Short communication

Characterization of biogenic phosphorus in sediments from the multi-polluted Haihe River, China, using phosphorus fractionation and ^{31}P -NMR

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ABSTRACT

We studied the phosphorus (P) pollution, as described by concentrations, distribution and transformation potential, of sediments of the water scarce and heavily polluted Fuyang River, a tributary of the Haihe River, using P fractionation and phosphorus-31 nuclear magnetic resonance (^{31}P -NMR). In terms of their contribution to total P, the rank order of the P fractions was as follows: $\text{H}_2\text{SO}_4\text{-P} > \text{NaOH-Pi} > \text{Res-P} > \text{NaOH-Po} > \text{KCl-P}$. Seven P compounds were detected by the ^{31}P -NMR analysis. Orthophosphate (45.2–92.4%) and orthophosphate monoesters (6.6–45.7%) were the dominant forms. Smaller amounts of pyrophosphates (0.1–6.6%), deoxyribonucleic acid (0.3–3.9%), phosphonates (0–3.3%), phospholipids (0–2.7%) and polyphosphates (0–0.04%) were observed in the sediments. Results of P fractionation and ^{31}P -NMR analysis showed that 35% of Pi was labile P, including KCl-P and NaOH-Pi (Fe-P and Al-P). Biogenic-P accounted for 24% of P in the sediments. Analysis of the relationships between P species and water quality indicated that the Po compounds would mineralize to form *ortho*-P and would be potentially bioavailable for recycling to surface water, supporting further growth of phytoplankton and leading to algal blooms.

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1. Introduction

Phosphorus (P) is a limiting element in freshwater systems. Excessive imports of P cause eutrophication (Ahlgren et al., 2005). Eutrophication of freshwater systems has become one of the most severe environmental problems in developing countries (Pernet-Coudrier et al., 2012). The issue is particularly serious in northern China, which is experiencing increasingly severe water shortages due to the rapid growth in population, industry and agriculture (Jiang, 2009). The consequences of eutrophication include algal blooms, oxygen depletion, aquatic ecosystem deterioration and increasing water treatment costs to ensure freshwater is suitable for human use (Vörösmarty et al., 2010).

The release of P from sediment is an important nutrient source that will induce continuous eutrophication in freshwater systems even if external inputs are reduced (Wu and Hua, 2014). Sediment P includes inorganic P (Pi) and organic P (Po). The mineralization of Po into Pi has a direct effect on P bioavailability in freshwater systems (Wang and Pant, 2010). However, until now, investigations of the species, concentrations, dynamics and effects of Po in sediment have been limited because of its complexity and limitations of analytical methods (Cade-Menun, 2005; Turner et al., 2005).

Phosphorus-31 nuclear magnetic resonance spectroscopy (^{31}P -NMR) is a non-destructive, non-invasive technique for identifying chemical forms that has the advantage of enabling multiple P compounds to be characterized simultaneously with distinct binding properties (Cade-Menun, 2005). Several P compounds have been detected by ^{31}P -NMR, including phosphonates (phon-P), orthophosphate (*ortho*-P), orthophosphate monoesters (mono-P), orthophosphate diesters (diesters-P: lipid-P and DNA-P),

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pyrophosphates (pyro-P) and polyphosphates (poly-P) (Turner et al., 2005). Therefore, it is an ideal technique to analyze Po species in marine or freshwater sediments, as it will not only provide useful information pertaining to P biogeochemical cycling in aquatic environments, but will also yield sufficient insight into the identification of specific P compounds.

The Haihe River is characterized by a high population density, rapid socioeconomic development and serious water pollution, caused by discharges of industrial and domestic wastewater. Because of the water shortages and the high nutrient (P) inputs, the river is highly eutrophic. Therefore, the objectives of this study were to detect and analyze the P species in river sediments by P fractionation and ^{31}P -NMR, predict the P bioavailability.

