

Levels and distribution of organochlorine pesticides in shellfish from Qiantang River, China

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Received 9 February 2007; received in revised form 28 July 2007; accepted 30 July 2007

Available online 6 August 2007

Abstract

Various shellfish collected from different locations along the Qiantang River in 2006 were analyzed for the levels of 13 organochlorine pesticides (OCPs) in order to elucidate the status of OCPs pollution in shellfish for human consumption. Total concentrations of OCPs in shellfish ranged from 16.9 to 78.6 ng/g wet weight (ww), with HCHs (α -, β -, γ -, δ -HCH), DDTs (*p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, *o,p'*-DDD) and other OCPs (aldrin, dieldrin, endrin, heptachlor and heptachlor epoxide) in the range of 3.33–13.2, 8.38–40.1 and 2.32–14.3 ng/g ww, respectively. The dominant OCPs in shellfish were *p,p'*-DDE among DDTs, β -HCH among HCHs and heptachlor epoxide among other OCPs. It is noticeable that higher OCPs biota-sediment accumulation factor (BSAF) occurred at site with high concentration of OCPs in sediments. The field bioconcentration factor (BCF) increased exponentially with the increase of K_{ow} (octanol–water partition coefficients) of the OCPs. Concentrations of DDTs and HCHs in shellfish from Qiantang River kept at middle level compared with those from marine environment. The concentrations of DDTs in more than 50% of edible shellfish in this study were higher than the limit of 14.4 ng/g ww for human consumption recommended by US EPA (2000).

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Keywords: OCPs; HCHs; DDTs; BSAF; BCF; Qiantang River

1. Introduction

In the previous decades, organochlorine pesticides (OCPs) were produced and used widely in the world. Due to their persistence, bioaccumulation, and adverse effect on wild-life and human, production and application of these chemicals were banned in the early 1970s in developed countries but some developing countries are still using these compounds because of their low cost and versatility in industry, agriculture and public health [1,2]. China, a developing country, is one of the largest producer and consumer of pesticides in the world. Large amounts of OCPs were used to obtain high yield to sustain the overpopulation in past decades in China. Even after the ban of technical HCH and DDT in 1983, 3200 t of lindane (99% γ -HCH) was used from 1991 to 2000 [3–5].

OCPs can enter the aquatic environments and can be transferred into food chains and accumulated in aquatic organism.

Eventually, OCPs might reach human beings through consumption of aquatic product, drinking water and agriculture food [6–8].

Organisms that live in aquatic environments are suitable representative for assessing pollution. Shellfish were suggested to use in many pollution monitoring and assessment studies because they have world-wide geographical distribution, relatively stationary to reflect contamination better than mobile species, sediment-dwelling, and pronounced ability to concentrate persistent organic substance (POPs) from sediment/water [9]. Shellfish are also preferred food for many people [10]. Therefore, data on distribution of OCPs in shellfish is important not only for ecological aspects, but also for human health perspectives.

Qiantang River is a typical river in China flowing through agricultural areas and important source for drinking water and edible aquatic products in Yangtze River Delta, where OCPs were used heavily in the past years. There exists a pesticides factory ever producing OCPs near Lanxi upstream of the river.

OCPs contamination in shellfish has been reported for coastal areas and estuarine environment [11–17,9] as well as lake

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[18,19]. However, most studies on OCPs levels in shellfish are from marine environment, and little information is available for OCPs contamination in shellfish from river. Though the consumption of shellfish in the world is mainly from sea, shellfish from river are very accessible in China and are exported to foreign countries. Therefore it is essential to examine the concentrations of OCPs in river shellfish.

In this study, the levels of OCPs in four shellfish from Qiantang River were investigated and compared with those observed in coast and estuary environment. Furthermore, the distribution of OCPs in shellfish was related with that in water and sediment using bioconcentration factor (BCF) and biota-sediment accumulation factors (BSAF), respectively. In addition, the estimated daily intake (EDI) through shellfish species was estimated. As far as the authors know, this is the first study on concentration of OCPs in various shellfish from Qiantang River. The study also provided basic data for health risk assessment of shellfish consumption.

2. Materials and methods

2.1. Sample collection

Shellfish were taken by grab sampler from riparian areas along Qiantang River in 21–24 April 2006, including Jinhua (JH), Lanxi (LX), Meicheng (MC), Fuchunjiang (FC), Fuyang (FY), Wenyan (WY), Hangzhou (HZ) sites. The sampling sites are shown in Fig. 1. The selected shellfish were common mussels in studied river including *Corbicula fluminea* (A), *Bellamyia purificata* (B), *Cipangopaludina cathayensis* (C) and *Anodonta arcaiformis* (D). Each animal contained at least 100 individuals. Associated sediments (0–5 cm) and water were

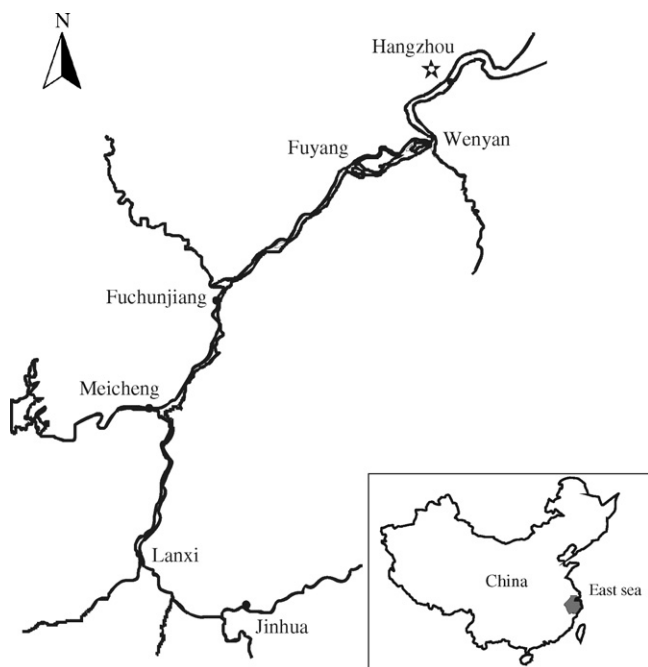


Fig. 1. Map of Qiantang River and sampling sites.

