



Distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in surface water and sediments from Baiyangdian Lake in North China

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Abstract

Persistent organochlorine compounds, including hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs) and polychlorinated biphenyls (PCBs) were analyzed in surface water and sediments from Baiyangdian Lake, North China. Total concentrations of HCHs, DDTs and PCBs in surface water were in the range of 3.13–10.60, 4.05–20.59 and 19.46–131.62 ng/L, respectively, and total concentrations of HCHs, DDTs and PCBs in sediments were 1.75–5.70, 0.91–6.48 and 5.96–29.61 ng/g dry weight, respectively. Among the groups of HCHs (sum of α -HCH, β -HCH, γ -HCH and δ -HCH) and DDTs (sum of DDT, DDD and DDE), the predominance of β -HCH, DDE and DDD in water and sediment samples was clearly observed. This observation suggested that β -HCH was resistant to biodegradation and the DDTs had been transformed to its metabolites, DDE and DDD. For PCBs, penta-, hexa- and hepta-chlorinated congeners were the most abundant compounds in the both phases. Furthermore, the partitioning of chlorinated compounds between sediment and water was investigated to understand their transport and fates in aquatic ecosystems. The results indicated that average logs of organic carbon-normalized sediment-water partition coefficients ($\log K'_{oc}$) for OCPs varied between 3.20 and 5.53, and for PCBs, $\log K'_{oc}$ values ranged from 3.19 to 5.57. The observed $\log K'_{oc}$ was lower than their equilibrium $\log K_{oc}$ predicted from linear model, which may be attributed to the solubility enhancement effect of colloidal matter in water phase and the disequilibrium between sediment and water.

Key words: organochlorine pesticides; polychlorinated biphenyls; water; sediment; Baiyangdian Lake; North China

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Introduction

Organochlorine compounds (OCs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are ubiquitous pollutants in the aquatic environment, and have been of great concern owing to their persistence, chronic toxicity and bioaccumulation (Tanabe et al., 1994). Hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) were the most widely used pesticides in China between 1950s and 1980s. The amounts of HCHs and DDTs produced in China were 4.9 and 0.4 million tons, respectively, accounting for 33% and 20% of the total worldwide productions (Zhang et al., 2002). Even after the ban on the use and production of technical HCHs and DDTs in 1983, 11 400 tons of lindane (γ -HCH) was still produced between 1991 and 2000 (Li et al., 2001). Furthermore, DDTs has been continuously

produced for about 20 years due to export demands and dicofol production (Qiu et al., 2005). It was reported that approximately 10 000 tons of PCBs were produced from 1965 to the early 1980s in China, accounting for about 1% of the global production (Zheng et al., 2010). The environmental risks and hazards of OCs should be paid more attention, as high residual levels of OCs in various environmental media were frequently detected in China (Mai et al., 2002; Zhang et al., 2003; Chen et al., 2004; Zhou et al., 2006).

In China, the OCs surveys have mostly been focused on harbors, rivers and estuaries (Mai et al., 2002; Zhou and Maskaoui, 2003; Zhou et al., 2006; Wang et al., 2007), however, little information is available on OCs pollution in the inland lakes that play important roles in the economic development of China. Baiyangdian Lake is the largest shallow lake in North China, and located about 150 km southwest of Beijing. Currently, there are more than

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243,000 people living in 39 villages scattered around the lake. As an important base of aquaculture in North China, Baiyangdian Lake provides aquatic products for nearly seven million people. The lake, with a surface area of 366 km² and a maximum depth of 6 m, consists of more than 100 small and shallow lakes linked by ditches. There were rivers in the upstream of Baiyangdian Lake in the past, and most of them have dried up in recent years. The only surviving tributary, the Fuhe River, carries large amounts of industrial and domestic sewage from Baoding City into the lake. With the rapid economic development and population rise, the water quality of the Baiyangdian Lake has deteriorated and the water contamination has threatened water supply. Although a few studies have investigated the contamination status of OCPs in Baiyangdian Lake (Dou and Zhao, 1998; Hu et al., 2010), these studies mostly focused on bioaccumulation and biomagnifications in the food web. Up to now, there has been no comprehensive investigation of pollution by OCPs and PCBs in water and sediments from Baiyangdian Lake.

The main objectives of this article are to determine the levels of OCPs and PCBs in water and sediment from Baiyangdian Lake and to assess their partitioning between the sediment and water phase. The current contamination levels are essential for us to make a better assessment of the likely impacts of these organic contaminants on the ecosystem and the sustainability of aquaculture in the area.

1 Materials and methods

1.1 Sampling

Fifteen sampling sites (Fig. 1) throughout the lake were selected based on hotspots of pollution in the lake, such as the entrance of river, the aquaculture areas, areas near

the villages, or areas slightly affected by human activities. Sampling from Baiyangdian Lake was conducted in July, 2008. Surface sediment samples (0–5 cm deep) were collected with a stainless steel static gravity corer. The top 1 cm surface layer was carefully removed with a stainless steel spoon, and stored in aluminium containers. At the same time, surface water samples were collected at the sediment sampling sites using pre-cleaned aluminium jars. The basic physicochemical parameters of water and sediment samples collected from the Baiyangdian Lake are shown in Table 1. All samples were transported on ice to the laboratory immediately. Sediment samples were freeze-dried using a freeze drier (FD-1A, China), and water samples were stored at –20°C. Freeze-dried sediments were ground with a mortar, sieved through a 100-mesh sieve, and then stored at –20°C in pre-cleaned dark glass bottles before extraction.

1.2 Chemicals

OCPs standards (α -HCH, β -HCH, γ -HCH, δ -HCH, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, heptachlor, aldrin, heptachlor epoxide B, heptachlor epoxide A, α -endosulfan, β -endosulfan, dieldrin, endrin and methoxychlor), PCBs standards (PCB-17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208 and 209), internal standard of pentachloronitrobenzene (PCNB), and surrogates of 4,4'-dichlorobiphenyl and 2,4,5,6-tetrachloro-*m*-xylene were all purchased from AccuStandard Inc. (USA). All solvents (hexane, acetone, ethyl acetate, methanol and dichloromethane) used for sample processing and analysis, were HPLC grade and purchased from Dikma Technologies (USA).



