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Spatial and temporal variations of organochlorine pesticides (OCPs) in water and sediments from Honghu Lake, China

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ABSTRACT

Honghu Lake in Jiangnan Plain, central China is an important habitat for many migratory birds and an important site for freshwater fishery, and Honghu Lake region is also a main area for rice and cotton production in China. To understand the status and changes of organochlorine pesticide (OCP) contamination, and to assess the OCPs' risks for the ecosystem in Honghu Lake, thirty surface water samples, fifteen surface sediments, and a sediment core were collected in January and July, 2005. OCPs, such as DDTs, HCHs and chlordanes, were determined by GC-ECD in all samples. Concentrations of OCPs in surface water collected during the wet season (July 2005) were relatively higher than those collected during the dry season (January 2005), indicating that the increasing land runoff during the summer might bring the chemical residues from soils to Honghu Lake. The relatively low α -HCH/ γ -HCH ratio and the relatively high *o,p'*-DDT/*p,p'*-DDT ratio indicated the application of lindane on regional agricultural lands in late spring and summer (April–August), which increased the increasing contribution of dicofol to DDT in Honghu Lake, respectively. The levels of Σ HCHs and Σ DDTs in the surface sediments were relatively lower than those from the Yangtze River Delta, but comparable to those from other lakes and rivers in China. The composition of HCHs and DDTs in the surface sediments showed that there was fresh input of lindane (γ -HCH), and DDT residues in Honghu Lake were aged and probably mainly originated from weathered agricultural soils of surrounding Jiangnan Plain. Wash out of HCHs and DDTs from soil was the possible process which caused the increasing concentrations of these chemicals in recent years.

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1. Introduction

Organochlorine pesticides (OCPs) were extensively used for pest and disease control since the 1940s, but OCPs can be bioaccumulated through food chains and cause adverse impacts on the environment and human health (Li and Macdonald, 2005; Nizzetto et al., 2010). OCPs are persistent in the environment and subject to long range transport due to their semi-volatile property (Jones and de Voogt, 1999). Many OCPs have been included in the list of Persistent Organic Pollutants (POPs) developed at the Stockholm Convention. Their uses and manufacture have been banned or restricted in the 1980s in most countries (Voldner and Li, 1995). However, from the 1950s to 1983, about 400,000 tons of dichlorodiphenyltrichloroethanes (DDTs) and 4,900,000 tons of hexachlorocyclohexanes (HCHs) were produced in China, accounting for 20% and 33% of the world total production, respectively (Fu et al., 2003). Although their production and application

have been banned since 1983 in China, high levels of OCPs are still detectable in water, soil, and plants due to their persistence in the environment (Chen et al., 2011; Qian et al., 2006; Wang et al., 2007a, 2007b, 2012; Xu et al., 2000).

OCPs can enter the aquatic environment through different pathways, including effluent discharge, agricultural runoff, atmospheric deposition, and air/water exchange (Li and Macdonald, 2005; Macdonald et al., 2005). Because of high hydrophobicity, OCPs have a strong affinity to suspended particles. When suspended particles deposit, OCPs can subsequently settle down from water to sediment (Yang et al., 2005). As a result of water turbulence, dredging and bioturbation, OCPs accumulated in sediment could be remobilized and released from sediment to the water column (Gong et al., 2007; Lee et al., 2001; Zeng and Venkatesan, 1999). Therefore, the lake sediments could become a potential secondary source of OCPs in the aquatic system (Gong et al., 2007; Lee et al., 2001; Nizzetto et al., 2010; Zeng and Venkatesan, 1999).

Honghu Lake is the seventh largest freshwater lake in China, and is located in Jiangnan Plain between Yangtze River and its longest tributary Han River (Fig. 1). As a main area for rice and cotton production