Table 1
Selected characteristics of shellfish in this study ($n = 100$)

Date	Sites	Species	Length (cm)	Weight (g)	Lipid (%)
21 April 2006	JH	A	2.1 ± 0.2	4.36 ± 1.15	3.1
		B	2.5 ± 0.2	5.32 ± 1.22	3.2
22 April 2006	LX	A	2.5 ± 0.1	4.51 ± 1.15	3.1
		B	2.7 ± 0.3	5.71 ± 1.54	3.2
22 April 2006	MC	A	2.6 ± 0.1	4.86 ± 1.15	3.1
		B	2.7 ± 0.3	5.85 ± 1.37	3.2
		C	5.1 ± 0.4	15.4 ± 3.22	3.0
23 April 2006	FC	A	2.5 ± 0.1	4.45 ± 1.25	3.1
		B	2.7 ± 0.3	5.32 ± 1.22	3.2
		C	5.2 ± 0.4	16.4 ± 4.18	3.0
24 April 2006	FY	A	2.5 ± 0.1	4.36 ± 1.15	3.1
		B	2.7 ± 0.3	5.32 ± 1.22	3.2
		C	5.3 ± 0.4	17.2 ± 5.10	3.0
		D	4.3 ± 0.4	15.6 ± 3.18	2.9
24 April 2006	WY	A	2.5 ± 0.1	4.36 ± 1.15	3.1
		B	2.7 ± 0.3	5.32 ± 1.22	3.2
24 April 2006	HZ	A	2.8 ± 0.3	4.36 ± 1.15	3.0
		B	3.0 ± 0.3	6.32 ± 1.22	2.9

A: *Corbicula fluminea*; B: *Bellamyia purificata*; C: *Cipangopaludina cathayensis*; D: *Anodonta arcaiformis* flavotincta. Jinhua (JH), Lanxi (LX), Meicheng (MC), Fuchunjiang (FC), Fuyang (FY), Wenyan (WY) and Hangzhou (HZ).

sampled simultaneously. Water was taken using clean glass barrel. In the laboratory, all biota samples were placed overnight in filtered freshwater without sediment to empty gut, without eliminating hydrophobic contaminants. The following morning, all animals were blotted dry and stored at -20°C before further processing [20,21]. Information on shellfish length, weight and lipid content is given in Table 1. All the equipments used for sample collection, transportation, and preparation were free from organochlorine contamination. Suppliers of the analytical reagents (such as hexane, dichloromethane, etc.) for organic trace analysis are from Hangzhou refinery in China.

2.2. Extraction and clean-up procedure

Shellfish samples were shucked and the soft tissues were homogenized in a blender. Ten grams of homogenized tissues were grinded with 30 g of anhydrous sodium sulphate and extracted with 200 ml of hexane:acetone (3:1, v:v) mixture in a Soxhlet apparatus for 8 h. The extracts were concentrated with a rotary evaporator at 40°C . After concentrating the extracted solvents, lipid content (in Table 1) was determined gravimetrically from an aliquot of the extract. For the clean up, the residue was dissolved in 1.5 ml hexane modified by Manirakiza's method [22].

For acid-stable pesticides, a 25 ml empty cartridge was filled with 3 g of ashed, activated and H_2SO_4 impregnated silica (45%, w/w) and washed with 6 ml hexane. The fat residue was loaded onto the cartridge and the elution was done with 2×5 ml hexane:dichloromethane (3:1, v/v) in a 25 ml conical flask. The

eluates were finally reduced to 200 μ l with nitrogen for GC analysis.

For non-acid-stable analytes, such as dieldrin and endrin, a 25 ml empty cartridges was filled successively with 2 g alumina, 2 g silica gel and 2 g Florisil (60–100 mesh, Wenzhou Chemical Reagent Factory, China), impregnated with an 15% KOH methanolic solution (50%, v/w). Before the extract was loaded, 1 g of Na_2SO_4 was added at the top and the cartridge washed with 6 ml hexane. The elution was done with 2×5 ml fraction of hexane–dichloromethane (3:1) in a 25 ml conical flask. The eluates were concentrated to 200 μ l for GC injection.

Sediment samples were extracted by ultrasonication. Water sample were extracted by solid phase extraction (SPE). The extracts of OCPs from sediments and water were described elsewhere [23].

2.3. Sample analysis

The OCPs residues were analyzed by a GC (Shimadzu GC-14B, Japan) with ^{63}Ni ECD and a DB-5 fused silica capillary (30 m length \times 0.32 mm i.d. \times 0.25 μ m film thickness, J&W Scientific Co., Folsom, CA, USA). The column temperature, increased from 100 to 190 $^\circ\text{C}$ at a rate of 20 $^\circ\text{C}/\text{min}$, held for 1 min, and then programmed to 235 $^\circ\text{C}$ at 4 $^\circ\text{C}/\text{min}$, held for 7 min. The temperature of injector and detector was 220 and 300 $^\circ\text{C}$, 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. Samples (1 μ l) were injected under splitless injection mode. The correlation coefficients of OCPs calibration curves were all greater than 0.998. Peak identification was conducted by the accurate retention time of each standard (National Research Center for Certified Reference Materials of China) and further confirmed by an Agilent 6890N GC–MS system.

2.4. Quality control and quality assurance

The limits of detection (LOD) of OCPs were defined as three times of the signal-to-noise ratio (S/N). For every set of 10 samples, a procedure blank and a spiked sample consisting of all chemicals were run to check for interference and cross contamination. Ten grams of quartz sands were analyzed as blanks by the same procedure as for the samples and did not reveal any contamination. OCPs recovery studies were undertaken to demonstrate the efficiency of the method. The recoveries of 13 OCPs in spiked shellfish using 100 ng of composite standard varied from 78% to 89% and the relative standard derivation (R.S.D.) was in the range of 5–10%. LOD of the procedure were 0.1–0.6 ng/g ww. The recoveries of OCPs in spiked sediments using 100 ng of composite standard were in the range of 82–106%. The LOD and R.S.D. for sediments were 0.10–0.46 ng/g dw and 5–10%, respectively. The spiked recoveries of OCPs in 11 water using 100 ng of composite standard were in the range of 82–106%. The LODs for water were 0.10–0.15 ng/l and R.S.D. was in the range of 5–10%.

