

Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China

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Abstract

The levels of 13 organochlorine pesticides (OCPs) in surface water and sediments from Qiantang River in East China were investigated to evaluate their potential pollution and risks. A total of 180 surface water samples at 45 sampling sites and 48 sediment samples at 19 sampling stations were collected along the river in four seasons of 2005. Soil samples and wet deposition samples were also collected to provide evidence on the source of OCPs pollution. The total OCPs concentrations in surface water and sediments were 7.68–269.4 ng/L and 23.11–316.5 ng/g-dry weight (dw), respectively. The concentrations of OCPs in sediments were in the range of 8.22–152.1 ng/g-dw for HCHs (α -, β -, γ -, δ -HCH), 1.14–100.2 ng/g-dw for DDTs (*p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT *o,p'*-DDD), 9.41–69.66 ng/g-dw for other OCPs (aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide). The total OCPs concentrations in soils and wet deposition were 5.04–214.9 ng/g-dw and 16.18–242.4 ng/L, respectively. Among the OCPs, HCHs, DDTs and heptachlor were the most dominant compounds in the sediments. The dominant OCPs in water were γ -HCH among HCHs, heptachlor among other OCPs and *p,p'*-DDE among DDTs. Also, different contamination patterns among sampling seasons were found. The concentrations of OCPs in sediment collected in spring were higher than those in summer and autumn. In contrast, the concentrations of OCPs in surface water in summer and autumn were higher among four sampling seasons. Distribution of HCHs, DDTs and other OCPs were different indicating their different contamination sources. The notable contamination was found in Fuchun reservoir. Composition analyses in sediments indicated a recent usage or discharge of lindane into the river.

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1. Introduction

Organochlorine pesticides (OCPs) are one of the most important persistent organic pollutants (POPs) and have been of great concern around the world owing to their chronic toxicity, persistence and bioaccumulation [1]. These compounds pose great threats to ecosystems and human health. Although the application of these chemicals has been banned or restricted in many countries especially the developed ones, some developing countries are still using these compounds because of their low cost and versatility in industry, agriculture and public health [2,3].

The input pathways of OCPs into the river environments include runoff from non-point sources, discharge of industrial wastewater, wet or dry deposition and other means. Therefore,

the residues of OCPs might ultimately pass onto people through consumption of drinking water, fish and agriculture food [4–6]. Furthermore, OCPs have an affinity for particulate matter and one of their main sinks is thought to be river and marine sediments. Therefore, the investigation of distribution of OCPs in water and sediments can indicate the status of aquatic contamination [7–9].

China is a large producer and consumer of pesticides in the world. Large amounts of OCPs were used in past decades to obtain high yield to sustain overpopulation in China. HCH and DDT were widely used in China from 1952 to 1983. The total production of technical HCH and DDT is around 4 and 0.27 million tonnes, respectively. Even after the ban of technical HCH and DDT in 1983, 3200 t of lindane (almost pure γ -HCH) was still in use between 1991 and 2000, and DDT production also continues due to export demand and dicofol production [10–12]. OCP pollution of aquatic environment was universe in China [8,9,13–18].

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Qiantang River is one of the two important rivers in the Yangtze Delta of East China and the largest river in Zhejiang province. It flows 688 km from the west peak to Hangzhou Bay with an approximately length of one ninth of the Yangtze River. Qiantang River Basin drains a populous area of 55558 km² and has been rice and orange fields for several centuries. In addition to being used for agriculture and the generation of electricity, Qiantang River is main source of drinking water and industrial water in this basin. However, no information was available for OCPs in Qiantang River. In order to understand the pollution of OCPs in Qiantang River, surveys were carried out in Qiantang River from Jinhua city (upstream) to Hangzhou city (downstream) in 2005.

The objectives of this research are to (1) survey the levels and distributions of OCPs in water and sediments of Qiantang River; (2) discuss their contamination profiles and possible sources of certain important OCPs.

2. Material and methods

2.1. Sampling and sample treatment

Qiantang River has two important sources (Xin'an River and Lan River). The two rivers meet in Meichen, called Fuchun River. To Hangzhou city, it is also named Qiantang River. Hangzhou is the capital of Zhejiang province, located downstream of Qiantang River. It is a traditional agriculture production area which has large scale grain farms. Also this river is a major source for drinking water supply in Zhejiang province and receives massive industrial discharge and domestic sewage at the same time.

Forty-five sampling sites along the river were selected and one water sample from each site was collected for one survey. A total of 180 surface water samples at 0.5 m below the water surface from Qiantang River were collected, upstream to downstream, during four axial surveys on January 19–20 (winter), April 13–14 (spring), July 27–29 (summer) and October 13–14 (autumn), 2005. Average temperature of surface water was 6, 12, 32 and 22 °C, respectively, in above four seasons. A total of 48 sediment samples in 19 sites along Qiantang River were collected during the last three surveys. Fig. 1 shows the study area and the sampling locations. Through the surveys a globe position system (GPS) was used to locate the sampling positions and temperature was detected. Samples were taken using a cleaned glass barrel with an upward-open door at the bottom. The 4.5 L glass bottles were rinsed twice with samples then carefully filled just to overflowing, without passing air bubbles through sample or trapping air bubbles in sealed bottles. Preparation of these bottles included washing with detergent, rinsing with tap water and ultra pure water. All samples were filtered through 0.45 μm fiber glass filters to remove sand and debris after returning to the laboratory and extracted immediately.