Fig. 1 Sampling locations in Baiyangdian Lake.

Table 1 Physicochemical properties of water and sediment samples collected from Baiyangdian Lake

Sites	Water				Sediment			
	pH	E_h (mV)	DO (mg/L)	DOC (mg/L)	TOC (g/kg)	BC (g/kg)	Mud content ^a (%)	CEC (cmol/kg)
1	8.62	145	5.36	15.45	15.76	1.42	24.59	4.81
2	9.22	150	3.79	15.31	19.95	1.80	31.97	4.90
3	8.65	138	5.21	12.59	11.37	1.02	20.35	4.86
4	8.85	167	5.52	14.62	17.36	1.56	17.23	4.98
5	9.11	156	5.96	14.92	16.56	1.49	33.11	5.32
6	9.01	161	7.15	14.12	9.88	0.89	21.12	6.00
7	8.40	177	5.05	14.64	34.71	3.12	39.65	5.03
8	8.77	145	5.43	14.57	14.17	1.28	30.15	4.92
9	8.69	180	4.70	13.60	10.87	0.98	29.22	5.41
10	9.38	164	6.78	15.13	25.95	2.34	36.42	5.69
11	8.67	131	7.45	12.34	8.58	0.77	38.60	5.09
12	8.85	111	5.20	12.75	12.57	1.13	28.38	4.94
13	9.27	101	7.50	10.78	11.97	1.08	34.37	5.29
14	8.51	121	4.23	11.12	10.38	0.93	19.12	4.76
15	9.50	130	6.40	13.42	17.96	1.62	13.48	4.71

^a Sum of silt and clay. E_h : redoxpotential; DO: dissolved oxygen; DOC: dissolved organic carbon; TOC: total organic carbon; BC: black carbon; CEC: cation exchange capacity.

1.3 Sample extraction and preparation

1.3.1 Sediment samples

Sample extraction for OCPs was largely based on established procedures (Zhang et al., 2002). Briefly, 20 g of homogenized samples spiked with 4,4'-dichlorobiphenyl as surrogate, was Soxhlet-extracted with a 1:1 (V/V) hexane and dichloromethane solvent mixture for 48 hr. The extract was concentrated and solvent-exchanged to hexane and further reduced to approximately 1 mL under a gentle nitrogen stream. A 1:2 aluminum/silica gel column (1 cm i.d.) was used to clean up and fractionate the extract. The column was flushed with 15 mL of hexane. Then it was eluted with 70 mL of dichloromethane/hexane (3:7, V/V) to yield the OCPs fraction. This fraction was concentrated and solvent-exchanged to hexane. The PCNB solution (10 µg/mL) of 10 µL was added as an internal standard prior to gas chromatograph mass spectrometer (GC-MS) analysis.

Sample extraction for PCBs was also based on established procedures (Mai et al., 2002). Briefly, 20 g freeze-dried sample spiked with surrogate standard (4,4'-dichlorobiphenyl), was Soxhlet-extracted with hexane and acetone solvent mixture (1:1, V/V) for 24 hr. Cleanup was done by treating the concentrated extract with 12 g florisil wet column and eluted with 100 mL hexane. The hexane fraction was then reduced to 1 mL and spiked with PCNB as an internal standard prior to GC-MS analysis.

1.3.2 Water samples

Filtered water samples, which spiked with surrogate standard 2,4,5,6-tetrachloro-*m*-xylene, were extracted using a solid phase extraction (SPE) system (Supelco, USA), following established procedures (Zhou et al., 2000). The C18 SPE cartridges (500-mg, Waters, USA) were first conditioned with 5 mL of ethyl acetate, then 5 mL of methanol followed by 2×5 mL of deionised water. Water samples (1.0 L) were passed through the cartridges at a flow rate of 6 mL/min using vacuum. Following extraction, the cartridges were eluted with 10 mL of ethyl acetate. Then, the extracts were dehydrated with anhydrous Na₂SO₄, concentrated to 1 mL using a gentle nitrogen

stream, and 10 µL (10 ng/mL) PCNB was added for GC-MS analysis.

1.4 Instrument analysis

OCPs and PCBs were analyzed by a Varian CP-3800 gas chromatograph, equipped with a Varian 4000 mass spectrometer. Separations were carried out using a VF-5MS column (30 m × 0.25 mm i.d. 0.25 µm film thickness, Varian, USA). Helium (99.999% pure) was used as carrier gas at a constant flow of 0.1 mL/min. For analysis of OCPs, the oven temperature began at 100°C, and was increased to 190°C at a rate of 20°C/min; this temperature was maintained for 1.0 min, then was raised to 235°C at a rate of 4°C/min, and held for 10 min. For analysis of PCBs, the oven temperature was set at 150°C for 2 min, and was then increased at a rate of 4°C/min to 290°C, at which it was held for 2 min.

For sediment samples, silt and clay contents of sediment were determined with a laser particle size analyzer (Malvern Mastersizer 2000, England). Total organic carbon (TOC) was measured using an Elementar Liqui-TOC (Hanau, Germany) after removal of carbonates. Black carbon (BC) was also measured using the Elementar Liqui-TOC (Hanau, Germany) after removal of the non-BC organic matter by chemical oxidation method. Cation exchange capacity (CEC) of sediment was determined referring to the standard procedures (International Organization for Standardization, 11260). For water samples, the pH, oxidation-reduction potential (E_h or ORP) and dissolved oxygen (DO) were determined by pH/ORP and DO sensor (Hach Company, USA). Dissolved organic carbon (DOC) was analyzed by Elementar Liqui-TOC (Hanau, Germany) after filtration and acidification.

