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Organochlorine compounds and polycyclic aromatic hydrocarbons in surface sediment from Baiyangdian Lake, North China: Concentrations, sources profiles and potential risk

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Abstract

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) were determined in nineteen surface sediment samples collected from Baiyangdian Lake and its inflowing river (Fuhe River) in North China. Total concentrations of OCPs, PCBs and PAHs in sediments ranged from 5.4 to 707.6 ng/g, 2.3 to 197.8 ng/g, and 101.3 to 6360.5 ng/g, respectively. The levels of contaminants in Fuhe River were significantly higher than those in Baiyandian Lake. For hexachlorocyclohexane (HCHs) and dichlorodiphenytrichloroethanes (DDTs), α-HCH and *p,p′*-DDT were predominant isomers; while for PCBs, PCB 28/31, PCB 40/103, PCB 60, PCB 101, and PCB 118 were predominant congeners. Possible sources derived from historical usage for OCPs and incomplete combustion fuel, wood, and coal and exhaustion of boats or cars for PAHs. Risk assessment of sediment indicated that sediments in Fuhe River were likely to pose potential biological adverse impact.

Key words: persistent organic pollutants; concentrations; profiles; risk assessment; Baiyangdian Lake
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Introduction

With the rapid development of agriculture and industry, persistent organic pollutants (POPs), such as organochlorinated pesticide (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), have been detected in various environmental matrixes and biota in China (Zhang et al., 2004; Wu et al., 2005; Xu et al., 2007; Hu et al., 2008; Li et al., 2008). In freshwater ecosystems, sedimentation has been identified as an important fate of contaminants. Sediments act both as a pollutant sink and as a carrier and secondary source of contaminants. These contaminants are not necessarily fixed permanently to sediments, but may be recycled via chemical and biological processes. The identification of POPs affecting aquatic ecosystem is critical to sound assessment and management of water bodies. In China, OCPs, such as dichlorodiphenytrichloroethanes (DDTs) and hexachlorocyclohexane (HCHs), were widely applied to agricultural production till they were banned in 1983 (Zhang et al., 2002). Because of their persistence, bioaccumulation, and long-distance transport, DDTs and HCHs have been detected in sediments from different regions in China (Zhang et al., 2003; Yang et al., 2005). PCBs have been widely used as dielectric fluids in transformers and capacitors, heat exchange fluids because of their insulating and nonflammable properties. In China, approximately 10,000 tons of PCBs were produced from 1965 to 1974. Following the ban on the production and use of PCBs, most of the outdated PCB-containing equipment was removed from use and stored. Unfortunately, PCBs in some of the equipment have recently been found leaking into the surrounding environment. The study of PCBs contamination is an important approach to the risk assessment, due to their toxic effects on humans and wildlife. PAHs, identified by U.S. EPA as priority pollutants, are a group of compounds which include the largest known class of chemical carcinogens and mutagens. The incomplete combustion of fossil fuel and biomass material is the main anthropogenic source of PAHs, which exhibits acute toxicity and sub-lethal effects on terrestrial and aquatic organisms. A series of anthropogenic and industrial activities, such as wastewater effluents, incomplete combustion of fuel, petrochemical industrial practices, vehicular emissions,

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power plant emissions, and domestic heating, constitute the main sources of PAHs.

Recent investigations showed that these POPs are widespread in water (Li et al., 2006; Shi et al., 2007), sediment (Mai et al., 2002; Wu et al., 2003; Chen et al., 2006; Qiao et al., 2006; Liu et al., 2008; Luo et al., 2008), and air (Wu et al., 2005; Chang et al., 2006) in China. However, most studies examined the POPs in sediment from marine and estuary environment, and little information is available on POPs contamination in sediment from inland lakes in China (Qiao et al., 2006).

The main objective of the study was to investigate the occurrence and distribution patterns of DDTs, HCHs, PCBs and PAHs in sediments from Baiyangdian Lake and Fuhe River in North China, which gave the information about status of contamination. Meanwhile, potential biological effects of DDTs, PCBs and PAHs in sediment samples were also evaluated. The results from the present study would have significant implications to understand the environmental changes, to determine reasonable ways for further development, and to maintain a sustainable development in the Baiyangdian regions.

1 Materials and methods

1.1 Study region

Baiyangdian Lake is the largest natural freshwater body in the North China Plain (Fig. 1). The lake consists of more than 100 small and shallow lakes linked to each other by thousands ditches with surface area of 366 km^2, a catchment of 31,200 m^2. It is semi-enclosed lake with scarce water circulation. Fuhe River is a major inflowing river of Baiyangdian Lake with 63 km long, flowing through Baoding City. Both the Baiyangdian Lake and Fuhe River are strongly influenced by human activities. In addition, Baiyangdian Lake is likely playing an important role in the South-to-North Water Division Project under construction because of its geographic location.

