Phosphorus characteristics, distribution, and relationship with environmental factors in surface sediments of river systems in Eastern China

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Abstract Phosphorus (P) is an essential nutrient for aquatic organisms. However, too much P discharged into limnetic ecosystems can induce eutrophication. The concentration of P in freshwater ecosystems has escalated in Eastern China due to overuse of fertilizer and excess emission of sewage, which is the result of the development of industry and agriculture in this area. However, little is known about the P characteristics and its environmental factors in river systems. Here, we present the results of P characterization and its relationships with environmental factors in Eastern China by applying SMT and ³¹P-NMR methods. The results showed that the concentrations of P in surface sediments varied with the river system, and more than 50 % of the samples had P concentrations exceeding 500 mg kg⁻¹. HCl-Pi was the dominant Pi in surface sediments, with the highest percentage (96.5 %) in the Yellow River System. Mono-P was the dominant Po in river sediments, followed by DNA-P. The PCA approach indicated that NaOH-Pi and ortho-P clustered in one group, with a second group including mono-P, diesters-P, and HCl-Pi. Phon-P and pyro-P belonged to different groups. On a regional scale, NaOH-Pi and Po showed a negative relationship with pH in sediments. Continuous eutrophication was induced by the presence of dams, and oxygen-consuming pollutants, such

as NH₃-N and COD_{Cr}, even when external P input was cut in heavily polluted rivers. The research revealed the characteristics of P in different river systems and proposed a conceptual model of P biogeochemical cycles in heavily polluted rivers. Results from this study may provide insight into P characteristics in Eastern China and would set a scientific basis for effective P management in developing countries.

Keywords Phosphorus · Sediment · SMT · ³¹P-NMR · River · Eastern China

Introduction

Phosphorus (P) is an essential element to all life, and thus its availability can impact primary production rates in aquatic ecosystems (Adina and Karen 2007; Carpenter 2008). Excessive P in aquatic environments can cause eutrophication (Schindler et al. 2008). Since the middle twentieth century, urbanization and agriculture intensification have led to eutrophication in aquatic environments, which induces environmental, ecological, social, and economic problems, including algal blooms, oxygen depletion, infectious disease, aquatic ecosystem deterioration, and freshwater becoming unsuitable for human use (Smith and Schindler 2008; Vörösmarty et al. 2010).

There are many rivers in Eastern China, total length of which is 42×10^4 km. Because of the effect of topography, the flow direction of rivers in Eastern China is from west to east. Cities and towns in the region are connected by large and small rivers. Within the last two decades, China has become the fastest-growing country in terms of economy, with a GDP growth rate of nearly 10 % (Liu and Raven 2010). Human activities in agriculture and industry greatly accelerate the rate of P bioactivity (Qu and Kroeze 2010). Rapid population

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growth, industrial development, and increased agricultural production have led to a greater inflow of untreated sewage and waste into the environment. As a result, anthropogenically mobilized P in watersheds flows into the rivers, lakes and marine systems, which increase the risk of surface water eutrophication (Pernet-Coudrier et al. 2012). For more than 30 years, nutrient management has been taken to improve water quality in China. The Chinese government pays close attention to controlling pollution inputs, and has set up rules and projects such as the National Water Pollution Control and Management Technology Major Projects of China. Despite sustained efforts, eutrophication still occurs in freshwater ecosystems, and water quality has deteriorated to the extent that it is unsuitable for many uses (Zhang et al. 2009). Although the external input of P is decreasing, the release of internal P from sediments continues, providing reactive P for harmful algal blooms (Read et al. 2014). Therefore, a systematic study of P in the sediment of different river systems is important to formulate a scientifically driven and effective policy for eutrophication management.

