	7.0(5.5)	119.6(94.5)	0.7(0.6)	n.d.	6.3(4.9)	n.d.	0.0	n.d.
4	130.7	3.2(2.4)	127.5(97.6)	1.2(0.9)	n.d.	2.0(1.5)	n.d.	0.0	n.d.
5	3838.1	801.3(20.9)	3036.8(79.1)	25.9(0.7)	n.d.	690.0(18.0)	11.4(0.3)	74.0(1.9)	n.d.
6	490.0	82.4(16.8)	407.5(83.2)	5.5(1.1)	n.d.	60.5(12.4)	3.9(0.8)	12.4(2.5)	n.d.
7	200.1	18.0(9.0)	182.0(91.0)	8.0(4.0)	n.d.	2.3(1.1)	0.5(0.3)	7.3(3.6)	n.d.
8	253.2	47.2(18.7)	205.9(81.3)	1.0(0.4)	n.d.	35.0(13.8)	0.8(0.3)	10.4(4.1)	n.d.
9	175.6	15.9(9.1)	159.6(90.9)	n.d.	n.d.	14.3(8.1)	1.1(0.6)	0.6(0.3)	n.d.
10	653.3	34.6(5.3)	618.7(94.7)	n.d.	n.d.	28.0(4.3)	2.4(0.4)	1.5(0.2)	2.4(0.4)
11	285.8	22.8(8.0)	263.3(92.1)	1.1(0.4)	0.6(0.20)	18.3(6.4)	n.d.	2.6(0.9)	n.d.
12	4961.0	689.1(13.9)	4271.9(86.1)	130.0(2.6)	n.d.	495.9(10.0)	22.0(0.4)	41.3(0.8)	n.d.

DNA-P = deoxyribonucleic acids (orthophosphate diesters), lipid-P = phospholipid (orthophosphate diesters), mono-P = orthophosphate monoesters, ortho-P = orthophosphate, phon-P = phosphonate, poly-P = polyphosphate, pyro-P = pyrophosphate.

^a The value was calculated from the concentration in the NaOH-EDTA extract and the dry weight.

^b The figures in brackets are the Po to TP concentrations in the NaOH-EDTA extracts.

^c The proportion of individual P fraction to TP in sediment (%).

Fig. 3. Biplot of phosphorus, sediment properties, metal concentration in sediments and sample sites.

3.3. Eutrophication risk

In order to evaluate the eutrophication risk of the different sediments, the Xm, SPS and ERI were determined and the results are shown in Table 1 and Fig. 4. The sorption data fitted well to the Langmuir equation. The calculated Xm values ranged from 100.4 to 1000.0 mg P kg⁻¹. The high Xm values were for sites 5 and 12, which were 1000.0 and 934.6 mg P kg⁻¹ and values had a similar trend with values for sediment P. The SPS values varied considerably from 38.7 to 84.6, with an average SPS value of 65. The ERI values ranged from 3 to 83 and the average was 24. The values for samples at 5 sites exceeded 20 (sites 1, 3, 4, 6 and 7), which meant the sites were at a high risk of eutrophication.

4. Discussion

4.1. Phosphorus pollution in the sediments

Phosphorus concentrations in the various sediments were quite different. In general, the concentrations of TP were higher in river sediments than other sediments. The concentrations of TP were 3837.2 and 5127.3 mg kg⁻¹ in the Haihe and the Zhujiang, respectively. The the Haihe River Basin and the Zhujiang both have a large population and rapid economic growth rate and many

large cities are located there. Moreover, environmental legislation, investment and sewage treatment has not kept pace with economic growth and the population increase. Therefore, large amounts of untreated wastewater and rubbish have been directly discharged to the environment. Consequently a large loading of P will be carried into the rivers (Liu and Raven, 2010; Qu and Fan, 2010). The river sampling sites in this research were in the flood plain. It should be noted that dams and irrigation channels have been constructed along the river, which makes the main water body flow much more slowly than would otherwise be the case. In some rivers in the Haihe River Basin for instance, there are some 18 dams in the Beiyunhe River over a 100 kilometer stretch (Pernet-Coudrier et al., 2012; Li et al., 2012; Zhang et al., 2013). The P concentrations in the wetlands, lakes, reservoirs and estuaries were lower than that in the rivers. The average concentration of TP for the 8 sites was 500 mg kg⁻¹ (sites 1–6, 12, and 10). The Po contents in the lakes, wetlands and reservoirs were higher than that in the rivers and the estuaries, and these values for Po surpassed 22% of the TP values. The Po in the estuaries was less than 10% of the TP values. The estuary is the region where seawater and freshwater mix, and where the pH and redox chemistry become complex, hence there would be an acceleration in the speed of Po transformation (Suzumura and Kamatani, 1993; Monbet et al., 2009). Sites 10 and 11 represented the water inlet and water outlet in an artificial wetland, respectively. The TP concentration was high in the water inlet but low in the water outlet, being 902 and 395 mg kg⁻¹, respectively. On the contrary, the concentration of Po was low in the water inlet and high in the water outlet, being 27 and 107 mg kg⁻¹, respectively. This result indicated that the wetland can withhold large amounts of Pi, but the Po will increase after the wetland, because of plant and microorganism metabolic activity (Cheesman et al., 2010).