2. Materials and methods

2.1. Description of study area

The Haihe River Basin is located in the north of China, and has an area of about 300,000 km² and a population of 145 million. Beijing, Tianjin and many other cities are included in this river basin. The Fuyang River (N36°23′–38°14′, E114°19′–116°7′) is an important tributary of the Haihe River System. It is 402 km long, and flows through the cities of Hengshui, Handan and Xingtai. Wagyanggou River, Shaocunpaigan River and Xiao River are three important tributaries of the Fuyang River. They receive large amounts of domestic wastewater from Shijiazhuang, the capital of Hebei Province. The Niuwei River is another important tributary of the Fuyang River system that mainly flows through Xingtai (Fig. 1). We chose the Fuyang River for sediment sampling because it is heavily polluted with P and it is representative of rivers in northern of China.

2.2. Sample collection and analysis

Water quality was monitored trimestral from 2010 to 2012. Sediment samples were collected in July 2012. Three surface (top 5 cm) sediment samples were collected at each site using a Peterson grab sampler. Samples taken from the same site were pooled and homogenized to obtain a representative sample. All samples were frozen and stored at –18 °C immediately upon returning from the field.

The pH of sediment samples was determined on sediments suspended in deionized water at a sediment:water ratio of 1:2.5 (Bai et al., 2009). Organic matter (OM) in sediments was determined by loss of ignition at 550 °C for 4 h (Jensen et al., 1992). Total Fe, Al, Mg, Mn and Ca were measured using ICP-OES after digesting sediments with HNO₃–HCl–HF (MARSPress, CEM, USA), the ratio of HNO₃:HCl was 3:1 (6 mL), and then 2 mL HF was added in the digesting tube. The limit of the ICP-OES was 0.1 mg kg^{–1}. The recoveries varied, but all fell within the range of 90–95%. Total P (TP) in sediments was determined by 1 mol L^{–1} HCl extraction (16 h) after pretreatment for 2 h at 500 °C. Pi was determined by direct extraction with 1 mol L^{–1} HCl (16 h). Po concentrations in the sediments were calculated as the difference between TP and Pi (Aspila et al., 1976). TP in the surface water were analyzed using the molybdenum blue method after digestion by K₂S₂O₈ under high temperature (120 °C) and high pressure (1.1 kg cm^{–2}) at least 30 min, the limit of this method was 0.01 mg L^{–1} (Wei, 2002). An annual average TP concentration in surface water was calculated for each site by using monitoring data from 2010 to 2012. Three replicates were analyzed for each sampling event, from which the mean value was calculated.

2.3. Phosphorus fractionations

The P fractionation procedure was based on the method of Hietjes and Lijklema (1980). This fractionation procedure separates the P in the sediment into five groups: (1) P in porewater and loosely sorbed P were extracted with 1 M KCl at room temperature for 1 h (KCl–P), and then the sediment was shaking with 0.1 M NaOH for 17 h at room temperature, the extractant was determined using molybdenum blue method before (NaOH–Pi) and after (NaOH–TP) digestion by K₂S₂O₈. (2) The NaOH–Pi was the P adsorbed to iron and manganese, and the difference between NaOH–TP and NaOH–Pi was (3) NaOH–Po, which was assumed to be Po and bacteria-incorporated P. Finally, (4) H₂SO₄ was used for extracting the P mostly apatite, which was stable withhold in the sediment (H₂SO₄–P). (5) The Res-P fraction was the difference between TP in sediment (HCl extracted–P) and the sum of KCl–P, NaOH–TP and H₂SO₄–P. The P concentration in all the extracts was estimated colorimetrically using the method of Murphy and Riley (Murphy and Riley, 1962).

2.4. NaOH–EDTA extraction and ^{31}P -NMR analysis

Sediment samples (5.0 g) were pre-treated for 16 h at room temperature with a 50-mL solution of 0.05 mol L^{–1} EDTA and 0.25 mol L^{–1} NaOH (Turner et al., 2003b). An aliquot of the NaOH–EDTA extract was used for Pi (Pi in NaOH–EDTA) and TP (TP in NaOH–EDTA) analyses using the molybdenum blue method before and after digestion with K₂S₂O₈. Po in the NaOH–EDTA extract was calculated as the difference between these two fractions. The Fe, Al, Mg, Mn and Ca in the NaOH–EDTA extract were measured using ICP-OES. The remaining solution was frozen and lyophilized to be used for ^{31}P -NMR analysis.

