

Distribution and sources of organochlorine pesticides in sediments of the Xiangjiang River, south-central China

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Abstract The Xiangjiang River (XR), the second largest tributary of the Yangtze River, is mainly located in Hunan province in south-central China. Nineteen surface sediment samples (the top 3-cm layer) collected from XR were analyzed to determine the concentrations, distribution, sources, and ecological risk of organochlorine pesticides (OCPs). The concentrations of OCPs were 3.0–29.8 ng/g (dry weight) with a mean of 12.6 ± 7.7 ng/g. The widely detected compounds included HCHs, DDTs, HCB, and dieldrin. Overall, the dominant OCPs in the sediments were mainly composed of residual and degradation products, e.g., β -HCH with a mean of 42.2 % in HCHs and p, p' -DDE with a mean of 43.5 % in DDTs, implying that OCPs in the sediments had suffered from long-term aging without fresh inputs in XR. However, there was a high

proportion of p, p' -DDT to DDTs in three sites, suggesting that there was use of technical DDT from their surrounding areas at present. The ratios of α -HCH/ γ -HCH and p, p' -DDD+ p, p' -DDE/DDTs increase from the upper reaches to the lower reaches of XR, suggesting sediments enriched with α -HCH and metabolites DDD and DDE during sediment transport process and could be attributed to the transformation of γ -HCH to α -HCH and DDT to DDE or DDD. The assessment of the ecological risk indicates that the OCPs in the sediments of XR have a moderate adverse biological effect on organisms.

Keywords OCPs · Distribution · Sources · Ecological risk · Surface sediments · Xiangjiang River

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Introduction

Organochlorine pesticides (OCPs), an important group of persistent organic pollutants, have been a wide concern due to their bioaccumulation, persistence, and chronic toxicity (Jones and de Voogt 1999; Hu et al. 2009). OCPs tend to accumulate in sediment due to their low aqueous solubility, low volatility, and high affinity for particulate matter. Thus, sediment in aquatic environment can serve as one of the major sinks of OCPs (Aigner et al. 1998; Doong et al. 2002; Tang et al. 2007; Zhao et al. 2010).

China had produced 4.9 and 0.4 million tonnes HCH and DDT, respectively, accounting for 33 and 20 % of the total world production since the 1950s (Li et al. 1998; Campoy et al. 2001; Gong et al. 2004; Li et al.

2006). Although OCPs were banned in 1983, HCB, DDT, and chlordane were still in production with limited use in China under the exemption in the Stockholm Convention (Xing et al. 2004; Qiu et al. 2005). At present, the residues of those OCPs are still widely detected in soils and aquatic environment in China (Li et al. 2006; Hu et al. 2010).

The Xiangjiang River (XR) in Hunan province in south-central China is the second largest tributary of the Yangtze River (the largest river in Asia) in terms of water discharge. Its length is 856 km and the watershed is 94,600 km². It is the largest river into the Dongting Lake, the second largest freshwater lake in China with the surface area of 2,820 km². Hunan province is a primary grain-producing region in China, and large amounts of pesticides have been used in this area until now. The usage of pesticides in Hunan province began in 1957 with an amount of 2,300 tonnes in this year and then increased to 220,600 tonnes in 1982. OCPs were widely detectable in various media including water, soil, and air in this area. Li et al. (2008) reported that concentrations of DDT residues up to 111.1 ng/g in an average were found in soils in the XR watershed. Wang et al. (2010b) found that concentrations of the major pollutants in surface water from the Changsha section of XR were 0.9–5.8 ng/L for HCHs, 1.4–4.4 ng/L for heptachlor, 0.7–1.8 ng/L for heptachlor epoxide, and 1.4–1.7 ng/L for endrin aldehyde. Thus, a high occurrence level of OCPs in the XR sediments would be expected.

Due to the developed mining and smelting industries in the XR watershed, XR has been widely concerned on the heavy metals (e.g., Cu, Cr, Cd, Hg, Pb, As, Zn) both in water and sediments (Zhang et al. 2009, 2010). As a result of intensive mining activities and subsequently increased soil erosion into the aquatic environment, more OCPs with soil erosion are also released into XR. Thus, the OCP contamination in XR should have the same concern; however, the dataset of OCPs in the region is very limited. The objectives of this work are to determine the occurrence levels, distribution, and sources of OCPs in the sediments of XR and to assess their biological risk on organisms.

Materials and methods

Sampling

Nineteen surface sediment samples were collected using a grab sampler in April 2010. The locations of sampling

sites are shown in Fig. 1. The depths of water at the sampling sites varied from 1 to 1.5 m. The top 3-cm layer was carefully removed with a stainless steel spoon for subsequent analysis. All sediment samples were wrapped in aluminum foil and stored at –20 °C until analysis.