1.5 Quality assurance and quality control

Strict quality control procedures were conducted throughout the whole process. For every set of 10 samples, procedural blanks, spiked blanks (standards spiked into solvent), matrix spikes/matrix spike duplicates, and sample duplicates were processed. None of the target compounds

were detected in the procedural blanks for both water and sediments. Spiked water and sediment samples were determined with good precision and recoveries. Relative standard deviations of the analytical methods for both OCPs and PCBs were less than 26%, and the mean values were used as the representative values for the sample. For OCPs, recoveries of surrogate ranged from 71.36%–84.32% and 54.31%–77.64% for water and sediment, respectively. For PCBs, recoveries varied from 74.15%–91.36% and 61.34%–88.31% for water and sediment, respectively. The limits of detection (LOD) of OCPs ranged from 0.17–1.31 ng/L for water samples, and 0.08–0.24 ng/g for sediment samples. The LOD of PCBs varied from 0.11–0.79 ng/L for water samples, and 0.06–0.32 ng/g for sediment samples.

2 Results

2.1 Concentrations of OCs in water

Ten OCPs (α -HCH, β -HCH, γ -HCH, δ -HCH, o,p' -DDD, p,p' -DDD, o,p' -DDE, p,p' -DDE, o,p' -DDT and p,p' -DDT) were detected at all 15 sites. The residual concentrations in surface water are summarized in Table 2. The total concentrations of OCPs in water ranged from 11.37 to 30.43 ng/L, with a mean value of 17.46 ng/L. The greatest concentration was observed at site 6.

Among OCPs, residues of total HCHs (Σ HCHs, the summation of α -, β -, γ - and δ -HCH) and DDTs (Σ DDTs, summation of o,p' -DDD, p,p' -DDD, o,p' -DDE, p,p' -DDE, o,p' -DDT and p,p' -DDT) in water varied from 3.13 to 10.60 ng/L (mean 6.18 ng/L), and 4.05 to 20.59 ng/L (mean 11.28 ng/L), respectively. Among HCHs, β -HCH isomer was much higher than α -, γ - and δ -HCH.

The mean concentrations of the HCHs isomers in water decreased in the following order: β -HCH (3.68 ng/g) > α -HCH (1.12 ng/g) > γ -HCH (1.08 ng/g) > δ -HCH (0.41 ng/g). The isomer of β -HCH made up of 60% of the total HCHs in water. For DDTs, DDE (sum of o,p' -DDE and p,p' -DDE, mean concentration 4.59 ng/L) were the dominant DDTs followed by DDD (o,p' -DDD and p,p' -DDD, 4.63 ng/L) and DDT (o,p' -DDT and p,p' -DDT, 2.60 ng/L). DDE and DDD occupied 41% and 40% of total DDTs in water, respectively. Comparing with other regions around the world, the levels of HCHs in surface water from Baiyangdian Lake were much lower than those in the Qiantang River, China (Zhou et al., 2006) and Minjiang River, China (Zhang et al., 2003), but were higher than that reported in the Baikal Lake, Russia (Iwata et al., 1995) (Table 3). The status of DDTs in water from the Baiyangdian Lake was similar to that of HCHs. According to the guideline recommended by the State Environment Protection Agency of China (GB3838-2002), the criteria maximum concentration of HCHs and DDTs in the surface water should be less than 2000 and 1000 ng/L, respectively. Concentrations of HCHs and DDTs in all water samples from the Baiyangdian Lake were within the required range of the guideline, indicating that HCHs and DDTs residues in the study area might be neglected.

The total concentrations of PCBs (Σ PCBs, sum of 39 congeners) in water ranged from 19.46 to 131.62 ng/L, with mean value of 45.35 ng/L (Table 2). Concentration at site 1 was significantly elevated compared to the other 14 sites. The levels of PCBs in water from Baiyangdian Lake were higher than those of Baikal Lake, Russia (Iwata et al., 1995) and Xiamen Harbor, China (Zhou et al., 2000), but were lower than that of Minjiang River,

Table 2 OCPs and PCBs concentrations in surface water and sediments from Baiyangdian Lake