The surficial sediments (top 0–20 cm) were collected with a stainless steel grab. All the samplers were immediately transferred to the laboratory and kept at –20 °C in the refrigerator. The samples were freeze-dried, homogenized and passed through a 63 μm sieve. All the equipments used for sam-

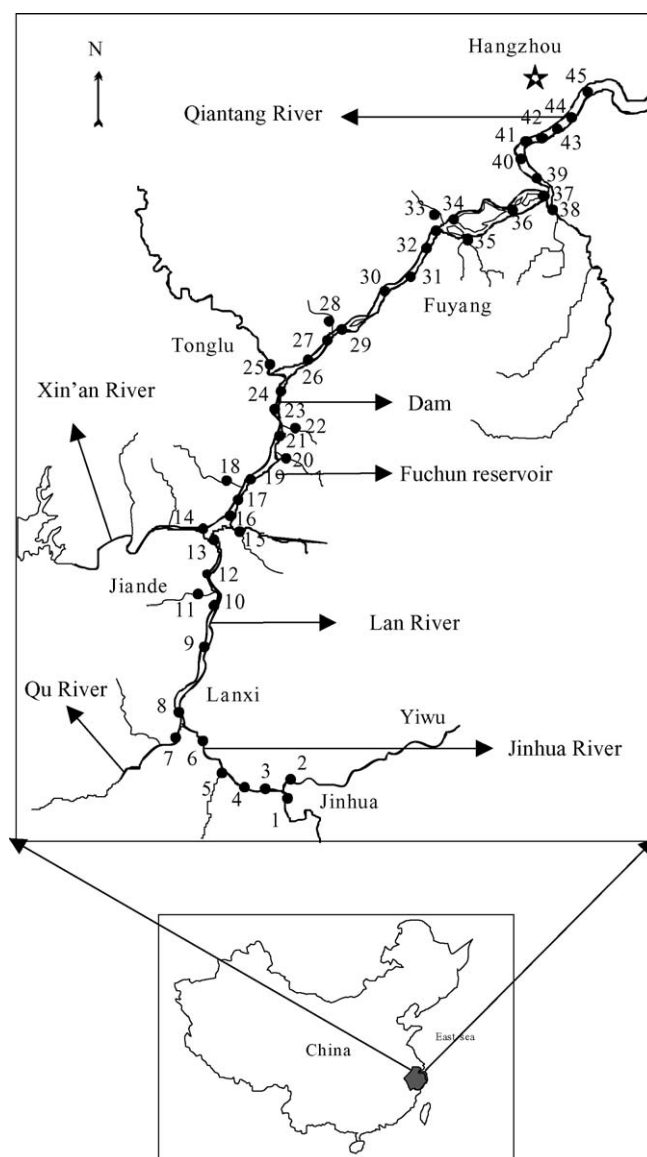


Fig. 1. Location of Qiantang River in China and the sampling sites.

ple collection, transportation, and preparation, were free from organochlorines contamination.

Thirty agricultural soil samples (top 0–3 cm) were collected with a stainless steel spoon near Qiantang River bank. Eighteen wet deposition samples (snow or rain water) were collected with a glass bucket and were treated by the same procedure with surface water.

2.2. Extraction procedure

Solid phase extraction (SPE) cartridges system from Supelco was used to extract water samples and wet deposition samples according to the method of Zhou et al. [16]. Before the extraction, the C₁₈-bonded phase containing 500 mg reversed phase octadecyl were first washed with 5 mL of ethyl acetate and conditioned by 5 mL of methanol, then washed with 2 mL × 5 mL of ultra pure water. The water samples (1000 mL) were percolated through the cartridges with a flow rate of 5 mL/min under

Table 1
Mean recovery, relative standard deviation (R.S.D.) and detection limit (DL) of OCPs in water (at 5 ng/L) and sediments (at 10 ng/g-dw)

OCPs	Water (<i>n</i> = 5)			Sediment (<i>n</i> = 5)		
	Recovery (%)	R.S.D. (%)	DL (ng/L)	Recovery (%)	R.S.D. (%)	DL (ng/g-dw)
α-HCH	76	6	0.08	90	7	0.10
β-HCH	87	3	0.16	88	5	0.40
γ-HCH	83	5	0.08	85	8	0.18
δ-HCH	85	4	0.08	83	6	0.24
Heptachlor	75	8	0.15	90	4	0.30
Aldrin	78	7	0.08	88	9	0.36
Heptachlor epoxide	76	3	0.08	89	10	0.20
<i>p,p'</i> -DDE	80	7	0.08	106	8	0.12
Dieldrin	78	4	0.15	92	7	0.15
Endrin	87	6	0.10	90	9	0.16
<i>p,p'</i> -DDD	79	5	0.08	90	6	0.16
<i>o,p'</i> -DDT	84	6	0.08	87	8	0.40
<i>p,p'</i> -DDT	87	5	0.08	85	11	0.46

a vacuum pump. After extraction, the pesticides trapped with in the cartridges were eluted by passing 6 mL ethyl acetate. Water was eliminated by anhydrous sodium sulfate (roasted at 300 °C) from the extracts before the solution in the glass tube was evaporated to 0.1 mL by gentle stream of nitrogen.

