Distribution and Sources of Organochlorine Pesticides in Taihu Lake, China

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Abstract Thirty surface sediments, corresponding overlying water and porewater samples were collected for analysis of organochlorine pesticides (OCPs) from Taihu Lake, China in May 2010. Altogether six OCPs, i.e. hexachlorobenzene (HCB), β-hexachlorohexane (β-HCH), p,p'-DDE, p,p'-DDD, p,p'-DDT, and o,p'-DDT were detected, and the total OCPs varied from 7.84 to 32.23 ng g^{-1} in sediments, from 136.97 to 2,185.14 ng L^{-1} in porewater and from 24.27 to 154.07 ng L^{-1} in overlying water, respectively. The highest levels of contamination in sediment was observed in southeast of the lake, while in water and porewater samples highest levels were found in Zhushan Bay, the seriously polluted area in the north part of Taihu Lake. The partition coefficient of measured OCPs between sediment-overlying water was five and six fold higher than that between sediment-porewater, indicating the different distribution patterns of OCPs among sediment, overlying water and porewater matrices. The ratios of DDT/(DDD + DDE) ranged from 0.57 to 2.28 in sediments, 0.93–13.02 in porewater and 0.84–15.98 in overlying water, respectively, suggesting the potential new source of DDTs into the lake. The ratios of o,p'-DDT/ p,p'-DDT in the three matrices were centered around 0.2–0.3, indicating the o,p'-DDT in the lake was originated from historical usage of technical DDTs.

Contamination of organochlorine pesticides (OCPs) in the environment has been of great significance for decades, due to their physicochemical properties such as semi-volatility, persistence, hydrophobicity, bioaccumulation and adverse effects on human health and animals. During 1950s–1980s, approximately 4,460,000 t of technical HCHs and 435,200 t of DDTs were produced in the world (Cao et al. 2007; Zhang et al. 2009). The worldwide historical application of OCPs has raised severe environmental problems, although the application of OCPs has been banned in many developed countries since 1980s.

Sediment is one of the main sinks of OCPs in the environment, since OCPs are readily adsorbed onto suspended particulate matter and subsequently precipitate into river, lake and marine sediments due to their high hydrophobicity and low water solubility (Yang et al. 2005; Sun et al. 2010). However, OCPs in sediment are still harmful to benthic organisms due to their possibility to release back to water column. A full understanding of the fate of OCPs requires information on their concentration and distributions in the aquatic environment among different phases.

Taihu Lake is the third largest freshwater lake in China, with an average depth of 1.9 m. With the rapid urbanization around the Taihu region, it receives large amounts of wastes from agricultural non-point sources, municipal sewage, industrial wastewater, aquaculture, etc., causing the pollution of the lake a great concern by both scientific

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and public communities (Zhang et al. 2011). The contamination of OCPs in water, sediments, biota and surrounding agricultural fields and airs in Taihu region has been extensively investigated by many researchers (Qiu et al. 2004; Zhao et al. 2010), however, information on the distribution of OCPs between sediment-overlying water and sediment-porewater, and their sources is still limited. This study investigated the distribution of OCPs in sediment and corresponding overlying water and porewater samples in Taihu Lake, interpreted the partition of OCPs between sediment-porewater and sediment-overlying water matrices, and identified the possible sources of pollution. Results will be helpful for better understanding the environmental behavior and fate of OCPs in the sediment–water system.

Materials and Methods

A mixture standard solution of OCPs containing o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, α-HCH, β-HCH, γ-HCH, δ-HCH, hexachlorobenzene (HCB), oxy-chlordane, $trans$-chlordane, cis-chlordane, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, methoxychlor, and mirex at a concentration of 100 mg/L was purchased from Chem Service, Inc., USA. The surrogate (^{13}C-p,p'-DDT) and the internal standard (deuterated phenanthrene, deuterated pyrene, and deuterated chrysene) were purchased from AccuStandard, Inc., USA. Organic solvents including acetone, n-hexane and methylene chloride were purchased from Fisher Scientific, USA.

Thirty surface sediment (0–10 cm) and corresponding overlying water samples were collected from Taihu Lake in May 2010, and the sampling locations were shown in Fig. 1. Surface sediments were grab sampled, and placed in glass bottles with Teflon-lined caps. Overlying water was taken 1 m beneath the surface, and stored in 4-L glass amber bottles. Samples were transported to the laboratory on ice. Porewater from each sediment was obtained by high-speed centrifugation. Both overlying water and the isolated porewater were stored in the dark at 4°C, and the remainder of sediment samples was frozen at −20°C before treatment. All samples were analyzed within one week.

