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Concentrations and Accumulation Features of Organochlorine Pesticides in the Baiyangdian Lake Freshwater Food Web of North China

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Abstract Organochlorine pesticides (OCPs), such as hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), are ubiquitous anthropogenic environmental contaminants. They are persistent, broad-spectrum toxicants that accumulate in the food web with potential risks to the ecosystem and human health. HCHs were the predominant contaminants in Baiyangdian Lake, North China. Concentrations of HCHs and DDTs ranged from 58 to 563 ng/g lipid weight (lw) and 21 to 401 ng/g lw, respectively, for aquatic biota samples. The highest levels of HCHs and DDTs were observed in muscles of yellow catfish. The mean concentrations of OCPs were 4.6 ng/L for water, 95 ng/g dry weight (dw) for aquatic plants, and 14 ng/g dw for sediments. Among the isomers and metabolites, α-HCH and *p,p*′-1,1-di(*p*-chlorophenyl)-2,2-dichloroethylene (*p,p*′-DDE) were the predominant congeners in biota samples. Correlations between log lipid-normalized concentrations of HCHs and DDTs and trophic levels (TLs) based on analysis of stable isotopes of nitrogen confirmed that persistent organic pollutants were magnified in the Baiyangdian Lake food web. Significant positive relationships were found for α-HCH and *p,p*′-DDT and their trophic magnification factors, which were 1.6 and 1.7, respectively. These results provide evidence of biomagnification of persistent organic pollutants (POPs) in freshwater food webs.

Organochlorine pesticides (OCPs) were used to control insects during increased crop production after World War II, but intensive worldwide usage now poses potential hazards to the environment and human health. OCPs, such as hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), represent an important group of persistent organic pollutants (POPs) and are of great concern around the world as a result of their chronic toxicity, persistence, and bioaccumulation (Willett et al. 1998). These compounds are ubiquitous contaminants in the aquatic environment. Because of their persistence and bioaccumulation, OCPs in the water can transfer into the food chain and accumulate in aquatic organisms. Eventually, OCPs may reach humans through the consumption of aquatic organisms, drinking water, and agricultural food products. Although the application of these chemicals has been banned or restricted in developed countries, some developing countries still use them because of their low cost and versatility in industry, agriculture, and public health.

OCPs were produced and widely used in China between the 1950s and 1980s (Li et al. 1998). Production of HCH and DDT in China was 4.9 and 0.4 million tons, respectively, accounting for 33% and 20% of the total world production (Zhang et al. 2002). Although agricultural use of HCHs and DDTs has been banned in China since 1983, relatively large concentrations of HCHs and DDTs have been detected in air (Luo et al. 2004; Qiu et al. 2004), water (Zhou et al. 2001; Luo et al. 2004), sediment (Yuan et al. 2001; Marvin et al. 2004), soils (Gong et al. 2004), and aquatic species (Guo et al. 2008; Li et al. 2008). Some

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evidence has suggested that new sources of DDTs may be present in some regions (Guo et al. 2008). Furthermore, production of DDT has continued due to export demands and dicofol production (Qiu et al. 2004). Because aquatic animals directly ingest contaminants from water and diet, aquatic organisms are used extensively for environmental monitoring. The low activity of metabolic enzymes in some aquatic organisms limits their ability to metabolize OCPs. Therefore, contaminant loading in aquatic organisms is reflective of the state of pollution in the surrounding environment. Fish, shrimp, crabs, and mussels are food sources for many people. While aquatic products generally account for only a small portion of the human diet, they represent a major route of human exposure to organic contaminants. Almost all of the aquatic species investigated in this study are consumed by the Baiyangdian population because they are accessible to fishermen and sold cheaply in local markets.

Inland lakes are useful examples of the exposure of aquatic ecosystems to long-range transported contamination in real environments because biota living in these ecosystems constitutes stable communities that develop under chronic atmospheric pollution inputs. Thus, contaminants accumulated in the organisms from these lakes can be uniquely related to atmospheric deposition in these areas. 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 of ditches with a surface area of 366 km^2 and a catchment of 31,200 m^2 (Xu et al. 1998). Situated centrally in the North China Plain, this lake plays important roles in water supply, aquaculture, tourism, and recreation, as well as being of great conservation value for wildlife and wetland vegetation. The lake was well known as “the pearl of North China” due to its beautiful scenery, convenient transportation facilities, and biodiversity, including species such as fish, shrimp, crabs, mussels, turtles, and economically important aquatic plants before the 1960s. In recent years, heavy pollution and consecutive droughts led to a decrease in biodiversity. Chemical plants, paper mills, battery plants, and oil chemical plants poured 250,000 tons of sewage per day into Baiyangdian Lake in past decades. Although numerous studies have investigated the presence of OCPs in various matrices of the Baiyangdian Lake, data on bioaccumulation and biomagnification in the food web are limited (Dou and Zhao 1998). Few reports have quantified OCP concentrations in the trophic levels using stable isotope analysis in the freshwater food web.