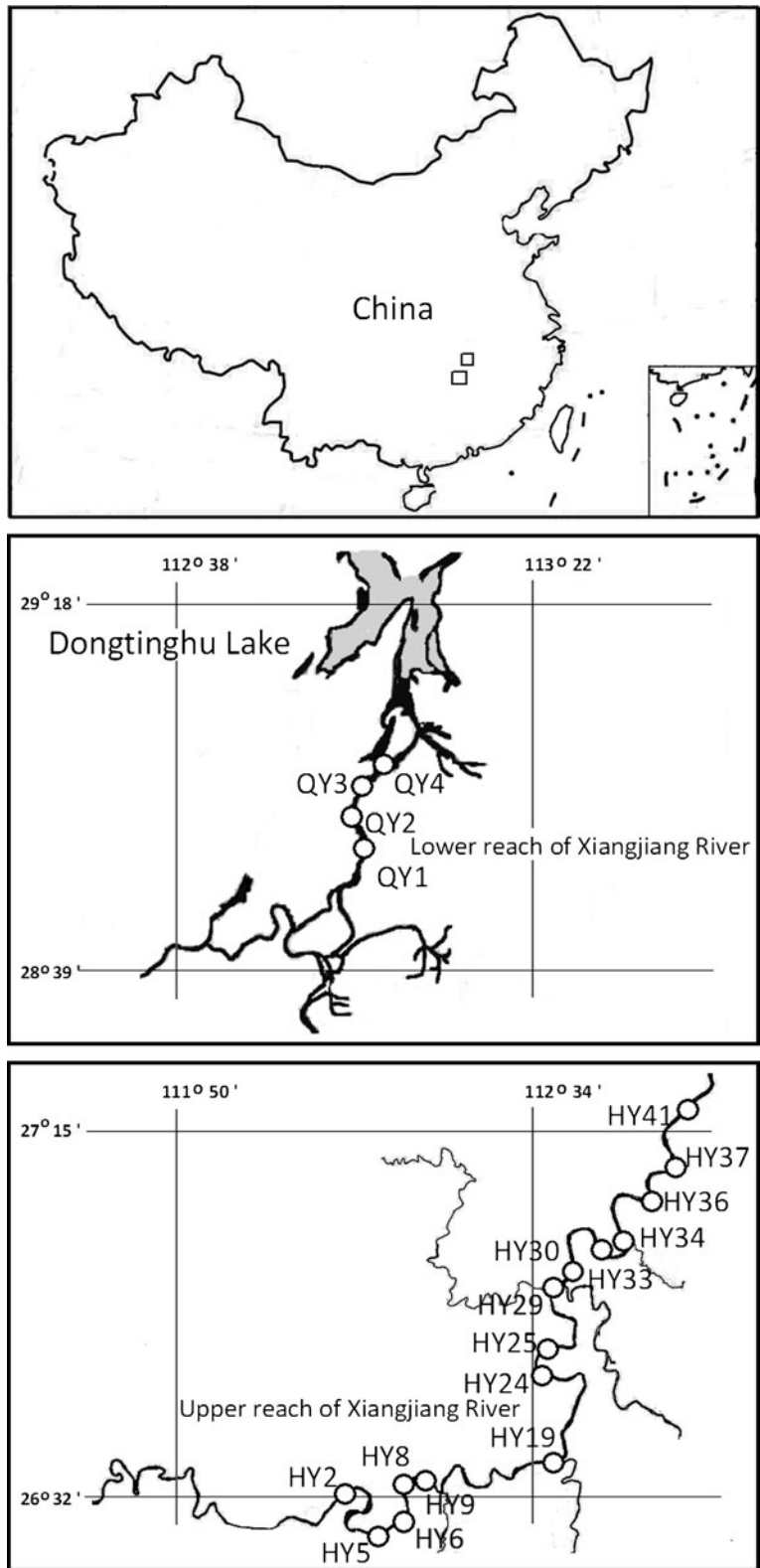
OCP analysis

The OCP analysis procedure followed that described by Hu et al. (2009). In the laboratory, sediment samples were freeze-dried for 24 h, pulverized, and sieved through 80-mesh stainless steel mesh. About 10 g of the subsamples was Soxhlet-extracted for 48 h with dichloromethane (DCM) at a rate of 4–6 cycles/h. A mixture of surrogate standards of 2,4,5,6-tetrachloro-*m*-xylene (TCmX) and decachlorobiphenyl (PCB209) was added to each of the samples prior to extraction. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract was concentrated and solvent-exchanged to hexane and purified on an 8-mm-i.d. alumina/silica column packed, from the bottom to top, with neutral alumina (6 cm, 3 % deactivated), neutral silica gel (10 cm, 3 % deactivated), 50 % (on a weight basis) sulfuric acid silica (10 cm), and anhydrous sodium sulfate. Alumina, silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 48 h with DCM and then baked for 12 h in 250, 180, and 450 °C, respectively, before use. The column was eluted with 50 mL of dichloromethane/hexane (1:1) to yield the organochlorine pesticide fraction. The fraction was concentrated to 0.5 mL under a gentle nitrogen stream. A known quantity of PCB54 was added as an internal standard prior to gas chromatography–mass spectrometry (GC–MS) analysis.