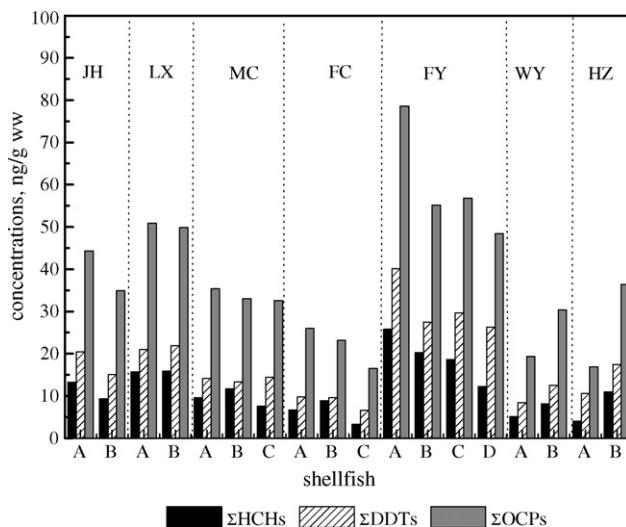


Fig. 2. Concentrations of OCPs in shellfish from Qiantang River (A: *Corbicula fluminea*; B: *Bellamya purificata*; C: *Cipangopaludina cathayensis*; D: *Anodonta arcuiformis flavotincta*).

3. Results and discussion

3.1. Levels and profiles of OCPs in shellfish

Most OCPs investigated were observed in shellfish from Qiantang River. The residual levels of OCPs in shellfishes on wet weight basis (Fig. 2 and Table 2) were dominated by DDTs, followed by HCHs and other OCPs. The mean composition of HCHs, DDTs, and other OCPs in shellfish were <32%, <50% and <25%, respectively (Fig. 3(1)). Concentrations of OCPs were in the range of 16.9–78.6 ng/g ww. The maximum level of OCPs was observed in *C. fluminea* collected from FY. The highest concentration of OCPs in shellfishes from FY site could attribute to surrounding agricultural fields and high influx of runoff as well as industrial effluents into the river through many tributary rivers.

3.1.1. HCHs

Total HCHs in shellfish were in the range of 3.33–13.2 ng/g, with a mean value of 4.5 ng/g (Table 2). Isomers of α -, β -, γ - and δ -HCH were observed to contribute about <10%, <55%, <35% and <20%, respectively (Fig. 3(2)). The highest concentration for total HCHs was observed in *C. fluminea* at FY, followed by LX, JH and MC. The β -HCH (the most toxicological active HCH isomer) was the predominant isomer in HCHs for all shellfishes. The most striking difference of the composition in the investigated organisms compared to the technical mixtures (approximately 55–80% α -HCH, 5–14% β -HCH, 12–14% γ -HCH and 2–10% δ -HCH) [24] is the considerably lower fractions of the α -HCH in the shellfish, which is later explained by its lower persistence. β -HCH can exist in the environment several years or longer because they are stable and resistant to microbial degradation and long half-life with low solubility and vapor pressure [25,26]. The β -HCH isomer was dominant of HCHs in all shellfishes, followed by γ -HCHs and δ -HCH. The high ratio of γ -HCH to HCHs (29%) was also found in sediment.

Table 2
Concentration of OCPs in shellfish from Qiantang River (ng/g ww)

Sites	Shellfish	α -HCH	β -HCH	γ -HCH	δ -HCH	Heptachlor	Aldrin	Heptachlor epoxide	<i>p,p'</i> -DDE	Dieldrin	Endrin	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	Σ HCHs ^a	Σ DDTs ^b	Σ other OCPs ^c	Σ OCPs ^d
JH	A	0.40	8.34	2.69	1.82	4.83	0.52	4.40	8.99	0.27	0.68	2.18	1.45	7.75	13.23	20.4	10.7	44.3
	B	0.48	4.42	2.61	1.78	1.56	0.45	2.17	7.55	0.78	5.71	2.45	1.60	3.38	9.30	15.0	10.7	34.9
LX	A	1.23	6.98	5.07	2.36	5.96	0.84	6.63	12.2	0.30	0.59	1.66	1.62	5.45	15.64	20.9	14.3	50.9
	B	0.81	5.05	4.45	5.61	4.00	0.54	5.52	11.9	0.37	1.69	1.49	1.27	7.16	15.91	21.8	12.1	49.9
MC	A	0.41	4.83	1.65	2.66	1.27	0.39	2.44	10.5	1.95	5.58	1.34	0.91	1.36	9.56	14.2	11.7	35.4
	B	1.15	5.22	3.43	1.80	2.68	0.76	3.83	8.09	0.19	0.68	1.65	0.63	2.91	11.6	13.3	8.13	33.0
	C	0.57	2.78	2.73	1.42	2.07	0.51	7.17	7.65	0.40	0.54	1.37	0.42	4.91	7.50	14.3	10.7	32.5
FC	A	0.48	3.50	2.67	0.64	2.54	0.47	4.65	5.93	0.92	1.04	2.32	0.45	1.02	6.65	9.72	9.62	26.0
	B	0.20	3.31	3.84	1.49	1.50	0.24	1.90	4.22	0.19	0.86	1.84	0.60	2.91	8.85	9.58	4.69	23.1
	C	0.48	1.14	1.06	0.65	1.20	0.43	2.37	2.05	0.96	1.62	1.25	0.60	2.65	3.33	6.56	6.58	16.5
FY	A	1.82	12.38	7.81	3.76	4.35	0.38	5.49	20.5	0.27	2.23	5.60	2.20	11.8	25.8	40.1	12.7	78.6
	B	0.88	11.35	6.73	1.27	3.72	0.33	1.72	15.3	1.05	0.68	2.60	1.60	7.91	20.2	27.4	7.49	55.2
	C	0.85	10.35	5.45	1.92	0.97	0.71	4.15	18.4	0.73	2.03	6.75	0.67	3.82	18.58	29.6	8.58	56.8
	D	1.76	6.35	4.13	3.61	3.93	0.72	3.19	14.5	0.22	1.82	3.78	1.20	6.82	12.2	26.3	9.88	48.4
WY	A	0.24	2.46	2.43	0.42	1.07	1.96	1.76	2.52	0.33	0.73	2.30	1.11	2.45	5.13	8.38	5.85	19.4
	B	0.51	3.97	2.05	1.59	3.96	0.19	2.82	6.86	1.24	1.52	3.25	0.60	1.82	8.12	12.5	9.73	30.4
HZ	A	1.09	1.83	0.47	0.59	0.70	0.47	0.29	5.67	0.25	0.59	2.65	0.84	1.43	3.98	10.6	2.32	16.9
	B	0.81	5.61	4.45	3.05	4.00	0.54	1.52	6.92	0.37	1.69	1.49	1.86	7.16	10.9	17.4	8.11	36.4