1.2 Sample collection and materials

Nineteen surface samples were collected, of which seven from Baiyangdian Lake and twelve samples from Fuhe River, in August, 2007 and March 2008, respectively, using a stainless steel grab sampler. The top 5-cm layer of sediments was scooped using a precleaned stainless steel scoop into solvent-rinsed aluminum containers. All samples were placed on ice and transported to the laboratory, then frozen and stored at –20°C until further analysis.

OCPs standard (*p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, α-HCH, β-HCH, γ-HCH, and δ-HCH), PAHs standard and perdeuterated PAH surrogates (phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were purchased from Ultra Scientific, Inc. (North Kingstow, USA). PCBs and *o,p′*-DDT, *o,p′*-DDE, *o,p′*-DDD were purchased from AccuStandards (New Haven, USA). All organic solvents were re-distilled using a glass system. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were extracted with dichloromethane for 72 hr using a Soxhlet extractor.

1.3 Analytical protocols

The procedures for OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, *o,p′*-DDD, *o,p′*-DDE), PCBs (PCB 28/31, 40/103, 60, 99, 101, 105, 110, 118, 128, 138, 153, 164) and 16 PAHs extraction, purification and instrumental analysis were described in detail elsewhere (Mai et al., 2002). In brief, freeze-dried sediment was accurately weighed, homogenized, and quantitatively transferred into a pre-cleaned extraction thimble. After spiked with surrogated standards (PCB 30 and PCB 65 for OCPs and PCBs, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} for PAHs), sediments were Soxhlet extracted with 180 mL of the mixture of acetone and hexane (*V/V*, 1:1) for PCBs, and with 180 mL dichloromethane for OCPs and PAHs. Activated copper was added for desulfurization. After concentrated, the extract was subjected to multilayer silica/alumina column for cleanup and fractionation. The column was eluted with 15 mL hexane, which was discarded. The second fraction containing target contaminants was eluted with 70 mL of dichloromethane and hexane (*V/V*, 30:70). The fractions were concentrated under a gentle flow of high-purity nitrogen to appropriate volumes, spiked with appropriate internal standards and then adjusted to accurate pre-injection volumes (200 μL) for instrumental analysis.

Identification and quantification of OCPs, PCBs and PAHs were performed on an Agilent 6890 gas chromatograph (GC) system equipped with an Agilent 5975B mass selective detector (MSD) operating in selective ion monitoring (SIM) mode, using a DB-5 capillary column (60 m length × 0.25 mm i.d × 0.25 μm film thickness). Splitless injection of 1 μL of sample was conducted with an autosampler. The carrier gas was an ultra high purity N_2. For OCPs and PCBs, the column oven was programmed from an initial temperature of 120 to 180°C at a rate of

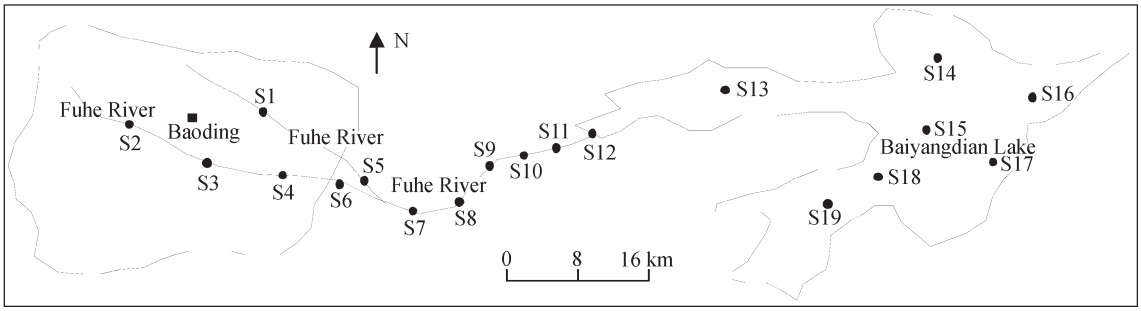

Fig. 1 Maps of sampling sites. S1–S12 located in Fuhe River, S13–S19 located in Baiyangdian Lake.