The lyophilized NaOH–EDTA extract (0.3 g) was 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 bicarbonate buffered dithionite (0.11 M NaHCO₃ + 0.11 M Na₂S₂O₄) was added to the extract to reduce interference from paramagnetic ions, such as Fe and Mn. The supernatants were centrifuged for 15 min at 14,000 rpm and transferred to 5-mm NMR tubes. ^{31}P -NMR 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 observe pulse, a relaxation delay of 2 s and an acquisition time of 0.6 s (Liu et al., 2009). Spectra were collected with around 20,000 scans (Beijing NMR Center, Beijing, China). Chemical shifts were recorded relative to an 85% H₃PO₄ standard (δ = 0 ppm). Signals were assigned to P species based on data in the literature (Cade-Menun, 2005; Turner et al., 2003a). The peak area was determined by visual inspection and an automated peak analysis tool. For the different P species areas, the contribution of each P compound group was calculated relative to the TP in the NaOH–EDTA extraction, determined by molybdenum blue method (Zhang et al., 2013). All NMR-spectra showed peaks in the area of phon-P (12 to 23 ppm), ortho-P (6 to 7 ppm), mono-P (4 to 6 ppm), lipid-P (1 to 3 ppm), DNA-P (0 ppm), pyro-P (–3.5 to –4.5 ppm) and poly-P (–17 to –19 ppm) (Cade-Menun, 2005; Turner et al., 2003a).

3. Results

3.1. Phosphorus in surface water and sediment samples

Sediment properties are shown in Table 1. The concentration of TP varied greatly, and ranged from 462 to 9829 mg kg^{–1}. Pi was the main P fraction. Po concentrations ranged from 22 to 2040 mg kg^{–1}, accounting for between 4.8 and 51.3% of TP. OM

Fig. 1. Location of sampling sites in Fuyang River. We divided the Fuyang River system into five parts that incorporated the main stem and the four main tributaries. A total of 18 sampling sites were selected throughout the river basin. Sites 1 to 7 were in the Fuyang River, sites 8 and 9 were in the Niuwei River, sites 10 and 11 were in the Xiao River, sites 12 to 15 were in the Wangyanggou River and sites 16 to 18 were in the Shaocunpaigan River.

Table 1
Physical and chemical properties of sediments in Fuyang River.

River	Site	OM (%)	C/P	pH	Sediment						
					TP (mg kg ⁻¹)	Po (%) (mg kg ⁻¹)	Al (g kg ⁻¹)	Ca (g kg ⁻¹)	Fe (g kg ⁻¹)	Mg (g kg ⁻¹)	Mn (g kg ⁻¹)
Fuyang River	1	6.55	44.38	7.65	1186	274 (23.1)	32.51	13.38	30.06	2.95	0.38
	2	8.47	21.07	7.84	3848	547 (14.2)	5.51	25.80	42.42	5.26	0.53
	3	6.44	27.10	7.35	1338	210 (15.7)	28.43	20.97	42.50	3.13	0.63
	4	25.19	14.37	7.17	9829	3787 (38.5)	17.35	14.78	44.72	4.05	0.57
	5	4.87	41.04	7.54	734	160 (21.8)	18.21	15.29	36.27	3.88	0.57
	6	20.81	25.62	8.27	4190	2109 (50.3)	7.18	11.17	55.54	5.53	0.52
	7	3.27	28.05	8.06	720	88 (12.3)	18.81	12.95	41.02	3.89	0.65
Niuwei River	8	4.03	32.10	7.43	733	87 (11.8)	32.59	18.26	32.78	3.81	0.40
	9	11.28	35.62	6.69	2048	569 (27.8)	22.41	13.12	45.29	5.58	0.30
Xiao River	10	5.67	26.32	7.73	1460	301 (20.6)	35.19	18.42	34.77	4.62	0.43
	11	5.43	41.24	7.48	818	145 (17.7)	34.57	14.16	45.90	4.07	0.41
Wangyanggou River	12	20.69	17.24	6.95	7366	3686 (50.0)	9.89	20.49	36.74	5.26	0.56
	13	2.87	33.54	8.53	574	96 (16.7)	15.27	20.29	33.46	4.25	0.58
	14	2.78	33.69	7.84	462	22 (4.8)	27.15	23.52	37.44	4.60	0.46
Shaocunpaigan River	15	9.83	19.75	7.75	3060	1570 (51.3)	19.60	20.89	30.88	5.18	0.45
	16	5.69	51.40	8.02	935	200 (21.3)	20.20	12.70	34.69	3.48	0.49
	17	1.99	25.88	8.52	534	51 (9.6)	27.08	21.97	32.69	4.59	0.49
	18	12.09	15.78	7.25	4228	2134 (50.5)	27.12	14.15	57.59	3.90	0.63