Water samples were passed through 0.45 μm glass fibers to remove suspended particles, and concentrated by solid phase extraction (SPE). The HyperSep C18 cartridges (500 mg/6 mL, Thermo Electron Corporation) were preconditioned by 5 mL of ethyl acetate, 5 mL of methanol and 5 mL of distilled water sequentially. Filtered water samples were loaded onto cartridges at a flow rate of approximate 8 mL min^{-1}. After the sample loading, 10 mL of distilled water were used to wash the cartridges, followed with the vacuum on for about 1 h till the
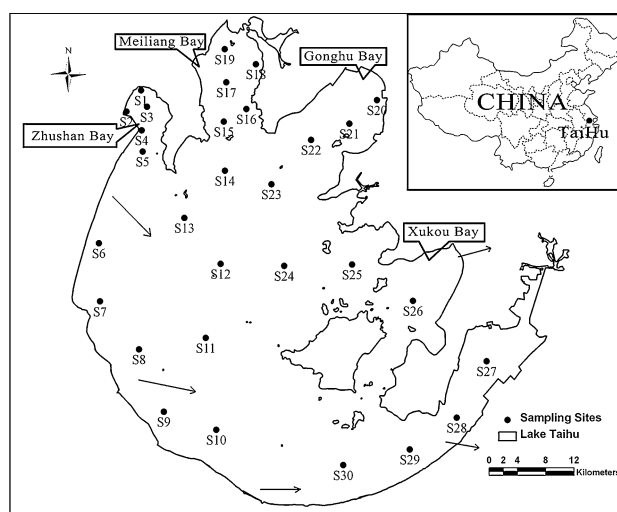

Fig. 1 The sampling sites in the study area (*arrows* show the inflows and outflows of the lake)

cartridges were all dry. The cartridges were eluted by 4 mL of 1:1 dichloromethane/n-hexanes and 4 mL of n-hexanes. The extract was concentrated to less than 1 mL with a gentle nitrogen stream, reconstituted with 8 mL of n-hexanes, and again concentrated to less than 1 mL. Anhydrous sodium sulfate was used to remove water residue. The extract was finally concentrated to 200 μL for analysis.

Sediments were extracted with an automated Dionex ASE 300 accelerated solvent extractor (Sunnyvale, CA, USA) (Zhang et al. 2009). Surface sediments were freeze-dried and ground in a mortar to pass through a sieve with 0.5 mm openings. Five grams of each sediment sample were weighed accurately, combined with 2 g of copper powder and 2 g of diatomite, and placed into the steel cells. Samples were extracted using 1:1 methylene chloride/acetone as extracting solvent. Extraction temperature was 100°C and extraction pressure was 1,500 psi. Preheating time and static time were both set to 5 min. A total flush volume of 100 % the cell volume and a purge time of 60 s with nitrogen was used. The final extraction volume was approximately 20 mL with two extraction cycles. The extracts were concentrated to approximately 1 mL and further cleaned up with a Florisil SPE cartridge (1 g, 6 mL, Supelco, USA). After sample loading, the cartridge was eluted with 12 mL acetone/hexane (2/98, v/v). The eluate was concentrated to 1 mL under a centrifugal vacuum evaporator system (CVE3100, Eyala, Japan). The internal standards, 20 μL of deuterated phenanthrene, deuterated pyrene, and deuterated chrysene mixture standard solution (10 ng μL^{-1}) was added prior to GC analysis.

OCPs were analyzed on a Shimadzu GCMS-QP2010 equipped with a fused silica capillary DB-5MS column (30 m, 0.25 mm i.d., 0.25 μm film thickness) using

electron ionization with selective ion monitoring mode. Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. The injector, transfer line, and ion source temperature were set at 250, 260 and 230°C, respectively. The GC oven temperature was programmed from 70°C (1 min) to 180°C at 20°C min^{-1}, then to 260°C at 4°C min^{-1}, and to 300°C at 15°C min^{-1} and held for 6 min. Two microliters of samples were injected in the split mode with 1:14.1. Quantification was performed by internal standard.

All analytical procedures were monitored with strict quality assurance and control measures. The instruments were calibrated daily with calibration standards. Procedural blanks were analyzed concurrently with the water and sediment samples and showed no detectable target compounds. The detection limit of OCPs ranged from 0.014 to 0.178 μg kg^{-1} for sediment, and from 0.228 to 0.567 ng L^{-1} for water. The recoveries of ^{13}C-p,p'-DDT fell within the range of 75 %–125 % for sediment and 73 %–108 % for water, respectively. For statistical analysis, two-tailed t test was used to compare the average concentrations between samples in the present study.