The analytical procedure of OCPs residues in sediments was as follows. Firstly, 10 g sample was extracted for 30 min with ultrasonication using 60 mL dichloro-methane–acetone (1:1 v/v) two times. The two extracts were combined and the activated Cu was added to remove element sulfate and then dehydrated with anhydrous sodium sulfate. The extracts were concentrated to about 1–2 mL by a rotary evaporator, and further purified with a glass column (12 mm i.d.) loaded with 10 g activated Florisil (60–100 mesh, Wenzhou Chemical Reagent Factory, China). The elution was subsequently carried out using 10 ml hexane containing 10% acetone (v/v). The effluents were concentrated to 0.1 mL under a gentle stream of pure nitrogen for GC analysis. The analytical procedure of OCPs residues in soils was similar to that in sediments.

2.3. Sample analysis

The OCPs residues were analyzed with a GC (Shimadzu GC-14B, Japan) with a ⁶³Ni ECD and a DB-5 fused silica capillary (30 m length × 0.32 mm i.d. × 0.25 μm film thickness, J&W Scientific Co., Folsom, CA, USA). The column temperature, increased from 100 to 190 °C at a rate of 10 °C/min, held for 1 min, and then programmed to 235 °C at 4 °C/min, held for 7 min. The temperature of injector and detector was 220 and 300 °C, respectively. High pure nitrogen was used for both carrier gas and make-up gas at a flow rate of 2.25 and 35.5 mL/min, respectively, after it was filtered with moisture and oxygen. Samples (1 μL) were injected under splitless injection mode. The concentrations of OCPs were determined by comparing the peak height of the samples and the calibration curves of the standards. The correlation coefficient of calibration curves of OCPs were all greater than 0.998. Peak identification was conducted by the accurate retention time of each standard (±1%) and also confirmed by GC–MS (Aligent 5975). Total organic carbon (TOC)

of water samples and sediments were analyzed by using TOC analyzer (TOC-V_{CPH}, Shimadzu Corp., Japan).

2.4. Quality control and quality assurance

The residue levels of OCPs were quantitatively determined by the external standard method using peak height. For every set of 10 samples, a procedural blank and spike sample consisting of all reagents was run to check for interference and cross contamination. The detection limits (DL) of OCPs were determined as the concentration of analyses in a sample that gives rise to a peak with a signal-to-noise ratio (*S/N*) of 3. The pesticides recoveries were determined relative to the ratio of direct injection of extract and the working standards prepared in hexane. The mean recovery of OCPs was estimated at mean concentration levels.

A strict regime of quality control was employed before the onset of the sampling and analysis program. OCPs recovery studies were undertaken to demonstrate the efficiency of the method. The standard solution of composite OCPs including α-, β-, γ-, δ-HCH and *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD as well as heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin was purchased from National Research Center of certified reference material in China. Five separate clean waters were spiked with the working solution including all the 13 OCPs, then extracted and analyzed in the same way as the real samples. Mean recoveries of OCPs ranged from 76% to 87% for water samples. The spiked recoveries of OCPs in sediments and soils using 100 ng of composite standard were in the range of 82–103%. Table 1 listed the detection limits (DL), mean recovery and relative standard deviation (R.S.D.) of the methods. The datum confirmed the practicability of the analytical protocols herein in the determination of OCPs residues in the water and sediments.

3. Results and discussion

3.1. Concentration of organochlorine pesticides in water

The concentrations of 13 organochlorine pesticides ranged from 7.68 to 269.4 ng/L in surface water from Qiantang River.

Table 2

Range, mean and standard deviation (S.D.) of concentration of OCPs (ng/L) detected in surface water of the Qiantang River ($n=45$)

OCPs	January 19–21			April 14–16			July 27–29			October 13–14		
	Range	Mean	S.D.	Range	Mean	S.D.	Range	Mean	S.D.	Range	Mean	S.D.
α -HCH	<0.08–12.46	1.28	2.56	<0.08–6.38	1.26	1.31	<0.08–72.24	7.84	11.66	0.80–22.87	4.13	3.81
β -HCH	<0.16–19.99	1.83	3.64	<0.16–4.95	2.01	1.19	<0.16–13.06	1.76	2.58	0.49–15.36	4.00	19.25
γ -HCH	<0.08–44.88	10.81	12.33	0.54–67.69	17.42	17.99	<0.08–173.11	23.42	32.15	0.89–77.56	20.57	3.06
δ -HCH	<0.08–4.39	1.07	1.09	<0.08–3.50	0.90	0.95	<0.08–24.05	4.24	5.07	0.18–46.26	7.70	10.31
Heptachlor	<0.15–18.09	5.79	3.78	1.40–24.48	7.82	4.89	<0.15–23.21	5.25	4.67	4.13–88.34	21.01	18.20
Aldrin	<0.08–27.59	3.17	4.58	<0.08–22.39	4.97	6.21	0.23–103.9	12.29	20.86	<0.08–19.31	6.78	5.07
Heptachlor epoxide	<0.08–35.32	2.82	5.43	<0.08–20.38	1.72	3.31	0.14–58.65	5.12	11.24	1.56–111.8	19.98	22.19
p,p' -DDE	<0.08–7.86	2.07	1.60	<0.08–3.08	0.80	0.71	<0.08–93.40	5.12	14.34	<0.08–3.72	0.80	0.72
Dieldrin	<0.15–9.88	1.52	2.05	<0.15–20.41	6.13	4.68	<0.15–34.20	5.38	8.34	<0.15–42.06	3.82	6.63
Endrin	<0.10–28.46	2.63	6.74	<0.10–5.73	0.59	1.36	<0.10–12.53	1.57	2.57	<0.10–6.30	0.37	1.14
p,p' -DDD	<0.08–1.91	0.19	0.38	<0.08–3.03	0.18	0.33	<0.08–13.56	2.08	2.57	<0.08–3.92	0.68	0.75
o,p' -DDT	<0.08–0.98	0.06	0.18	<0.08–0.85	0.25	0.28	<0.08–10.88	1.36	2.10	1.56–6.79	0.70	1.26
p,p' -DDT	<0.08–2.60	1.01	0.72	<0.08–1.58	0.45	0.40	<0.08–11.22	2.01	2.04	<0.08–24.70	1.89	4.98
Σ HCH ^a	1.81–61.95	14.99	16.06	0.74–75.21	21.48	19.24	0.79–202.8	37.26	38.45	4.85–141.4	35.77	29.02
Σ DDT ^b	0.60–8.11	3.34	1.69	0.40–4.25	1.58	0.94	0.80–97.54	10.57	15.09	0.45–24.70	4.09	5.89
Σ Other OCP ^c	1.65–55.59	15.94	12.53	5.12–47.61	21.24	10.28	2.62–114.0	29.61	29.55	17.95–163.8	50.30	28.45
Σ OCP ^d	7.68–93.03	34.27	25.25	11.96–108.4	44.30	23.19	9.61–269.4	77.44	61.83	28.30–238.7	90.15	47.27