Compounds	Water (ng/L)			Sediments (ng/g dw)			Compounds	Water (ng/L)			Sediment (ng/g dw)		
	Mean	SD ^a	Range	Mean	SD	Range		Mean	SD	Range	Mean	SD	Range
α -HCH	1.12	0.63	0.17–2.32	0.58	0.70	0.13–2.94	PCB110	1.04	0.82	nd–3.21	1.04	1.01	0.21–4.20
β -HCH	3.68	1.39	1.26–6.00	1.25	0.62	0.38–2.29	PCB118	1.88	2.14	0.23–8.10	0.95	0.71	nd–2.95
γ -HCH	1.08	0.84	0.36–3.54	0.63	0.32	nd–1.05	PCB128	4.32	4.68	nd–16.84	0.51	0.27	nd–0.99
δ -HCH	0.41	0.15	nd ^b –0.67	0.26	0.08	0.13–0.42	PCB132	2.09	1.58	nd–4.86	0.48	0.20	nd–0.87
Σ HCHs	6.18	2.26	3.13–10.60	2.68	0.10	1.75–5.70	PCB138/158	1.50	0.87	nd–3.21	0.40	0.20	nd–0.75
o,p' -DDD	2.47	1.52	nd–6.31	0.33	0.19	nd–0.85	PCB149	1.57	0.93	nd–3.74	0.47	0.25	nd–0.88
p,p' -DDD	2.16	2.14	0.17–8.88	0.76	1.22	0.26–5.11	PCB151	0.93	0.15	nd–1.26	0.56	0.20	nd–0.95
o,p' -DDE	2.43	1.10	0.98–5.26	0.32	0.07	nd–0.46	PCB153	1.21	0.70	nd–2.84	0.46	0.30	nd–1.03
p,p' -DDE	2.16	1.00	1.28–4.32	0.43	0.21	nd–0.77	PCB156	1.82	2.23	0.13–8.78	0.79	0.41	0.25–1.65
o,p' -DDT	1.40	0.32	nd–2.14	0.27	0.11	nd–0.54	PCB169	5.58	1.84	2.63–10.32	0.64	0.31	nd–1.24
p,p' -DDT	1.20	0.30	0.68–1.64	0.52	0.40	0.24–1.54	PCB170	2.40	1.68	nd–4.36	0.79	0.32	nd–1.25
Σ DDTs	11.28	3.96	4.05–20.59	2.26	1.32	0.91–6.48	PCB171	6.14	12.58	nd–39.38	0.57	0.30	nd–1.14
Σ OCPs	17.46	4.77	11.37–30.43	4.93	1.56	3.32–8.64	PCB177	3.33	5.12	nd–15.68	0.58	0.41	nd–1.67
PCB17/18	1.84	1.62	nd–5.53	0.61	0.30	nd–1.11	PCB180	2.11	2.02	nd–6.32	0.49	0.31	nd–1.32
PCB28/31	1.50	0.94	nd–3.56	0.80	0.64	0.13–2.63	PCB183	1.16	0.69	nd–2.41	0.57	0.25	nd–0.97
PCB33	1.58	1.33	0.38–5.46	0.82	0.54	nd–1.95	PCB187	4.01	5.10	nd–16.94	0.55	0.27	nd–0.98
PCB44	1.68	1.02	nd–3.27	0.80	0.81	nd–3.47	PCB191	1.14	0.50	nd–2.14	0.45	0.30	nd–0.99
PCB49	1.25	1.45	nd–4.53	0.41	0.25	nd–0.96	PCB194	1.13	0.49	nd–2.08	0.68	0.23	nd–0.93
PCB52	0.55	0.16	nd–0.94	0.40	0.30	nd–1.15	PCB195	1.14	0.94	nd–3.45	0.41	0.19	nd–0.64
PCB70	1.32	0.83	nd–3.12	0.36	0.25	nd–0.98	PCB199	1.86	1.55	nd–4.80	0.50	0.28	nd–0.97
PCB74	1.09	0.70	nd–2.86	0.38	0.27	nd–1.01	PCB205	1.02	0.27	nd–1.36	0.39	0.21	nd–0.74
PCB87	1.64	1.11	nd–3.65	1.38	1.40	0.23–6.15	PCB206	2.09	1.36	nd–4.21	0.50	0.26	nd–1.00
PCB99	1.53	0.73	nd–2.91	0.96	0.65	nd–2.65	PCB208	0.82	0.43	nd–1.41	0.41	0.28	nd–0.97
PCB101	1.21	0.50	nd–2.12	0.73	0.30	0.36–1.21	PCB209	0.89	0.50	nd–1.32	0.39	0.14	nd–0.65
PCB105	1.19	0.69	0.43–3.24	0.54	0.30	nd–1.08	Σ PCBs	45.35	25.40	19.46–131.62	18.91	6.35	5.96–29.61

^a SD: standard error of mean ($n = 30$); ^b nd: not detected.

Table 3 Concentrations of HCHs, DDTs and PCBs in surface water and sediments from lakes, rivers and estuaries around the world

	Location	Year	∑HCHs	∑DDTs	∑PCBs	Reference
Water (ng/L)	Baiyangdian Lake, China	2008	3.13–10.60	4.05–20.59	19.46–131.62	This study
	Baikal Lake, Russia	1992	0.056–0.96	nd ^a –0.015	0.018–0.59	Iwata et al., 1995
	Qiantang River, China	2005	0.74–202.8	0.40–97.54	NA ^b	Zhou et al., 2006
	Minjiang River, China	1999	52.09–515.0	40.61–233.5	203.9–2473	Zhang et al., 2003
	Xiamen Harbor, China	1998	3.4–27.8	0.9–2.3	0.1–1.7	Zhou et al., 2000
Sediment (ng/g dw)	Baiyangdian Lake	2008	1.75–5.70	0.91–6.48	5.96–29.61	This study
	Baikal Lake, Russia	1992	0.019–0.12	0.014–2.70	0.08–6.1	Iwata et al., 1995
	Taihu Lake, China	2006	53.95	0.07–5.75	NA	Zhao et al., 2009
	Hanoi area, Vietnam	2006	<0.2–36	4.4–1100	1.3–384	Hoai et al., 2010
	Xiamen Harbor, China	1998	<0.01–0.14	<0.01–0.06	<0.01–0.32	Zhou et al., 2000
	Minjiang River, China	1999	2.99–16.21	1.57–13.06	15.14–57.93	Zhang et al., 2003
	Pearl River Delta, China	1997	nd–17.0	2.6–1629	10.2–486	Mai et al., 2002

^a nd: not detected; ^b NA: no data available.

China (Zhang et al., 2003) (Table 3). According to the guideline of US Environmental Protection Agency (<http://www.epa.gov/waterscience/criteria/wqcriteria.html>), surface water that is considered to pose no hazard to the aquatic and human health, the concentration of PCBs should be less than 14 ng/L. Therefore, the quality of surface water of Baiyangdian Lake has been seriously contaminated by the presence of PCBs, indicating risk to the aquatic environment and human health.