GC–MS analysis was carried out on an Agilent-5975 GC-MSD system (Agilent, USA) with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μm), operating under single-ion monitoring mode. Helium was used as the carrier gas at 1.2 mL/min under constant flow mode. Helium was filtered with moisture, hydrocarbon, and oxygen filters before entering the GC system. The oven temperature began at 60 °C for 1 min and increased to 290 °C (10-min hold time) at a rate of 4 °C/min. Split/splitless injection of a 1-μL sample was performed with a 5-min solvent delay time. Injector temperature was at 250 °C. The inlet degradation of individual OCP was checked daily and controlled within 15 %.

Targeted OCPs include α -HCH, β -HCH, γ -HCH, δ -HCH and *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD

Fig. 1 Map of sampling sites



as well as HCB, heptachlor, aldrin, heptachlor epoxide, dieldrin, and endrin. All data were subjected to strict quality control procedures, including procedural blanks, and duplicate samples were analyzed. Method detection limit (MDL) ranged from 0.01 to 0.05 ng/g for individual OCPs. Concentrations lower than MDLs were considered nondetectable for quantified OCPs. The average surrogate recoveries were 74 ± 9 and 87 ± 15 % for TCmX and PCB209, respectively. All reported values were corrected by the field blanks and surrogate recovery.

Total organic carbon analysis

Dried samples were treated with 1 M hydrochloric acid to remove carbonate and dried overnight at 60 °C. The carbonate-free samples were then analyzed for total organic carbon (TOC) with a Vario EL-III Elemental Analyzer (Elementar, Germany), and average values were reported. Replicate analysis of one sample ($n=6$) gave a precision of ± 0.02 wt% for TOC.

Results and discussion

Concentration profiles of OCPs in sediments

The residual concentrations of OCPs in surface sediments are shown in Fig. 2. All concentrations were calculated on a dry weight basis. Among the OCPs detected, β -HCH, γ -HCH, p,p' -DDE, p,p' -DDD, o,p' -DDT, and HCB were detected in all sediments (detection frequency 100 %), followed by α -HCH (89.5 %), p,p' -DDT (89.5 %), dieldrin (84.2 %), and δ -HCH (68.4 %). Endrin, aldrin, heptachlor, and heptachlor epoxide were not detected in the sediments in this study. The concentrations of the measured OCPs in the sediments were <0.04 –1.6 ng/g (mean 0.6 ± 0.5 ng/g) for α -HCH, 0.09–2.2 ng/g (mean 0.8 ± 0.7 ng/g) for β -HCH, 0.1–0.4 ng/g (mean 0.3 ± 0.1 ng/g) for γ -HCH, <0.08 –0.9 ng/g (mean 0.3 ± 0.2 ng/g) for δ -HCH, 0.8–4.0 ng/g (mean 2.1 ± 0.9 ng/g) for p,p' -