6°C/min, then ramped to 240°C at a rate of 1°C/min, and finally increased at a rate of 6°C/min to 290°C and hold for 15 min. For PAHs, the GC oven temperature was programmed from 90 to 180°C at a rate of 10°C/min, to 220°C at a rate of 2°C/min, and further to 290°C at a rate of 8°C/min holding for 30 min. Fluorobiphenyl and terphenyl-d_{14} were used as internal standards for the quantification of PAHs, PCB 82 for OCPs and PCBs. Quantification was based on internal calibration curves made from standard solutions at six concentration levels.

1.4 Quality assurance/quality control

The surrogate standard recoveries in 19 samples ranged from 64.1% to 115.6% for phenanthrene-d_{10}, 70.2% to 121.1% for chrysene-d_{12}, and 68.7% to 115.9% for perylene-d_{12}, 86.2% to 134.2% for PCB 30, and 97.6% to 132.2% for PCB 65. For quality control, a procedural blank, triplicate spiked blanks; triplicate spiked matrices (a mixture of 16 PAHs and 8 PCB congeners were added to sediment) were analyzed. The recoveries of the spiked blanks ranged from 61.6% to 108.7% for PCBs and 41.7% to 114.3% for PAHs. The recovery of spiked matrices ranged from 63.5% to 97.7% for PCBs and 42.5% to 120.9% for PAHs. The limit of detection, defined as a signal to noise ratio of 3, ranged from 0.02 to 0.09 ng/g dry weight (dw) for OCPs, 0.40 to 3.4 ng/g dw for PCBs, and 0.004 to 0.12 ng/g dw for PAHs. All the results were expressed on a dry weight basis. Only trace levels of targets were detected in blanks. OCPs and PCBs data were not corrected by surrogate recovery and blank, and PAHs data were corrected.

1.5 Data analysis

In the present study, concentration values less than detection limits were set to zero. Comparisons of concentrations were performed using Two-Sample Kolmogorov-Smirnov nonparametric tests. All statistical analyses were performed with SPSS 11.0 for Windows. The level of significance was set at $\alpha = 0.05$ in this study.

2 Results and discussion

2.1 OCPs in sediment

The total OCPs concentrations ranged from 5.4 to 707.6 ng/g with 1.3 to 51.3 ng/g for DDTs and 4.7 to 678.6 ng/g for HCHs in Fu River (Table 1). The concentrations of OCPs in sediments from Fuhe River (5.4–707.6 ng/g, mean 161.3 ng/g) were significantly higher than those in Baiyangdian Lake (12.1–15.8 ng/g, mean 14.2 ng/g) ($p < 0.05$). The highest level of OCPs (707.6 ng/g) was found at site 4 in Fuhe River and the lowest level (5.4 ng/g) was found at site 12 in Baiyangdian Lake. The ubiquitous distribution of DDTs and HCHs in sediments suggested an extensive use of these pesticides in the regions.

Compared with data acquired by studies conducted in other regions in China, the total DDTs concentrations (2.2–3.1 ng/g) in the sediments from Baiyangdian Lake were comparable to those of Guanting Reservoir, Beijing (3.3–17.2 ng/g) (Xue et al., 2006), and lower than those of Gaobeidian Lake, Beijing (10.3–15.6 ng/g) (Li et al., 2008), but higher than those of Taihu Lake (0.2–0.7 ng/g) (Nakata et al., 2005). The total HCHs concentrations of Baiyangdian Lake (9.8–12.8 ng/g) were close to those of Guanting Reservoir, Beijing (0.3–10.8 ng/g) (Xue et al., 2006), but higher than those of Gaobeidian Lake, Beijing (1.02–1.48 ng/g) (Li et al., 2008).

Composition differences of HCH isomers or DDT congeners in the environment could indicate different contamination sources (Doong et al., 2002). Technical-grade HCH consists principally of four isomers, α-HCH (60%–70%), β-HCH (5%–12%), γ-HCH (10%–15%), and δ-HCH (6%–10%). The mainly composition of lindane is γ-HCH (> 99%). Among the HCH isomers, α-HCH is

Table 1 Concentrations of persistent organic pollutants in sediments from Baiyangdian Lake and Fuhe River (ng/g dry weight (dw))