Data points below the detection limit were regarded as half of the detection limit during the statistical analysis.

^a Σ HCH = α -HCH + β -HCH + γ -HCH + δ -HCH.

^b Σ DDT = p,p' -DDE + p,p' -DDD + o,p' -DDT + p,p' -DDT.

^c Σ Other OCP = heptachlor + aldrin + heptachlor epoxide + dieldrin + endrin.

^d Σ OCP = Σ HCH + Σ DDT + Σ Other OCP.

Table 2 illustrated results of the water sample analyses. It can be seen that the concentrations of HCHs and other OCPs were much higher than that of DDTs.

Fig. 2 delineated the distribution of total OCPs residues in water along the Qiantang River. It clearly revealed that the OCP residues in July and October were higher in four sampling seasons. This meant that some OCPs could be released from wet deposition or soil eroding to waters with much rainfall during the summer and autumn season in Zhejiang province. Higher concentration of OCPs in upriver five areas-Jinhua, Lanxi, Jiande, Tonglu, Fuyang (sites 1–36) probably resulted from farmland runoff along riverside. The above five areas are traditional agriculture areas in Zhejiang province. Lower concentration of OCPs occurred in Hangzhou area (sites 37–45) due to large flux dilution effect in downriver. For example, flux in

sites 13 and 41 ranged from 50 to 350 m³/s and from 500 to 750 m³/s, respectively, in four seasons according to Hangzhou hydrology record. The highest OCP concentrations were found at site 23 (269.4 ng/L), which was in Fuchun reservoir just before the dam, where a water power station is situated. Other higher OCP concentration occurred in site 8 (near Lanxi) and site 35 (near Fuyang). In four sampling periods, the highest concentration of OCPs in the river was 202.8 ng/L for HCHs (site 9) in July, 97.54 ng/L for DDTs (site 37) in July and 163.8 ng/L for other OCPs (site 23) in October.

It was observed that the HCHs concentration had positive correlation relationship with OCPs ($OCPs = 1.415 \times HCHs + 22.867$, $R = 0.7078$, $n = 180$, $p < 0.05$) in water in four sampling periods. Also, Σ Other-OCPs had significant correlation with OCPs ($OCPs = 1.561 \times \Sigma$ Other-OCPs + 16.09, $R = 0.6869$, $n = 180$, $p < 0.05$) but DDT content had no linear relation with others. It can be inferred that the content of 13 OCPs can be estimated by the content of HCH in surface water of Qiantang River. The TOC content in water ranged from 1.03 to 8.80 mg C/L in the first sampling time, having poor correlation with OCPs in water.

Other OCPs (including aldrin, dieldrin, endrin, heptachlor and heptachlor epoxide) had never been used in large amounts in East China, but was detected in most of water samples from Qiantang River. The results showed that these compounds probably originated from other regional atmospheric flow transport into Qiantang River. Other OCPs such as heptachlor are still used in some developing countries around the tropical belt and may potentially move into other relatively colder regions.

Pesticide pollution of surface waters from agriculture use has been well documented around the world in recent years. Because of limited research data on these 13 total OCPs,

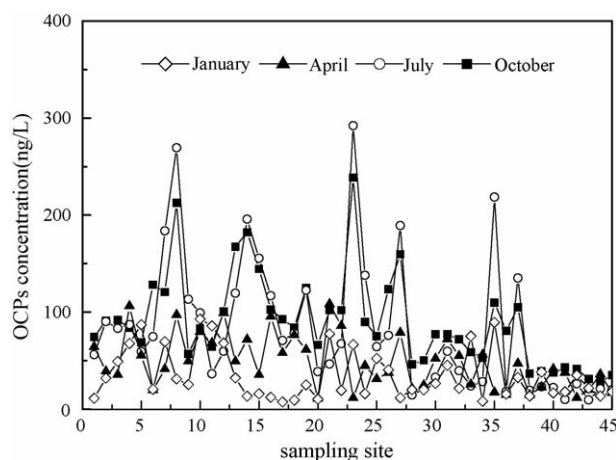


Fig. 2. Distribution of OCPs concentration in water from Qiantang River.

only Σ HCH and Σ DDT in Qiantang River were compared with other rivers in China, such as Mingjiang River (52.1–515.0 ng/L for Σ HCH, 40.6–233 ng/L for Σ DDT), Jiulong River (31.95–129.8, 19.24–96.64 ng/L), Tonghui River (70.12–992.6, 18.79–663.3 ng/L), Yangtse River (4.2–5.5, 1.9–2.3 ng/L) [8,9,15]. The results showed that waters in Qiantang River were some moderately polluted by OCPs. Σ HCH and Σ DDT in short rivers kept at higher levels in China. Because of a lack of previous studies in Qiantang River, it is difficult to assess the temporal variation of water quality in Qiantang River during recent years.