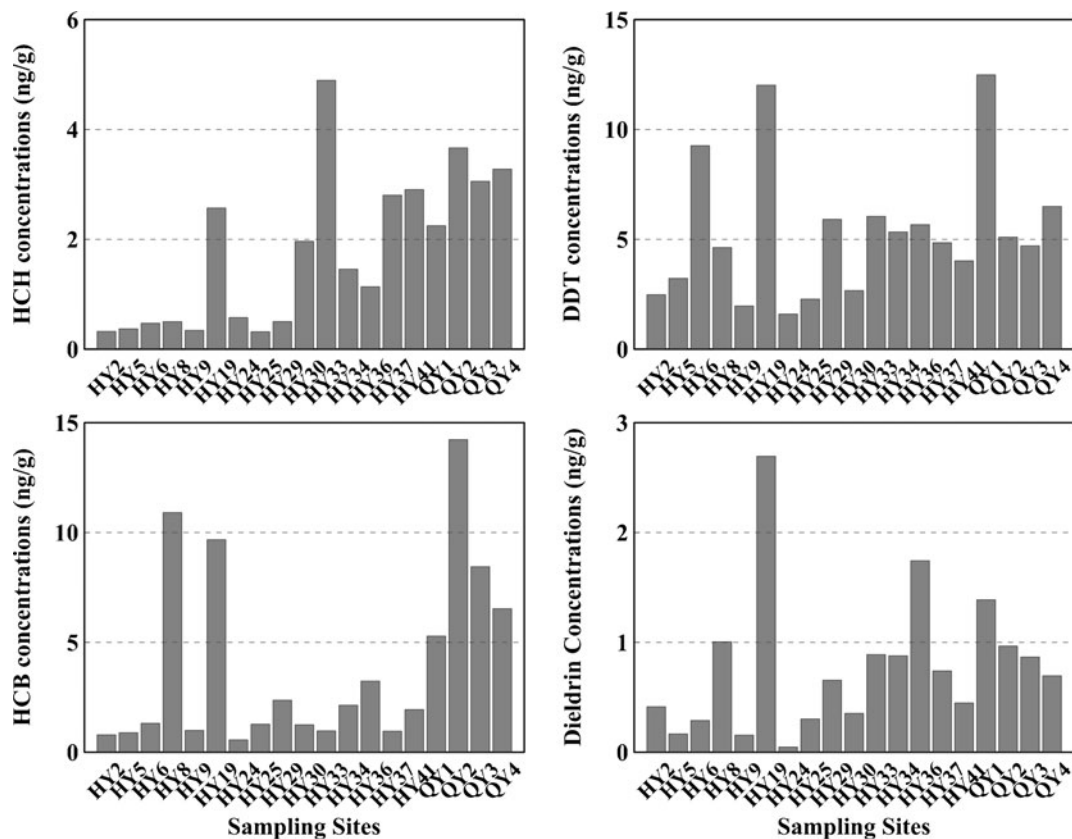


Fig. 2 Distributions of OCPs in the sediments of XR

DDE, 0.2–2.2 ng/g (mean 0.7±0.5 ng/g) for *p,p'*-DDD, <0.3–5.8 ng/g (mean 1.4±1.9 ng/g) for *p,p'*-DDT, 0.4–3.2 ng/g (mean 1.1±0.6 ng/g) for *o,p'*-DDT, 0.6–14.2 ng/g (mean 3.9±4.1 ng/g) for HCB, and <0.3–2.7 ng/g (mean 0.9–0.7 ng/g) for dieldrin. The results indicate a wide occurrence of HCHs, DDTs, and HCB in the sediments of XR. This is consistent with the data on the use of OCPs in China (Wang et al. 2005).

The levels of HCHs, DDTs, and HCB in the sediments in XR and other various rivers in China are shown in Table 1. Concentrations of HCHs (0.3–4.9 ng/g, *n*=19) in XR were relatively similar to those in other rivers, but lower than those in the Haihe River (1.0–1,620 ng/g, *n*=25) as well as Qiantang River (8.2–152.1 ng/g, *n*=48). For DDTs (1.6–12.5 ng/g, *n*=19), they were lower than those in the Haihe River (nd–155 ng/g, *n*=25) and Qiantang River (1.1–100.2 ng/g, *n*=48) while similar to those detected in the upper reaches of the Huaihe River (4.1–23.9 ng/g, *n*=16), Wuhan section of the Yangtze River (0.8–35.6 ng/g, *n*=36), and Anqing–Nantong section of the Yangtze River (0.3–32.8 ng/g, *n*=28), but higher than those in the Daliaohe River Watershed (0.5–2.8 ng/g, *n*=12), Huangpu River (0.7–4.4 ng/g, *n*=8), and the middle and lower reaches of the Yellow River (0.05–5.0 ng/g, *n*=23). HCB

has never been used directly as a pesticide in China, but it has been released into the environment as an unintended by-product in chemical processes and incomplete combustion and an impurity in pesticides (Wei et al. 2007). HCB in the sediments from XR (0.6–14.2 ng/g, *n*=19) had relatively lower concentrations compared with those from the Haihe River (nd–835 ng/g, *n*=25), Anqing–Nantong section of the Yangtze River (0.05–30.3 ng/g, *n*=28), and Dagu Drainage River (17.5–1315.2 ng/g, *n*=12). These regions were major HCB production bases in China. They were similar to those in the Wuhan section of the Yangtze River (0.9–4.4 ng/g, *n*=12).

Distribution

The distributions of HCHs, DDTs, HCB, and dieldrin are shown in Fig. 2. The highest concentrations of HCHs and DDTs appeared at sites HY33 (4.9 ng/g) and QY1 (12.5 ng/g), while the highest concentrations of HCB and dieldrin were found at sites QY2 (14.2 ng/g) and HY19 (2.7 ng/g), respectively. The higher concentrations of individual OCPs found at these sites indicate that there was significant input of OCPs from the surrounding area or benefited from good depositional setting for OCP enrichment. Besides, compounds of HCHs, DDTs, HCB, and dieldrin all had higher concentrations at site

Table 1 Comparison of HCHs, DDTs, and HCB concentrations in sediments in various rivers in China