The present study examined the concentration, distribution, and characteristics of OCP residues in various

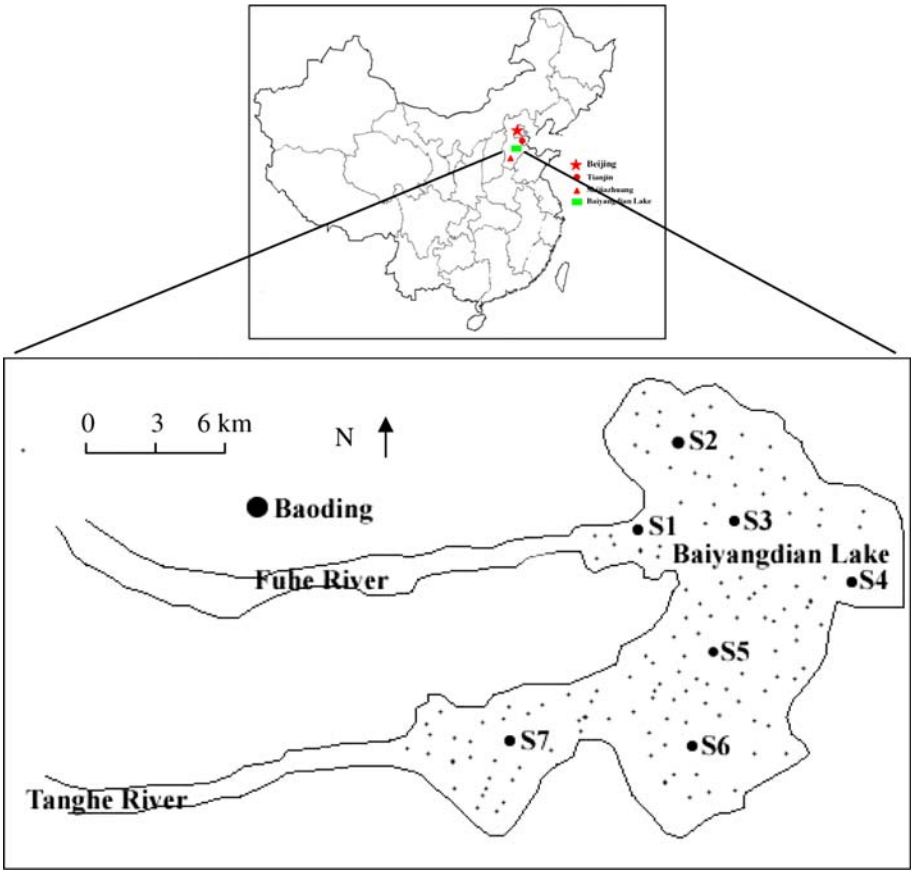

Fig. 1 Location of Baiyangdian Lake for the study (S1–7 represent sampling sites of sediment)

organisms, including zooplankton, shrimp, crab, mussels, fish, turtle, duck, and aquatic plants. Water and sediment samples from Baiyangdian Lake were also investigated. The accumulation status for the pollutants in organisms was determined by calculating bioaccumulation factors (BAFs). At the same time, trophic magnification factors (TMFs) were used to predict biomagnification of HCHs and DDTs in the Baiyangdian Lake food web.

Materials and Methods

Sample Collection

Samples were collected from the Baiyangdian Lake on July 25–30, 2007. The sampling sites are shown in Fig. 1. The organisms selected were as follows: zooplankton, shrimp (*Macrobrachium nipponense*), crab (*Eriocheir sinensis*), river snail (*Viviparus*), swan mussel (*Anodonta*), common carp (*Cyprinus carpio*), crucian carp (*Carassius auratus*), bighead carp (*Aristichthys nobilis*), grass carp (*Ctenopharyngodon idella*), northern snakehead (*Channa argus*), oriental sheatfish (*Parasilurus asotus*), yellow catfish (*Pelteobagrus fulvidraco*), loach (*Misgurnus anguillicaudatus*), ricefield eel (*Monopterus ablus*), turtle (*Pelodiscus sinensis*), and ducks (*Anatidae*). Common aquatic plants included *Nelumbo nucifera* and *Typha angustifolia*. Morphological parameters and habitat of the aquatic organisms are given in Table 1. Fish muscle was taken from dorsal part of the body. Shrimp, crab, river snail, and swan mussel were dissected to obtain the soft tissues. Fifteen individuals of each species were pooled to analyze OCPs in shrimp and river snail. The tissues were washed, wrapped in aluminum foil, placed in polyethylene bags, and then stored at −20° until analysis.

Sample Preparation and Extraction

Animal samples were extracted as described in previous studies (Chen et al. 2007; Hu et al. 2008). Approximately 1.0 g freeze-dried tissue was spiked with a surrogate standard (PCB 30 and PCB 65) and Soxhlet-extracted with 50% acetone in hexane for 48 h. The lipid content was determined by gravimetric measurement from an aliquot of extract. Another aliquot of extract was subjected to gel permeation chromatography to remove lipids. The cleaned extract was concentrated to approximately 0.5 mL. The extract was further purified on 2 g silica gel solid-phase extraction columns (Isolute, International Sorbent Technology, UK). The extracts were further concentrated, the solvent was exchanged to isooctane, and the extracts were finally concentrated to 50 μL under a gentle stream of nitrogen. A known amount of internal standard (PCB 82) was added to all extracts prior to instrumental analysis. Sediment and plant samples were processed as described elsewhere (Mai et al. 2002; Zhu and Hites 2006). Water samples were extracted by solid-phase extraction (SPE) as described in previous studies (Peng et al. 2008).

Instrumental Analysis

Instrument analysis was performed on an Agilent 6890 gas chromatograph (GC) system equipped with an Agilent 5973 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; J&W Scientific, Folsom, CA) for separation. Quantification was based on internal calibration curves made from six concentrations of standard solutions.

Stable isotope analysis of the animal samples was done according to a previously described method (Wu et al.