According to Chinese official guideline (GH3838–2002), for grades 1–3 surface water used for drinking water source, which is considered to pose low hazard to the aquatic and human health, the concentration of HCHs should be less than 5000 ng/L, and DDTs less than 1000 ng/L. The present observation showed both DDTs and HCHs were much lower than the guideline values (DDTs, up to 8.11 ng/L, HCHs up to 75.2 ng/L).

3.2. Residual levels of OCPs in sediments

The total OCPs concentration in sediments varied from 23.11 to 316.5 ng/g-dw. Table 3 illustrates the OCP concentration statistic in surface sediments from Qiantang River in three sampling seasons. Total organic carbon (TOC) of these sediments ranged from 0.88% to 2.55%, having no good correlation with the concentration of OCPs. The detection rates of HCHs, DDTs and other OCPs in the sediments were up to 100%, which indicates wide occurrence of these compounds in Qiantang River. Concentrations of OCPs in the sediments from Qiantang River in three sampling seasons ranged from 23.11 to 316.5 ng/g, 9.23 to 152.1 ng/g for HCHs, 1.14 to 100.2 ng/g for DDTs.

Table 3
Range, mean and standard deviation (S.D.) of concentration of OCPs (ng/g-dw) detected in the sediments from Qiantang River

OCPs	April 14–16 (<i>n</i> = 12)			July 27–29 (<i>n</i> = 19)			October 13–14 (<i>n</i> = 17)		
	Range	Mean	S.D.	Range	Mean	S.D.	Range	Mean	S.D.
α -HCH	<0.10–9.65	1.47	2.74	0.79–11.55	5.47	3.45	<0.10–7.05	2.46	2.19
β -HCH	6.02–83.92	17.53	6.55	2.35–78.60	13.10	6.07	1.22–37.24	11.12	8.96
γ -HCH	3.62–54.49	19.28	14.00	2.16–32.42	14.44	10.55	<0.24–45.16	16.92	10.27
δ -HCH	0.95–30.11	12.48	8.44	0.34–17.47	4.08	3.65	1.49–22.29	8.14	5.11
Heptachlor	0.30–17.89	7.69	5.78	2.58–28.10	12.41	6.46	1.34–16.95	7.88	4.49
Aldrin	0.21–14.89	3.76	4.63	0.36–19.56	3.92	4.37	0.63–17.80	6.32	4.16
Heptachlor epoxide	<0.20–29.14	10.13	8.13	<0.20–25.11	4.94	7.61	1.37–24.25	5.74	5.94
<i>p,p'</i> -DDE	2.75–36.27	9.60	4.82	0.75–40.07	8.08	6.70	<0.12–20.39	5.77	7.74
Dieldrin	<0.15–17.83	7.20	5.54	<0.15–28.40	6.23	7.47	<0.15–8.31	1.64	2.45
Endrin	<0.16–52.37	5.84	13.83	<0.16–2.54	0.36	0.65	<0.16–5.46	0.92	1.58
<i>p,p'</i> -DDD	3.57–59.47	12.31	7.08	1.05–52.82	8.46	7.03	<0.16–22.44	6.41	8.14
<i>o,p'</i> -DDT	0.28–6.77	2.09	2.01	0.40–9.61	2.07	2.40	0.40–3.21	0.81	0.77
<i>p,p'</i> -DDT	0.46–8.38	2.46	2.31	0.46–22.78	5.44	6.24	0.46–18.45	3.63	4.58
Σ HCH ^a	19.74–152.1	44.10	25.56	9.23–120.2	34.70	16.78	8.22–75.53	34.49	18.44
Σ DDT ^b	8.64–100.2	25.13	12.26	4.47–95.77	23.10	16.49	1.14–55.09	16.63	18.48
Σ Other OCP ^c	9.41–83.51	34.63	20.29	7.92–69.66	27.86	16.08	9.90–46.65	22.49	10.44
Σ OCP ^d	54.30–316.5	113.85	47.41	27.14–285.6	90.42	39.15	23.11–179.5	76.75	41.95

Data points below the detection limit were regarded as half of the detection limit during the statistical analysis.

^a Σ HCH = α -HCH + β -HCH + γ -HCH + δ -HCH.

^b Σ DDT = *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT.

^c Σ Other OCP = heptachlor + aldrin + heptachlor epoxide + dieldrin + endrin.

^d Σ OCP = Σ HCH + Σ DDT + Σ Other OCP.