Results and Discussion

The range and average concentrations of individual OCPs in sediments, porewater and overlying water matrices from Taihu Lake were summarized in Table 1. Altogether 6 OCPs, i.e. HCB, β-HCH, p,p'-DDE, p,p'-DDD, p,p'-DDT, and o,p'-DDT were detected in all samples. In sediments, the total OCPs varied from 7.84 to 32.23 ng g^{-1} dry weight, with a mean value of 17.59 ng g^{-1}. The sediment concentrations and compositions of OCPs in different regions around the lake differed significantly, with the increasing trend along the direction of water flow (as shown in Fig. 1 with arrows indicating the water flow directions). The highest concentration was discovered at S28 (32.23 ng g^{-1}), situated in the southeast part of Taihu

Lake, where water met and was the grass-dominated regions. This result was consistent with that reported by Zhao et al. (2009) and Fan and Wang (2007).

For lipophilic organic compounds, their concentrations in sediments/soils were generally closely related to the sediment/soil organic matter contents, because sediment with high organic carbon content is more likely to adsorb hydrophobic compounds by a partition way (Xu et al. 2007, 2009a, b; Yu et al. 2009). However, no correlations were found in this study between OCPs residues and organic matter content (R^2 = 0.0119) in the sediment from Taihu Lake. Zhao et al. (2009) also observed this phenomenon and explained it by three reasons: the complex process of OCPs accumulation, the higher microbial activities and biodegradation of OCPs in sediments with high organic matter contents, and the complex organic matter sources. The different OCPs application history in different regions around the lake may also partially contribute to the spatial distribution of OCPs in the sediments.

For aqueous phases, the total OCPs ranged from 136.97 to 2,185.14 ng L^{-1} in porewater and from 24.27 to 154.07 ng L^{-1} in overlying water, respectively. The highest concentrations of total OCPs for both porewater and overlying water were found at S2. S2 located in Zhushan Bay, one of the most polluted areas in Taihu Lake, where there were two severely polluted rivers (Taige Canal and Caoqiao River) carrying contaminants directly into the lake (Zhang et al. 2011). Agricultural runoff from adjacent fields entered the rivers and contributed to the total OCPs in the lake water.

To better understand the distribution of OCPs between different matrices, two partition coefficients, sediment-overlying water (K$_{SW}$) and sediment-porewater (K$_{SP}$) were calculated:

$$K_{SW} = C_S/C_W$$

$$K_{SP} = C_S/C_P$$

where C$_S$ is the sediment concentration, C$_w$ is the water concentration, C$_p$ is the porewater concentration. The results were shown in Table 2. It was observed that all K$_{SW}$

Table 1 OCPs concentrations in different matrices from Taihu Lake (May 2010)

PAHs	Sediment (ng g^{-1} dw) [n = 30]		Porewater (ng L^{-1}) [n = 27]		Water (ng L^{-1}) [n = 30]	
	Range	Mean	Range	Mean	Range	Mean
HCB	0.05–0.91	0.22	nd–7.83	2.70	0.22–0.85	0.41
β-HCH	0.05–1.28	0.30	2.06–20.19	6.17	0.43–1.65	0.97
p,p'-DDE	0.87–7.41	4.37	nd–290.62	77.52	nd–34.09	13.84
p,p'-DDD	1.04–10.82	3.07	nd–152.70	54.10	nd–18.35	9.16
o,p'-DDT	0.29–3.69	1.61	31.07–304.80	93.16	6.49–24.89	14.59
p,p'-DDT	4.00–17.50	8.03	78.67–1,409.0	362.59	17.13–103.55	57.27
$\sum$OCP	7.84–32.23	17.59	136.97–2,185.14	575.57	24.27–154.07	93.78

nd not detected

Table 2 Distribution coefficients of OCPs between sediment-overlying water (K_{SW}) and sediment-porewater (K_{SP})