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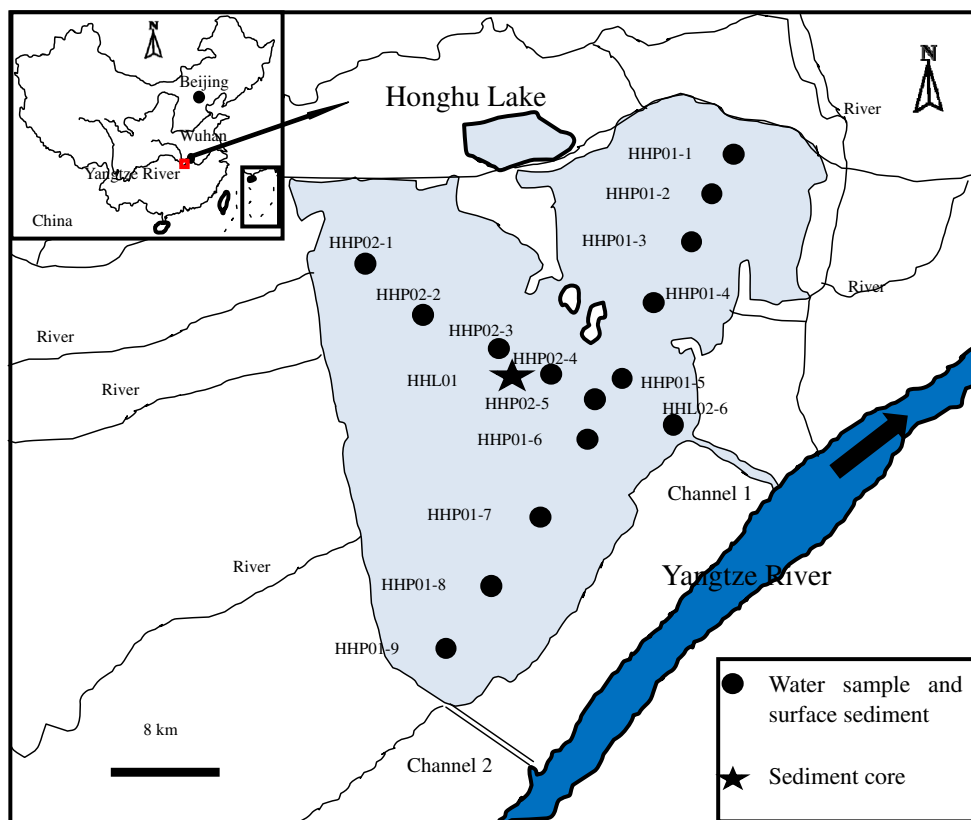


Fig. 1. Map of Honghu Lake and the sampling locations.

in China, organochlorine pesticides (OCPs), such as DDTs, HCHs and chlordanes, have been extensively used around the Honghu Lake region during 1950s–1970s (Li et al., 1999, 2001). Although the production and agricultural usage of technical DDTs and HCHs have been banned officially in China since 1983, lindane and DDTs containing dicofol are still illegally produced and used because of low cost and high efficiency in pest control (Li et al., 2001; Qiu et al., 2005, 2008).

Due to the rapid development of the local economy near Honghu Lake, water quality and aquatic biological resources have decreased dramatically since the 1980s. For protection and restoration purposes, the Honghu Wetland Nature Reserve was founded in 1996 and added to the Ramsar List of Wetlands of International Importance in 2008. Currently Honghu Lake is an important habitat for many migratory birds and an important site for freshwater fishery. To understand the status and changes of OCP contamination in Honghu Lake, the specific objectives of this study were to (1) investigate the levels, spatial distribution of DDTs, HCHs and chlordanes in water and sediments in Honghu Lake and (2) study the contamination profiles to identify possible sources of OCPs. This study also reconstructed the contamination history based on the temporal changes of OCPs in the sediment.

2. Methodologies

2.1. Field sampling

Honghu Lake is located in central Hubei Province and has a catchment area of about 3000 km² with a population of over 1.5 million. The lake has an average altitude of 22 m and can exchange water with Yangtze River through two channels (Fig. 1). Honghu Lake used to exchange water with Yangtze River freely. However, two dams were constructed on the channels in 1957 for agricultural irrigation. Since then water exchange only occurs in flood seasons (Huang et al., 2007).

To study the distribution of OCPs in Honghu Lake, two transactions were selected for sample collection: One started from the inlet located Northeast, through channel 2 (HHP01); the other one started from the inlet located Northwest through channel 1 that connected to Yangtze River (HHP02) (Fig. 1). These two transactions were along the major shipping channels of the lake. At the time of sampling the lake was divided into several segments by enclosed nets for aquaculture. Therefore, it was difficult to access other areas except for the shipping channels.

In January and July, 2005, 30 water samples were collected from 15 sampling sites along the two transactions. All the water samples were collected in pre-cleaned 5 L glass bottles. The water samples were stored at $-20\text{ }^{\circ}\text{C}$ before chemical analysis. Surface sediment samples (0–2 cm) were collected in July 2005 using a stainless steel grab. Meanwhile, a sediment core with a length of 70 cm was collected at site HHL01 using a KC Kajak sediment core sampler (Silkeborg, Denmark). This sediment core was sectioned at 1 cm intervals. The sectioned sediment core and surface sediment samples were sealed in polyethylene bags and stored at $-20\text{ }^{\circ}\text{C}$ till chemical analysis.

2.2. Chemicals

Pesticide grade dichloromethane (DCM) and *n*-hexane were purchased from Tedia Co. (Fairfield, Ohio, USA). HPLC grade acetone was from Fisher Scientific (Waltham, Massachusetts, USA). The mixed standard of organochlorine pesticides, 2,4,5,6-tetrachloro-*m*-xylene (TCMX), decachlorobiphenyl (PCB 209) and pentachloronitrobenzene (PCNB) were obtained from Ultra Scientific (North Kingstown, Rhode Island, USA). Other chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Silica gel and alumina gel (100–200 mesh) were activated at $180\text{ }^{\circ}\text{C}$ and $240\text{ }^{\circ}\text{C}$ for 12 h, respectively, deactivated with 3.0% purified water, and stored in desiccators. Anhydrous sodium sulfate was baked at $450\text{ }^{\circ}\text{C}$ for 6 h before it was used.