Concentrations of OCPs in sediment were <0.10–11.55 ng/g for α -HCH, 1.22–89.92 ng/g for β -HCH, <0.24–54.49 ng/g for γ -HCH, 0.34–30.11 ng/g for δ -HCH, 0.46–22.78 ng/g for *p,p'*-DDT, 0.28–9.61 ng/g for *o,p'*-DDT, <0.15–28.20 ng/g for dieldrin, <0.16–52.37 ng/g for endrin, 0.21–19.56 ng/g for aldrin, 0.30–28.10 ng/g for heptachlor, <0.20–29.14 ng/g for heptachlor epoxide. Several biological metabolites of the parent DDT were also detected. The concentrations were <0.12–36.27 ng/g for *p,p'*-DDE, <0.16–59.47 ng/g for *p,p'*-DDD. Concentration of HCHs in sediments was much higher than those of DDTs. Also, same situation occurred in water. This trend is consistent with the fact that the amount of technical HCH used was significantly larger than that of DDT in Zhejiang province.

The status of OCPs contamination of in sediments in this study was compared with those in other rivers. Amongst the Chinese rivers, the levels of HCHs and DDTs in sediments from the Qiantang River ranked considerably higher (8.22–152.1 ng/g-dw for HCHs, 1.14–100.2 ng/g-dw for DDTs), Only Pearl River Estuary can surpass which (11.95–352.62 ng/g-dw for HCHs, 11.37–599.78 ng/g-dw for DDTs) [17].

Other OCPs such as heptachlor, aldrin, dieldrin have ever been used in small amounts in Zhejiang province and they can also be detected in water and sediment from Qiantang River. It may be resulted from agricultural runoff and wet deposition entering water environment. Tables 4 and 5 showed the concentration range, mean and standard deviation (S.D.) in agricultural soils near Qiantang River bank and in wet deposition near S41, respectively. The total OCPs concentrations in soil and wet deposition were 5.04–214.9 ng/g-dw and 16.18–242.4 ng/L, respectively. Other OCPs was above 50% in wet deposition samples and below 30% in soil samples.

Table 4

Range, mean and standard deviation (S.D.) of concentration of OCPs (ng/g-dw) detected in the agricultural soils near Qiantang River

OCPs	April 14–16 (n = 10)			July 27–29 (n = 10)			October 13–14 (n = 10)		
	Range	Mean	S.D.	Range	Mean	S.D.	Range	Mean	S.D.
α-HCH	<0.10	0.05	0.00	<0.10–0.62	0.06	0.20	0.58–3.38	1.44	0.88
β-HCH	<0.40–3.52	0.85	1.08	<0.40–6.84	0.91	2.12	1.01–2.91	1.83	0.64
γ-HCH	<0.18–12.99	3.07	3.85	<0.18–10.43	2.05	3.13	1.65–9.76	6.40	3.27
δ-HCH	<0.24–1.56	0.22	0.49	<0.24–2.56	0.70	0.98	0.60–5.48	2.48	1.60
Heptachlor	<0.30–11.62	2.86	3.40	<0.30–19.48	6.81	7.00	<0.30–6.19	2.68	2.84
Aldrin	<0.36–1.18	0.30	0.39	<0.36–5.74	1.13	2.13	<0.36–37.91	4.85	13.36
Heptachlor epoxide	0.70–18.14	10.14	6.63	<0.15–4.33	0.76	1.34	0.70–8.23	3.27	2.78
p,p'-DDE	<0.12–3.21	0.66	0.98	<0.12–47.60	9.41	14.97	0.47–77.68	17.04	26.38
Dieldrin	<0.15–3.15	1.03	1.31	<0.15–25.16	4.88	9.02	<0.15–60.54	11.00	21.35
Endrin	<0.16–17.89	2.90	6.32	<0.16–3.55	0.87	1.21	<0.16–15.17	1.90	5.36
p,p'-DDD	<0.16–6.63	1.20	2.31	<0.16–31.05	4.23	9.55	<0.16–32.31	5.82	11.09
o,p'-DDT	<0.40–0.83	0.40	0.26	<0.40–13.71	2.03	4.21	<0.40–34.21	5.14	11.82
p,p'-DDT	<0.46–2.78	0.83	0.89	<0.46–98.76	16.34	30.43	<0.46–84.34	25.33	34.18
ΣHCH ^a	0.46–18.06	4.01	5.36	0.46–14.45	3.72	4.54	4.56–19.29	12.14	5.36
ΣDDT ^b	0.57–10.99	2.38	3.84	0.57–191.1	32.00	57.83	1.71–189.9	53.32	72.76
ΣOther OCP ^c	5.29–36.14	17.13	9.25	2.57–41.15	14.46	13.50	4.03–59.14	16.88	19.23
ΣOCP ^d	6.32–42.53	23.51	12.32	5.04–203.4	50.18	60.58	28.16–214.9	82.35	74.39

Sampling sites of soil was near S1, S2, S3, S4, S6, S9, S14, S22, S26, S34, S37 and S39, respectively. Data points below the detection limit were regarded as half of the detection limit during the statistical analysis.

^a ΣHCH = α-HCH + β-HCH + γ-HCH + δ-HCH.

^b ΣDDT = p,p'-DDE + p,p'-DDD + o,p'-DDT + p,p'-DDT.

^c ΣOther OCP = heptachlor + aldrin + heptachlor epoxide + dieldrin + endrin.

^d ΣOCP = ΣHCH + ΣDDT + Σother OCP.