Phosphorus in sediments can be divided into inorganic P (Pi) and organic P (Po), which both contain many P speciations. However, not all forms of P in sediments will be released, and will support algae growth (Carpenter 2008). According to the combination of P, it can be divided into exchangeable P, the fraction of which associated with Al, Fe, and Mn oxides and hydroxides, and apatite-P, the fraction of which in Ca-bound compounds. According to its bond characteristics, P can be further divided into orthophosphate, phosphonates, pyrophosphate, orthophosphate monoesters, DNA-P, and phospholipids (Ruban et al. 2001a; Turner et al. 2005). Although several analytical methods have been developed to elucidate information on P, lack of uniformity in analytical procedures means that results from different studies cannot be compared. The most commonly used procedure is the Standards, Measurements and Testing (SMT) procedure, launched by the European Commission through the Standards, Measurements, and Testing Program (Ruban et al. 2001b). This method has the advantage of a simple operation, easily accessible reagents, and less interference between various forms. However, the SMT method can only measure total Po, and it is unable to thoroughly understand Po. Alternatively, ^{31}P -NMR is a non-destructive, non-invasive technique for identifying chemical forms and can completely analyze Po components. Therefore, it is an ideal technique for analyzing Po species in marine or freshwater sediments (Cade-Menun 2005; Turner et al. 2005; Cade-Menun and Liu 2013). Several Po compounds, including phosphonates, orthophosphate monoesters and orthophosphate diesters, have been detected by ^{31}P -NMR (Turner et al. 2005). From the above analysis, a combination of SMT and solution ^{31}P -NMR will offer a deep and comprehensive understanding of P in sediments.

A knowledge of P distribution and characteristics will contribute to nutrient management and improve water quality, as well as enhancing the knowledge of P biogeochemistry. Thus, the goal of this study was to investigate P characteristics in surface sediment in different river systems by SMT fractionations and solution ^{31}P -NMR. We also studied the relationships between P speciation and environmental factors, with the aim of providing a basis for appropriate mitigation strategies in the environment and P management policies in developing countries.

Materials and methods

Study areas and sediment sampling

To obtain representative sediment samples, 50 samples were collected from Eastern China in September 2013, according to the pollution level and watershed area (Fig. 1). The watershed includes the Songhua River, Liao River, Hai River, Yellow River, Huai River, Yangtze River, Mindongnan River, and Pearl River. According to the river system size, three to twelve samples were collected in each area. Three surface sediments (about 5 cm) were collected by a Peterson grab sampler. Each sub-sampling site was within a 500-m radius. Samples from the same site were pooled and homogenized to obtain a representative sample. Sediments samples were kept in a sealed plastic bag under 0 °C in a vehicular refrigerator. Samples were freeze-dried at −50 °C by FD-1 freeze-dryers upon their arrival in the laboratory. Freeze-dried sediment samples were ground and passed through a 100- μm mesh sieve. Samples were quartered, and representative samples were stored in sealed plastic bags at room temperature until analysis.

Sediment sample analysis

P speciations were determined according to the SMT protocol (Ruban et al. 2001a, b). P in the sediment was classified into TP, Pi, Po, HCl-Pi, and NaOH-Pi. (1) TP: 0.2-g samples were placed in crucibles at 450 °C in a muffle furnace for 3 h. The cool ash was transferred into a centrifugal tube with 20 mL 3.5 mol L^{−1} HCl. HCl can be added directly to the crucible to ease the transfer of the ash. The tube was covered and stirred for 16 h, and then centrifuged at 2000 g for 15 min. After centrifugation, the extract was collected in a test-tube for determination of the concentrated TP in sediments. (2) Pi and Po: 0.2-g samples were weighed and placed into a centrifugal tube and 20 mL 1 mol L^{−1} HCl was added with a pipette. Tubes were covered and stirred for 16 h, and then centrifuged at 2000 g for 15 min. After centrifugation, the extract was collected in a test-tube for the determination of Pi. The Po content was calculated as the difference between TP and Pi. (3) HCl-Pi and NaOH-Pi: 0.2-g samples were accurately

Fig. 1 Location of the 50 sample sites in Eastern China. These sites are distributed in Heilongjiang Province, Liaoning Province, Hebei Province, Beijing Municipality, Tianjin Municipality, Shandong Province, Jiangsu Province, Shanghai Municipality, Anhui Province, Hubei Province, and Guangdong Province. These sites represent eight watersheds, which are the most affected ecology systems in Eastern China. These regions also have the largest population density and fastest economic development, which include the Bohai Sea Economic Rim, Pearl River Delta Economic Rim, and Yangtze River Delta Economic Rim