	Baiyangdian Lake		Fu River			Baiyangdian Lake		Fu River	
	Mean	Range	Mean	Range		Mean	Range	Mean	Range
α-HCH	7.3	5.8–8.3	96.0	2.4–583.3	Naphthalene	10.1	6.0–21.7	121.8	3.8-654.2
β-HCH	0.8	0.5–1.1	14.8	0.4–107.7	Acenaphthylene	4.0	2.2–5.6	11.1	0.7–42.1
γ-HCH	3.6	2.7–4.2	48.5	1.9–254.8	Acenaphthene	2.6	0.8–5.4	19.9	1.1–59.8
∑HCHs[a]	**11.6**	**9.8–12.8**	**146.3**	**4.7–678.6**	Fluorene	8.5	7.2–10.5	76.9	8.5-262.7
o,p′-DDE	0.2	0.17–0.22	0.7	0.2–2.4	Phenanthrene	35.3	20.6–52.2	383.7	23.7-1206.3
p,p′-DDE	0.5	0.4–0.6	4.5	0.4–13.0	Anthracene	5.3	1.9–10.9	67.1	4.7–176.6
o,p′-DDD	0.4	0.2–0.8	1.4	0.2–4.5	Fluoranthene	26.9	13.9–46.9	417.6	26.0–1054.1
p,p′-DDD	0.7	0.4–1.1	4.7	0.4–15.8	Pyrene	20.2	10.1–36.9	328.0	24.7–858.7
p,p′-DDT	0.9	0.7–1.2	4.9	0.6–16.6	Benzo[a]anthracene	9.1	3.1–19.2	131.9	7.6–344.4
∑DDTs[b]	**2.6**	**2.2–3.1**	**15.0**	**1.3–51.3**	Chrysene	12.5	5.5–26.9	182.8	18.1–444.6
∑OCPs	**14.2**	**12.1–15.8**	**161.3**	**5.4–707.6**	Benzo[b]fluoranthene	26.7	12.5–53.9	401.9	33.9–1075.9
∑PCBs[c]	**3.6**	**2.3–7.6**	**46.3**	**4.2–197.8**	Benzo[k]fluoranthene	4.8	0.3–13.6	161.4	10.2–786.0
					Benzo[a]pyrene	5.0	1.2–12.7	217.8	11.3–664.7
					Dibenzo[a,h]anthracene	2.8	0.8–5.8	15.9	1.7–45.2
					Indeno[1,2,3-cd]pyrene	7.3	3.5–13.8	66.9	6.1–190.0
					Benzo[g,h,i]perylene	8.8	4.5–17.0	57.2	3.2–181.6
					∑PAHs	**189.9**	**101.3–322.8**	**2661.9**	**191.6–6360.5**

[a] ∑HCHs include α-HCH, β-HCH, and γ-HCH;
[b] ∑DDTs include *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, and *p,p′*-DDT;
[c] ∑PCB congeners include PCB 28/31, PCB 40/103, PCB 60, PCB 99, PCB 101, PCB 105, PCB 110, PCB 118, PCB 128, PCB 138, PCB 153, and PCB 164.

more likely to be transported by air for a long distance, while β-HCH is more resistant to hydrolysis and environmental degradation. Moreover, γ-HCH can be converted to α-HCH in environment. Therefore, the profiles of HCH isomers can reflect the sources and the fate of HCHs in the environment. As shown in Fig. 2a, the predominant HCH isomer was α-HCH in Baiyangdian Lake, accounting for 62.6% of the total HCHs, followed by γ-HCH and β-HCH, accounting for 30.8% and 6.6% of the total HCHs, respectively. The compositional profile of HCH isomers in Fuhe River was similar to that of Baiyangdian Lake, α-HCH, γ-HCH, and β-HCH accounting for 61.4%, 32.0% and 6.7% of the total HCHs, respectively. The results suggested that contamination of HCHs in Baiyangdian Lake and Fuhe River may be attributed to the long-range transport and the erosion of the weathered agricultural soils containing HCH compounds. The ratio of α/γ-HCH was lower than that of technical HCH, which indicated that technical HCH contamination was mainly due to historical usage.

Among the DDT isomers, *p,p′*-DDT was the predominant compound accounting for more than 30% of the total DDTs in the sediment samples (Fig. 2b). DDT can be biodegraded to DDE under aerobic condition and to DDD under anaerobic condition, the relative concentration of the parent DDT compound and its metabolites, DDD and DDE, can be used to indicate possible pollution sources. There was almost no difference in ratios of DDT/(DDE+DDD) between Baiyangdian Lake and Fuhe River ($p > 0.05$). The ratios of DDT/(DDE+DDD) were lower than one in majority of samples. The results possibly indicated that the DDTs in soils nearby Baiyangdian Lake and Fuhe River were subjected to a long-term weathering. Degradation of HCHs and DDTs in sediments and soils occurred significantly after official ban of HCHs and DDTs in 1983. In addition, industrial sewage from Baoding City was another source of HCHs and DDTs.