A: *C. fluminea*; B: *B. purificata*; C: *C. cathayensis*; D: *A. arcaiformis* flavotincta. Jinhua (JH), Lanxi (LX), Meicheng (MC), Fuchunjiang (FC), Fuyang (FY), Wenyan (WY) and Hangzhou (HZ).

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

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

^c Σ other OCPs = heptachlor + aldrin + heptachlor epoxide + dieldrin + endrin.

^d Σ OCPs = Σ HCHs + Σ DDTs + Σ other OCPs.

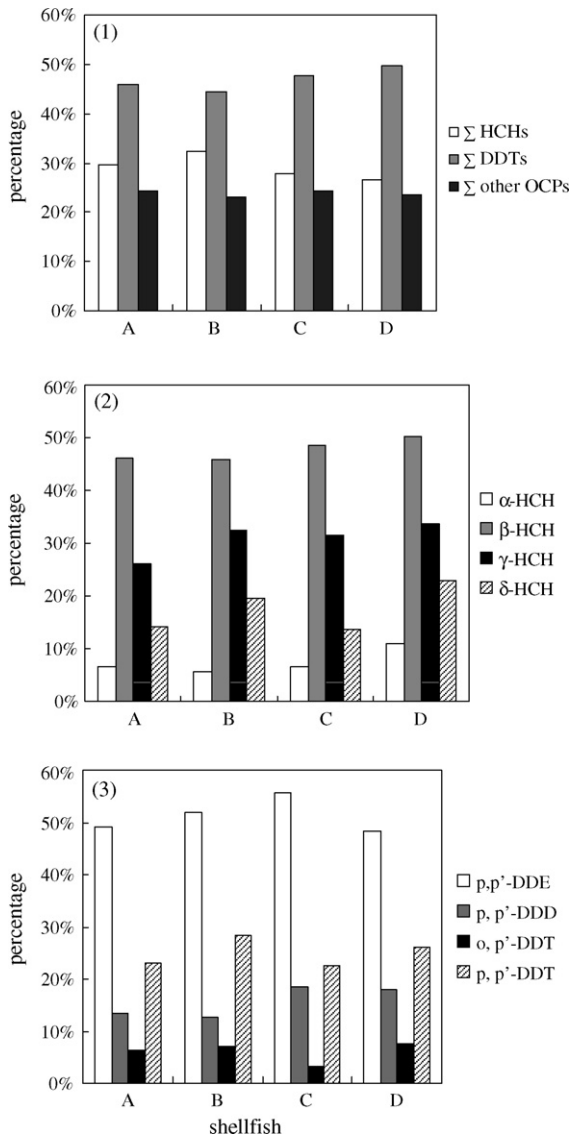


Fig. 3. Percentages of OCPs (1), HCHs (2) and DDTs (3) in shellfish from Qiantang River (A: *C. fluminea*; B: *B. purificata*; C: *C. cathayensis*; D: *A. arcaiformis flavotincta*).

The observed results in sediments were agreement with those observed from Qiantang River in 2005 [23]. Considering the persistence order of HCH isomers ($\beta > \gamma > \alpha$) [27], a relatively recent use of lindane (γ -HCH > 99%) on Qiantang rivershores farms could be suggested as a possible source.

3.1.2. DDTs

Total DDTs concentrations in shellfish ranged from 8.38 to 40.1 ng/g ww, with a mean value of 17.7 ng/g ww (Fig. 2 and Table 2). The mean compositions of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD in this study were <30%, <10%, <55% and <20%, respectively (Fig. 3(3)). The highest concentration for total DDTs was also found in *C. fluminea* at FY. The levels of *p,p'*-DDE levels were higher than that of *p,p'*-DDD suggested that DDTs endured the aerobic transform in organisms. Relative to HCHs, shellfish soft tissues show high levels of DDTs at all sampling sites. Similarly to total HCHs, shellfish at FY site had

the highest level of total DDTs while the lowest level at FC site (near which is Fuchunjiang reservoir). This fact indicated that HCHs and DDTs levels in shellfish not only depend on geographical position but also on shellfish species. *C. fluminea* is bivalve widely distributed in river environment.

3.1.3. Other OCPs

With regard to the residues levels of other OCPs (aldrin, dieldrin, endrin, heptachlor and heptachlor epoxide) in shellfish, total other OCPs concentrations ranged from 2.32 to 14.3 ng/g ww and lowered than that of HCHs. Heptachlor epoxide was dominant among other OCPs with the range of 0.29–7.17 ng/g ww. Other OCPs had never been used in large amounts in Zhejiang province, but was detected in most of water and sediment samples from Qiantang River [23]. 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 [28].