weighed in the centrifuge tubes with 20 mL 1 mol L⁻¹ NaOH. Tubes were stirred (16 h) and then centrifuged (2000 g, 15 min). Thorough mixing was necessary to keep the sediment in suspension. After centrifugation, the supernatant was used to continue extract NaOH-Pi, and the residue was used to extract HCl-Pi. The extract was collected, with 10 mL of extract removed with a pipette. In order to achieve 10 mL, 4 mL 3.5 mol L⁻¹ HCl was added and the tube was covered. The sample was then stirred energetically for 20 s and left to stand for 16 h. A brown precipitate appeared and settled, and the sample was then centrifuged at 200 g for 15 min. NaOH-Pi was then determined in the supernatant. The residue of the previous centrifugation was washed with 12 mL 1 mol L⁻¹ NaCl, and stirred for 5 min. The sample was then centrifuged at 2000 g for 15 min, and the supernatant discarded. The washing step was repeated once, and then 20 mL 1 mol L⁻¹ HCl was added to the tube and stirred for 16 h. After centrifugation at 2000 g for 15 min, HCl-Pi was determined in the extract. All P in the extract was measured by molybdate colorimetry method (Aspila et al. 1976).

The pH was determined by pH electrode, with a sediment-to-water ratio of 1:2.5 (McDowell et al. 2006). Loss-on-ignition (LOI) refers to the standard methodology (Heiri et al. 2001).

NaOH-EDTA extraction and solution ³¹P-NMR

Po analysis consisted of two parts: NaOH-EDTA extraction and ³¹P-NMR analysis. After being ground into powder and sieved through a 100 mesh, sediment samples were pre-

extracted with a solution composed of 0.05 mol L⁻¹ EDTA and 0.25 mol L⁻¹ NaOH for 16 h at room temperature, with a ratio of sediment sample to extract of 1:10 (Turner et al. 2003a). An aliquot of extracts was used to analyze Pi (Pi in NaOH-EDTA) and TP (TP in NaOH-EDTA) using the molybdate colorimetry method before and after digestion by K₂S₂O₈. Differences between TP and Pi were Po in NaOH-EDTA. The remaining solution was frozen and lyophilized for ³¹P-NMR analysis.

Although freeze-drying and re-dissolving has the risk of losing Po, lyophilized samples in this research were completely re-dissolved due to the incomplete dissolution. Lyophilized NaOH-EDTA extracts (300 mg) were re-dissolved in 0.6 mL D₂O and 0.1 mL 10 mol L⁻¹ NaOH, ultrasonicated for 30 min, and then equilibrated for 5 min. 2 % (v/v) of BD (0.11 M NaHCO₃ + 0.11 M Na₂S₂O₄) was added to the extracts for reducing paramagnetic ion (Fe³⁺, Mn²⁺) interference. Supernatants were centrifuged for 15 min at 14,000 rpm and transferred into 5-mm NMR tubes. All of the preparation procedures were completed within 1 h to reduce Po loss. The ³¹P-NMR solution spectra were obtained using a Bruker 400 MHz spectrometer (Bruker, Billerica, MA, USA) operating at 129.53 MHz at 25 °C. We used a 90 °C observation pulse, a relaxation delay of 3 s and an acquisition time of 0.6 s. Spectra were collected with around 3000 to 20,000 scans, according to the concentration of Po. Although T₁ relaxation times were not analyzed explicitly in this study, for most samples (70 %) analyzed for Mn and Fe, a T₁ relaxation time of 3 s should be adequate for quantitative spectra for a variety of P forms (McDowell et al. 2006). Chemical shifts were recorded

relative to an 85 % H_3PO_4 standard ($\delta=0$ ppm). Signals were assigned to P compounds based on data in the literature (Turner et al. 2003b; Cade-Menun 2005). Peak assignments were made using ^{31}P -NMR chemical shifts of phosphonate (phon-P: 12 to 23 ppm), orthophosphate (ortho-P: 6 to 7 ppm), orthophosphate monoesters (mono-P: 4 to 6 ppm), phospholipids (lipids-P: 1 to 3 ppm), deoxyribonucleic acid phosphorus (DNA-P: 0 ppm), and pyrophosphate (pyro-P: -3.5 to -4.5 ppm). Visual inspection and an automated peak analysis tool calculated the peak area. From different P species areas, the contribution of each P compound group was calculated relative to TP in the NaOH-EDTA extraction, determined by the molybdate colorimetry method (Turner et al. 2003b; Shinohara et al. 2012).