The Biplot of phosphorus, sediment properties, metal concentration in sediment and sample sites are shown in Fig. 3. The first principal component account for 35.47%, and second principal component account for 30.79%. Two principal components accounted for 66.26%, which belongs to batter fitting level (Wang et al., 2013a,b,b). The angles between environment variable show that TP and Po, OM and Xm have positive relationship. The results indicated the OM is vital factor for P distribution. The positive relationship are also found between SPS and Ca, indicating the SPS

Fig. 4. Phosphorus-induced up-water eutrophication risk index for surface sediment in various sites.

Table 3Pearson correlation coefficients for physicochemical characteristics, P and metal concentrations in the sediment ($n = 132$).

	pH	OM	TP	Po	Al	Ca	Fe	Mg	Mn	Xm	SPS
pH	1	-.394	-.112	-.140	-.499	.206	-.644*	-.289	-.606*	-.486	.569
OM		1	.669*	.815**	-.088	.213	.536	-.341	.145	.916**	-.067
TP			1	.616*	.138	-.145	.334	-.307	-.341	.698*	.521
Po				1	-.240	.084	.520	-.237	-.130	.669*	.208
Al					1	-.827**	.408	.684*	-.010	-.013	-.259
Ca						1	-.465	-.706*	.138	.107	.021
Fe							1	.344	.355	.573	-.289
Mg								1	.112	-.270	-.446
Mn									1	.342	-.788**
Xm										1	-.125
SPS											1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

may affected by the concentration of Ca in sediment. The sample sites divide into four groups. The first group is site 5, which is a high polluted sediment sample and have high P concentration. The second group including sites 2 and 12, the concentration of OM in these sites are higher than other sites. Sites 3, 4, 6 and 7 belong to third group, which have high and similar SPS. The last groups including sites 1, 8, 9, 10 and 11. The relationship between physicochemical characteristics, P and metal concentration was analyzed by Pearson's correlation (Table 3). The results also show that the Po and Xm were found to be significant positively correlated with OM ($p < 0.01$), which indicated the organic matter is vital element for the TP ($p < 0.01$) and Po ($p < 0.01$) distribution.

The P compounds showed diversity in the different sediments. The ortho-P was most prominent in the surface sediment. Pyro-P was detected in most sediment. Poly-P was only found in the water outlet of the artificial wetland. Some studies suggested that the pyro-P may originate from poly-P and esters, which can be hydrolyzed during alkaline extraction (Hupfer et al., 1995, 2004), so the poly-P may be hydrolyzed during NaOH-EDTA extraction and not detected by the ^{31}P -NMR in most of samples. The majority of Po originated from mono-P compounds, and this species was detected at all sites. Mono-P comprised 1.1%–18% of TP in NaOH-EDTA extract. Mono-P represents an important Po compounds in the sediment, which includes inositol P, sugar phosphates and mononucleotides. Inositol phosphates were considered to be the most abundant Po in aquatic sediment, and these compounds can be mineralized under anaerobic or aerobic conditions (Turner et al., 2002). Diester-P is a mixture of numerous compounds with varying liability, including DNA-P and lipid-P, and these components were detected in rivers, lakes and wetlands but not in the estuaries. DNA-P and lipid-P were considered to have originated from an organism's basic metabolism (Shinohara et al., 2012). Rivers, lakes and wetlands have large algae and hydrophytes, which may have been the main sources of the DNA-P and lipid-P. DNA-P and lipid-P were not detected in the estuaries. The reason for this may be that the complex physical and chemical conditions existing in the estuary would induce the hydrolysis of the DNA-P and lipid-P (Monbet et al., 2009). The phon-P, which is a chemically stable compound because of the direct C–P bond, was only found in the artificial wetland (Turner et al., 2005). Wetzel (2001) suggested that the pH may be important for the existence of phon-P, because the bacteria which produce the phosphonate enzyme would be controlled by the high pH conditions. In this study, however, the pH varied greatly.