Parentheses indicate the proportion of Po to TP in sediments (%).

content varied with TP concentrations. The average OM content was 8.78% and ranged from 1.99 to 25.19%. The pH in sediments ranged from 6.69 to 8.53. The concentrations of other metals in the sediments were as follows: total Al concentrations ranged from 5.51 to 35.19 g kg⁻¹, total Ca from 11.17 to 25.8 g kg⁻¹, total Fe from 30.06 to 57.59 g kg⁻¹, total Mg from 2.95 to 5.58 g kg⁻¹ and total Mn from 0.30 to 0.65 g kg⁻¹. The ratio of TC to TP in the sediments ranged from 14.37 to 51.40. Total P and soluble reactive phosphorus (SRP) in surface water samples was ranging from 0.17 to 7.29 mg L⁻¹ and 0.06 to 6.44 mg L⁻¹, respectively.

3.2. Phosphorus fractionation in sediments

Sediment P was mainly composed of H₂SO₄-P and NaOH-Pi. H₂SO₄-P concentrations ranged from 344.4 to 2941.7 mg kg⁻¹, and had a relative contribution of between 20.2 and 74.5% to TP, while concentrations of NaOH-Pi ranged from 54.4 to 5749.2 mg kg⁻¹ and had a relative contribution of 7.6 to 65.1% to TP. Res-P ranged from 33.6 to 1257.9 mg kg⁻¹, and had a relative contribution of 1.4 to 18.8%. NaOH-Po ranged from 0.3 to 243.9 mg kg⁻¹, and had a relative contribution of between 0.1 and 5.2% to TP, while KCl-P ranged from 1.2 to 31.0 mg kg⁻¹, and had a relative contributions of between 0.1 and 2.1% to TP. The rank order and average relative proportions of the P fractions were as follows (the proportion was based on the average proportion of the KCl-P): H₂SO₄-P (69.7%) > NaOH-Pi (47.5%) > Res-P (15.9%) > NaOH-Po (2.9%) > KCl-P (1.0%).

3.3. ³¹P-NMR spectra of NaOH-EDTA extracts of sediments

The NMR spectra of the surface sediments are shown in Fig. 2. Seven P compounds were detected in the NaOH-EDTA extract by ³¹P-NMR. The concentrations of the various P compound groups in surface sediments are presented in Table 2. TP in the NaOH-EDTA extracts ranged from 179.7 to 5712.9 mg kg⁻¹, which represented recovery of between 27.2 and 87.1% of the TP in the sediments. Po in the NaOH-EDTA ranged from 15.4 to 2578.3 mg kg⁻¹, representing a recovery ranging from 30.0 to 73.0%. In the NaOH-EDTA extracts, *ortho*-P was the main component of TP, which ranged from 140.8 to 4061.6 mg kg⁻¹, accounting for 45.2 to 92.4% of TP. Pyro-P ranged from 0.3 to 44.2 mg kg⁻¹, accounting for 0.1 to 6.6% of the TP. Poly-P was only detected in sediments from site 1, and had a concentration of 0.2 mg kg⁻¹ and a relative contribution of 0.04% to TP. Mono-P was the main component of Po, which ranged from 13.1 to 2220.9 mg kg⁻¹, accounting for between 6.6 and 45.7% of TP. Lipid-P ranged from 0 to 141.1 mg kg⁻¹, accounting for 0 to 2.7% of the TP. DNA-P ranged from 0.5 to 124.2 mg kg⁻¹, accounting for 0.3 to 3.9% of the TP. The levels of phon-P ranged from 0 to 141.4 mg kg⁻¹, accounting for up to 3.3% of TP.