Additional data

To obtain a clear understanding of environmental factors and P in surface sediments of different river systems, the concentrations and distribution of $\text{NH}_3\text{-N}$ and COD_{Cr} were also collected by consult data. The oxygen deficit values were calculated by oxygen consumption of COD_{Cr} and transformation of $\text{NH}_3\text{-N}$ to $\text{NO}_3\text{-N}$.

The river morphology is a vital factor affecting biogeochemical cycles of P in river systems. Rivers can generally be divided into faster-flowing rivers, slower-moving rivers, and standing waters. Dams are the main factor affecting river flow regimes. We thus obtained the distribution and numbers of dams by consult datum. We thus conducted a preliminary analysis of the combined impact of $\text{NH}_3\text{-N}$, COD_{Cr} and dams on P speciations and distribution in different river systems in Eastern China.

Results and discussion

Phosphorus in the river sediment

Characteristics of P distribution and concentration are shown in Table 1 and Fig. 2. P concentration exceeded 500 mg kg^{-1} in more than 50 % of the sampling sites in river systems in Eastern China, which indicated the surface sediment was “polluted” by P (Jin et al. 2004). Sediment became the “source” of P in freshwater ecosystems, when the external inflow of P decreased.

The concentration of P in surface sediments varied with the river system. The highest average concentration of TP was in the Hai River System, which was 1922.0 mg kg^{-1} . The TP concentration in the Hai River System was higher than any other river systems, including the Songhua River System, the Yellow River System and the Yangtze River System, which were 567.4 , 552.4 and 736.8 mg kg^{-1} , respectively. The main

reason for the high P concentration in the Hai River System was that sewage was the predominant P source in this watershed. With the development of population and economy, there is an increasing tendency of sewage production and water scarcity which threatens the health of the Hai River System (Pernet-Coudrier et al. 2012). Meanwhile, plenty of dams built in the river basin aggravated the P accumulation in the sediment. The Beiyun River is an important river in the Hai River System, which has a dozen of dams within 100 km of the rivers. Large numbers of dams in the Hai River System can slow down the river flow and inflow into many reservoirs (Zhang et al. 2014). We also collected historical data to analysis the trend of TP variation regulation in different river systems. The TP concentration in the surface sediment were 1713, 1760 and 1922 mg kg^{-1} in the Hai River System, which indicated the TP was increased as the large of pollutant input (An 2007; Sun and Huang 2008). For the Yangtze River System and the Mindongnan River System, TP presented a downward tendency, the concentration of which were 1466, 1058, 736 mg kg^{-1} and 1010, 723, 433 mg kg^{-1} (Hou et al. 2001; Liu et al. 2001; Jia 2009; Hu et al. 2009). The TP in the surface sediment in other river systems showed un conspicuous variation regulation.

Pi was the main component identified, which led to variations in TP concentrations in different river systems. The concentration of Pi accounted for 71.5 to 96.5 % of TP. The highest percentage, 96.5 %, appeared in the Yellow River System. Po was an important compound and accounted for 3.5 to 28.5 % of TP in the surface sediment in Eastern China. The LOI showed the same variation regulation with Po in Eastern China. The pH ranged from 4.6 to 8.9, and the sediment showed neutral properties on a regional scale.

P recovery by NaOH-EDTA extract

TP in NaOH-EDTA extract and TP in river sediments showed positive relationships, the same as Po in NaOH-EDTA extract and river sediments (Fig. 3a). Although the average recovery rate of NaOH-EDTA was not high (21–66 %), the extraction rate of TP in NaOH-EDTA ranged from 15.5 to 87.6 %, with an average rate of 49.5 %. The extraction rate of Po in NaOH-EDTA ranged from 9.6 to 100.3 %, with an average rate of 39.5 %. The high range may be due to the extraction and analysis methods not being suitable and effective for different sediment analysis on such large scale. However, better relationships ($R^2_{\text{TP-sediment and TP-NaOH-EDTA}}=0.80, p<0.0001$; $R^2_{\text{Po-sediment and Po-NaOH-EDTA}}=0.95, p<0.0001$) demonstrated that two methods can determine the speciations and distribution characteristics. Systematic procedures for the analysis of different sediments are needed in the future.