2.2 Concentrations of OCs in sediments

HCHs and DDTs were detected in all sediment samples, with total concentrations ranging from 1.75 to 5.70 ng/g, and 0.91 to 6.48 ng/g, respectively (Table 2). In HCHs, the mean concentrations of the HCHs isomers in sediments decreased in the following order: β -HCH (1.25 ng/g) > γ -HCH (0.63 ng/g) > α -HCH (0.58 ng/g) > δ -HCH (0.26 ng/g), and the isomer of β -HCH constituted about 50% of total HCHs in sediments. For DDTs, DDD was detected at the highest level (0.26–5.52 ng/g), followed by DDE (0.20–1.14 ng/g) and DDT (0.17–2.08 ng/g). DDD and DDE constituted 45% and 31% of total DDTs in sediments, respectively. In comparison, the levels of HCHs in sediments from Baiyangdian Lake were higher than those observed in sediments of Baikal Lake, Russia (Iwata et al., 1995) and Xiamen Harbor, China (Zhou et al., 2000), were similar to those in Minjiang River, China (Zhang et al., 2003) and Hanoi area, Vietnam (Hoai et al., 2010), but were lower than in Taihu Lake, China (Zhao et al., 2009) (Table 3). The levels of DDTs in sediments from the Baiyangdian Lake were much lower than those in the Hanoi area, Vietnam (Hoai et al., 2010) and Pearl River Delta, China (Mai et al., 2002), and were similar to that in the Taihu Lake, China (Zhao et al., 2009) and Minjiang River, China (Zhang et al., 2003) (Table 3). Compared with the previous studies in Baiyangdian Lake, concentrations of HCHs and DDTs in sediments were a little greater than the levels found in 1995, which ranged from 0.69 to 2.26 ng/g for HCHs and 0.56 to 2.61 ng/g for DDTs (Dou and Zhao, 1998).

Total PCBs concentrations in sediments ranged from 5.96 to 29.61 ng/g, with a mean value of 18.91 ng/g (Table 2). The distribution pattern of PCBs in sediments was consistent with that in water, and the greatest con-

centration was also observed at site 1. The PCBs levels in sediments from Baiyangdian Lake were greater than those of sediments from Baikal Lake, Russia (Iwata et al., 1995) and Xiamen Harbor, China (Zhou et al., 2000), and were similar to that of Minjiang River, China (Zhang et al., 2003), but were lower than those of Hanoi area, Vietnam (Hoai et al., 2010) and Pearl River Delta, China (Mai et al., 2002) (Table 3). As no data is available for past levels of PCBs in the studied area, no conclusion can be made concerning temporal changes in PCB levels in Baiyangdian Lake.

3 Discussion

3.1 Distribution of OCs in water and sediments

Overall, the concentrations of HCHs, DDTs and PCBs in water and sediments varied with the sampling locations. The greatest concentration of OCPs including HCHs and DDTs in water was found at site 6, which is surrounded by many villages. Relatively higher levels (≥ 20 ng/L) were also found at sites 2, 3, 5, 10 and 15. Three possible explanations can be provided. First, sites 2 and 3 are located on the entrance way of Fuhe River. Fuhe River, which running through a heavy industrial city of Baoding, carries about 250,000 tons untreated industrial and domestic wastewater per day produced by Baoding into the Baiyangdian Lake (Hu et al., 2010). Second, sites 5, 6, 10 and 15 are all close to villages and fish or duck aquaculture areas, suggesting agricultural non-point source pollution at these sites represent a major input for OCPs into the Baiyangdian Lake. Third, numerous shipping for tourism, fishery and cargo transport around these sites during sampling, might result in sediment resuspension, and contaminants might be released from sediment into the water. This seems to be a local source of OCPs for these sites. Levels of OCPs in the relatively pristine sites 11 and 14, however, were much lower than those mentioned above. The greatest OCPs concentration in sediments occurred at site 15, which was different from the concentration distribution in water. This may be due to the different historical input and deposit, pesticides chemical and physical properties, and environmental characteristics.

The greatest concentration of PCBs in water was found at site 1, which agreed with the concentration distribution

in sediments. Therefore, site 1 was the most seriously polluted location by PCBs in the lake. Site 1 is situated near the estuary of Baigou River, which is mainly stressed by the non-point source pollutants in the past (Li et al., 2005). High contamination level could also be linked to the emission of PCBs by ships since there are intensive boat activities for tourism and fishery around site 1. PCB has been used as paint additive used on the bottom of boats in the past (Wang et al., 2007). Jin et al. (2002) reported that in China, about 1000 tons PCBs were produced as paint additive before their absolute prohibition in 1980s. Other sites show similar spatial pattern of PCBs in water and sediments. The possible reasons for such a pollution pattern are difficult to be evaluated precisely since the environment of Baiyangdian Lake is impacted by a variety of local activities, such as discharge of sewage, aquaculture and frequent shipping, agricultural activities from the surrounding countryside, and industry activities from the nearby city of Baoding.

To understand further the distribution of OCs in water and sediments, the potential influence of certain parameters on the levels of these compounds has also been discussed. The distribution of hydrophobic organic contaminants such as HCHs, DDTs and PCBs have been shown to be related by dissolved organic carbon (DOC) contents in water and by total organic carbon (TOC) and mud (silt + clay) contents in sediments (Iwata et al., 1995). However, there are still no consistent results concluded about the relationship between OCs and physicochemical characteristics of environment (Zhao et al., 2009). In this study, the concentrations of OCPs and PCBs in water did not show any correlation with DOC contents ($p > 0.05$). This relationship was also observed in the previous work (Mai et al., 2002), showing that many factors contributed to the OCs distribution in water. Pearson's correlation between organochlorine pollutants and physicochemical parameters was also performed in sediments, and significant correlation was obtained between PCBs and mud ($p < 0.05$), but not between PCBs and TOC content. This suggests that distributions of PCBs were not dependent on the content of TOC, but dependent on the content of mud in this area. However, both TOC and mud contents do not appear to correlate well with the HCHs and DDTs concentrations ($p > 0.05$), suggesting that sediment contamination in the study area may be predominantly by anthropogenic inputs than by natural processes (Mai et al., 2002).