Table 1 Basic characteristics and trophic levels for the fish species from the Baiyangdian Lake, North China in 2007 (mean ± SD)

Species	Body weight (g)	Body length (cm)	Trophic levels	Habitat and diets[b]
Common carp	882.1 ± 152.0	29.3 ± 3.0	2.0 ± 0.1	Omnivorous (zooplankton, insects, worms, and fungi)
Crucian carp	244.5 ± 21.3	19.7 ± 0.3	2.2 ± 0.1	Omnivorous (zooplankton, insects, worms, and fungi)
Grass carp	2051.2 ± 124.2	48.4 ± 1.6	2.2 ± 0.04	Herbivorous (aquatic plant)
Bighead carp	618.3 ± 118.0	31.1 ± 2.5	3.2 ± 0.04	Filter feeder (zooplankton, phytoplankton, and detritus)
Northern snakehead	440.7 ± 189.4	31.0 ± 4.9	4.9 ± 1.5	Carnivorous (crustaceans, invertebrates, and amphibians)
Oriental sheatfish	618.3 ± 118.2	48.4 ± 1.9	3.1 ± 0.3	Carnivorous (crustaceans, invertebrates, and amphibians)
Yellow catfish	70.1 ± 43.9	16.2 ± 4.0	4.0 ± 0.3	Carnivorous (crustaceans, invertebrates, and amphibians)
Loach[a]	22.7	13.3	3.8[c]	Carnivorous (insects, worms, bacteria, and detritus)
Ricefield eel	36.1 ± 8.7	35.8 ± 3.3	3.8 ± 0.4	Carnivorous (insects, worms, bacteria, and detritus)

[a] The sample number is two

[b] Information from Wang (2006)

[c] Mean value

2009). All samples were analyzed for stable nitrogen isotope composition using an elemental analyzer–isotope ratio mass spectrometer (CE flash EA1112-Finnigan Delta plus XL; Thermo Fischer Scientific Bremen, Germany). Two replicates of each sample were analyzed, and the relative standard deviation was less than 0.5%. The isotope ratio was standardized against air according to $\delta^{15}N = [R_{sample}/(R_{air} - 1)] \times 1000‰$, where R is the ratio of $^{15}N/^{14}N$. The $\delta^{15}N$ values were based on an ammonium sulfate standard.

Quality Assurance and Quality Control (QA/QC)

For each batch of 20 samples, a procedural blank, triplicate spiked blanks, triplicate spiked matrices, and duplicate experimental samples were processed. The recovery from the spiked blanks was 87.5 ± 1.1% for 1,1-di(*p*-chlorophenyl)-2,2-dichloroethylene (DDE) and 105.4 ± 1.3% for DDT. The recovery from the spiked matrices was 88.9 ± 2.5% for DDE and 110.1 ± 7.6% for DDT. The recoveries of surrogate standards PCB 30 and PCB 65 ranged from 63.3 to 103.1%. No surrogate corrections were made to the final results. A low concentration of *p,p*′-DDE (1.1 ng/mL) was found in procedural blanks, but the blank value was not subtracted from the sample measurements. Target analytes included α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p*′-DDE, *p,p*′-DDE, *p,p*′-DDD, *o,p*′-DDT, *o,p*′-DDE, and *o,p*′-DDD. The limit of detection (LOD), defined as a signal-to-noise ratio (S/N) of 3, ranged from 0.03 to 7.19 ng/g lw for OCPs.

Data Analysis

All concentrations were normalized to lipid weight unless indicated. A random number between zero and LOD was used for calculations if a concentration was below the LOD. Differences among various species were examined using the Kruskal–Wallis test. Statistical significance was defined at $p < 0.05$. Analyses were conducted using SPSS 11.0.

Results and Discussion

Levels and Profiles of OCPs in Water and Sediments

The HCH isomers β-HCH and δ-HCH, and *p,p*′-DDE, *o,p*′-DDD, and *o,p*′-DDT were not detected in water samples from Baiyangdian Lake. The concentrations in water, sediments, and biota are presented in Table 2. Concentrations of OCPs in water and sediments from seven sampling sites ranged from 2.6 to 5.9 ng/L (mean 4.6 ng/L) and from 12 to 16 ng/g dry weight (mean 14 ng/g dw), respectively. OCPs in sediment were predominantly HCHs; the mean proportion of HCHs and DDTs in sediment was 81.8 and 18.2%, respectively. The α-HCH isomer was predominant in both water and sediment, ranging from 55.1 to 66.2% in water and from 57.5 to 69.8% in sediment. The predominant contributor to the sum of DDTs in water and sediment was *p,p*′-DDE, ranging from 50.0 to 52.3% in water and 25.8 to 38.9% in sediment. The *o,p*′-DDE and *o,p*′-DDD congeners were minor DDT contributors in water and sediment. Farmland predominates in the watershed of Baiyangdian Lake, where major crops are vegetables, grains, and fruit. The extensive agricultural activities of the region have caused increasing pesticide use. OCPs are still used for agriculture in areas around Baiyangdian Lake (Dou and Zhao 1998). The residues of HCHs and DDTs in water and sediment from Baiyangdian Lake probably result from agricultural runoff or atmospheric deposition. The higher contributions of α-HCH and *p,p*′-DDE suggest that pesticide residues in the samples were largely derived from recent input instead of historical discharge.

Concentrations and Profiles of OCPs in Specific Organisms

Concentrations in Invertebrates

Mollusks and crustaceans have unique characteristics that are different from fish species and turtles. Mollusks and crustaceans have long been used as potential bioindicators and biomonitors, such as in the Mussel Watch Program, because of their high accumulation capacity (Soto et al. 2000). In the present study, the invertebrates included zooplankton, shrimp, crab, river snail, and swan mussel. Zooplankton is an important component that affects food web transfer of organic pollutants. The mean concentrations of HCHs and DDTs in zooplankton samples were 65 and 95 ng/g dw, respectively. The concentrations in zooplankton were 1–2 orders of magnitude higher than those reported from Gaobeidian Lake, Beijing (Li et al. 2008). These findings may be due to different environmental conditions. Gaobeidian Lake was exposed to the effluent of wastewater treatment plants, and the water temperature was higher than in Baiyangdian Lake. Higher temperatures could enhance the rate of metabolism of contaminants in organisms and, thus, increase the presence of contaminant metabolites in organisms (Buckman et al. 2007).