Table 1 Characteristics of the sediments used in this study

River	Value	pH	LOI %	TP ^a mg kg ⁻¹	Po (%) ^b	NaOH-Pi	HCl-Pi
Songhua River	Range	4.6–7.7	1.2–4.9	465.0–726.3	58.2–150.5	86.2–313.3	204.7–400.9
	Mean	6.8	3.3	567.4	104.1(18.3)	177.6	285.8
Liao River	Range	8.2–8.9	0.5–2.1	126.1–356.3	6.1–100.5	36.5–63.7	83.5–192.1
	Mean	8.6	1.5	252.4	51.3(20.3)	50.3	150.7
Hai River	Range	7.2–8.3	1.3–13.7	221.8–7125.6	23.0–1350.9	66.1–1430.3	87.2–4344.4
	Mean	7.9	5.0	1922.0	340.2(17.7)	491.4	1090.5
Yellow River	Range	8.8–8.9	0.7–2.5	497.4–641.4	15.9–4.4	16.8–24.5	454.3–595.2
	Mean	8.8	1.7	552.4	19.7(3.5)	21.0	511.7
Huai River	Range	7.6–7.9	1.3–6.3	319.9–470.3	27.9–80.7	51.0–96.6	195.4–328.8
	Mean	7.9	3.6	411.8	57.5(14.0)	75.1	279.2
Yangtze River	Range	7.8–8.7	1.7–6.1	568.7–1123.2	23.8–135.5	67.9–139.2	443.4–848.5
	Mean	8.3	4.0	736.8	75.5(10.2)	105.4	555.8
Mindongnan River	Range	5.2–7.2	5.4–9.6	311.4–624.8	82.2–170.7	117.3–309.5	91.7–159.6
	Mean	6.4	7.5	433.4	123.4(28.5)	187.0	123.0
Pearl River	Range	6.8–7.6	3.6–9.7	202.2–1234.3	32.4–237.1	89.2–713.3	76.1–237.0
	Mean	7.2	6.6	488.2	136.8(28.0)	238.4	141.5

^a The concentrations are based on the dry weight

^b The figures in round brackets are the proportions of the Po to the TP concentrations in the sediment

P speciations by SMT and ³¹P-NMR analysis

The SMT fraction results are shown in Table 1. In general, NaOH-Pi was considered as P bound to Al, Fe, and Mn oxides or hydroxides, and Fe-P was the main P component in the sediment (Ruban et al. 2001a). Fe-P and Al-P were also easily affected by pH and the oxidation reduction potential (Ruban et al. 1999), and released into pore water and surface water

under reductive conditions. The average concentration of NaOH-Pi ranged from 21.0 to 491.4 mg kg⁻¹. For most river systems, NaOH-Pi was not the primary component, and only accounted for 7 to 50 % of TP in the sediment. However, the concentration of NaOH-Pi was high in the Mindongnan River and the Pearl River: 187.0 mg kg⁻¹ (72 % of TP) and 238.4 mg kg⁻¹ (71 % of TP), respectively. The HCl-Pi showed positive relationships with TP in the sediment ($R^2_{\text{HCl-Po}}$ and

Fig. 2 The distribution of P in surface sediments from river systems in Eastern China (ArcGIS 10.0). *TP* total phosphorus, *Pi* inorganic phosphorus, *Po* organic phosphorus

Fig. 3 **a** Relationships between TP, Po in NaOH-EDTA extract and TP, and Po in river sediments. **b** Relationship between Po, NaOH-Pi, LOI, and pH in surface river sediments

$T_P = 0.87$, $p < 0.0001$), which indicated that HCl-Pi was the main component of TP in sediments. The HCl-Pi was Ca-bound P in sediment, and Ca-bound P is often referred to as apatite-P (Ruban et al. 2001a, b). This result showed that most of the Pi in the river sediment was stable P.