3.3. Spatial and temporal distribution of OCPs in sediment

The distribution of OCPs in sediments in three seasons along the Qiantang River was shown in Fig. 3. The two highest concentrations of OCPs including HCHs and DDTs were found in

stations 21 and 16, which agreed with the concentration distribution in surface water. It may be due to the similar historical input and deposit indicating important sources of OCPs in this region. In fact, these two sites were located in the Fuchun reservoir. Large amounts of farms and villages were flooded to cumulate water in 1970. A mass application of OCPs happened in the area before this time. This can be probably the severest OCP pollution source. Moreover, natural water flow was hold back before the man-made dam in a long time, which is not good for OCP pollutant dilution and diffusion. The third highest OCPs concentration occurred in station 14 (S14), located in the end of Xin'an River, one of two important sources of Qiantang River.

Table 5

Range, mean and standard deviation (S.D.) of concentration of OCPs (ng/L) detected in the wet deposition in Hangzhou (near S41) in 2005 (n = 18)

OCPs	Range	Mean	S.D.
α-HCH	0.13–25.06	9.13	8.06
β-HCH	<0.16–23.82	4.06	6.01
γ-HCH	<0.08–99.36	24.15	25.45
δ-HCH	<0.08–54.01	9.67	15.66
Heptachlor	<0.15–33.55	7.85	8.86
Aldrin	<0.08–70.84	19.54	18.25
Heptachlor epoxide	<0.08–137.34	16.11	32.17
p,p'-DDE	<0.08–10.69	2.36	2.45
Dieldrin	<0.15–18.76	4.55	4.67
Endrin	<0.10–8.38	1.38	2.29
p,p'-DDD	<0.08–5.88	1.32	1.77
o,p'-DDT	<0.08–3.37	0.88	1.21
p,p'-DDT	<0.08–11.03	2.82	3.21
ΣHCH ^a	1.36–139.34	47.02	42.08
ΣDDT ^b	0.30–16.52	7.25	5.38
ΣOther OCP ^c	8.35–166.46	49.01	42.66
ΣOCP ^d	16.18–242.4	103.8	69.60

Wet deposition was collected in Hangzhou (near S40) in snowy or rainy days. Data points below the detection limit were regarded as half of the detection limit during the statistical analysis.

^a ΣHCH = α-HCH + β-HCH + γ-HCH + δ-HCH.

^b ΣDDT = p,p'-DDE + p,p'-DDD + o,p'-DDT + p,p'-DDT.

^c ΣOther OCP = heptachlor + aldrin + heptachlor epoxide + dieldrin + endrin.

^d ΣOCP = ΣHCH + ΣDDT + Σother OCP.

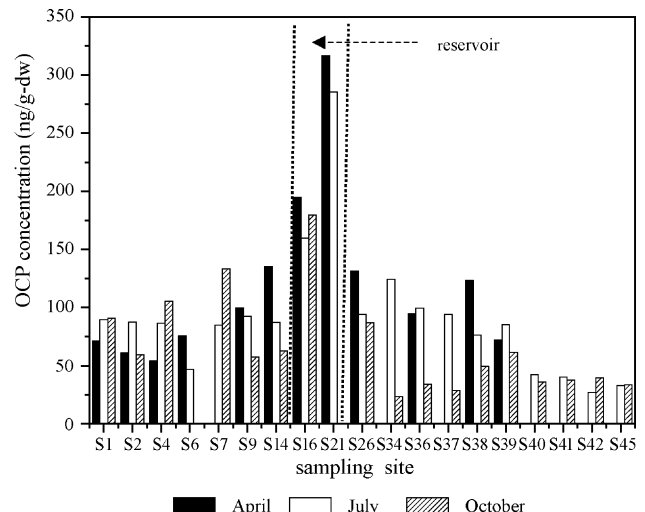


Fig. 3. Distribution of OCPs concentration in sediment from Qiantang River.

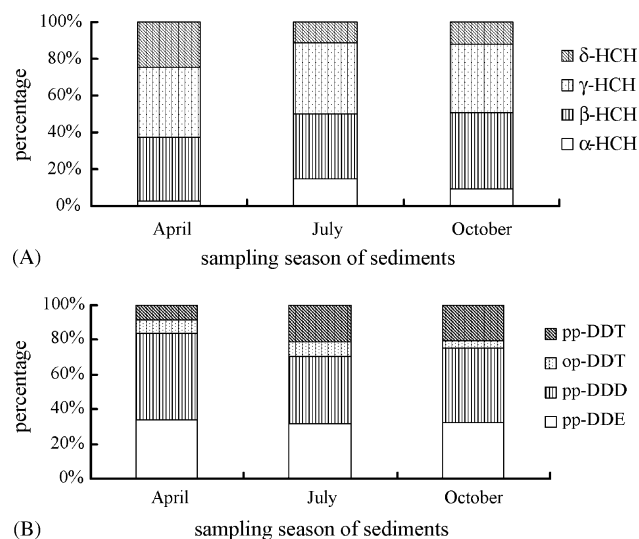


Fig. 4. Composition of OCPs (A in HCHs, B in DDTs) in sediments from Qiantang River.

The results showed Xin'an River was some moderately polluted by OCPs. Xin'an River drainage area is also intense agricultural area. Sediment in S7 held the relative higher OCP concentration, which showed Qu River was also contaminated by OCPs relatively severer.

It was interesting that OCPs concentration of water in above four stations also kept maximal level. As a whole, OCPs concentration upriver (S1–39) was higher than that downriver (S40–45) for sediments. The highest OCPs concentration in sediments occurred in April, which may be due to weaker desorption of sediment pollutant at lower temperature compared with July and October in Zhejiang province.