The concentrations of OCPs in mollusks (river snail and swan mussel) ranged from 148 to 1,018 ng/g lw and in crustaceans (shrimp and crab) ranged from 64 to 407 ng/g lw. The mean concentration of OCPs in invertebrates (345 ng/g lw) was higher than that of sediments (14 ng/g dw), suggesting that, even at relatively low levels, these compounds may be bioavailable for sediment-dwelling organisms. These invertebrate organisms may provide an important link in the transfer of dissolved and particle-bound POPs to higher levels in the freshwater food web.

Table 2 Concentrations (mean ± SD) of HCHs and DDTs in water, sediments, and aquatic biota samples (ng/g lipid weight) from Baiyangdian Lake in 2007

	N	Lipid%	α-HCH	β-HCH	γ-HCH	p,p'-DDE	p,p'-DDD	p,p'-DDT	$\sum$HCHs[b]	$\sum$DDTs[b]	$\sum$OCPs[b]
Zooplankton1			16	6.8	11	51	8.9	8.1	34	78	112
Zooplankton2			37	21	36	45	20	22	96	112	208
Shrimp	3[45][a]	6.3 ± 1.7	27 ± 4.2	15 ± 2.8	16 ± 1.4	196 ± 30	73 ± 18	20 ± 8.3	58 ± 5.5	303 ± 44	361 ± 46
Crab	3	6.9 ± 1.3	49 ± 37	18 ± 24	53 ± 58	24 ± 3.6	2.3 ± 1.7	6.2 ± 7.3	120 ± 118	34 ± 13	131
River snail1	1[15][a]	4.2	139	92	216	19	7.2	14	447	44	492
River snail2	1[15][a]	3.7	161	71	237	26	21	40	469	96	565
Swan mussel	5	5.8 ± 0.6	174 ± 112	77 ± 49	172 ± 84	32 ± 42	23 ± 24	36 ± 33	423 ± 242	99 ± 104	522 ± 335
Common carp	5	12 ± 3.2	78 ± 41	20 ± 14	43 ± 17	10 ± 3.1	12 ± 9.5	6.7 ± 3.0	142 ± 66	31 ± 14	173 ± 73
Crucian carp	4	9.1 ± 1.4	59 ± 6.7	41 ± 15.5	67 ± 20	24 ± 1.4	11 ± 5.2	16 ± 1.8	167 ± 37	55 ± 5.3	222 ± 38
Grass carp	5	7.1 ± 1.9	88 ± 25	29 ± 105	56 ± 20	7.2 ± 1.5	8.8 ± 1.6	3.9 ± 1.4	174 ± 54	23 ± 2.5	196 ± 56
Bighead carp	4	4.5 ± 1.0	241 ± 55	25 ± 2.6	82 ± 26	37 ± 13	8.9 ± 1.4	13 ± 0.8	348 ± 79	64 ± 15	413 ± 86
Northern snakehead	14	9.3 ± 1.2	85 ± 86	22 ± 32	26 ± 18	67 ± 32	63 ± 32	84 ± 42	132 ± 131	221 ± 102	353 ± 176
Oriental sheatfish	5	38 ± 7.6	39 ± 14	16 ± 6.8	29 ± 15	17 ± 5.9	7.3 ± 5.6	5.5 ± 6.8	84 ± 33	32 ± 17	116 ± 46
Yellow catfish	4	4.6 ± 1.8	315 ± 89	117 ± 35	130 ± 37	295 ± 135	49 ± 24	38 ± 13	562 ± 153	401 ± 178	963 ± 323*
Ricefield eel	8	10 ± 2.2	170 ± 64	92 ± 23	136 ± 61	78 ± 42	19 ± 6.4	17 ± 6.0	398 ± 76	119 ± 49	517 ± 64
Loach1	1	12	140	50	125	57	8.4	12	315	81	396
Loach2	1	8.9	157	41	139	62	11	14	337	91	429
Turtle	4	4.8 ± 1.9	153 ± 121	33 ± 11	120 ± 74	10 ± 5.3	2.7 ± 1.6	10 ± 9.5	307 ± 209	26 ± 16	332 ± 217
Duck	5	9.0 ± 1.8	66 ± 10	27 ± 17	72 ± 21	9.6 ± 2.5	1.2 ± 0.6	9.6 ± 2.4	165 ± 33	21 ± 5.0	186 ± 31
Aquatic plant[c]	5		13 ± 3.5	11 ± 5.0	61 ± 44	2.0 ± 1.5	0.7 ± 0.5	0.6 ± 0.2	92 ± 54	3.8 ± 2.0	95 ± 56
Water[d]	7		1.2 ± 0.5	ND	0.7 ± 0.4	ND	0.7 ± 0.04	1.2 ± 0.5	2.1 ± 0.8	2.4 ± 0.6	4.6 ± 1.2
Sediment[c]	7		7.3 ± 0.8	0.8 ± 0.2	3.6 ± 0.6	0.5 ± 0.1	0.7 ± 0.2	0.9 ± 0.3	12 ± 1.2	2.6 ± 0.4	14 ± 1.3

ND not detected

* Significant difference at $p < 0.05$ level

[a] [45] and [15] represents the number of analyzed pool samples for shrimp and river snail, respectively

[b] $\sum$HCHs = α-HCH + β-HCH + γ-HCH + δ-HCH, $\sum$DDTs = p,p'-DDT + p,p'-DDE + p,p'-DDD + o,p'-DDT + o,p'-DDE + o,p'-DDD, $\sum$OCPs = $\sum$HCHs + $\sum$DDTs

[c] Units are ng/g dry weight

[d] Units are ng/L

Invertebrate organisms are indicative of the contamination at collection sites because of their small range of movement and water-respiring filtration.