3.2. Levels and profiles of OCPs in sediments and water

The levels of OCPs in sediments were in the range of 11.0–46.4 ng/g dry weight (dw) (Table 3). HCHs isomers in sediments have a high contribution of β -HCH (29–40%), followed by γ -HCH and α -HCH. DDT was found at higher concentration than HCHs. The parent compound, *p,p'*-DDT, could be detected only in low concentrations (up to 1.3 ng/g dw) and contributed less than 18% to the sum of DDTs. The principal contributors to Σ DDTs in sediments were *p,p'*-DDE (range 26–54%) and *p,p'*-DDD (28–53%). The *o,p'*-DDT and *p,p'*-DDT were minor contributors to Σ DDTs (0–17%). Significant concentration of *p,p'*-DDE in sediments may be attributed to the presence of various species of riparian benthic organisms which can accelerate the biodegradation process [29]. The concentrations of other OCPs in sediments ranged between 2.60 and 15.89 ng/g dw, lower than that of DDTs on average.

The levels of OCPs in surface water were in the range of 44.1–265 ng/l (Table 4). Concentrations of HCHs and DDTs ranged from 6.3 to 81.4 ng/l and 5.3 to 24.4 ng/l, respectively. The highest OCP concentration was found in FY both in water and sediment.

3.3. Biota-sediment accumulation factor (BSAF) and bioconcentration factor (BCF)

3.3.1. BSAF

BSAF is a valuable parameter for predicting bioaccumulation of lipophilic compounds, which is primarily associated with tissue lipid and sediment organic carbon [30,31]. In the study, BSAF was taken as a measure of the biotic fate of OCPs and defined as the following equation [32]:

$$\text{BSAF} = \frac{C_b/f_l}{C_s/f_{oc}} \quad (1)$$

Table 3

BSAF and sediment characteristics of Σ HCHs, Σ DDTs and Σ other OCPs in shellfish from seven sites

Sites	Species	BSAF				Sediment (ng/g dw)				
		Σ HCHs ^a	Σ DDTs ^b	Σ other OCPs ^c	Σ OCPs ^d	Σ HCHs	Σ DDTs	Σ other OCPs	Σ OCPs	f_{oc} (%)
JH	A	0.33	0.51	0.23	0.35	14.0	13.75	15.9	43.65	1.07
	B	0.22	0.36	0.22	0.27	14.0	13.75	15.9	43.65	1.07
LX	A	0.68	0.46	0.58	0.54	10.1	19.9	10.8	40.8	1.35
	B	0.66	0.46	0.47	0.51	10.1	19.9	10.8	40.8	1.35
MC	A	0.53	0.48	0.50	0.50	5.18	8.52	6.73	20.4	0.89
	B	0.62	0.43	0.33	0.45	5.18	8.52	6.73	20.4	0.89
	C	0.42	0.48	0.46	0.46	5.18	8.52	6.73	20.4	0.89
FC	A	0.33	0.35	0.65	0.41	3.52	4.93	2.60	11.0	0.57
	B	0.46	0.36	0.33	0.38	3.52	4.93	2.60	11.0	0.57
	C	0.17	0.23	0.45	0.26	3.52	4.93	2.60	11.0	0.57
FY	A	1.50	1.52	0.62	1.23	12.5	19.1	14.8	46.4	2.25
	B	1.13	1.00	0.35	0.83	12.5	19.1	14.8	46.4	2.25
	C	1.08	1.13	0.42	0.89	12.5	19.1	14.8	46.4	2.25
	D	0.68	0.96	0.47	0.73	12.5	19.1	14.8	46.4	2.25
WY	A	0.19	1.00	0.73	0.93	4.70	6.83	2.96	14.5	0.53
	B	0.28	0.30	0.54	0.34	4.70	6.83	2.96	14.5	0.53
HZ	A	0.23	0.20	0.10	0.18	5.86	17.9	7.56	31.3	1.05
	B	0.60	0.32	0.35	0.38	5.86	17.9	7.56	31.3	1.05

A: *C. fluminea*; B: *B. purificata*; C: *C. cathayensis*; D: *A. arcaiformis* flavotincta. Jinhua (JH), Lanxi (LX), Meicheng (MC), Fuchunjiang (FC), Fuyang (FY), Wenyan (WY) and Hangzhou (HZ).

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

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

^c Σ other OCPs = heptachlor + aldrin + heptachlor epoxide + dieldrin + endrin.

^d Σ OCPs = Σ HCHs + Σ DDTs + Σ other OCPs.

where C_b is the biota contaminant concentration (ng/g wet weight), f_l the biota lipid concentration (fraction by weight), C_s the sediment contaminant concentration (ng/g dry weight), and f_{oc} is the organic carbon fraction of the sediment (fraction by weight).

BSAF of Σ HCHs in shellfish ranged from 0.17 to 1.50 (Table 3), with the highest BSAF of Σ HCHs and concentration of Σ HCHs in sediments from FY. In contrast, there was the

lower BSAF of 0.17 for Σ HCHs in samples from WY, with the lowest HCHs concentration in its associated sediment. BSAF of Σ DDTs were in the range of 0.20–1.52. Similarly to Σ HCHs, there were the highest BSAF in shellfish from FY, in which the concentration of Σ DDTs were the highest, whereas at HZ site there was the lowest BSAF although Σ DDTs level was lower. It is noticeable that higher BSAF occurred at more severely polluted site with higher sediment organic carbon content (f_{oc}),