2.3. Sample preparation

The water sample of 1000 ml was extracted three times with 20 ml of dichloromethane (DCM) solution for each extraction. Before extraction, samples were spiked with 20 ng of 2,4,5,6-tetrachloro-m-xylene (TCMX) and PCB 209 as the surrogate standards. Extracts were added with activated copper granules, solvent-exchanged to hexane, evaporated to about 2–3 mL and then purified by elution with 30 mL of hexane and DCM mixture (3:2 v/v) through a chromatographic column of deactivated alumina/silica gel (1:2 v/v). Elutes were concentrated to 0.2 ml under a nitrogen stream and spiked with pentachloronitrobenzene (PCNB) as an internal standard prior to instrumental analysis.

Surface sediment and sediment core samples were homogenized and freeze-dried. Ten grams of dried sediment samples were spiked with 20 ng of TCMX and PCB 209, and then were Soxhlet-extracted with DCM for 24 h. Elemental sulfur was removed by adding activated copper granules to the collection flasks. The purification of sediment samples was performed the same as that for the water samples described above. All extracts were kept in sealed vials at $-20\text{ }^{\circ}\text{C}$ prior to instrumental analysis.

2.4. Instrumental analysis

A HP 6890 GC with a ^{63}Ni ECD and a HP-5 (30 m \times 0.32 mm i.d. \times 0.25 μm film thickness) capillary column was used to detect the concentrations of OCPs in water and sediment samples. High purity nitrogen was used as carrier gas at 2.5 ml/min under a constant flow mode. Injector and detector temperatures were maintained at 290 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. The oven temperature change was programmed as follows: began at 100 $^{\circ}\text{C}$ (equilibrium time 1 min), raised to 200 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$, then to 230 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$, and at last reached to 280 $^{\circ}\text{C}$ at a rate of 8 $^{\circ}\text{C}/\text{min}$, then held for 15 min. The extract sample of 2 μl was injected into GC-ECD for chemical analysis. A 6-point calibration curve was established to quantify the target elements. Then, the concentrations of OCPs were corrected by surrogates. In the present study, the following standard compounds were included: α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT, α -chlordane (cis), and γ -chlordane (trans). The detailed description of the procedure was given by Gong et al. (2007) and Chen et al. (2011).

2.5. Sediment core dating

The sediment core dating was accomplished by using the previously established methods (Gong et al., 2007; Zhang et al., 2002). In

brief, the Pb activities in the sediment samples were determined by analyzing the α -radioactivity of its decay product ^{210}Po , based on the assumption that the two were in equilibrium. The Po was extracted, purified, and self-plated onto silver disks at 75–80 $^{\circ}\text{C}$ in 0.5 M HCl, with ^{209}Po used as yield monitor and tracer in quantification. Counting was conducted by computerized multichannel α -spectrometry with gold-silicon surface barrier detectors. Supported ^{210}Po was obtained by indirectly determining the α -activity of the supporting parent ^{226}Ra , which was carried by co-precipitated BaSO_4 . A constant rate of supply (CRS) model was used to obtain the average sedimentation rate.

2.6. Quality assurance

The OCP concentrations were quantitatively determined by comparing the area under each peak with the area of the standard. For quality assurance (QA) samples, a procedural blank and a spiked sample containing all chemicals were analyzed to determine potential interference and cross-contamination. The correlation coefficients for the calibration curves of the OCPs were all >0.99 . The limits of detection (LDs) for OCPs were based on a signal-to-noise ratio (S/N) of 3. The method detection limits (MDL) of OCPs in the sediment samples ranged from 0.01 to 0.05 ng/g DW. The MDL of OCPs in the water samples ranged from 0.01 to 0.1 ng/L. The spiked recoveries of the OCPs ranged between 75% and 113%, and the recovery of surrogates (TCMX and PCB209) were $85 \pm 13\%$ and $75 \pm 5\%$, respectively.

2.7. Statistical analysis

Normality test, two sample *t* tests on different means, nonparametric test on different means (two sample Kolmogorov–Smirnov test/K–S test), and correlation analyses were performed by OriginPro 8.

3. Results and discussion

3.1. Distribution and potential sources of OCPs in surface water

Concentrations of OCPs in surface water in Honghu Lake are shown in Table 1. During the dry season in January, 2005, the average value of ΣOCPs in the water samples was 4.06 ± 1.38 ng/L. ΣHCHs , ΣDDTs , and $\Sigma\text{chlordanes}$ contributed 73%, 5.9% and 21% to ΣOCPs , respectively. During the wet season in July, 2005, the average value of ΣOCPs was 4.82 ± 1.25 ng/L. ΣHCHs , ΣDDTs , and $\Sigma\text{chlordanes}$ contributed 49%, 8.5% and 42% to ΣOCPs , respectively. Overall, HCHs were the dominant chemicals detected in water samples. The relatively

Table 1
OCP concentrations of surface water (ng/L) and surface sediments (ng/g DW) in Honghu Lake (n = 15).