Concentrations in Fish and Other Organisms

Large interspecies variations were found in concentrations of HCH, DDT, and OCP (Table 2). The concentrations of OCPs in different fish species were dominated by α-HCH, followed by *p,p′*-DDE. The concentrations of α-HCH and *p,p′*-DDE ranged from 39 to 315 ng/g lw and from 7 to 296 ng/g lw, respectively, in the nine fish species studied from Baiyangdian Lake. The concentrations of total OCPs in fish species ranged from 53 to 1,319 ng/g lw. Significantly different concentrations of OCPs were observed among various fish species. The concentration of OCPs (963 ng/g lw) in yellow catfish was significantly greater than those of other species ($p < 0.05$). The smallest mean concentration of OCPs (116 ng/g lw) was detected in oriental sheatfish. The mean concentrations of OCPs in different fish species from Baiyangdian Lake generally decreased in the order: yellow catfish > ricefield eel > bighead carp = loach > northern snakehead > crucian carp > grass carp > common carp > oriental sheatfish. Yellow catfish, ricefield eel, loach, and northern snakehead had a greater tendency to bioaccumulate OCPs than did common carp, crucian carp, and grass carp. The variation of concentrations of HCHs and DDTs in different species may be attributed to the different trophic position and specific feeding characteristics of these species. In addition to fish and invertebrates, the concentrations of OCPs in the muscle of turtles and ducks from Baiyangdian Lake ranged from 114 to 632 ng/g lw and from 132 to 233 ng/g lw, respectively. The concentrations of OCPs in aquatic plants ranged from 35 to 175 ng/g dw.

Generally, yellow catfish, northern snakehead, oriental sheatfish, ricefield eel, and loach, all of which are benthic carnivorous species, were at relatively higher trophic levels and prey on small fish or other organisms. Benthic fish play a significant role in the process of resuspension of contamination adsorbed on sediment and recycling these contaminants into the water column. Consistent with this role, higher concentrations of OCPs in the samples of the benthic carnivorous fish species were observed in the present study. A similar tendency was observed in a previous study (Zhou et al. 1999). The OCP levels in all carnivorous fish (yellow catfish, northern snakehead, ricefield eel, and loach), except oriental sheatfish, were higher than those of herbivorous and detritivorous fish species, suggesting that OCPs bioaccumulate through the food chain of the freshwater ecosystem. It was interesting to note that the lowest concentration of OCPs was found in oriental sheatfish, which has higher lipid content (38.3%) than the other fish. The linear regression analysis indicated that negative correlations between the concentrations of OCPs and lipid content were found in different organisms from Baiyangdian Lake ($R^2 = 0.18$, $p = 0.11$). Redistribution of OCPs in the fish body was a potential confounding process. During periods of spawning, stored body fat is metabolized, and lipophilic organochlorines are mobilized and distributed through blood circulation. Grass carp, an herbivorous species, feed mainly on residues of agricultural crops and grass commonly grown on the dykes. In addition, the uncontrolled use of DDTs may have contributed to the high concentrations detected in aquatic plants (Hong et al. 1999). OCPs were also detected in the freshwater microbial community (Li et al. 2008) and suspended particulate matter (Hong et al. 1999). The presence of OCPs in freshwater microbial community may be the reason for the high levels of OCPs detected in the bighead carp, which is a filter feeder.

Compared with other reports, the magnitude of $\sum$HCHs (32–707 ng/g lw) and $\sum$DDTs (12–612 ng/g lw) in the aquatic organisms in the present study was lower than in organisms from Qiantang River (109–3,651 ng/g lw for $\sum$HCHs, 331–16,133 ng/g lw for $\sum$DDTs) (Zhou et al. 2008) and Rio de la Plata in Argentina (1,000–25,000 ng/g lw for $\sum$DDTs) (Colombo et al. 1990). Levels in this study were similar to those of organisms from Taihu Lake (16–90 ng/g lw for $\sum$HCHs, 350–4,700 ng/g lw for $\sum$DDTs) (Nakata et al. 2005) and the Bangkok region (10–360 ng/g lw for $\sum$DDTs) (Kannan et al. 1995).

Compositional Profiles of HCHs and DDTs

The relative abundance of HCH congeners is shown in Fig. 2a. The compositional profiles of HCHs were similar among aquatic organisms except for river sail and duck. The average concentrations of α-HCH, β-HCH, and γ-HCH contributed 32.6–69.2% (mean 47.6%), 7.5–25.8% (mean 17.5%), and 23.3–49.5% (mean 34.9%), respectively, to the total HCH concentration. The technical mixture of HCH usually contains 55–80% α-HCH, 5–15% β-HCH, 8–15% γ-HCH, and 2–16% δ-HCH (Willett et al. 1998). α-HCH was the most predominant isomer, which indicated the extensive application of technical HCH in China in the past (Yang et al. 2007). The compositional profiles of HCHs in fish species from Baiyangdian Lake were in agreement with previous reports (Yang et al. 2007). The compositional profiles of DDTs are shown in Fig. 2b. The congener of *p,p′*-DDE was a major component, ranging from 29.6 to 71.0% (mean 49.8%) in all animal samples except for river snail, swan mussel, and northern snakehead. The amount of *p,p′*-DDE as a percentage of total DDTs was 35.9% for river snail, 37.8% for swan mussel, and 36.8% for northern snakehead. The relative abundance