Table 4

Residues of HCHs and DDTs in shellfish in references and this study

Study area	Water	Species	Σ HCHs ^a (ng/g)	Σ DDTs ^b (ng/g)	References
Bohai, China	Marine	20	<0.08–5.92 ww	<0.12–151 ww	[16]
Coastal water of China	Marine	2	0.73–0.96 ww	0.72–36.88 ww	[17]
Coastal water of South Korea	Marine	5	Nd–34.56 dw	1.67–102.76 dw	[11]
Black sea, Turkey	Marine	1	<0.022–4.5 ww	<0.15–4.14 ww	[14]
Red sea, Egypt	Marine	1	16.2–183.4 ww	125–772 ww	[15]
Coastal water of India	Marine	1	N/A	0.9–40	[36]
Coastal water of Philippines	Marine	1	N/A	0.19–9.5	[36]
Coastal water of Thailand	Marine	1	N/A	1.3–38	[36]
Xiamen, China	Marine	1	N/A	<0.5–220 ww	[13]
Coastal area of Xiamen, China	Marine	5	0.18–345 dw	75.2–2143 dw	[12]
Ming River, China	Estuary	3	Nd–5.07 dw	21.5–2396 dw	[12]
Yangtze River, China	Estuary	2	1.2–5.5 ww	25.6–68.8 ww	[9]
Lake Faro, Italy	Lake	1	N/A	7.00–15.37 ww	[19]
Lake Maggiore, Italy	Lake	1	N/A	7.76–34.76 ww	[18]
Qiantang River, China	River	4	4.0–25.8 ww	6.6–40.1 ww	This study

N/A: No data is obtained.

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

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

while lower BSAF found at lower contaminated site with lower f_{oc} . This result is different from that in Yangtze Estuary [9], which probably was due to specific estuarine hydrodynamics. It means that where there was a higher BSAF, there probably was a higher value of contaminant concentration (Σ HCHs or Σ DDTs) and a higher f_{oc} ; where there was a lower BSAF, there probably was a lower value of contaminant concentration and a lower f_{oc} . This effect was due to HCHs and DDTs having greater affinity for organism lipid; therefore, the hydrophobic organic contaminants (HOCs) would be more accumulative in organisms. As sensitive sentinel organisms, shellfish are useful in the surveillance of OCPs contamination in riverine ecosystems. The field correlation between $\log K_{ow}$ and \log BSAF was calculated in all shellfish at seven sampling sites but correlation coefficient was very low ($R < 0.2$).

3.3.2. BCF

Bioaccumulation of compounds in shellfishes is also the process by which chemicals are enriched in the organism relative to the water in which they reside. It is well accepted for shellfishes and many other mussels that hydrophobic compounds preferential accumulate in lipids relative to other compartments [33]. The bioconcentration of hydrophobic compounds in shellfishes has been modeled as a simple partition process between water and lipids, which can be predicted by K_{ow} [34].

Bioconcentration factor (BCF), defined as the ratio of the OCPs concentration in shellfish soft tissue (ng/g lipid) and water (ng/L), were calculated. It also describes the equilibrium reached between uptake and depuration of a contaminant by shellfishes and is the ratio of the respective rate constants for those processes.

The field correlation between $\log K_{ow}$ and \log BCF was calculated in all shellfish at seven sampling sites. Higher correlation coefficients was observed between the \log BCF and $\log K_{ow}$ in shellfish A (*C. fluminea*, $R = 0.76$, Fig. 4A) and shellfish B (*B. purificata*, $R = 0.80$, Fig. 4B) at HZ. The BCFs reported here agreed with literature [34] and have small discrepancies with predictions on the basis of the $\log K_{ow}$. The best fit of the line is

$$\log \text{BCF} = 0.29 \log K_{ow} + 3.44$$

$$R = 0.80 \text{ (for } Bellamya \text{ purificata \text{ in HZ)} \quad (2)$$

DDE showed an extremely high BCF. This is probably due to its high lipid affinity. Differences in shellfish physiology and in the compounds utilized for the calculation could contribute to this divergence. The field BCF data are expectedly more complicated because the contaminant concentration may vary significantly with time and with location. There would be large uncertainties concerning the achievement of equilibrium of contaminants between biota and water in natural systems [35].

3.4. Compared with other surveys in shellfish from various water environment

When compared with other surveys in shellfish from various world locations, concentrations of total HCHs and DDTs in shellfish were listed in Table 4. Σ HCHs concentrations for shell-

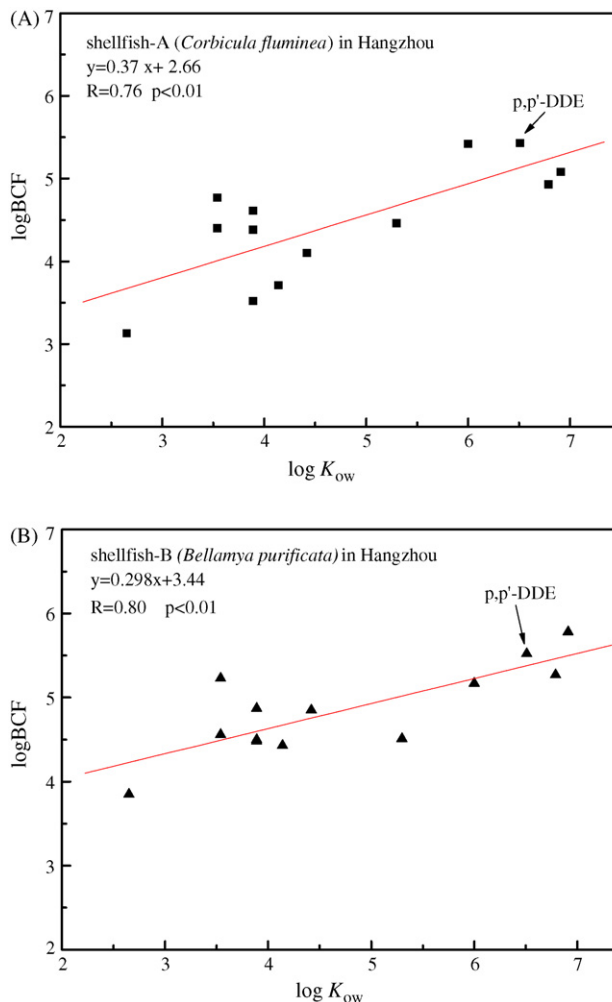


Fig. 4. Correlations between octanol–water partition coefficients (K_{ow}) and BCF for OCPs (BCF normalized by lipid content).

fish in Qiantang River kept in middle level compared with those in marine and estuary environment such as Red Sea in Egypt and coast of Korea. While Σ DDTs for shellfish in Qiantang River also kept in middle level compared with those in marine and estuary environment such as Red Sea in Egypt and Mingjiang Estuary in China.