Sampling site	Year	HCHs	DDTs	HCB	<i>N</i>	Reference
Xiangjiang River	2010	0.3–4.9 ^a	1.6–12.5 ^b	0.6–14.2	19	This study
Daliaohe River Watershed	2005	1.9–21.5 ^a	0.5–2.8 ^b	NA	12	Wang et al. (2007)
Haihe River	2007	1.0–1620 ^a	nd–155 ^b	nd–835	25	Zhao et al. (2010)
Huaihe River	2007	2.0–11.1 ^a	4.1–23.9 ^b	NA	16	Sun et al. (2010)
Huangpu River	2003	0.1–0.8 ^a	0.7–4.4 ^c	NA	8	Hu et al. (2005)
Qiantang River	2005	8.2–152.1 ^a	1.1–100.2 ^b	NA	48	Zhou et al. (2006)
Yangtze River (Wuhan)	2005	0.1–21.1 ^d	0.8–35.6 ^b	NA	36	Tang et al. (2007)
Yangtze River (Anqing–Nantong)	2005	NA	0.3–32.8 ^e	0.05–30.3	28	Shi et al. (2010)
Yellow River	2005	0.09–12.9 ^a	0.05–5.0 ^b	NA	23	Wang et al. (2010a)
Dagu Drainage River	2006	NA	NA	17.5–1315	12	Ding et al. (2007)

nd not detected, NA not available

^a α-HCH+β-HCH+γ-HCH+δ-HCH

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

^c *p,p'*-DDE+*p,p'*-DDD+*p,p'*-DDT

^d α-HCH+β-HCH+γ-HCH

^e *o,p'*-DDE+*p,p'*-DDE+*p,p'*-DDD+*o,p'*-DDT+*p,p'*-DDT

HY19. This could be due to the contribution of the local sewage outfalls directly discharged into this site. From Fig. 2, it is found that the concentrations of DDTs are higher than those of HCHs, HCB, and dieldrin at most sampling sites. This is consistent with the result of soils from the XR watershed (Li et al. 2008). Compared with HCH isomers, DDTs are the most persistent, less volatile, and lower water-soluble isomers that tend to sink and accumulate in sediments. Basically, the upper reaches of XR had lower values than the lower reaches. The mean concentrations of HCHs, DDTs, HCB, and dieldrin in surface sediments in the upper reaches (Hengyang section) were 1.4 ± 1.4 , 4.8 ± 3.0 , 2.6 ± 3.2 , and 0.7 ± 0.7 ng/g, respectively, while those in the lower reaches (the river mouth) were 3.1 ± 0.6 , 7.2 ± 3.7 , 8.6 ± 4.0 , and 1.0 ± 0.3 ng/g, respectively.

The correlations of HCHs, DDTs, HCB, and dieldrin with TOC are shown in Fig. 3. It is observed that dieldrin has a good correlation with TOC ($R^2=0.70$, $p<0.05$). However, HCHs, DDTs, and HCB do not show any correlation with TOC. Higher TOC contents help in the accumulation of OCPs in sediments due to

the strong sorption of compounds to organic carbon which may play an important role in OCP distribution in sediments (Doong et al. 2002; Hung et al. 2006). As Hu et al. (2011) pointed out, correlation between TOC and organic pollutants was hardly detected in sediment, where pollutants and TOC sources were heterogeneous or the pollutant input was continuous and strong in aquatic environment. It indicates that there is still input of HCH, DDT, and HCB into XR. Good correlation between dieldrin and TOC indicates that the accumulation of dieldrin in the sediments of XR is more regulated by TOC without continuous input. It is consistent that dieldrin was also hardly detected in the soils in the surrounding region (Li et al. 2008).

Composition and sources

Compositional differences of HCHs or DDTs in the environment could reveal respective different contamination sources (Sun et al. 2010). HCHs were contained mainly in two forms in China during the period of wide application, technical HCH and