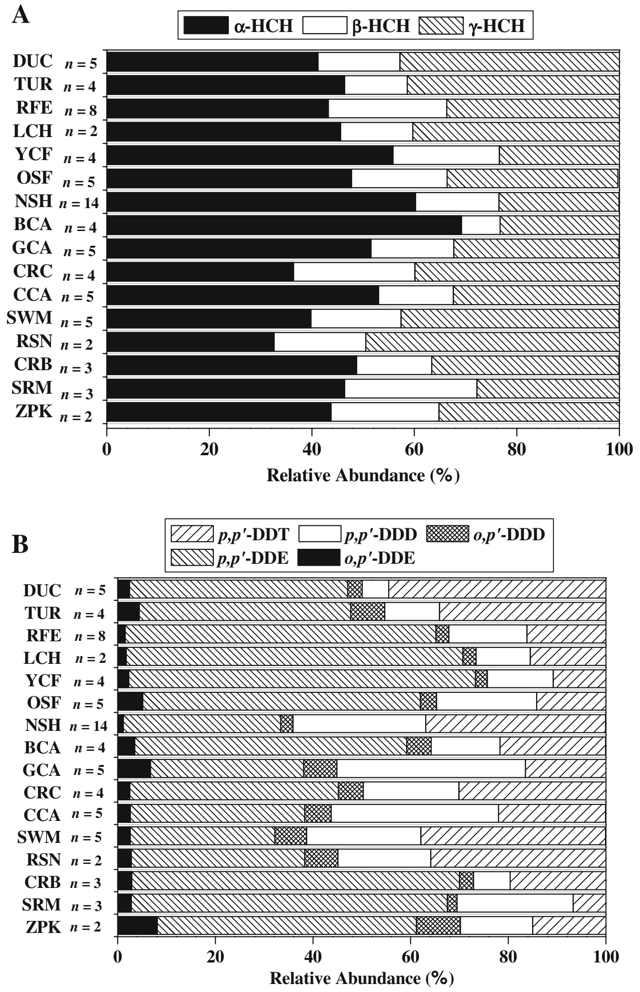

Fig. 2 HCHs (**a**) and DDTs (**b**) compositional profiles in organisms collected from Baiyangdian Lake, North China. *ZPK* zooplankton, *SRM* shrimp, *CRB* crab, *RSN* river snail, *SWM* swan mussel, *CCA* common carp, *CRC* crucian carp, *GCA* grass carp, *BCA* bighead carp, *NSH* northern snakehead, *OSF* oriental sheatfish, *YCF* yellow catfish, *LCH* loach, *RFE* ricefield eel, *TUR* turtle, *DUC* duck

of *p,p′*-DDE in water and sediment samples was greater than that of animal samples from Baiyangdian Lake. River snail, swan mussel, and northern snakehead from Baiyangdian Lake are benthic habitat species and may have more chances to touch suspended particles in water, to which persistent organic pollutants adsorb. Thus, the *p,p′*-DDE was predominant in tissues of river snail, swan mussel, and northern snakehead from Baiyangdian Lake.

Sources of HCHs and DDTs

China is a large producer and consumer of pesticides. Technical HCH and DDT have been widely used in China since the 1950s. From 1952 to 1984, the total production of technical HCH was around 4 million tons, and from 1951 to 1983 the production of DDT was 0.27 million tons (Li et al. 2001). Although HCHs and DDTs were banned in 1983, OCP residues in aquatic organisms from Baiyangdian Lake deserve particular attention.

Generally speaking, α-HCH (55–80%) was the predominant isomer in technical HCH (Willett et al. 1998). In the present study, the concentration ratios of α/γ-HCH in animal samples ranged from 0.6 to 4.6 (mean 1.7), and were lower than the ratio of technical HCH. The use of both technical HCH and lindane (the commercial name of γ-HCH) contribute to environmental HCHs in North China (Li et al. 1996). Significantly different ratios of α/γ-HCH were found in various aquatic organisms ($p < 0.05$). The ranking order of the ratios was as follows: duck (1.0) < mollusks and crustaceans (1.1) < turtle (1.2) < zooplankton (1.3) < detritivorous and herbivorous fish (1.8) < carnivorous fish (2.2). This difference in ratio of α/γ-HCH may reflect different metabolic mechanisms and specific habitats in which the different species live. In addition, the relative low concentrations of γ-HCH may be partly attributed to a possible transformation of γ-HCH to α-HCH in the environment (Haugen et al. 1998).

DDT is degraded into DDD under anaerobic conditions and DDE in aerobic environments (Hitch and Day 1992; Maldonado and Bayona 2002). The ratios DDD/DDE and DDT/(DDD + DDE) can be used to assess the living environment of aquatic organisms, estimate the extent of DDT decomposition, or identify recent input of DDTs (Lee et al. 2001). Higher DDT/(DDD + DDE) ratios were found in tissues of duck (0.8) and turtle (0.6). Lower DDT/(DDD + DDE) ratios were observed in tissues of invertebrates and fish species (0.2–0.4). These results indicated that duck and turtle had more potential for exposure to DDTs in their habitats, which may have new inputs of DDTs. Fish species living in Baiyangdian Lake were polluted by residues of historic applications of DDTs in various environmental matrices (Dou and Zhou 1996, 1998). The DDD/DDE ratios in tissues of fish, mollusks, and crustaceans (0.6–1.2) were greater than those of other species. The highest DDD/DDE ratio (1.2) was found in grass carp. These results suggest that DDTs can be biotransformed under anaerobic conditions in sediments or in aquatic species, such as invertebrates, duck, and turtle.

Bioaccumulation of OCPs in Aquatic Organisms

Bioaccumulation Factors (BAFs)

To determine whether concentrations of OCPs in animal samples were in equilibrium with those in water, we used bioaccumulation factors (BAFs) of the compounds in the organisms to assess the partition process between water and lipids. The BAF is defined as the ratio of the OCP concentration in tissues (ng/g wet weight) divided by the concentration of compounds in the dissolved phase of water (ng/L).