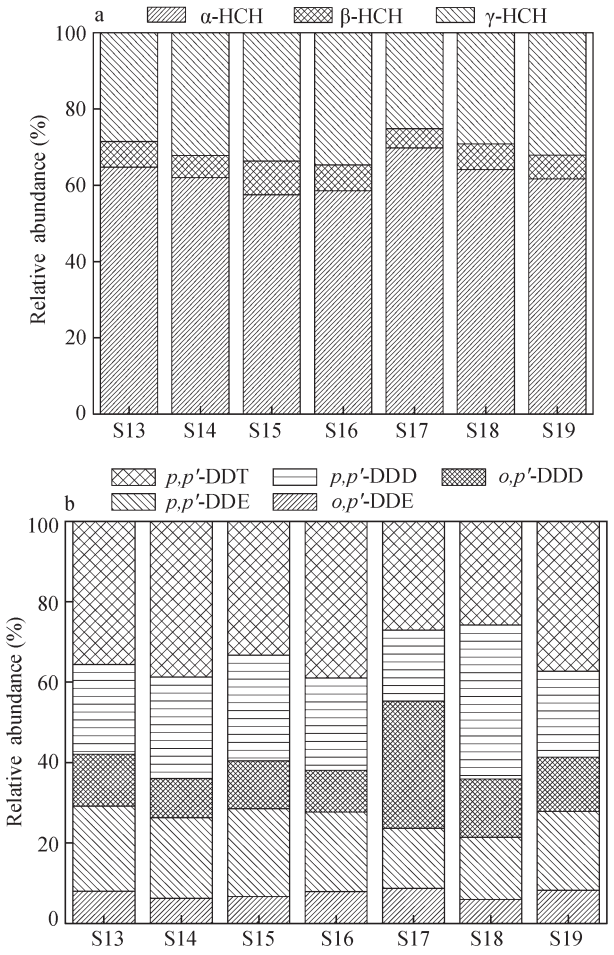

Fig. 2 Composition of HCH isomers (a) and DDT isomers (b) in surface sediments from Baiyangdian Lake.

2.2 PCBs in sediment

The concentrations of PCBs ranged from 2.3–7.6 ng/g (mean 3.6 ng/g) and 4.2–197.8 ng/g (mean 46.3 ng/g) in sediments of Baiyangdian Lake and Fuhe River, respectively (Table 1). The PCB concentrations in Fuhe River were significantly higher than those in Baiyangdian Lake ($p < 0.05$). The spatial distribution of PCB concentrations in sediment suggested the presence of sources along the sites of Fuhe River (Fig. 1). The total concentrations of PCBs greater than 100 ng/g dw were found at sites 4, 6, 9 situated along Fuhe River. There were steel factories, power plants, paper mills and electric cables dismantling and smelting plants along the bank of Fuhe River. The outflow from industrial facilities was discharged into Fuhe River, which was a primary sedimentation reservoir.

The PCB concentrations of in sediments of Baiyangdian Lake were comparable to those of Tonghui River (0.8–8.5 ng/g) (Zhang et al., 2004), Gaobeidian Lake (0.9–3.7 ng/g) (Li et al., 2008), Haihe River (0.8–7.5 ng/g) (Liu et al., 2007), Nanpaiwu River (0.5–7.4 ng/g dw) (Hu et al., 2005), and Yellow River (1.4–5.2 ng/g) (He et al., 2006), but were lower than those of Dagu Drainage River (44.3–153.7 ng/g) (Liu et al., 2007), Pear River (48.3–486 ng/g) and Macao Harbor (339 ng/g) (Mai et al., 2002), and Eire Lake (43 ng/g) (Marvin et al., 2004). The concentrations of PCBs in sediments of Fuhe River were higher than those of Tonghui River (Zhang et al., 2004), Haihe River (Liu et al., 2007), Nanpaiwu River (Hu et al., 2005), and Yellow River (He et al., 2006). The findings suggested that the contaminations of PCBs for Fuhe River and Baiyangdian Lake were moderate or relatively low levels.