4. Discussion

4.1. Sediment P pollution

The Haihe River basin has high population, economic and agricultural growth rates, and as a result, faces increasingly severe water-related issues. Human and industrial water consumption and irrigation of intensely farmed land has led to water shortages. Meanwhile, the nutrient concentrations in this region's rivers have increased dramatically in the past 40 years (Pernet-Coudrier et al., 2012). The average and maximum TP concentrations in surface water were 1.68 and 7.29 mg L⁻¹, while the average and maximum SRP concentrations were 1.21 and 6.44 mg L⁻¹, respectively. All of these values far exceed the water quality criteria

for both the USA (0.1 mg L⁻¹: US EPA. Quality criteria for water-1986, EPA 440/5-86-001) and China (0.4 mg L⁻¹: National Standard of the People's Republic of China, Environmental quality standards for surface water, GB3838-2002), which means that the water is unsuitable for any use. Sediment TP concentrations ranged from 462 to 9829 mg kg⁻¹. The average sediment TP concentration was 2448 mg kg⁻¹ and TP concentrations exceeded 1000 mg kg⁻¹ at 55.6% of sampling sites. Because of the excessive P inputs, significant amounts of P have accumulated in the river sediments, and exceed what has been reported for Bronx River (Wang and Pant, 2010), Yellow River (Pan et al., 2013), Illinois River (Haggard and Soerens, 2006) and Amazon River (Berner and Rao, 1994).

The ratio of TC to TP (*C/P*) gives information on the origin of the OM and the Po biogeochemical cycle (Zhang, 2007). A high *C/P* value implies P losses. Po degrades when OM degrades. A low *C/P* value means that the P input is mainly from human activities and that P is accumulating in the sediments. In this study, a negative correlation between the *C/P* values and TP in the sediments indicated that the high TP concentrations were mainly due to anthropogenic inputs. Correlations between TP and OM ($R^2_{TP-OM} = 0.87$) and Po and OM ($R^2_{Po-OM} = 0.89$) indicated that the P and OM in the sediments are homologous, and that the majority of Po was most likely associated with OM, such as fulvic and humic acids (Bai et al., 2009). High values of TP and Po appeared in the Fuyang River. The concentrations of TP and Po were 9829 and 3787 mg kg⁻¹ at sampling point 4, the location of the Aixinzhuang Dam. The dam interferes with river flow and reduces velocity, which results in sediment P accumulation at the dam wall.

4.2. ³¹P-NMR spectroscopy and P fractions

Ortho-P was the dominant P fraction in NaOH-EDTA extracts of the river sediments. This could be because of the continuous inputs of either industrial and domestic wastewater, or non-point pollution from agriculture. A proportion of the *ortho*-P may also be the result of in-river transformations. For example, some Po that entered the river systems may have been hydrolyzed to *ortho*-P by phosphatase (Turner et al., 2006). Mono-P were the main form of Po in the sediments. It represents a wide range of important Po compounds, such as inositol phosphate and sugar phosphates, and has a long half-life in sediments (23 years) (Ahlgren et al., 2005). The *ortho*-P may originated from sediment (e.g. Inositol hexaphosphate) or the degradation of diesters. In this study, we also found that the residual P fraction was positively correlated with the mono-P and phon-P fractions, which ranged from 6.57 to 29.20% of TP in the NaOH-EDTA extracts ($R^2 = 0.79$, $p < 0.01$). Diesters-P were a form of labile P in the sediments. It has a half-life of 21 years, and is a mixture of compounds such as DNA-P, lipid-P and teichoic-P (Cade-Menun, 2005; Turner et al., 2003b). A positive correlation between diester-P in NaOH-EDTA and the NaOH-Po in sediment by P fractionation indicated that the NaOH-Po by P fractionation was mostly labile P ($R^2 = 0.77$, $p < 0.01$).