The NMR spectra for river sediments are shown in Fig. 4. Six ³¹P-NMR peaks were detected in the NaOH-EDTA extracts of river sediments. All NMR spectra showed peaks in areas of phon-P, ortho-P, mono-P, lipids-P, DNA-P, and pyro-P. Concentrations and relative distributions of various P compound groups in different river sediments are presented in Table 2. Po in the NaOH-EDTA fraction ranged from 18.5 to 219.2 mg kg⁻¹ (average value, similarly hereafter). Ortho-P was the dominant form of P in NaOH-EDTA extracts of river sediment, and ranged from 52.8 to 804.3 mg kg⁻¹,

accounting for 62.7 to 88.4 % of TP in NaOH-EDTA extracts. Biogenic-P compounds are analyzed as the molybdenum-non-reactive P in sediment (Rydin 2000; Shinohara et al. 2012). For different river sediments, concentration biogenic-P ranged from 21.8 to 228.2 mg kg⁻¹, which included pyro-P, mono-P, DNA-P, lipids-P and phon-P. Concentrations of mono-P ranged from 14.8 to 182.6 mg kg⁻¹, accounting for 8.0 to 22.0 % of TP in NaOH-EDTA extracts. As the main composition of diesters-P, DNA-P accounted for 0.1 to 2.2 % of TP in NaOH-EDTA extracts, with the concentration ranging from 0.1 to 22.7 mg kg⁻¹. Pyro-P and phon-P were not detected in the Liao River and the Huai River sediments, respectively. Lipid-P was detected only in the Songhua River, the Hai River, the Yangtze River and the Pearl River.

Combination analysis of SMT and ³¹P-NMR

The PCA approach was applied to analyze relationships among different P forms in SMT fraction and ³¹P-NMR, and a $\lambda > 0.5$ of KMO (0.807) and significant Bartlett's test (< 0.0001) demonstrated its validity (Fig. 5). Three eigenvalues were significantly higher than one and three components explained 97.0 % of the total variance. P speciations assembled into four groups; NaOH-Pi and ortho-P were clustered in one group, which indicated that NaOH-Pi was mostly composed of ortho-P, and NaOH-Pi and ortho-P had the same combination phase. The second group included mono-P, diesters-P (DNA-P and lipids-P) and HCl-Pi. The stability of mono-P and diesters-P was higher than ortho-P in the ³¹P-NMR analysis, and HCl-Pi was mostly composed of Ca-bound P and apatite-P. Thus, this result indicated that HCl-Pi and Po in sediments had the same activity. Phon-P and pyro-P belonged to different groups. Phon-P is thought to be produced by cyanobacteria, and is much more stable in the environment (Read et al. 2014). Pyro-P has strong bioactivity in the environment, and can be accumulated in the organism cell as energy or nutrient storage molecules (Brown and Kornberg 2008).

Fig. 4 Parts of ³¹P-NMR spectra of NaOH-EDTA extracts of surface sediments in river systems. *Phon-P* phosphonate, *Ortho-P* orthophosphate, *Mono-P* orthophosphate monoesters, *Lipid-P* phospholipid, *DNA-P* deoxyribonucleic acid phosphorus, *Pyro-P* pyrophosphates

Table 2 Concentrations for P compounds in NaOH-EDTA extracts of the sediments by ^{31}P -NMR (mg kg^{-1})