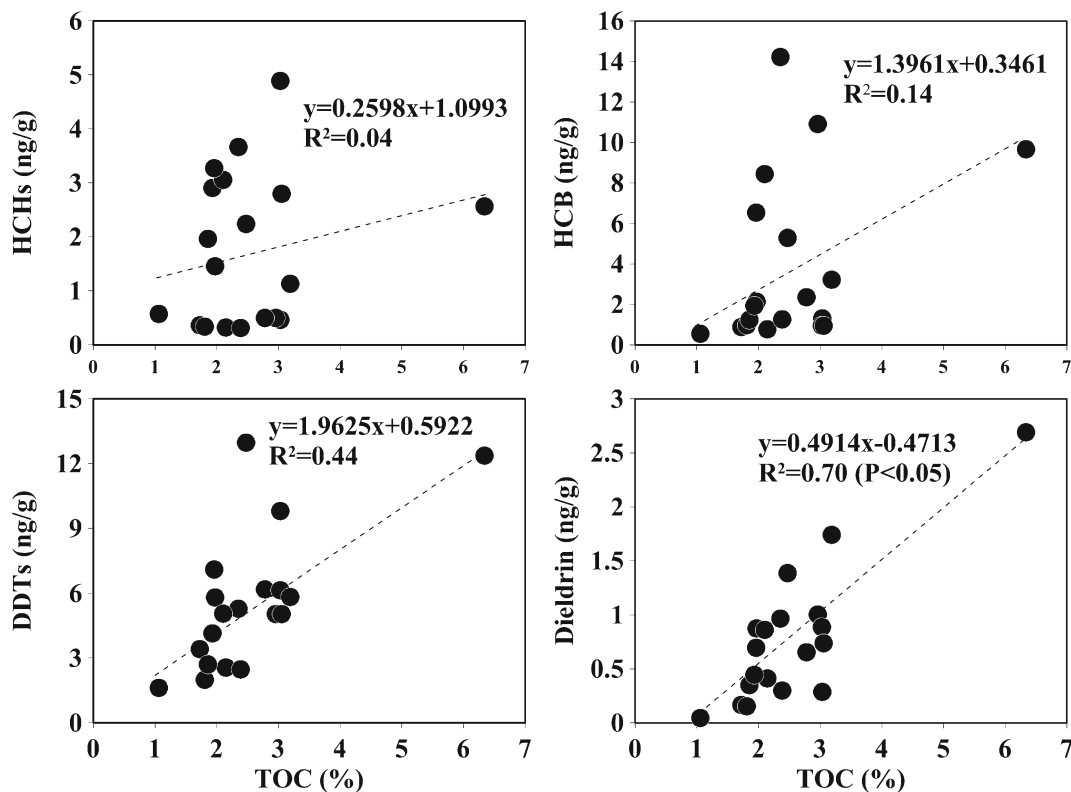
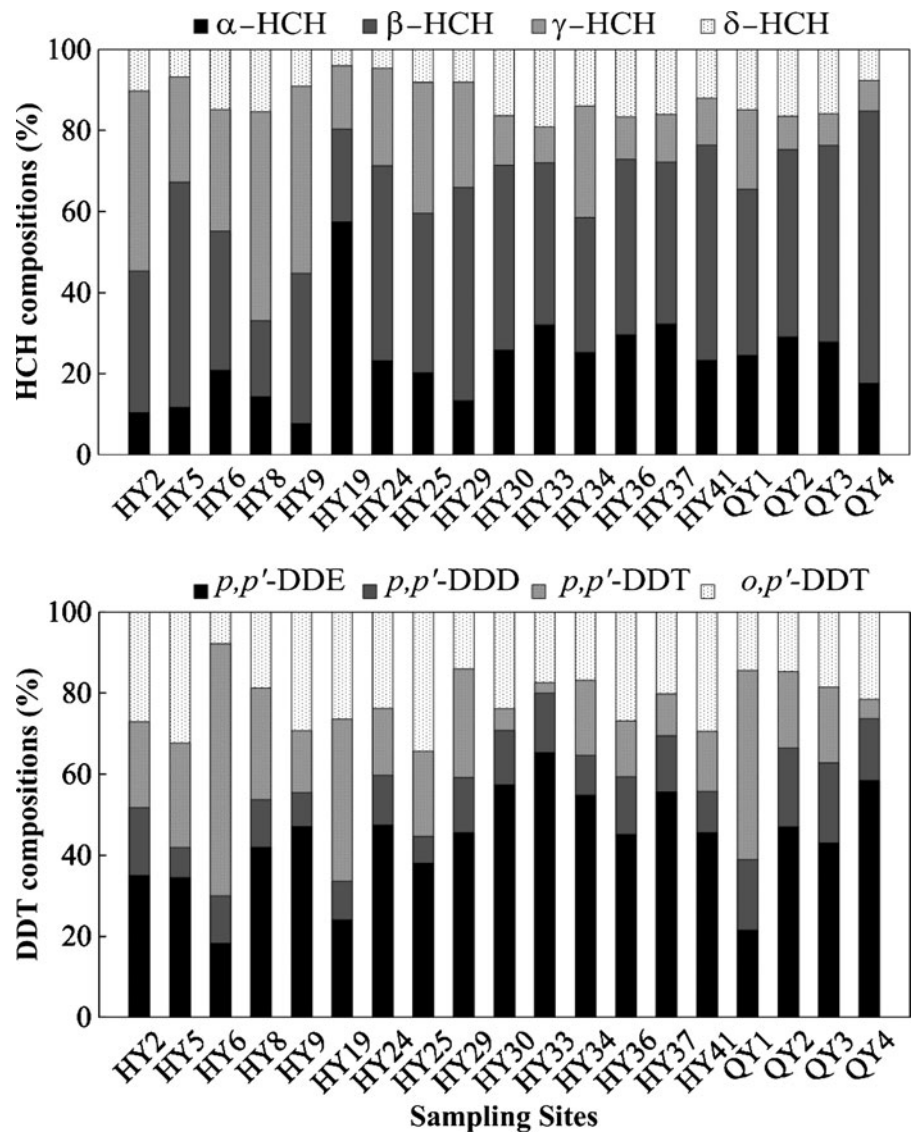