3.2 Compositions of OCs in water and sediments

The compositions of HCH isomers in water and sediment are shown in Fig. 2. The typical technical HCHs contains α -, β -, γ -, δ -HCH isomers of 60%–70%, 5%–12%, 10%–15%, and 6%–10%, respectively, while lindane consists of 99% γ -HCH (Iwata et al., 1993). Hence, the ratios of α -HCH to γ -HCH (α/γ) might be between 4 and 7 for the technical mixture, and nearly zero for lindane. In this study, β -HCH was the predominant isomer and was present in all water and sediment samples, while α , γ , δ -HCH were lower, with α/γ -HCH ratios ranging from 0.14 to 3.78 for water, and 0.13 to 8.65 for sediment.

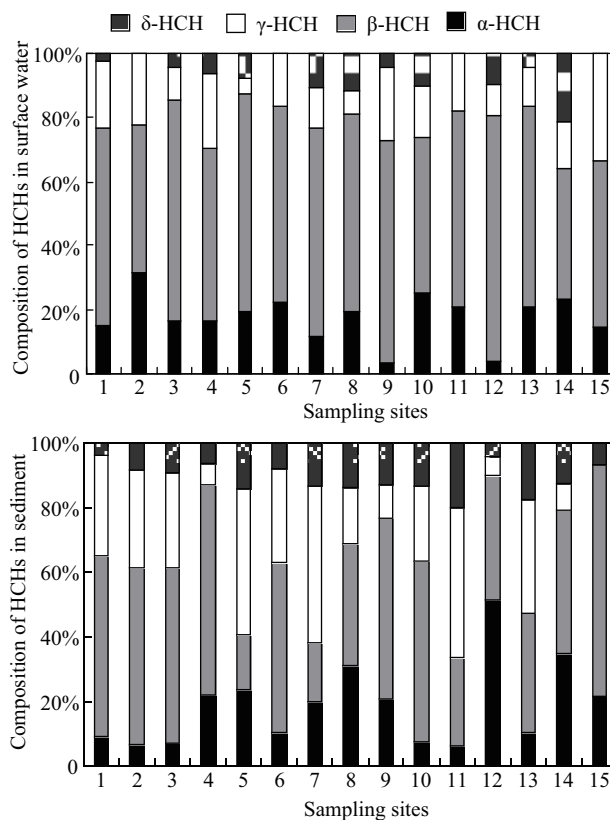


Fig. 2 Percentage composition of HCHs in surface water and sediment.

This indicates that the early usage pattern of HCHs is the mixture of technical HCHs and lindane (Iwata et al., 1995; Strandberg et al., 1998). For one site without γ -HCH detected in sediments, better transportability of α -HCH than γ -HCH or photochemical transformation and biodegradation of γ -HCH to α -HCH in environment may explain this observation (Strandberg et al., 1998). β -HCH was the most stable isomer in HCHs because of its lower vapor pressure, the abundance of β -HCH as the only isomer indicated that most HCHs came from older residues in the study area (Doong et al., 2002).

The compositions of DDT metabolites in water and sediments are shown in Fig. 3. Technical DDTs generally is composed of p,p' -DDT (75%), o,p' -DDT (15%), p,p' -DDE (5%), o,p' -DDE (< 0.5%), p,p' -DDD (< 0.5%), o,p' -DDD (< 0.5%), and unidentified compounds (< 0.5%) (WHO, 1979). DDT degrades to DDE and DDD in the aerobic and anaerobic condition, respectively (Doong et al., 2002). In general, a ratio of $(DDE+DDD)/\sum DDTs$ of more than 0.5 indicates long-term biotransformation of DDT to DDE and DDD, while a ratio of less than 0.5 may indicate recent input of DDT (Hitch and Day, 1992). The ratios of $(DDE+DDD)/\sum DDTs$ found in the Baiyangdian Lake ranged from 0.65 to 0.91 (mean 0.80) for water, and 0.34 to 0.97 (mean 0.74) for sediments, with most values being more than 0.5 (Fig. 4). This indicates that the degradation occurred significantly after the official ban of DDT in 1983, and the DDT compounds in Baiyangdian Lake may be mainly derived from DDT-treated aged and weathered agricultural sources. Moreover, a higher ratio of p,p' -DDE/ p,p' -DDT can be used to indicate the long-range atmospheric transport of DDT compounds, because

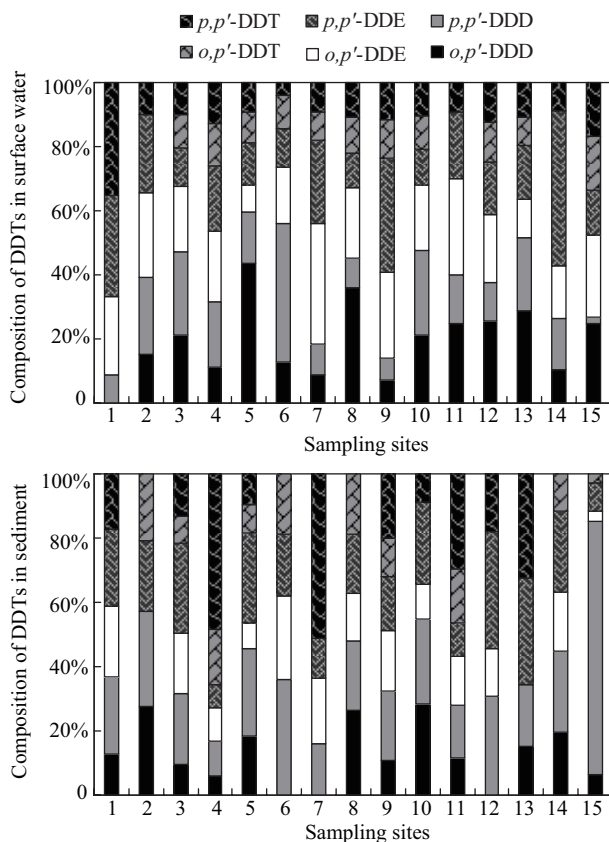


Fig. 3 Percentage composition of DDTs in surface water and sediments.

of more efficient transport of p,p' -DDE than p,p' -DDT (Iwata et al., 1993). The ratios of p,p' -DDE/ p,p' -DDT varied from 0.83 to 5.35 with an average value of 1.99 in water of Baiyangdian Lake, indicating that the DDTs in this area may also come from atmospheric deposition. This result can be confirmed by the fact that DDT is still used to eradicate contagious disease (such as malaria and dengue) in tropical countries, and is then globally redistributed through the atmosphere (Hoai et al., 2010). The DDE/DDD ratios of these two metabolites provide the basic biodegradable condition of the intended environmental compartments (Hitch and Day, 1992). Ratios of DDE/DDD ranged from 0.36 to 6.28 for water, and 0.14 to 2.04 for sediment (Fig. 4). Most of the ratios are greater than 1, indicating DDT had been biotransformed to DDE under aerobic conditions, which was consistent with observed E_h values (101–180 mV) in water (Table 1).