4.2. Eutrophication risk of the different sediments

The eutrophication risk is different for the river, wetland, lake, estuary and reservoir. The release of P in the surface sediment is governed by the sorption and desorption of P (Ramm and Scheps,

1997). According to the Chinese environmental dredging common standard, the sediments should be dredged and consequently have a high risk of P release (Liu et al., 1999). In this research, Xm, SPS and ERI were used to assess the P release risk in the different sediments. Generally, a high ERI means a high risk of P release, consequently there is a high eutrophication risk when the ERI surpass 25% (Huang et al., 2004; Jin et al., 2006). The TP concentrations in samples from two-thirds of all sites exceeded 500 mg kg^{-1} , including river water (sites 1, 5, 6, 12), estuary water (sites 3 and 4) and a reservoir water (site 2). The ERI values were greater than 25% for sites 1, 3 and 4, being 26, 59 and 83%, respectively. Sites 3 and 4 were on the Bohai estuary and are from a region where freshwater and sea-water mix, thus facilitating the release of P. So, the ERI in the estuary was higher than other regions. Although the concentrations of TP in site 3 (Miyun reservoir), which is a source of drinking water for Beijing, exceeded 500 mg kg^{-1} , the ERI value represented a low risk condition. The main reason was that the depth of the Miyun reservoir was over 40 m and the hypolimnetic anoxia molar Al:Fe ratio was < 3 (the value is 0.22), so the P was stable and not readily released from the sediment (Kopáček et al., 2005). The ERI values at sites 5 and 12, which exhibited high TP concentrations, were lower than 10% indicating that they have a low eutrophication risk. Kopáček et al., found that the P would be released from lake sediment during hypolimnetic anoxia, if the molar $\text{Al}_{\text{NaOH-25}}:\text{Fe}_{\text{BD}}$ ratio was > 3 , or the molar $\text{Al}_{\text{NaOH-25}}:\text{P}_{(\text{H}_2\text{O} + \text{BD})}$ ratio was > 25 . But oxidation–reduction processes are different in lakes, rivers, estuaries and reservoirs. The Xm and the ERI gave a good fit for the power function ($R_{\text{Xm-ERI}} = 0.89$, $p < 0.01$) for all 12 sites (Fig. 5). A positive relationship between Xm and OM in the sediment ($R_{\text{Xm-OM}} = 0.84$, $p < 0.01$) indicated that the chemical–physical conditions, such as concentrations of organic matter (humic acid, fulvic acid and humin), play a vital role on P sorption and desorption.

Fig. 5. Correlation between Xm and ERI for the sediment samples.

5. Conclusions

This research used ^{31}P -NMR and sorption experiments to provide an insight into the occurrence of P components, their distribution and the risk of eutrophication in different water ecosystems, such as wetlands, lakes, reservoirs, rivers and estuaries in Eastern China. Results showed that the river sediments had accumulated significant amounts of TP and Po. Seven P compounds were detected in NaOH-EDTA extracts from the ^{31}P -NMR analysis. Ortho-P (83.3–97.6%) and mono-P (1.1–18.0%) were the dominant P compounds, while smaller amounts of DNA-P (0–4.1%), pyro-P (0–4.0%), lipid-P (0–0.8%) were found in the surface sediment. Poly-P and phon-P were only detected at 3 sites (site 11 and site 10, respectively). The TP concentration in two-thirds of all sites exceeded 500 mg kg^{-1} , which included river samples (sites 1, 5, 6, 12), estuarine samples (sites 3 and 4) and reservoir water (site 2). The ERI values were greater than 25% at sites 1, 3 and 4, the values being 26, 59 and 83%, respectively, hence these sites (sediments) have a high eutrophication risk. The Xm and ERI values were fitted to a power function ($R_{\text{Xm-ERI}} = 0.89$, $p < 0.01$) for all 12 sites and a positive correlation between Xm and OM in the sediment ($R_{\text{Xm-OM}} = 0.84$, $p < 0.01$).

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