Log BAFs ranged from 2.5 to 3.8 for HCHs and from 1.8 to 3.5 for DDTs for all aquatic species. No significant difference in log BAFs for HCHs was found among the invertebrates in the present study ($p > 0.05$). The log BAF for DDTs of shrimp was significantly higher than that of crab, river snail, and swan mussel from Baiyangdian Lake ($p < 0.05$). Log BAFs for HCHs and DDTs were significantly different among the fish species from Baiyangdian Lake ($p < 0.05$). The highest log BAF of HCHs was found in oriental sheatfish, and the highest log BAF for DDTs was found in northern snakehead. The lowest log BAF of HCHs was found in northern snakehead, and the lowest for DDTs was found in grass carp. The log BAFs of HCHs in different fish species from Baiyangdian Lake generally decreased in the order: oriental sheatfish > ricefield eel = loach > yellow catfish > bighead carp > crucian carp = common carp > grass carp. The log BAFs of DDTs in different fish species from Baiyangdian Lake generally decreased in the order: northern snakehead > yellow catfish = oriental sheatfish > ricefield eel > loach > crucian carp > common carp > bighead carp > grass carp. The differences in log BAFs may reflect different capacity to metabolize POPs in various species in the present study.

Trophic Magnification Factors (TMFs)

The biomagnification of persistent organic pollutants is complicated in food webs. Previous studies have indicated that 1,1-di(*p*-chlorophenyl)-2,2-dichloroethylene (DDE) and 1,1-di(*p*-chlorophenyl)-2-chloroethylene (DDMU) can biomagnify in aquatic organisms, with higher DDT concentrations found in organisms with a higher trophic level than that of its prey (Hu et al. 2005). Based on the stable isotope values, Baiyangdian Lake organisms occupied three main trophic levels: zooplankton (5.9‰) and shrimps (5.8‰) were secondary consumers; crab (12.6‰), river snail (9.32‰), swan mussel (10.2‰), and herbivorous or detritivorous fish were tertiary consumers; and carnivorous fish, including northern snakehead (15.5‰), yellow catfish (12.8‰), ricefield eel (12.0‰), loach (11.3‰), and turtle (12.8‰), were quaternary consumers.

Trophic levels (TLs) of each aquatic organism were calculated using the previously defined relationship (Fisk et al. 2001a, b): $\mathrm{TL}_{\mathrm{consumer}} = 2 + (\delta^{15}\mathrm{N}_{\mathrm{consumer}} - \delta^{15}\mathrm{N}_{\mathrm{zooplankton}})/3.4$. The trophic level of zooplankton was assumed to be 2. The trophic level value (4.9) in the northern snakehead was higher than that of other organisms in the present study. The trophic magnification factors (TMFs) were based on the relationship between the trophic levels and natural log concentrations of OCPs (lipid-normalized) using simple linear regression: $\mathrm{Ln}\,[\mathrm{concentration}] = A + B \times \mathrm{TL}$. The slope B was used to calculate TMF values using $\mathrm{TMF} = e^{B}$. Generally speaking, biomagnification is defined by a TMF statistically >1 (Fisk et al. 2001a, b).

In order to ensure a meaningful relationship between the Ln[concentration] and trophic levels, we purposely omitted the concentrations of HCHs and DDTs in duck samples from Fig. 3. Significantly positive relationships were found between trophic levels and the concentrations of α-HCH and *p,p*′-DDT in aquatic organisms, indicating the potential for biomagnification of the contaminants in the freshwater food web in Baiyangdian Lake (Fig. 3a, e). The concentrations of α-HCH and *p,p*′-DDT significantly increased with trophic levels ($p < 0.05$), with TMF values of α-HCH and *p,p*′-DDT of 1.6 and 1.7, respectively (Table 3). The TMF values of β-HCH (1.3) and γ-HCH (1.4) were lower than that of α-HCH (1.6), which indicated that HCH isomers in aquatic organisms had a different extent of biomagnification in the Baiyangdian Lake food web, which may be related to different metabolism of isomers in organisms (Fisk et al. 2001a, b).

The TMFs of HCHs (1.5) and DDTs (1.3) in the Baiyangdian Lake food web were lower than those of the Northwater Polynya and Barents Sea food web (Fisk et al. 2001a, b; Hop et al. 2002). Fisk et al. reported TMF values for HCHs and DDTs of 2.7 and 10.8, respectively, for a marine food web that included zooplankton, benthic invertebrates, fish, seabirds, and marine mammals (Fisk et al. 2001a, b). Hop et al. also reported TMFs for α-HCH and *p,p*′-DDE of 1.6 and 3.7, respectively, for poikilotherms from the Barents Sea food web (Hop et al. 2002). Although *p,p*′-DDE was the predominant metabolite in the present study, the TMF of *p,p*′-DDE in Baiyangdian Lake (1.3) was lower than that in the Bohai Bay (3.3) (Hu et al. 2005), Northwater Polynya (13.7) (Fisk et al. 2001a, b), Barents Sea (3.7) (Hop et al. 2002), and White Sea (3.6) (Muir et al. 2003) marine food webs, which may be due to the different ecological factors of the various sites, such as the food web length, species that are present, and location. The trophic positions in Bohai Bay, Northwater Polynya, Barents Sea, and White Sea marine food webs included birds and aquatic mammals, and the length of food web was longer than that of the Baiyangdian Lake freshwater food web. In addition, differences in TMFs between freshwater and marine food webs have been observed in other studies (Kidd et al. 1998; Fisk et al. 2001a, b). The relationship between the biomagnification of persistent organic pollutants and trophic levels in freshwater food webs is not fully understood. The length of the food webs, feeding strategy, and lipid contents are potential factors that influence bioaccumulation of contaminants in freshwater ecosystems. Without water birds in the present study, the trophic level scale was narrow for the Baiyangdian freshwater food web. Clearly, further investigation of