The PCBs congeners which contained 3–10 chlorine atoms were all detected in water and sediment. From Fig. 5, it can be clearly observed that the highly chlorinated compounds (penta-, hexa- and hepta-chlorinated isomers) contribute more to the distribution of PCBs in the study area. On the average, penta- to hepta-chlorinated PCBs compounds collectively accounted for 73%, 65% of total PCBs concentration in water and sediments, respectively. In contrast, the residue levels of the octa-, septa- and deca-chlorinated PCBs congeners were low in all samples matrices, owing to their little usage in the study area. The finding of congener distribution towards more highly chlorinated compounds is consistent with previously published data (Iwata et al., 1995), indicating the preferential

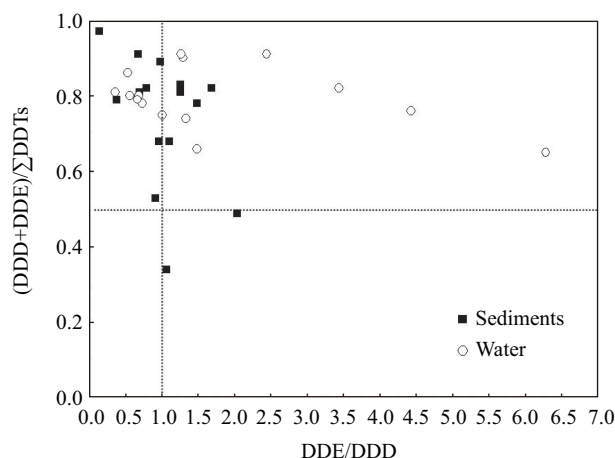


Fig. 4 Relationship between $(\text{DDD}+\text{DDE})/\Sigma\text{DDTs}$ and DDE/DDD from Baiyangdian Lake.

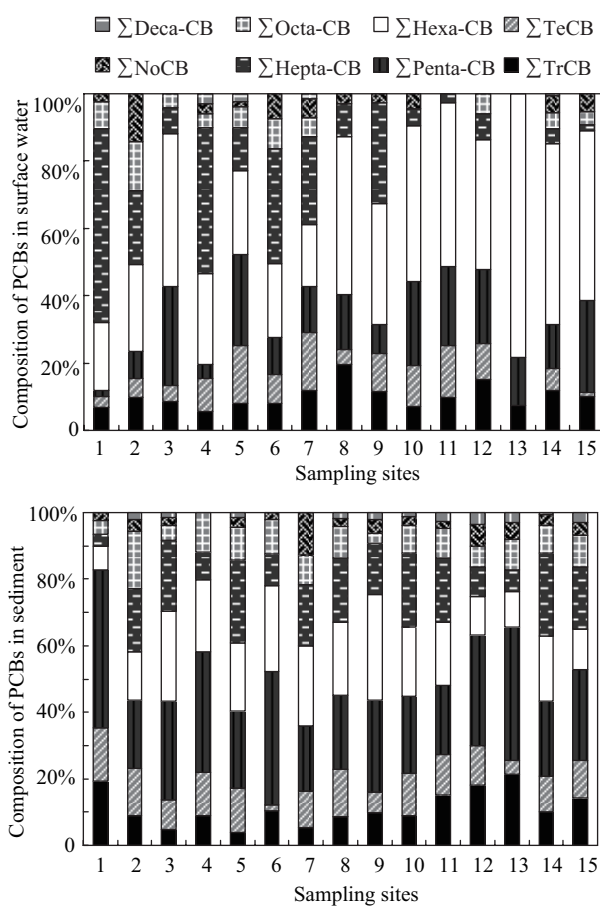


Fig. 5 Percentage composition of PCBs in surface water, and sediments.

retention of these less volatile and more un-degradable compounds in the aquatic environment (MacDonald et al., 1992; Bayarri et al., 2001). Pentachlorinated biphenyl is main PCBs in paint, and the total pentachlorinated biphenyl contents are the highest in Baiyangdian Lake. This suggests that paint in ship bottom is responsible for the PCBs residue in this lake.

3.3 Partition coefficient of OCs between sediment and water

Partitioning between the sediment and water can be quantitatively characterized by the partition coefficient

(K_d) or by an organic carbon-normalized partition coefficient (K_{oc}), that describes the ratio of a chemical's concentration in sediment to that in water at steady-state equilibrium conditions (Karickhoff et al., 1979):

$$K_d = f_{oc} K_{oc} = \frac{C_s}{C_w} \quad (1)$$

where, C_s (ng/g dw) is the concentration of a specific OCs compound in sediment, C_w (ng/L) is the concentration of the same compound in water, and f_{oc} is the mass fraction organic carbon in the sediment.