Fig. 3 Correlations between TOC and HCHs, DDTs, HCB, and dieldrin in the sediments of XR

lindane. Technical HCH contains 55–80 % α -HCH, 5–14 % β -HCH, 8–15 % γ -HCH, and 2–16 % δ -HCH. Lindane (>99 % γ -HCH because of its insecticidal property) is a kind of pesticide refined from technical HCH (Walker et al. 1999). The average HCH compositions measured in the sediment samples in this study were 23.5 ± 11.1 % for α -HCH, 42.2 ± 11.3 % for β -HCH, 22.2 ± 13.9 % for γ -HCH, and 12.1 ± 4.6 % for δ -HCH. It can be found that β -HCH had the highest percentage in most sites (Fig. 4), and they were all larger than the percentage of β -HCH in technical HCH (5–14 %). β -HCH has lower water solubility, vapor pressure, and microbial degradation

rate than other HCH isomers and tends to be enriched in sediment as the time passes by (Willett et al. 1998; Lee et al. 2001). Thus, the dominant β -HCH in this study suggests that HCHs in the sediments of XR had suffered from long-term aging without fresh inputs of technical HCH and lindane. Furthermore, the usage of technical HCH or lindane can be represented by the ratio of α -HCH/ γ -HCH (Calamari et al. 1991). Generally, α -HCH/ γ -HCH < 3 implies the usage of lindane, while it ranges from 3 to 7 for technical HCH (Pandit et al. 2006; Tang et al. 2007). In this study, α -HCH/ γ -HCH < 3 was found in most sampling sites (Fig. 5), indicating the final usage of lindane rather than

Fig. 4 Compositions of OCPs in the sediments of XR



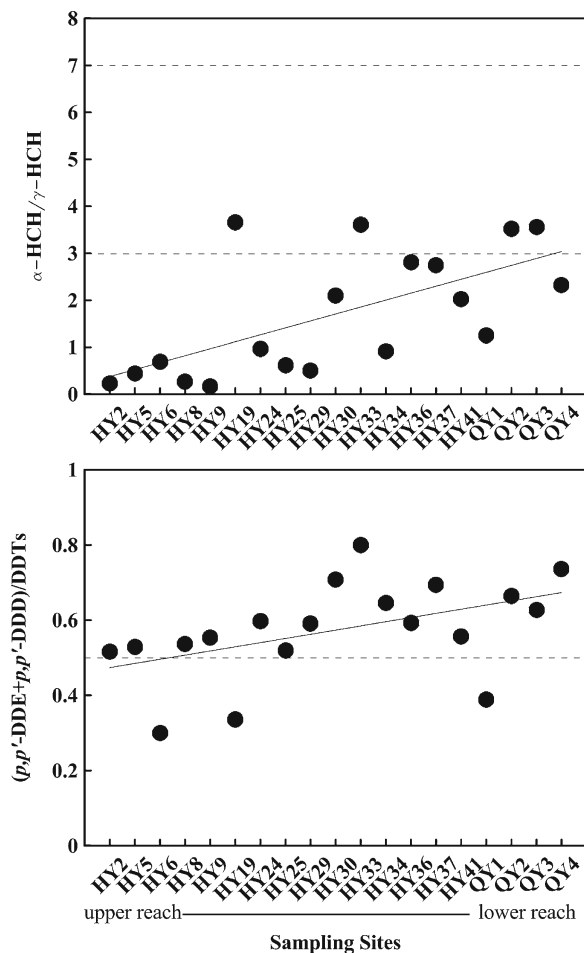


Fig. 5 Ratios of α -HCH/ γ -HCH and $(p,p'$ -DDE + p,p' -DDD)/DDTs in the sediments of XR

technical HCH in XR. Moreover, from Fig. 5, it is shown that the ratio of α -HCH/ γ -HCH increases from the upper reaches to the lower reaches of XR. This can be probably attributed to the transformation of γ -HCH to α -HCH with the process of sediment transport rather than change in sources.

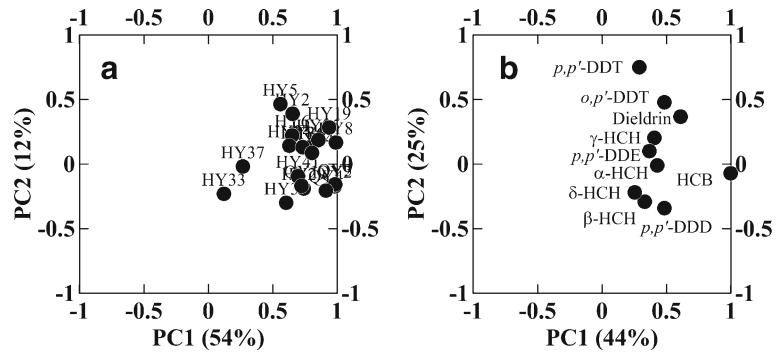
DDT can be biodegraded to DDE under aerobic conditions and DDD under anaerobic conditions, and the ratio of DDD/DDE denotes the condition of DDT biodegradation (Doong et al. 2002). The ratios of p,p' -DDD/ p,p' -DDE were <1.0 in all the samples in this study, indicating that the degradation of DDT might be under aerobic conditions. The compositions of DDTs in surface sediments are shown in Fig. 4. p,p' -DDE was the main congener (mean 43.5 %) in DDTs which was consistent with those in soil environment. This indicates that the residual DDTs in soil inputs may be