OCPs	Water in dry season				Water in wet season				Surface sediments			
	Average	STDEV ^a	Min	Max	Average	STDEV	Min	Max	Average	STDEV	Min	Max
α -HCH	1.23	0.88	0.35	3.43	0.24	0.21	0.06	0.81	2.35	3.33	0.27	13.63
β -HCH	0.33	0.14	0.12	0.60	1.12	0.41	0.49	1.71	2.24	1.24	0.00	4.44
γ -HCH	1.31	0.62	0.33	2.74	0.66	0.34	0.23	1.61	2.95	2.77	0.00	10.76
δ -HCH	0.10	0.27	ND ^b	0.89	0.33	0.48	ND	1.29	0.18	0.46	0.00	1.74
ΣHCHs^c	2.97	1.43	0.95	7.04	2.36	1.08	0.79	4.00	7.72	3.80	2.54	16.92
p,p'-DDE	0.10	0.04	0.04	0.18	0.12	0.06	0.06	0.28	7.12	5.40	1.30	22.23
p,p'-DDD	0.02	0.02	ND	0.06	0.04	0.05	ND	0.15	0.94	0.82	0.18	3.08
o,p'-DDT	0.07	0.08	ND	0.26	0.10	0.09	ND	0.26	0.00	0.01	0.00	0.05
p,p'-DDT	0.05	0.06	ND	0.15	0.15	0.05	0.07	0.24	1.14	0.60	0.31	2.21
ΣDDTs^c	0.24	0.13	0.06	0.49	0.41	0.19	0.15	0.82	9.19	6.75	1.84	27.52
α -chlordane	0.23	0.20	0.04	0.65	1.14	0.49	0.53	2.32	0.75	0.54	0.20	1.80
γ -chlordane	0.62	0.54	0.05	1.86	0.92	0.46	0.41	1.99	0.22	0.22	0.00	0.79
Chlordanes ^c	0.85	0.64	0.09	2.29	2.05	0.75	1.07	3.74	0.97	0.55	0.30	1.80
ΣOCPs^d	4.06	1.38	2.15	7.94	4.82	1.25	2.93	7.52	17.88	10.47	4.68	42.95

^a STDEV means standard deviation.

^b ND means the concentration is less than MDL. 0 is assigned to the value of ND when calculating the sum of OCPs and the average concentration.

^c $\Sigma\text{HCHs} = \alpha\text{-HCH} + \beta\text{-HCH} + \gamma\text{-HCH} + \delta\text{-HCH}$; $\Sigma\text{DDTs} = \text{p,p'-DDE} + \text{p,p'-DDD} + \text{o,p'-DDT} + \text{p,p'-DDT}$; $\Sigma\text{chlordanes} = \alpha\text{-chlordane} + \gamma\text{-chlordane}$.

^d $\Sigma\text{OCPs} = \Sigma\text{HCHs} + \Sigma\text{DDTs} + \Sigma\text{chlordanes}$.

high levels of OCPs found during the wet season (K-S test, $D = 0.87$, $Z = 0.32$, $P = 0.000006$) might be partially attributed to the increase of land runoff in the summer. The low levels of DDTs found in water samples may be caused by the large octanol/water partition coefficient of these chemicals ($\log K_{ow} \sim 6.5$) (Mackay et al., 2006).

Except δ -HCH, other HCH isomers (α -HCH, β -HCH, γ -HCH) were detected in all water samples. The levels of Σ HCHs in water samples ranged from 0.79 to 7.04 ng/L, with an average concentration of 2.67 ng/L. The spatial distribution of Σ HCHs in surface water is presented in Fig. 2. In the dry season, the highest concentration of Σ HCHs was found at site HHP01-4 which was in a narrow channel between a lake island and the northeast shore of Honghu Lake. The high concentration of Σ HCHs in this sample might due to the re-emission of these substances from suspended sediments caused by turbulence occurred in the narrow channel. During the wet season, the highest value of Σ HCHs was detected at site HHP02-3 which is located near a fish farming region. High bioactivities of aquatic organisms from this region could increase re-suspension of OCPs accumulated in the sediment, which could accelerate the release of previously adsorbed pollutants from suspended particles into water.