Regarding the composition of PCB congeners, PCB 28/31, PCB 40/103, PCB 60, PCB 101, and PCB 118 were predominant congeners in sediments of Baiyangdian Lake and Fuhe River (Fig. 3). Most sediment samples collected from Baiyangdian Lake and Fuhe River had higher proportions of tri-, tetra-, and penta-CBs, collectively accounting for more than 80% of total PCB concentrations. Lower chlorinated congeners, such as PCB 28/31, PCB 40/103, PCB 60, PCB 101, and PCB 118 were prevalent in sediments from Baiyangdian Lake and Fuhe River, which were in accordance with those reported in sediments from different locations in China (Mai et al., 2005). In contrast, the pattern was different from those observed in sediments from marine coastal regions in North America in which hexa-, hepta-, or octa-CBs contributed to greater proportions of the total PCBs (Kannan et al., 1997).

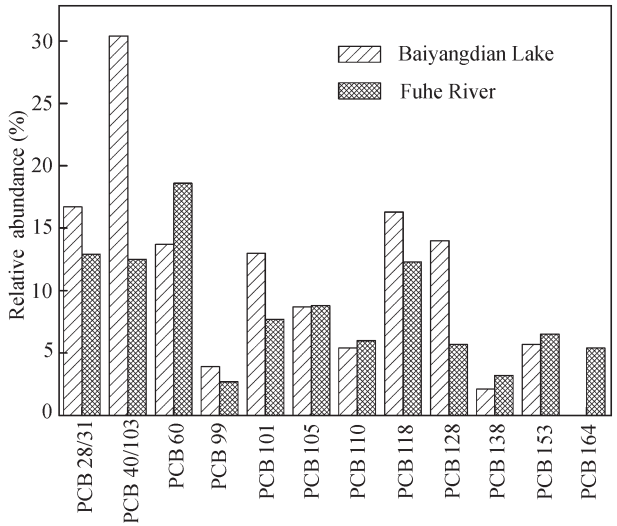

Fig. 3 Composition of PCB congeners in surface sediments from Baiyangdian Lake and Fuhe River.

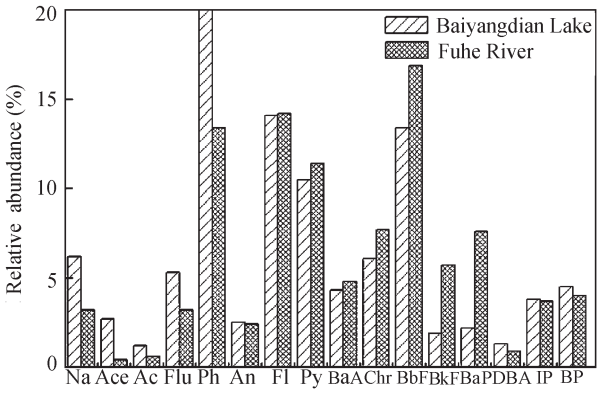

Fig. 4 Composition of PAHs in surface sediments from Baiyangdian Lake and Fuhe River. Individual 16 PAHs include naphthalene (Na), acenaphthylene (Ace), acenaphthene (Ac), fluorene (Flu), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), indeno[1,2,3- cd]pyrene (IP), benzo[g,h,i]perylene (BP).

2.3 PAHs in sediment

2.3.1 Concentrations of PAHs

All PAH target compounds were detectable in sediment samples collected from Baiyangdian Lake and Fuhe River. The concentrations of PAHs (sum of 16 EPA priority PAHs) in sediments of Baiyangdian Lake varied from 101.3 to 322.8 ng/g (mean 189.9 ng/g), which are significantly lower than those determined in Fuhe River sediments (191.6–6360.5 ng/g, mean 2661.9 ng/g) ($p < 0.05$). The highest PAHs concentration (6360.5 ng/g) was found in S3 in Fuhe River, the lowest concentration (101.3 ng/g) was found in S18 in Baiyangdian Lake (Table 1). The level of PAHs in sediments from Fuhe River was 14 times higher than that of sediments from Baiyangdian Lake, indicating that Fuhe River was seriously contaminated by PAHs. Generally, industrialized and urbanized region showed high level of PAHs contamination. The spatial distribution of PAHs in Baiyangdian Lake and Fuhe River was complicated due to the intricate ecosystem. Baiyangdian Lake is located in the lower of Fuhe River, and industrial contaminated sources are fewer than Fuhe River. Fuhe River flows through Baoding City, which is a medium-sized industrial city. Industrial activities are likely to be mainly sources of PAHs in Fuhe River.