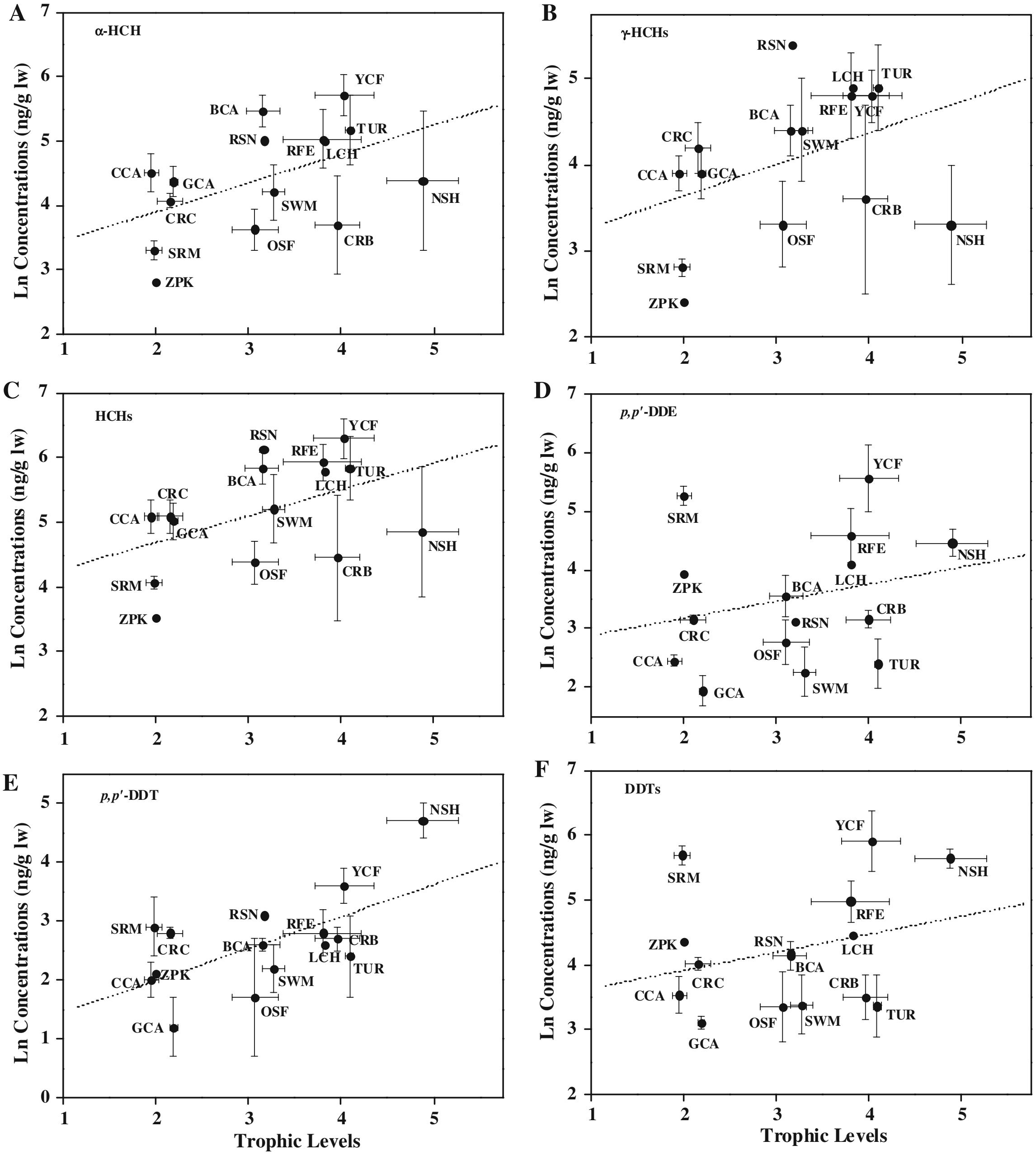

Fig. 3 Relationship of major persistent organochlorines in the Baiyangdian Lake food web and trophic levels (*TLs*) calculated from δ^{15}N values. *Vertical* and *horizontal bars* represent standard errors for mean values in each species. *ZPK* zooplankton, *SRM* shrimp, *CRB* crab, *RSN* river snail, *SWM* swan mussel, *CCA* common carp, *CRC* crucian carp, *GCA* grass carp, *BCA* bighead carp, *NSH* northern snakehead, *OSF* oriental sheatfish, *YCF* yellow catfish, *LCH* loach, *RFE* ricefield eel, *TUR* turtle. The duck samples were purposely omitted from the plot

biomagnification using large-scale and much longer food chains in the Baiyangdian Lake freshwater ecosystem is needed.

Conclusions

HCH and DDT concentrations were measured in water, sediment, and aquatic organisms from the Baiyangdian Lake food web. The level of DDTs in environmental matrices and aquatic organisms was relatively low compared with levels of HCHs. The profiles of HCHs and DDTs indicated sources of new inputs of HCHs and DDTs in the area of Baiyangdian Lake despite a long-time ban in China. Bioaccumulation factors (BAFs) suggested different rates of bioconcentrations for various aquatic organisms in the Baiyangdian Lake freshwater ecosystem. Regression analysis between OCP concentrations and trophic levels

Table 3 Slope and *p*-value of slope of regression analysis between logarithm of concentration and trophic levels, and TMFs for HCHs and DDTs

Compound	Slope	R^2	TMFs	*p*
α-HCH	0.45	0.26	1.57	0.05*
β-HCH	0.28	0.10	1.32	0.25
γ-HCH	0.37	0.16	1.44	0.14
HCH	0.41	0.22	1.50	0.08
p,p′-DDE	0.29	0.06	1.34	0.37
p,p′-DDT	0.54	0.38	1.72	0.01*
DDTs	0.28	0.08	1.32	0.31

* Statistically significant difference

suggested that α-HCH and *p,p′*-DDT exhibited a relatively high degree of biomagnification in the freshwater food web. TMF values of α-HCH and *p,p′*-DDT were 1.6 and 1.7, respectively.

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