3.5. Estimated daily intake (EDI) of OCPs

The residual levels presented on wet weight basis were compared with the edible hygienic criteria (2000 and 1000 ng/g wet weight for HCHs and DDTs, respectively) in China [12]. All the residual levels of DDTs and HCHs were far below the criteria. In China, with improvement of human life, consumption of fish and shellfish increased from 27.5 g/person day in 1989 to 30.5 g/person day in 1997 [17]. In the present study, the figure in 1997 was used to evaluate daily intake of OCPs by human in China through shellfish consumption. As shown in Table 5, the EDI of DDTs and γ -HCH by the people were far below the acceptable daily intake (ADI) recommended by the Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) indicating this intake would not pose

Table 5

Estimated daily intake (EDI) of OCPs through shellfish by human (average body wt. 60 kg) in China

Compounds	Average concentration (ng/g ww)	EDI (ng/kg body wt./day)	ADI (FAO/WHO) (ng/kg body wt./day)
Σ HCHs ^a	11.47	5.83	8,000 (γ -HCH)
Σ DDTs ^b	17.67	8.98	20,000 (DDT)

EDI = average concentration (ng/g) \times consumption (30.5 g/day)/body weight (60 kg). ADI: acceptable daily intake.^a Σ HCHs = α -HCH + β -HCH + γ -HCH + δ -HCH.^b Σ DDTs = *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT.

a health risk in China at present. But the concentrations of DDTs in more than 50% of edible shellfish were higher than the limit of 14.4 ng/g ww for human consumption recommended by US Environmental Protection Agency (EPA) (2000).

4. Conclusions

This work provided the first data on contamination status of OCPs in various shellfish of Qiantang River, East China. The results indicated that there still existed a variety of OCPs in shellfish. Among OCPs determined in the shellfish in the present study, residual levels of DDTs were predominant, followed by HCHs and other OCPs. The highest levels of β -HCH and *p,p'*-DDE in shellfish was due to their resistance to microbial degradation and thereby long half life. The higher level of γ -HCH in shellfish may be due to the fact that a large of lindane was produced in the immediate previous decades and the usage still continues in east China. Higher BSAF occurred at higher polluted site with higher f_{oc} , while lower BSAF found at lower contaminated site with lower f_{oc} . log BCF showed a positive correlation with log K_{ow} in shellfishes. Shellfish are useful in the surveillance of OCPs contamination in riverine ecosystems.

When compared with other surveys in various shellfish species from marine and estuary environment, Concentration of HCHs and DDTs in shellfish from Qiantang River kept in middle level.

The estimated daily intake of DDTs and γ -HCH by the people were far below the ADI recommended by FAO/WHO, suggesting no relevant health risk by consuming shellfish. But the concentrations of DDTs in more than 50% of edible shellfish were higher than the limit of 14.4 ng/g ww for human consumption recommended by US EPA (2000).

Acknowledgements

The research was supported by the national natural science foundation of China (20337010) and the natural science foundation of Zhejiang province (Z203111). The authors thank Dr Kun Yang for his improvement in the manuscript.

References

- [1] S. Tanabe, H. Iwata, R. Tatsukawa, Global contamination by persistent organochlorine and their ecotoxicological impact on marine mammals, *Sci. Total. Environ.* 154 (1994) 163–177.
- [2] A. Sarkar, R. Nagarajan, S. Chaphadkar, S. Pal, S.Y.S. Singbal, Contamination of organochlorine pesticides in sediments from the Arabian Sea along the west coast of India, *Water Res.* 31 (1997) 195–200.
- [3] G. Zhang, P. Andrew, H. Alan, B.X. Mai, Sedimentary records of DDT and HCH in the Pearl River Delta, South China, *Environ. Sci. Technol.* 36 (2002) 3671–3677.
- [4] X.H. Qiu, T. Zhu, J. Li, H.S. Pan, Organochlorine pesticides in the air around the Taihu Lake, China, *Environ. Sci. Technol.* 38 (2004) 1368–1374.
- [5] S. Tao, F.L. Xu, J. Wang, W.X. Liu, Z.M. Gong, J.Y. Fang, L.Z. Zhu, Y.M. Luo, Organochlorine pesticides in agriculture soil and vegetables from Tianjin, China, *Environ. Sci. Technol.* 39 (2005) 2494–2499.
- [6] M.T. Kawano, T. Inoue, H. Wada, H. Hidaka, R. Tatsukawa, Bioconcentration and residue patterns of chlordane compounds in marine animals: invertebrates, fish, mammals, and seabirds, *Environ. Sci. Technol.* 22 (1988) 792–797.
- [7] H. Iwata, S. Tanabe, N. Sakai, R. Tatsukawa, Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate, *Environ. Sci. Technol.* 27 (1993) 1080–1098.
- [8] M. Oehme, S. Mano, The long range transport of organic pollutants to the Arctic, *Fres. Z. Anal. Chem.* 319 (1984) 141–146.
- [9] Y. Yang, M. Liu, S. Xu, L. Hou, D. Ou, H. Liu, S. Cheng, T. Hofmann, HCHs and DDTs in sediment-dwelling animals from the Yangtze Estuary, China, *Chemosphere* 62 (2006) 381–389.
- [10] J.W. Farrington, E.D. Goldberg, R.W. Risebrough, J.H. Martin, V.T. Bowen, US “Mussel Watch” 1976–1978: an overview of the trace-metal, DDE, PCB, hydrocarbon, and artificial radionuclide data, *Environ. Sci. Technol.* 17 (1983) 490–496.
- [11] S.-K. Kim, J.R. Oh, W.J. Shim, D.H. Lee, U.H. Yim, S.H. Hong, Y.B. Shin, D.S. Lee, Geographical distribution and accumulation features of organochlorine residues in bivalves from coastal areas of South Korea, *Mar. Pollut. Bull.* 45 (2002) 268–279.
- [12] W. Chen, L. Zhang, L. Xu, X. Wang, L. Hong, H. Hong, Residue levels of HCHs, DDTs and PCBs in shellfish from coastal area of east Xiamen Island and Minjiang estuary, China, *Mar. Pollut. Bull.* 45 (2002) 385–390.
- [13] D.W. Klumpp, H. Hong, C. Humphrey, X. Wang, S. Codi, Toxic contaminants and their biological effects in coastal waters of Xiamen, China. I. Organic pollutants in mussel and fish tissues, *Mar. Pollut. Bull.* 44 (2002) 752–760.
- [14] P.B. Kurt, H.B. Ozkoc, A survey to determine levels of chlorinated pesticides and PCBs in mussels and seawater from the mid-Black Sea coast of Turkey, *Mar. Pollut. Bull.* 48 (2004) 1076–1083.
- [15] A. Khaled, A.El. Nemr, T.O. Said, A. El-Sikaily, A.M.A. Abd-Alla, Polychlorinated biphenyls and chlorinated pesticides in mussels from the Egyptian Red Sea coast, *Chemosphere* 54 (2004) 1407–1421.
- [16] R. Yang, Z. Yao, G. Jiang, Q. Zhou, J. Liu, HCH and DDT residues in mollusks from Chinese Bohai coastal sites, *Mar. Pollut. Bull.* 45 (2004) 795–805.
- [17] N. Yang, M. Matsuda, M. Kawano, T. Wakimoto, PCB and organochlorine pesticides (OCPs) in edible fish and shellfish from China, *Chemosphere* 63 (2006) 1342–1352.
- [18] A. Binelli, A. Provini, DDT is still a problem in developed countries: the heavy pollution of Lake Maggiore, *Chemosphere* 52 (2003) 717–723.
- [19] P. Licata, D. Trombetta, M. Cristani, D. Martino, F. Naccari, Organochlorine compounds and heavy metals in the soft tissue of the mussel *Mytilus galloprovincialis* collected from Lake Faro (Sicily, Italy), *Environ. Int.* 30 (2004) 805–810.
- [20] J. Kukkonen, P.F. Landrum, Effects of sediment-bound polydimethylsiloxane on the bioavailability and distribution of benzo(a)pyrene in lake