The observed partition coefficients (K'_d and K'_{oc}) for Baiyangdian Lake were calculated using the measured OCs concentrations in the sediment and water, through the following Eqs. (2) and (3):

$$K'_d = \frac{C_s}{C_w} \quad (2)$$

$$K'_{oc} = \frac{K'_d}{f_{oc}} \quad (3)$$

The partition coefficient was calculated only for those OCs detected and quantified in both sediments and water phases. The $\log K'_d$ for seven OCPs congeners (α -, β -, γ -, δ -HCH, p,p' -DDD, p,p' -DDE and p,p' -DDT) ranged from 1.74 to 4.48, with average values varying from 2.29 ± 0.31 (mean \pm standard deviation) to 2.85 ± 0.32 . The $\log K'_d$ value for 39 PCBs congeners ranged from 1.36 to 3.66, with average values varying from 2.04 ± 0.58 to 2.94 ± 0.46 . The K'_d values obtained for various OCs compounds were divided by sediment organic carbon content, to derive the organic carbon normalized partition coefficients (K'_{oc}). $\log K'_{oc}$ of OCPs varied between 3.20 and 5.53, with average values ranging from 4.12 ± 0.36 to 4.69 ± 0.32 , and, for PCBs, the $\log K'_{oc}$ values varied between 3.19 and 5.57, with average values ranging from 3.86 ± 0.52 to 4.77 ± 0.49 .

The values of $\log K'_{oc}$ were compared with equilibrium $\log K_{oc}$ values calculated using a linear model of Karickhoff et al. (1979):

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (4)$$

Observed $\log K'_{oc}$ values are significantly lower than equilibrium $\log K_{oc}$ values, as shown in Fig. 6. There are several possible explanations for the differences between observed and predicted partition coefficients. First, non-settling colloids and micro-particles not being separated from the dissolved species may contribute to the overestimation of dissolved phase OCs. Studies by Gschwend and Wu (1985) and Zhou et al. (2007) suggested that natural colloidal matter has an unnegligible "solubility enhancement" effect on the distribution of hydrophobic organic contaminants between aqueous and sediment-bound phases. Solubility enhancement is the reduction in the observed solid-solution distribution coefficient (K_d), in the presence of colloidal matter. This makes a compound appear to be more soluble in water, and reduces the total sediment-sorbed amount (Gao et al., 1997). Second, sediments and water under investigation may not have reached chemical

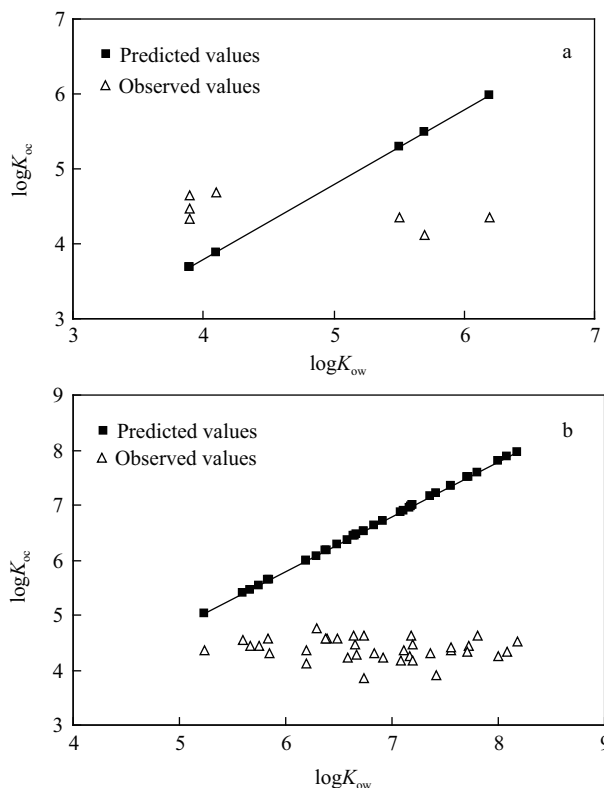


Fig. 6 Relationship between $\log K_{oc}$ and $\log K_{ow}$ for OCPs (a) and PCBs (b) at the sediment/water interface. The predicted values were derived from the relationship $\log K_{oc} = 1.00 \log K_{ow} - 0.21$ (Karickhoff et al., 1979).

equilibrium, as a result, K_d values are significantly lower than the equilibrium partition constant. It may also be due to the fact that in this study natural OCs were analyzed, while in many other reports from laboratory studies non-natural OCs were introduced through spiking. It is known that OCs found naturally and those freshly introduced may behave differently in their partition between sediment and water (Zhou and Maskaoui, 2003).

The observed $\log K'_{oc}$ values for OCPs and PCBs do not appear to show a statistically significant relationship with $\log K_{ow}$ (Fig. 6). This was similar to result obtained by Gobas and Maclean (2003) and Chen et al. (2004), suggesting that for any given chemical, an inherent variability in K_{oc} values is expected as a result of different environmental conditions and equilibration times. Thus it is unlikely that a highly accurate, generally applicable correlation for K_{oc} can be established (Seth et al., 1999).

4 Conclusions

This article provided basic data on OCPs and PCBs levels in the water and sediment from Baiyangdian Lake, North China. HCHs and DDTs were the dominant OCPs in water and sediment samples from the Baiyangdian Lake. The concentration of OCPs in Baiyangdian Lake was at a middle level, and PCBs was at a relatively high or similar level, compared to those of other areas. Among the HCHs and DDTs, β -HCH, DDE and DDD were predominant compounds in water and sediments of the lake. The congeners of PCBs containing penta

hepta chlorines were the dominant part of PCBs in both phases of the lake. Analysis of partition coefficients from Baiyangdian Lake shows that there was a greater deviation between observed values and predicted values. Laboratory-derived correlations between OCs partition coefficients and properties of the contaminants cannot be used to accurately predict the partition trends observed in Baiyangdian Lake. Data from Baiyangdian Lake may be explained by the presence of contaminant-associating colloidal matter and disequilibrium between sediment and water phases. To accurately describe the behavior of hydrophobic organic contaminants in aquatic environment, direct measurement of partition coefficients between hydrophobic compounds and colloidal matter at typical environmental concentrations is an urgent need in the future.

Acknowledgments

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