The positive correlation between NaOH-Pi (as determined by P fractionation) and NaOH-Fe and NaOH-Al indicated that the sediment P immobilization potential was controlled by Fe and Al hydroxides ($R^2 = 0.88$, $p < 0.01$) (Kopáček et al., 2005). Liu reported that BD-Fe and NaOH-Al together explained 68% of the variability in the maximum sorption capacity of sediment (Liu et al., 2009). P fractionation and ³¹P-NMR analysis showed that 35% of Pi was labile P, including KCl-P and NaOH-Pi (Fe-P and Al-P). Biogenic-P, which was considered molybdenum-non-reactive P in the NaOH extract, accounted for 24% in the sediments. There is a high risk of

Table 2Concentrations^{†‡} of P compounds in NaOH–EDTA extracts of the sediments determined by solution ³¹P-NMR.

River	Site	TP	Po (%)	Inorganic P			Organic P			
				<i>Ortho</i> -P (mg kg ⁻¹)	Pyro-P (mg kg ⁻¹)	Poly-P (mg kg ⁻¹)	Mono-P (mg kg ⁻¹)	Lipid-P (mg kg ⁻¹)	DNA-P (mg kg ⁻¹)	Phon-P (mg kg ⁻¹)
Fuyang River	1	512.7	129.1 (47.1) [*]	389.5 (75.9) ^{**}	33.7 (6.6)	0.2 (0.04)	66.7 (13.0)	4.2 (0.8)	18.4 (3.6)	n.d.
	2	2731.9	377.7 (69.0)	2340.5 (85.7)	20.8 (0.8)	n.d.	241.5 (8.8)	23.9 (0.9)	65.3 (2.4)	39.9 (1.5)
	3	857.7	113.0 (53.7)	746.8 (87.1)	6.2 (0.7)	n.d.	79.2 (9.2)	6.5 (0.8)	16.2 (1.9)	2.9 (0.3)
	4	5712.9	1657.3 (43.8)	4061.6 (71.1)	44.2 (0.8)	n.d.	1260.6 (22.1)	141.1 (2.5)	124.2 (2.2)	81.3 (1.4)
	5	314.1	94.3 (58.8)	256.9 (81.8)	3.1 (0.9)	n.d.	39.8 (12.7)	1.8 (0.6)	12.4 (3.9)	n.d.
	6	3299.4	1222.5 (58.0)	2056.8 (62.3)	41.3 (1.3)	n.d.	963.4 (29.2)	31.2 (0.9)	110.9 (3.4)	95.7 (2.9)
	7	195.7	64.2 (72.8)	172.6 (88.2)	1.1 (0.5)	n.d.	19.9 (10.2)	n.d.	2.2 (1.1)	n.d.
Niuwei River	8	357.5	55.5 (64.0)	330.2 (92.4)	0.8 (0.2)	n.d.	23.5 (6.6)	n.d.	3.1 (0.9)	n.d.
	9	1607.3	388.8 (68.3)	1237.2 (76.9)	8.3 (0.5)	n.d.	325.6 (20.3)	6.5 (0.4)	22.2 (1.4)	7.6 (0.5)
Xiao River	10	1008.2	219.7 (73.0)	786.9 (78.1)	13.7 (1.4)	n.d.	181.3 (17.9)	2.9 (0.3)	20.1 (1.9)	3.3 (0.3)
	11	487.3	52.8 (36.5)	427.2 (87.7)	1.1 (0.2)	n.d.	55.6 (11.4)	0.6 (0.1)	1.6 (0.3)	1.2 (0.2)
Wangyanggou River	12	4860.1	2578.3 (70.0)	2194.9 (45.2)	41.8 (0.9)	n.d.	2220.9 (45.7)	133.2 (2.7)	121.9 (2.5)	147.4 (3.0)
	13	186.4	28.8 (30.0)	154.4 (82.8)	0.3 (0.1)	n.d.	31.1 (16.7)	n.d.	0.5 (0.3)	0.1 (0.1)
	14	157.6	15.4 (70.1)	140.8 (89.4)	0.3 (0.2)	n.d.	13.1 (8.3)	0.6 (0.4)	1.9 (1.3)	0.9 (0.6)
	15	2171.9	755.9 (48.0)	1394.4 (64.2)	36.9 (1.7)	n.d.	539.1 (24.8)	53.4 (2.5)	75.6 (3.5)	72.5 (3.3)
Shaocunpaigan River	16	487.9	123.0 (61.6)	362.9 (74.4)	4.6 (0.9)	n.d.	104.6 (21.4)	1.9 (0.4)	10.9 (2.3)	2.8 (0.6)
	17	179.7	24.1 (47.1)	161.7 (90.0)	0.8 (0.4)	n.d.	15.1 (8.4)	n.d.	2.1 (1.2)	n.d.
	18	3684.5	1199.5 (56.2)	2527.5 (68.6)	32.8 (0.9)	n.d.	1009.2 (27.4)	14.5 (0.4)	92.5 (2.5)	8.2 (0.2)