3.4. Compositions analyses in sediments

Composition differences of HCH isomers or DDT congeners in the environment could indicate different contamination sources [7,19]. Technical HCH has been used as broad spectrum pesticides for agricultural purpose, which has been banned since 1983 in China. Technical-grade HCH consists principally of four isomers, α -HCH (60–70%), β -HCH (5–12%), γ -HCH (10–15%), δ -HCH (6–10%), while γ -HCH is above 99% in lindane. The physicochemical properties of these HCH isomers are different. β -HCH has the lowest water solubility and vapor pressure, which is the most stable and relatively resistant to microbial degradation [20]. Also it should be noted that α -HCH can be converted to β -HCH in the environment [21]. Therefore, the predominant of γ -HCH in the some environmental samples reflects the recent use of lindane. Regarding the composition of HCH isomers measured in this study, a high percentage of γ -HCH was recorded in three sampling seasons (Fig. 4A). The average composition of HCH isomers measured in the sediment samples are α -HCH: 9.0%, β -HCH: 37.2%, γ -HCH: 38.1%, δ -HCH: 15.8%. It can be concluded that lindane may be used recently in Qiantang River Region. Lindane is a kind of important intermediate in chemical factory.

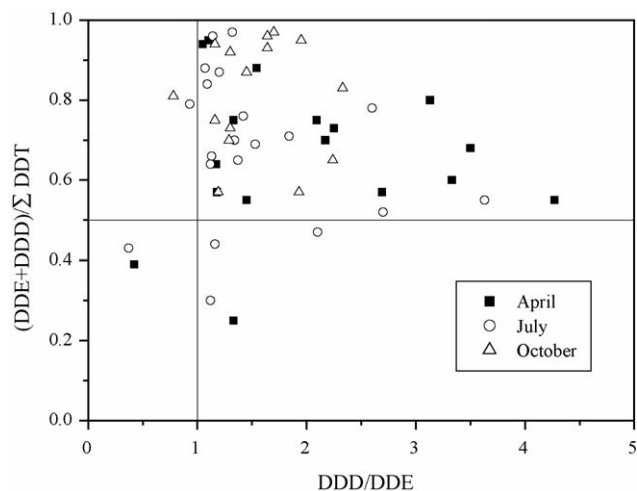


Fig. 5. Relationship between $(DDE+DDD)/\Sigma DDT$ and DDD/DDE in sediments from Qiantang River.

The average composition of DDT isomers measured in the sediment samples in three sampling seasons are p,p' -DDE: 32.6%, p,p' -DDD: 43.9%, o,p' -DDT: 6.7%, p,p' -DDT: 16.8% with the dominance of p,p' -DDD (Fig. 4B). Whereas technical DDT generally contains 75% p,p' -DDT, 15% o,p' -DDT, 5% p,p' -DDE, and <5% others [22]. The relative concentration of the parent DDT compound and its biological metabolites, DDD and DDE, can be used as indicative indices for assessing the possible pollution sources. Since DDT can be biodegraded under aerobic condition to DDE and under anaerobic condition to DDD [23], ratio of $(DDE+DDD)/DDTs > 0.5$ can be thought to be subjected to a long-term weathering [19,24,25]. Fig. 5 shows the relationship between the $(DDE+DDD)/DDTs$ and DDD/DDE in surface sediments collected from Qiantang River in three seasons. Ratios of $(DDE+DDD)/DDTs$ were in the range of 0.22–0.98 with most values being more than 0.5. This infers the degraded metabolites formed a significant proportion of total DDT compounds. Also, most values of DDD/DDE ratio were greater than the unity, indicating that the sediments was dominated by p,p' -DDD, the product of anaerobic degradation of p,p' -DDT. The results obtained from the indices clearly indicate that DDTs in sediments from Qiantang River may be derived from the aged and weathered agricultural soils and was retained under anaerobic conditions within the sediments in the rivers. A small quality of DDT source, such as dicofol (contains 20% p,p' -DDT) is still used for protecting fruit tree and cotton in some scattered sites along the river bank according to a recent investigation. There was no strong evidence to prove new input of abundant DDT in Zhejiang province. The DDT pollution in Qiantang River mainly came from residue of early applications.

4. Conclusion

This work provided the first systemic data on the contamination status of OCPs in surface water and sediments of Qiantang River, East China. Due to previous excessive agriculture application, industrial pollutant discharge, atmosphere transport and difficulty of degradation, there still existed a variety of OCPs

residues in the river water and sediments in East China. HCHs and DDTs were the dominant OCPs in water and sediments from the River. The predominant species was γ -HCH among HCHs, *p,p'*-DDD among DDTs and heptachlor among other OCPs in sediments. The dominance of γ -HCH in the most sediments samples reflects the recent use of lindane. The high concentration of biological metabolites-*p,p'*-DDD from the parent DDTs depict that OCPs contamination was mainly from the aged and weathered agricultural soils and was retained under anaerobic conditions in the sediment. The hydrological characteristic of Qiantang River, such as seasonal variation of flow and temperature, can influence the spatial and temporal distribution of OCPs in sediments. The results obtained in this study show that there still exist a variety of organochlorine pesticide residues in the sediments and water from Qiantang River in China. The results also indicated that there existed certain potential health risks to drinking water consumers and organism in Qiantang River basin. Further work is needed to determine the bioaccumulation of POPs in the food web and the associated risks to the ecosystems and human health.

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