The composition of HCH related isomers could be used as an indicator to determine the sources and fates of HCHs in the environment. Usually, the main sources of HCHs came from the usage of technical HCH, containing 60–70% α -HCH, 5–12% β -HCH, 10–15% γ -HCH and other minor isomers, and lindane, containing more than 99% of γ -HCH (Iwata et al., 1993; Li et al., 1998; Wu et al., 2010). The α/γ -HCH ratio is 5:7 in technical HCH but tends to increase over time due to a faster degradation of γ -HCH, compared to α -HCH. However, continued usage of lindane would lead to a decline in the α/γ -HCH ratios. Generally, a ratio of α/γ -HCH lower than 1 indicates recent input of lindane (Zhang et al., 2009). The most often detected HCH isomers in the water samples of Honghu Lake were α -, β - and γ -HCH. During the dry season, α - and γ -HCH were the dominant isomers and accounted for 41.41% and 44.11% of Σ HCHs, respectively. The pattern of HCHs during the wet season was different from that during the dry season. In the wet season, the dominant isomers were β - and γ -HCH which accounted for 47.46% and 27.97% of Σ HCHs, respectively. In the present study, the α/γ -HCH ratios in surface water during the dry and wet seasons were 1.3 ± 2.1 and 0.38 ± 0.31 , respectively. The relatively low levels of α/γ -HCH ratio observed in the wet season indicated the presence of lindane in the surrounding areas of Honghu Lake in late spring and summer. In addition, the predominant β -HCH in surface water during the wet season might suggest the input of technical HCH residues to Honghu Lake from local agricultural surface runoff, since β -HCH is more stable and resistant to microbial degradation compared with other isomers (Li et al., 2001, 2003). Furthermore, it might also suggest that technical HCH have not been used in the study area recently.

p,p' -DDT, o,p' -DDT, p,p' -DDD and p,p' -DDE had been detected in the majority of water samples. Σ DDT concentrations in water samples ranged from 0.06 to 0.82 ng/L with an average concentration of 0.33 ng/L (Table 1). In general, the spatial distribution of Σ DDTs in water was relatively uniform in Honghu Lake (Fig. 2). Similar to the distribution of Σ HCHs, the water samples collected at Site HHP02-3 which is located near a fish farming region had the highest concentration of Σ DDTs during the wet season. DDTs in lake water were predominated by p,p' -DDE and p,p' -DDT which contributed $41 \pm 22\%$ and $28 \pm 22\%$ of Σ DDTs, respectively. In the environment, p,p' -DDT will be converted to p,p' -DDE by bacteria under aerobic conditions (Kim et al., 2002). Hence, the ratio of DDT over DDE can be used to determine the degree of DDT biodegradation and to distinguish recent and historical inputs of DDTs (Wu et al., 2011). Commonly, DDT/DDE ratios greater than 1 indicate relatively fresh DDT inputs, while DDT/DDE ratios of <1 imply the presence of aged DDT material (Poza et al., 2006). In the present study, the ratio of p,p' -DDT/ p,p' -DDE in the water samples collected during the dry and wet seasons were 0.50 ± 0.64 and 1.5 ± 0.86 , respectively,