n.d. not detected. DNA-P=deoxyribonucleic acids (orthophosphate diesters), Lipid-P=phospholipid (orthophosphate diesters), Mono-P=orthophosphate monoesters, *Ortho*-P=orthophosphate, Phon-P=phosphonate, Pyro-P=pyrophosphates, Poly-P=polyphosphates.

[†]The concentration is based on the dry weight.

[‡]The value was calculated from the concentration in the NaOH–EDTA extract and the dry weight.

^{*} The proportion of Po in NaOH–EDTA extraction to total Po in sediments (%).

^{**} The proportion of individual P fraction to total P in NaOH–EDTA extraction.

Fig. 2. ^{31}P -NMR spectra of NaOH-EDTA extracts of the surface sediments in Fuyang River. (A) Phosphonate; (B) orthophosphate; (C) orthophosphate monoesters; (D) orthophosphate diesters; (E) phospholipid; (F) deoxyribonucleic acids; (G) pyrophosphates; (H) polyphosphates. Fuyang River: site 1, 2, 3, 4, 5, 6, 7; Niuwei River: site 8, 9; Xiao River: 10, 11; Wangyanghou River: 12, 13, 14, 15; Shaocunpaigan River: 16, 17, 18.

release of both labile P and biogenic-P to the water column, thereby leading to water eutrophication.

Apart from *ortho*-P, biogenic P is an important source of P in surface water. Biogenic P includes Po, poly-P and pyro-P, which were analyzed as molybdenum-non-reactive P in the NaOH extract (Ahlgren et al., 2005). Biogenic P could be released from the sediments under redox conditions and could induce water eutrophication (Qian et al., 2011). The positive relationship between biogenic-P and TP in the water column indicates that the biogenic-P compounds could be released into surface water and could support hydrophyte growth (Wang and Pant, 2010).

5. Conclusions

This research has used P fractionation and ^{31}P -NMR to provide an insight into the P species and distribution of P pollution in sediments of the heavily polluted and water scarce Fuyang River and their effects. Results show that the river sediments have accumulated significant amounts of Pi and Po. Sediment P was mainly composed of $\text{H}_2\text{SO}_4\text{-P}$ and NaOH-Pi . Seven P compounds were detected in NaOH-EDTA extract from the ^{31}P -NMR analysis. *Ortho*-P and mono-P were the dominant forms, while smaller amounts of pyro-P, DNA-P, phon-P, lipid-P and poly-P were found in the surface sediments. Results of the P fractionation and ^{31}P -NMR analysis showed that biogenic-P accounted for 24% of P in the sediments.

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