The concentrations of the 16 PAHs were compared with that in other areas. The concentration of PAHs in sediments from Baiyangdian Lake (101.3–322.8 ng/g) was comparable to those of Tonghui River (127–928 ng/g) (Zhang et al., 2004), Yangtze River Estuary (107–633 ng/g) (Liu et al., 2008), Yalvjiang River (68–1500 ng/g) (Wu et al., 2003), Minjiang River Estuary (175–817 ng/g) (Yuan et al., 2001), and Gulf of Trieste (35–682 ng/g) (Notar et al., 2001). However, the PAHs concentrations were lower than those reported in urbanized and industrialized areas, such as Pearl River (1434–10,811 ng/g) (Mai et al., 2002), and Meiliang Bay, Tai Lake (1207–4754 ng/g) (Qiao et al., 2006). The concentration of PAHs in Fuhe River was close to those obtained from Meiliang Bay, Taihu Lake (Qiao et al., 2006), and lower than those of urbanized and industrialized areas, such as Pearl River (Mai et al., 2002).

2.3.2 Profiles and sources of PAHs

Compositions and relative abundance of individual PAHs in sediments of Baiyangdian Lake and Fuhe River are shown in Fig. 4. Phenanthrene (20.2%), fluoranthene (14.1%) and benzo[b]fluoranthene (13.4%) were the most predominant PAHs in sediments of Baiyangdian Lake. For sediments in Fuhe River, benzo[b]fluoranthene (16.9%) was the most predominant followed by fluoranthene (14.2%) and phenanthrene (13.4%). The profiles were similar to those of Tonghui River (Zhang et al., 2004) and Taihu Lake (Qiao et al., 2006). In contrast, it was different profiles of sediments from marine environment (Ma et al., 2001).

Generally, biomass and fossil fuel combustion process and release of uncombusted petroleum products are the main sources of anthropogenic PAHs in the environment. Pyrogenic sources were depleted in low molecular weight (2–3 rings) PAHs (LMW) and enriched in high molecular weight (4–6 rings) PAHs (HMW), which led to LMW/HMW ratio < 1. Petrogenic sources such as fuel oil or light refined petroleum products, were dominated by LMW PAHs and had LMW/HMW > 1 (Wang et al., 2006). The ratio of anthracene (An) to sum of An and phenanthrene (Ph), and fluoranthene (Fl) to the sum of the fluoranthene (Fl) and pyrene (Py) had been distinguished pyrogenic and petrogenic sources of PAHs. The ratio of An/(An + Ph) < 0.1 were mainly from petroleum contamination (petrogenic source), while those with the ratio > 0.1 were typical of combustion sources (pyrogenic source) (Li et al., 2006). The ratio of Fl/(Fl + Py) < 0.4 suggests typical petroleum contamination, while Fl/(Fl + Py) > 0.5 indicates that PAHs are mainly from combustion of grass, wood and coal, and 0.4 < Fl/(Fl + Py) < 0.5 from liquid fossil fuel combustion (Yunker and Macdonald, 2003).

In the present study, the ratios of LMW/HMW in all sediment samples were less than 1, and the ratios of Fl/(Fl + Py) were greater than 0.5, indicating pyrogenic sources (combustion of biomass and coal) of PAHs. In past years, there were many chemical plants, paper mills, and cell

plants along Fuhe River. Although these plants were forced to close by local government in recent years because of contaminations, the PAHs in sediments derived from these plants many years ago are still abundant in Fuhe River. The ratios of An/(An + Ph) in sediments from Baiyangdian Lake were mostly less than 0.1 except S14, whereas the ratios of all the sediments from Fuhe River were higher than 0.1 within the range of 0.11–0.22. The result suggested that PAHs found in sediments of Baiyangdian Lake mainly derived from pyrogenic sources, and Fuhe River from petrogenic sources, such as leakage of oil or petroleum products. Accordingly, PAHs in Baiyangdian Lake mainly derived from pyrogenic sources, while PAHs in Fuhe River from mixed input of pyrogenic and petrogenic sources. The results were consistent with those of Haihe River, North China (Jiang et al., 2007).

2.4 Ecotoxicological concern

Despite many studies have been carried out the assessment on biological effects, there is no uniform standard available so far. Many publications reviewed the effects range low (ERL) and the effects range median (ERM) values for the assessment of biological adverse effects (Long et al., 1995). The ERL and ERM values are intended to define chemical concentration ranges that are rarely, occasionally, or frequently associated with adverse biological effects including altered benthic communities, histopathological disorders in fish, EC_{50} or LC_{50} concentrations and toxicity predicted by models. The levels of the contaminants in the present study were compared with the ERL and ERM values (Table 2). For DDTs, S1 had constituents frequently posing biological impairment with concentrations (51.3 ng/g) much greater than the value of ERM, and other sites occasionally posed possible adverse biological effects. For PCBs, S4, S10 and S12 posed possible adverse biological effects, with concentrations 103.6, 101.0, and 42.5 ng/g, respectively, which are greater than the value of ERL. For PAHs, the total concentrations of PAHs for most sites were lower than the values of ERL except for S1, S3, and S6, which may lead possible adverse biological effects.