River	Value	TP	Po	Inorganic P		Organic P			
				Ortho-P	Pyro-P	Mono-P	Lipid-P	DNA-P	Phon-P
Songhua River	Range	145.7–450.9	15.5–70.6	130.0–411.4	0.2–4.5	14.8–77.2	0.1–0.2	0.3–4.9	0.2–0.3
	Mean	301.5	48.2 (16.0) ^a	251.8 (83.5) ^b	1.5 (0.5)	46.0 (15.3)	0.1 (0.03)	2.0 (0.7)	0.2 (0.1)
Liao River	Range	19.6–126.6	6.1–81.6	13.4–92.5	nd	6.1–33.2	nd	0.1	0.9–81.6
	Mean	84.2	31.3 (37.2)	52.8 (62.7)	nd	18.5 (22.0)	nd	0.1 (0.1)	41.3 (49.0)
Hai River	Range	148.7–3069.7	5.2–1033.4	100.4–1991.9	0.6–44.4	5.0–871.4	1.0–61.2	0.3–94.4	0.5–26.4
	Mean	1032.5	219.2 (21.2)	804.3 (77.9)	10.1 (1.0)	182.6 (17.7)	21.8 (2.1)	22.7 (2.2)	10.5 (1.0)
Yellow River	Range	nd	nd	nd	nd	nd	nd	nd	nd
	Mean	nd	nd	nd	nd	nd	nd	nd	nd
Huai River	Range	136.1–172.3	10.3–24.2	111.9–150.4	0.8–1.8	10.3–22.4	nd	1.8–3.1	nd
	Mean	148.6	18.5 (12.5)	129.2 (86.9)	1.3 (0.9)	16.9 (11.4)	nd	2.4 (1.6)	nd
Yangtze River	Range	101.7–317.2	3.1–45.9	84.4–267.8	0.5–3.5	1.4–31.4	0.2	0.4–8.3	1.2–6.1
	Mean	185.5	20.2 (10.9)	163.9 (88.4)	1.7 (0.9)	14.8 (8.0)	0.2 (0.1)	4.1 (2.2)	3.5 (1.9)
Mindongnan River	Range	166.5–280.7	12.0–52.7	148.3–405.1	0.4–2.7	11.0–38.8	nd	1.0–10.7	3.2
	Mean	266.0	26.8 (10.1)	238.2 (89.5)	1.0 (0.4)	21.6 (8.1)	nd	4.4 (1.7)	3.2 (1.2)
Pearl River	Range	99.8–987.0	9.3–116.7	90.4–867.0	0.1–5.0	9.0–101.8	0.2–2.4	0.4–15.0	0.1–1.0
	Mean	338.3	39.0 (11.5)	298.1 (88.1)	1.6 (0.5)	34.3 (10.1)	1.2 (0.4)	4.2 (1.2)	0.4 (0.1)

The values were calculated from the concentration in the NaOH-EDTA extract and the dry weight

Ortho-P orthophosphate, *Mono-P* orthophosphate monoesters, *DNA-P* deoxyribonucleic acids, *Lipid-P* phospholipid, *Phon-P* phosphonate, *Pyro-P* pyrophosphate, *nd* not detected

^a The figures in round brackets are the Po to TP concentrations in the NaOH-EDTA extracts

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

P species and environmental factors

The characteristics of P in sediments are affected by environmental factors. On a regional scale, NaOH-Pi and Po showed negative relationships with sediment pH ($p < 0.01$, $n = 50$) (Fig. 3b). The relationship indicated sediment pH can affect

Fig. 5 Plot of loading of three principal components in PCA results

the form in which P exists. This study also found that LOI showed negative relationships with sediment pH ($p < 0.001$, $n = 50$). NaOH-Pi and Po were considered more labile than HCl-Pi in sediments (Zhang et al. 2012; Zhu et al. 2013). As pH decreased, the concentration of NaOH-Pi and Po increased. The result indicated the bioavailability of P increased as pH decreased in the sediment, which induced continuous eutrophication in the water. The pH increase has many potential causes, such as sewage discharge and global warming (McCulloch et al. 2012). We deduce that eutrophication will continue under the condition of pH decrease in the Eastern China freshwater system, even if external P sources are reduced.

Conceptual model of P biogeochemical cycle

Many studies have indicated that oxygen is the vital factor controlling P release in the sediment, which means the P generally has a higher release rate under anoxic conditions, via its effect on Fe (III) and Mn (IV) (Ahlgren et al. 2011; Kraal et al. 2013). There are also many researches indicated the dissolved oxygen (DO) is the vital environment factor for P release and burial (Ingall et al. 1993; Sulu-Gambari et al. 2015). Excessive nutrient inputs will consume oxygen and induce hypoxia in