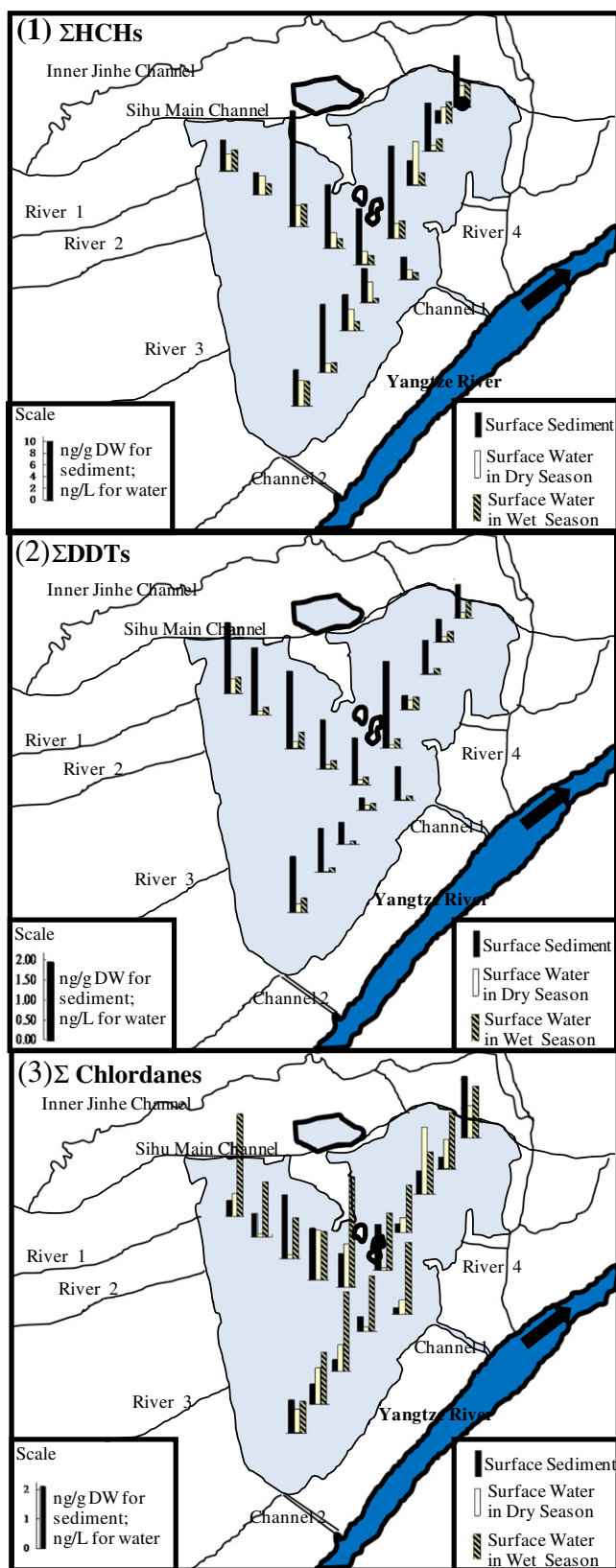


Fig. 2. Spatial distributions of Σ HCHs, Σ DDTs and Σ Chlordanes in surface water and surface sediments of Honghu Lake.

indicating fresh input of p,p' -DDT in the wet season. Since technical DDT has been banned in China in the middle of the 1980s, the usage of DDT-containing products, such as antifouling paint for ships, may

be the fresh source of DDT in the aquatic system (Wu et al., 2011; Zheng et al., 2010). Furthermore, agricultural application of dicofol containing high levels of *o,p'*-DDT as impurity may be another source of DDT input to the environment in China (Qiu et al., 2005; Zheng et al., 2010). The ratio of *o,p'*-DDT/*p,p'*-DDT in technical DDT and dicofol was reported to be 0.2–0.3 and 7, respectively (Qiu et al., 2004, 2005, 2008; Wu et al., 2011). In the present study, *o,p'*-DDT/*p,p'*-DDT in the water samples collected during the dry and wet seasons were 1.2 ± 1.1 and 0.73 ± 0.61 , respectively, which were 2–6 times higher than that in technical DDT, and 6–10 times lower than that in dicofol, suggesting a significant contribution of dicofol to DDT in the present study area.

α - and γ -Chlordane were detected in all water samples. Concentrations of Σ chlordanes in water samples varied between 0.09 and 3.74 ng/L, with an average concentration of 1.5 ng/L (Table 1). The spatial distributions of Σ chlordanes are shown in Fig. 2. In general, the levels of Σ chlordanes in the wet season (2.1 ± 0.75 ng/L) were significantly (*K-S* test, *D* = 0.73, *Z* = 0.27, *P* = 0.00035) higher than those found in the dry season (0.85 ± 0.64 ng/L). As mentioned above, agricultural application and/or increasing agricultural land surface runoff might contribute to the high levels of Σ chlordanes during the wet season. Moreover, the isomer ratio of γ/α -chlordane could be used to trace the source of chlordane in the environment since the ratio of γ/α -chlordane in technical chlordane mixtures is 1.17:1.41 (Bidleman et al., 2002; Jantunen et al., 2000; Zhang et al., 2009). In the present study, the average and standard deviation of γ/α -chlordane was 1.3 ± 0.95 , which was similar to the ratio in technical chlordane, likely indicating recent usage of technical chlordane in the Honghu Lake water basin.

3.2. OCP distribution in surface sediments and sediment core

All the selected OCPs except for *o,p'*-DDT were detected in the surface sediments of Honghu Lake. The concentration ranges, mean values and standard deviations of OCPs in the surface sediments are shown in Table 1. α -HCH, β -HCH, γ -HCH, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, α -chlordane and γ -chlordane were the most commonly found OCP compounds and in more than 80% of sediment samples. Σ HCHs, Σ DDTs and Σ Chlordanes in sediment contributed 43%, 51% and 5.4% to the total OCPs (Σ OCPs), respectively. Overall, HCHs and DDTs were the dominant chemicals detected in the sediment samples. Different from the concentrations in surface waters, concentrations of Σ DDTs in surface sediments with 9.19 ± 6.75 ng/g DW were not significantly (*K-S* test, *D* = 0.27, *Z* = 0.10, *p* = 0.68) different from the concentrations of Σ HCHs with 7.72 ± 3.80 ng/L. Historically, the total usage of technical HCH was about ten times more than that of DDT (Li et al., 1999, 2001). However, HCHs have smaller octanol/water partition coefficient and particle affinity but higher biodegradability and volatility, compared to DDTs (Mackay et al., 2006; Yang et al.,

2005), which contributed to the relative low residuals in the sediments. The highest level of Σ OCPs was found at site HHP02-3 where the concentrations of Σ HCHs and Σ DDTs in surface water were also the highest, while the lowest concentration of Σ OCPs was found at site HHP02-6 where the levels of Σ HCHs and Σ DDTs were also found to be the lowest (Fig. 2). Geographically, the high levels of OCPs were found in the sediments collected near the island in HHL. For DDTs, the concentrations in the sediments collected along the HHP02 profile were obviously higher than those collected along the HHP01. However, this distribution trend was not found for Σ HCHs and Σ Chlordanes (Fig. 2).