In order to roughly evaluate the ecotoxicological significance of OCPs contamination in Baiyangdian Lake and Fuhe River sediments, the data were compared with the Canadian environmental quality guideline for marine sediment (CCME, 2002). The guideline specifies the interim sediment quality guideline (ISQG) and the probable effect level (PEL). The ISQG represents the contaminants levels, below which an adverse effect would rarely be observed. PEL represents the concentration, above which adverse effect would frequently occur. In the present study, 58% and 26% of the stations showed DDT concentrations over the ISQG value (1.19 ng/g) and the PEL value (4.77 ng/g), respectively, and 26% and 5% of the stations for PCBs concentrations exceeded the ISQG value (21.5 ng/g) and the PEL value (189 ng/g), respectively. Among PAHs individuals, fluorene, naphthalene, and phenanthrene concentrations exceeded the PEL values in the 5%, 5%, and 21% of the stations, respectively. Based on these results, it could be concluded that DDTs were the main compound of concern in the Baiyangdian Lake and Fuhe River. Ecotoxicological effect of sediment from Fuhe River on benthic organisms was higher than that of Baiyangdian Lake. Therefore, the contamination of Fuhe River should be paid more attention.

3 Conclusions

OCPs, PCBs and 16 priority PAHs were determined in sediment samples collected from 19 sites from Baiyangdian Lake and its inflowing river Fuhe River, North China. The levels of PAHs in surface sediments were relatively high. Contamination levels of sedimentary POPs in Baiyangdian Lake and Fuhe River can be categorized as low to moderate compared to other urbanized regions worldwide. With regards to OCPs, α-HCH, and *p,p′*-DDT were the most abundant compounds in sediments of Baiyangdian Lake and Fuhe River. Among the PCB con-

Table 2 Effects range low (ERL) and effects range median (ERM) guideline values for DDTs, PCBs and PAHs (ng/g dw)

	ERL	ERM	Baiyangdian Lake		Fuhe River	
			Average	Maximum	Average	Maximum
∑DDTs	**1.6**	**46.1**	**2.6**	**3.1**	**16.2**	**51.3**
∑PCBs	**22.7**	**180**	**3.6**	**7.6**	**46.3**	**197.8**
Naphthalene	160	2100	10.1	21.7	121.8	654.2
Acenaphthylene	44	640	4.0	5.6	11.1	42.1
Acenaphthene	16	500	2.6	5.4	19.9	59.8
Fluorene	19	540	8.5	10.5	76.9	262.7
Phenanthrene	240	1500	35.3	52.2	383.7	1206.3
Anthracene	853	1100	5.3	10.9	67.1	176.6
Fluoranthene	600	5100	26.9	46.9	417.6	1054.1
Pyrene	665	2600	20.2	36.9	328.0	858.7
Benzo[a]anthracene	261	1600	9.1	19.2	131.9	344.4
Chrysene	384	2800	12.5	26.9	182.8	444.6
Benzo[b]fluoranthene	NA	NA	26.7	53.9	401.9	1075.9
Benzo[k]fluoranthene	NA	NA	4.8	13.6	161.4	786.0
Benzo[a]pyrene	430	1600	5.0	12.7	217.8	664.7
Dibenzo[a,h]anthracene	64.3	260	2.8	5.8	15.9	45.2
Indeno[1,2,3-cd]pyrene	NA	NA	7.3	13.8	66.9	190.0
Benzo[g,h,i]perylene	NA	NA	8.8	17.0	57.2	181.6
∑PAHs	**4000**	**44,792**	**189.9**	**322.8**	**2661.9**	**6360.5**

generers, PCB 28/31, PCB 40/103, PCB 60, PCB 110, and PCB 118 were predominant in sediments of Baiyangdian Lake and Fuhe River. For PAHs, phenanthrene, fluoranthene, pyrene, and benzo[b]fluoranthene were predominant congeners in sediments studied. Analysis of the possible sources of PAHs suggests mixed input of pyrogenic (combustion of wood and coal) and petrogenic (leakage of oil and petroleum products) PAH origin. Risk assessment of sediment indicated that sediments in Fuhe River were likely to pose potential biological impact. Further research should be performed to investigate the toxicological effects of POPs in sediments from Baiyangdian Lake and Fuhe River.

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