Fig. 6 Conceptual model of P biogeochemical cycle and environmental factors in a seriously polluted river system

the bottom waters, with the result that P is readily remobilized from sediments (Wang et al. 2016). This internal source of P will fuel high primary productivity and oxygen consumption; this is particularly relevant for the slow flowing rivers with numerous dams that are common in semi-arid regions of northern China (Gustafsson et al. 2012). Iron (Fe) and sulfur (S) may influence P adsorption and desorption. The reductive dissolution of Fe-oxides induces P release under seasonal hypoxia (Cowan et al. 1996; McManus et al. 1997). In addition, sulfur-oxidizing bacteria can accumulate P, which will be released from seasonally hypoxic sediment during summer (Schulz and Schulz 2005). Recently, it was discovered that a filamentous bacterium from the *Desulfobulbaceae* family (cable bacteria) could control iron–P dynamics in sediments in a coastal hypoxic basin (Pfeffer et al. 2012; Seitaj et al. 2015; Sulu-Gambari et al. 2015). According to the pollution levels in Eastern China and the basis of pro-study, we propose a

conceptual model of the P biogeochemical cycle (Fig. 6). The reasons for the oxygen deficit in these waters include dams and high concentrations of $\text{NH}_3\text{-N}$ and COD_{Cr} (Fig. 7).

Dam

Rivers in Eastern China flow from west to east due to the local topography. There are many plains in Eastern China, and the water in rivers moving steadily and slowly. There are also large populations and cities located along rivers. In this study, the sampling sites in rivers were located 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 slower than would otherwise be the case (Taylor et al. 2015). For instance, in the Beiyun River of the Hai River Basin, there are 18 dams on a 100-km stretch, with one dam per 2.28 km (Fig. 7). The dams in the river systems cause

Fig. 7 The distribution of COD_{Cr} , $\text{NH}_3\text{-N}$, oxygen deficit, and dams in Eastern China (ArcGIS 10.0)

remarkable features of “Reservoir type Rivers” (Pernet-Coudrier et al. 2012; Zhang et al. 2014), which cause the accumulation of P and other pollutants, such as $\text{NH}_3\text{-N}$ and COD_{Cr}.

NH₃-N and COD_{Cr}

Although there has been large population increase and rapid economic growth in the past two decades, environmental legislation, investment and sewage treatment has not kept pace with these developments. Therefore, large amounts of untreated wastewater and sewage have been directly discharged into the environment. Consequently, a large amount of pollutants is carried into rivers at the same time (Liu and Raven. 2010; Qu and Fan. 2010). The $\text{NH}_3\text{-N}$ and COD_{Cr} are the two main elements consuming oxygen (Li et al. 2012; Wang et al. 2016). The average concentrations of $\text{NH}_3\text{-N}$ and COD_{Cr} were $6.6 \pm 13.42 \text{ mg L}^{-1}$ (ranging from 0.6 to 119.5 mg L^{-1}) and $21.27 \pm 35.40 \text{ mg L}^{-1}$ (ranging from 0.2 to 447.8 mg L^{-1}), respectively, in the Hai River (unpublished data). A high concentration of pollutants leads to oxygen consumption, and induces anaerobic conditions at the interface between the water surface and sediments.

Thus, the combined effect of dams and oxygen-consuming pollutants induces sustained eutrophication, even when external P is reduced, especially in seriously polluted rivers such as the Hai River. Research is needed in the future to understand the mechanisms by which $\text{NH}_3\text{-N}$, COD_{Cr} and dams affect P biogeochemical cycles in seriously polluted river systems. It should be noted that the processes and mechanisms are complex, and biological and chemical processes need to be studied in detail (Seitaj et al. 2015; Sulu-Gambari et al. 2015).

Conclusions

The results of this study showed that the concentration of P in surface sediments varied with watersheds, with P concentration exceeding 500 mg kg^{-1} in more than 50 % of the sampling sites. The highest average concentration of TP, $1922.0 \text{ mg kg}^{-1}$, was in the Hai River System, which was higher than any other river system studied. HCl-Pi was the main Pi identified in the sediment, with its highest percentage of 96.5 % in the Yellow River System. Mono-P was the main Po in river sediments, followed by DNA-P. In this research, the combined application of SMT and ^{31}P -NMR for P analysis was proven to be effective. The PCA approach indicated NaOH-Pi and ortho-P were clustered in one group, with a second group including mono-P, diesters-P (DNA-P and lipids-P), and HCl-Pi. Phon-P and pyro-P belonged to different groups. On a regional scale, NaOH-Pi and Po showed negative relationships with sediment pH. The combined effect of dams and oxygen-consuming pollutants, such as $\text{NH}_3\text{-N}$

and COD_{Cr}, induced sustained eutrophication in seriously polluted rivers, even when external P was reduced.

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