HCHs and DDTs were ubiquitous in the sediments of Honghu Lake. Concentrations of Σ HCHs and Σ DDTs in the sediments of the Honghu Lake were in the range of 2.54–16.92 ng/g (with an average value of 7.72 ng/g) and 1.84–27.52 ng/g (with an average value of 9.19 ng/g), respectively. Table 2 compared the Σ HCHs and Σ DDTs in the sediments from lakes and rivers in China. Overall, the levels of Σ HCHs and Σ DDTs in the Honghu Lake were relatively lower than those from the Yangtze River Delta (i.e., Taihu Lake, Qiantang River), but comparable with those from the other regions. Yangtze River Delta is a traditional agricultural region and the most developed industrial region. The high levels of Σ HCHs and Σ DDTs in the Yangtze River Delta might be attributed to the industrial production and agricultural application in those areas. It is worth noting that the levels of Σ HCHs and Σ DDTs in Haihe River in 2007 were significantly higher than those in 2003, especially for Σ HCHs (Yang et al., 2005; Zhao et al., 2010), indicating a fast input of OCPs into Haihe River in recent years.

The average compositions of HCH isomers measured in the surface sediment samples from Honghu Lake were α -HCH with 30%, β -HCH with 29%, γ -HCH with 38% and δ -HCH with 2%. Previous studies carried out in the rivers or estuary environment often found that β -HCH was dominant in sediments (Kaushik et al., 2008; Said et al., 2008; Yang et al., 2010; Zhang et al., 2003; Zhong et al., 2011; Zhou et al., 2006). However, γ - and α -HCH also make large contributions to the levels of Σ HCHs in this study. According to the ratio of α/γ -HCH in the sediment from Honghu Lake, with the exception of three sites where the ratios could not be calculated, the ratios at all the sampling sites were less than 0.5, thereby implying that there may be new γ -HCH (lindane) input into the Honghu Lake. The γ -HCH input maybe associated with the input from agricultural surface runoff or atmospheric depositions.

The average compositions of DDT related substances in the sediments were 77% *p,p'*-DDE, 12% *p,p'*-DDT, and 10% *p,p*-DDD. The predominance of *p,p'*-DDE in the sediments indicated that the DDT residues in the Honghu lake were degraded and probably originated from weathered agricultural soils of surrounding areas.

Fig. 3 shows the concentration variations of DDTs and HCHs in the sediment core and the chronology determined by radiometric dating

Table 2

Comparison of Σ HCHs and Σ DDTs in surface sediments of Honghu Lake with other lakes/rivers of China (ng/g DW).

Sampling location	Sampling time	Σ HCHs	Σ DDTs	Reference
Peacock River, Northwest China	2006	0.13–6.6 (1.4)	0.10–1.5 (0.55)	Chen et al. (2011)
Daliaohe River, Northeast China	2005	1.86–21.49 (6.82)	0.21–2.81 (0.76)	Wang et al. (2007a)
Tonghui River, Beijing, North China	2002	0.06–0.38 (0.17)	0.11–3.8 (1.1)	Zhang et al. (2004)
Haihe River, North China	2003	1.9–19 (7.3)	0.32–80 (16)	Yang et al. (2005)
Haihe River, North China	2007	12–1600 (550)	Nd–155 (19)	Zhao et al. (2010)
Yellow River, North China	2005	0.09–12.89 (1.08)	0.05–5.03 (1.02)	Wang et al. (2010)
Baiyangdian Lake, North China	2007	0.15–3.11 (0.86)	0.03–1.41 (0.46)	Wang et al. (2012)
Qiantang River, East China	2005	8.2–150 (37)	1.1–100 (21)	Zhou et al. (2006)
Taihu Lake Region, East China	1999–2001	<0.1–66.5	<0.1–8.8	Feng et al. (2011)
Dongting Lake, Southeast China	2004	0.21–9.59 (5.33)	Nd–10.15 (5.31)	Qian et al. (2006)
Jiulong River, Southeast China	1999	0.48–9.0 (1.6)	0.01–0.43 (0.09)	Maskaoui et al. (2005)
Mingjiang River, Southeast China	1999	3.0–16 (8.6)	1.6–13 (6.7)	Zhang et al. (2003)
Pearl River, South China	2002–2003	0.18–1.4	0.057–2.2	Yu et al. (2008)
Yangtze River, Central China	1998	0.18–1.1	0.21–4.5	Xu et al. (2000)
Honghu Lake, Central China	2005	2.54–16.9 (7.72)	1.84–27.5 (9.19)	This study