	f_{OC}	HCB		β-HCH		p,p'-DDE		p,p'-DDD		o,p'-DDT		p,p'-DDT	
		K_{SW}	K_{SP}	K_{SW}	K_{SP}	K_{SW}	K_{SP}	K_{SW}	K_{SP}	K_{SW}	K_{SP}	K_{SW}	K_{SP}
S1	3.15	364	47	168	24	342		153	59	37	5	123	19
S2	2.32	404	28	103	8	219	10	215	15	34	3	93	7
S3	2.61	637	156	141	23	na	295	na	137	420	69	489	73
S4	3.08	325	64	212	61	na	na	1,106	234	149	43	245	85
S5	2.03	549	71	902	177	285	27	244	26	111	22	99	21
S6	1.85	490	54	702	52	442	na	331	na	48	4	160	10
S7	3.77	361	79	866	170	216	42	212	39	23	5	163	34
S8	1.56	333	37	127	15	238	37	590	78	132	16	341	45
S9	0.97	1,839	318	77	5	218	41	388	59	242	15	97	5
S10	3.77	773	32	163	4	na	122	na	72	513	11	640	8
S11	1.81	413	na	522	na	175	na	194	na	127	na	78	na
S12	0.58	364	na	272	na	442	na	432	na	120	na	135	na
S13	2.93	498	na	45	15	415	na	170	na	60	20	103	43
S14	1.81	248	34	111	35	206	22	291	39	66	21	66	24
S15	1.02	606	113	152	26	274	117	346	90	184	31	90	16
S16	2.61	158	na	247	45	370	38	268	29	75	14	94	19
S17	1.70	137	24	170	43	412	156	386	106	174	44	179	49
S18	2.03	436	89	278	90	363	225	198	71	121	39	141	53
S19	2.61	1,189	195	180	39	72	50	154	53	62	13	73	16
S20	2.06	205	18	886	95	1457	31	418	25	96	10	161	15
S21	2.10	457	73	185	27	na	98	893	43	203	30	227	29
S22	2.93	261	65	299	105	482	37	408	46	48	17	88	39
S23	3.01	945	117	498	67	809	58	740	75	181	24	182	25
S24	4.45	217	na	692	na	3,217	na	550	na	44	na	64	na
S25	1.49	1,699	420	64	13	188	357	216	120	69	14	99	21
S26	3.55	165	35	185	34	335	124	130	33	136	25	208	41
S27	5.17	181	39	201	65	485	118	259	57	23	8	84	31
S28	2.95	655	240	135	55	339	107	1,089	284	123	51	298	183
S29	2.17	1,608	na	193	77	1,158	na	518	na	66	26	110	79
S30	0.43	127	117	476	99	186	72	57	20	120	25	97	18
Mean	–	555	103	308	54	513	99	391	75	127	22	168	37

na not available

values of OCPs were higher than K_{SP} values, showing different distribution patterns. The monitoring data showed higher OCPs levels in porewater samples than in overlying water. OCPs belong to hydrophobic organic compounds, which have very low aqueous solubilities. The presence of dissolved organic colloids in porewater may enhance the aqueous concentrations of these hydrophobic compounds beyond their solubilities significantly (Luthy et al. 1997; Nam and Alexander 1998), resulting in the lower K_{SP} values compared to K_{SW}.

p,p'-DDT was the active ingredient in DDTs and typically made up approximately 80 % of the technical formulation, which was degraded to p,p'-DDE under aerobic conditions and to p,p'-DDD under anaerobic conditions

(Zhao et al. 2009). Thus, the ratio of DDT/(DDD + DDE) can be used as an indicator of the residence time of p,p'-DDT in the environment (Qiu et al. 2004; Cheng et al. 2008). A ratio over 1 meant the historical usage and a ratio less 1 indicated relatively recent input of the parent DDTs (Jaga and Dharmani 2003). In this study, the ratios of DDT/(DDD + DDE) in sediments were site-specific, fluctuating around 1 (ranging from 0.57 to 2.28), indicating that in some areas around Taihu Lake, technical DDTs were still used. The ratios were 0.93–13.02 in porewater and 0.84-15.98 in overlying water, respectively, suggesting the potential new source of DDTs into the lake.

The characteristics of DDT compositions may be used to distinguish the DDT pollution caused by technical DDTs

from that caused by dicofol (Cheng et al. 2008). In China, dicofol has been widely used in agriculture since DDT was banned in 1983 (Sun et al. 2010). Dicofol contained approximately 11.4 % of o,p'-DDT and 1.7 % of p,p'-DDT (Qiu et al. 2005). The ratio of o,p'-DDT/p,p'-DDT ranged from 0.2 to 0.3 in technical DDTs, and from 1.3 to 9.3 or higher in dicofol (Qiu et al. 2005). Results from this study showed that in the sediment samples the ratio varied from 0.04 to 0.66, with 0.18 as the median value, suggesting the important contribution of technical DDTs. The similar ratios were also found in aqueous phases, ranging from 0.22 to 0.44 in porewater and from 0.24 to 0.38 in over-lying water, respectively, confirming the contribution from technical DDTs.

This work revealed the distribution of OCPs in sediment, overlying water and corresponding porewater samples from Taihu Lake, which extended our understanding of the OCPs contamination status in this shallow freshwater lake in China. The OCPs levels at each sampling location were site-specific, which was related to the pesticide application history in surrounding areas. Sources of DDTs identified by specific molecular ratios indicated that DDT residues in Taihu Lake were mainly originated from technical DDTs from both historical usage and recent input.

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