- sediment to *Lunbriculus variegates*, Environ. Toxicol. Chem. 14 (1998) 523–531.
- [21] N.H.B.M. Kaag, M.C.T. Scholten, S.N.M. Van, Factors affecting PAH residues in the lugworm *Arenicola marina*, a sediment feeding polychaete, J. Sea Res. 40 (1998) 251–261.
- [22] P. Manirakiza, A. Covaci, L. Nizigiymana, G. Ntakimazi, P. Schepens, Persistent chlorinated pesticides and polychlorinated biphenyls in selected fish species from Lake Tanganyika, Burundi, Africa, Environ. Pollut. 117 (2002) 447–455.
- [23] R. Zhou, L. Zhu, K. Yang, Y. Chen, Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China, J. Hazard. Mater. A 137 (2006) 68–75.
- [24] H.R. Buser, M.D. Muller, Isomer and enantioselective degradation of HCH isomers in sewage sludge under anaerobic conditions, Environ. Sci. Technol. 29 (1995) 664–672.
- [25] K.L. Willett, E.M. Ulrich, A. Hites, Differential toxicity and environmental fates of hexachlorocyclohexane isomers, Environ. Sci. Technol. 32 (1998) 2197–2207.
- [26] S.L. Simonich, R.A. Hites, Global distribution of persistent organochlorine compounds, Science 269 (1995) 1851–1854.
- [27] A. Kouras, A. Zouboulis, C. Samara, T. Kouimtzi, Removal of pesticides from aqueous solution by combined physicochemical processes—the behavior of lindane, Environ. Pollut. 103 (1998) 193–202.
- [28] R.A. Doong, Y.C. Sun, P.L. Liao, C.K. Peng, S.C. Wu, Distribution and fate of organochlorine pesticide residues in sediments from the selected rivers in Taiwan, Chemosphere 48 (2002) 237–246.
- [29] G.G. Pandit, S.K. Sahu, S. Sadasivan, Distribution of HCH and DDT in the coastal marine environment of Mumbai, India, J. Environ. Monitor. 4 (2002) 431–434.
- [30] P.L. Ferguson, G.T. Chandler, A laboratory and field comparison of sediment polycyclic aromatic hydrocarbons bioaccumulation by the cosmopolitan estuarine polychaete *Streblospio benedicti* (Webster), Mar. Environ. Res. 45 (1998) 387–401.
- [31] T. Nilsson, S. Spörting, E. Björklund, Selective supercritical fluid extraction to estimate the fraction of PCB that is bioavailable to a benthic organism in a naturally contaminated sediment, Chemosphere 53 (2003) 1049–1052.
- [32] C.S. Wong, P.D. Capel, L.H. Nowell, National-scale, field-based evaluation of the biota-sediment accumulation factors, Environ. Sci. Technol. 35 (2001) 1709–1715.
- [33] D.L. Swackhamer, R.A. Hites, Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake, Isle Royale, Lake Superior, Environ. Sci. Technol. 22 (1988) 543–548.
- [34] J.C. Colombo, M.F. Khalil, M. Arnac, A.C. Horth, Distribution of chlorinated pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of the Rio de la Plata, Argentina, Environ. Sci. Technol. 24 (1990) 498–505.
- [35] C.T. Chiou, Partition and Adsorption of Organic Contaminants in Environmental Systems, John Wiley & Sons Inc., Hoboken, 2002, pp. 82–85.
- [36] S. Tanabe, M.S. Prudente, S. Kan-Atireklap, A. Subramanian, Mussel watch: marine pollution monitoring of butyltins and organochlorines in coastal waters of Thailand, Philippines and India, Ocean Coast Manage. 43 (2000) 819–839.