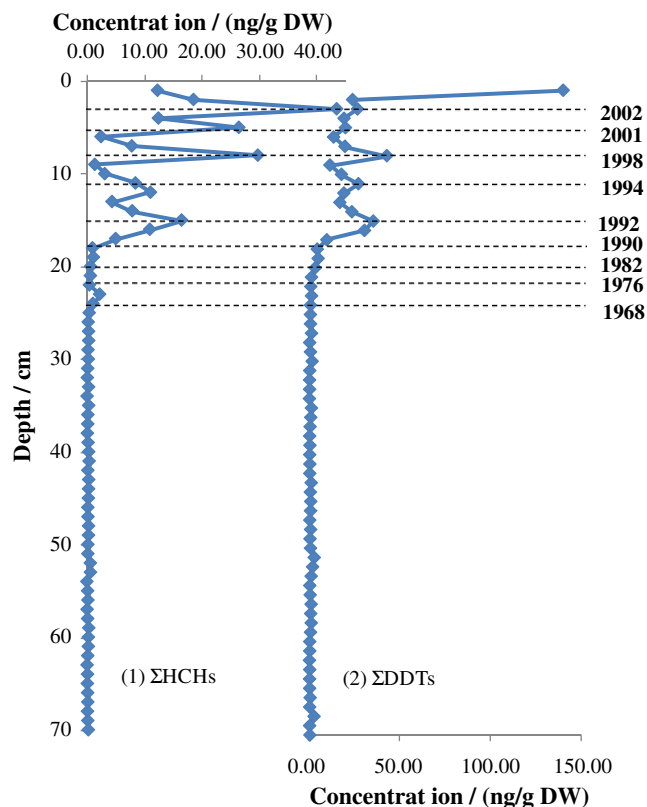


Fig. 3. Profile chronology and concentrations of Σ HCHs and Σ DDTs in sediment core of Honghu Lake.

of ^{210}Pb (data not shown). In China, technical HCH and DDT were widely used in the 1960s and 1970s. A previous report on the pesticides in sediment cores from Quanzhou Bay, southeast China found high levels of DDTs and HCHs in the 1970s, indicating the increasing usage of these pesticides in China (Gong et al., 2007). In this study, Σ HCHs showed a slight increasing trend in the 1970s, but no obviously increasing trend was found for Σ DDTs between 1968 and 1990. However, the levels of Σ HCHs and Σ DDTs both showed gradual increasing trends after the year 1990, which were similar to a previous study carried out in Quanzhou Bay and Pearl River delta of China (Gong et al., 2007; Zhang et al., 2002). Wash out of HCHs and DDTs from soil was the possible process which caused the increasing concentrations of these chemicals in recent years (Gong et al., 2007). Rapid economic development led to serious land reclamation in the Jiangnan Plain in the 1990s. Therefore, residues of OCPs in agriculture soil transported by enhanced surface runoff to the sediments of Honghu Lake may be the major reason for the increase in concentrations of DDT and HCH in the sediment.

It should be noted that concentrations of Σ HCHs overall increased from 0 ng/g DW in 1990 to 45 ng/g DW in 2002, and sharply decreased to 10 ng/g DW in recent years. However, there was a quite different trend in the concentrations of Σ DDTs with stable levels of about 50 ng/g DW during 1990–2002. But Σ DDTs showed a rapid increase to 150 ng/g DW in 2005. The historical records of Σ HCHs and Σ DDTs in the present study from 1990 to 2005 likely indicated that OCPs or some substitutes, especially those containing HCHs still were used extensively, although the use of OCPs has been banned or restricted in China since 1983 (Sarkar et al., 1997). In fact, extensive and continuous usage of OCPs in China has resulted in ubiquitous OCP pollution in various environmental matrices, including air, soils, sediments, water bodies, and biota samples (Feng et al., 2011; Lam et al., 2008; Lammel et al., 2007; Liu et al., 2009; Tang et al., 2007; Wang et al., 2007b; Zhang et al., 2011; Zhao et al., 2010; Zhong et al., 2011).

4. Conclusions

Concentrations of Σ OCPs in surface water in Honghu Lake varied from 2.15 to 7.94 ng/L (mean 4.06 ng/L) in the dry season, and from 2.93 to 7.52 ng/L (mean 4.82 ng/L) in the wet season. HCHs were the dominant compounds, followed by chlordanes and then DDTs. The low values of α/γ -HCH (0.38 ± 0.31), $o,p'/p,p'$ -DDT (1.5 ± 0.86) and γ/α -chlordane (1.3 ± 0.95) in surface water in the wet season might indicate the fresh/recent application of lindane, dicofol and technical chlordane in the surrounding agricultural areas. The levels of Σ HCHs and Σ DDTs in the surface sediments of Honghu Lake ranged from 4.68 to 42.95 ng/g DW, with a mean of 17.88 ng/g DW, which were comparable with those of other water bodies in the country, except for Taihu Lake in East China and Qiantang River in East China which had higher concentrations. Furthermore, the HCHs and DDTs were extensively used in Honghu Lake area during 1990–2005 as revealed by the historical record in the sediment core.

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