the main source of DDTs in XR. Generally, the ratio of DDT to DDE and DDD can be inferred whether there are fresh DDT inputs recently or not. $(DDE + DDD)/DDTs < 0.5$ could be considered that the samples have fresh DDT inputs, while the contrary indicates long-term weathering (Hitch and Day 1992). Here, $(p,p'$ -DDE + p,p' -DDD)/DDTs > 0.5 except for a few sites (HY6, HY19, and QY1), suggesting that DDTs in the sediments of XR mainly came from the degradation products of DDT without fresh DDT inputs (Fig. 5). For sites HY6, HY19, and QY1, the ratios of $(p,p'$ -DDE + p,p' -DDD)/DDTs < 0.5 , indicating that there were fresh DDT inputs from their surrounding areas. Technical DDT and dicofol are the two types of fresh DDT. Technical DDT generally contains 75 % p,p' -DDT, 15 % o,p' -DDT, 5 % p,p' -DDE, and <5 % others, while the content of o,p' -DDT is higher than that of p,p' -DDT in dicofol (Yang et al. 2005). The ratio of p,p' -DDT/ o,p' -DDT can be used for distinguishing different sources of DDT (Qiu et al. 2005). High ratios of p,p' -DDT/ o,p' -DDT in sites HY6, HY19, and QY1 (8.0, 1.5, and 3.3, respectively) imply that the fresh DDT input was derived from the usage of technical DDT. Although technical DDT was banned in agriculture for more than two decades, technical DDT used for other purposes, e.g., DDT-activated antifouling paint, and for public health may help to explain the observed high p,p' -DDT levels related to the technical DDT usage in XR. The Dongting Lake watershed had seriously suffered from the harm of schistosomes in history, and technical DDT was still used to kill schistosomes in the region (Li et al. 2008). Figure 5 shows that the ratio of $(p,p'$ -DDE + p,p' -DDD)/DDTs increases from the upper reaches to the lower reaches of XR probably due to the degradation of DDT to DDD or DDE during sediment transport.

Principal component analysis

In this work, PCA was conducted for four DDT compounds, four HCH compounds, HCB, and dieldrin from 19 samples in XR. As shown in Fig. 6, two factors were extracted which accounted for 66 % (loadings) and 79 % (scores) of the total variance in the dataset. The loading plot reveals a separation between upper reaches and lower reaches of XR (Fig. 6a), and the main compounds (scores) explaining the separation of the upper reaches are p,p' -DDT, o,p' -DDT, and γ -HCH (Fig. 6b), while the lower reach stations are clearly defined by p,p' -DDE, β -HCH, and δ -HCH which are considered as degradation

Fig. 6 Principal component analysis loading (a) and score (b) plot in the sediments of XR



and residual compounds. It suggests that different contamination patterns of OCPs in surface sediments were possibly related to the enrichment of degradation (*p,p'*-DDE) or residual (β -HCH and δ -HCH) compounds during sediment transport and deposition process.

Ecological risk

Sediment quality guidelines, the effects range low (ER-L) and effects range median (ER-M), are applied in this study. A value below the ER-L represents a minimal effect, that between the ER-L and ER-M represents a possible effect, and that above the ER-M represents a probable effect (Long et al. 1995). Table 2 shows that the maximum concentrations of individual OCPs do not exceed their respective ERL and ER-M values. Concentration levels of DDTs are higher than ER-L at all sites. Meanwhile, concentrations of *p,p'*-DDE and *p,p'*-DDT higher than ER-L are observed at 47.4 and 29.4 % of the sites, respectively. There is only one site (QY1) in which *p,p'*-DDD is higher than ER-L. Dieldrin concentrations are between ER-L and ER-M in all detected sites. Concentrations of γ -HCH at six sites are higher than ER-L. It could be considered that DDTs and dieldrin were the main pollutants possibly causing adverse biological risk in XR. Importantly, concentrations of dieldrin, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and γ -HCH are all found to be higher than ER-L at sites QY1 and HY19. This indicates that sites QY1 and HY19 need special concern for adverse biological effect of OCPs on benthic organisms.

Conclusions

This work reported the contamination status of OCPs in surface sediments in XR. HCHs, DDTs,

HCB, and dieldrin were widely detected in most sample sites. The levels of these compounds in XR were moderately polluted. HCHs and DDTs in the sediments were mainly composed of degraded or residual products, indicating that they had suffered from long-term aging. However, the high proportion of *p,p'*-DDT to DDTs in three sites implies that there was a current usage of technical DDT in surrounding areas when sampling. The sediments in the lower reaches of XR (the river mouth) had higher values of OCPs than those in the upper reaches, indicating that the sediment in the river mouth was an important sink of OCPs. Moreover, the sediments from the lower reaches were more concentrated with degradation or residual products mainly due to the transformation of OCPs with sediment transport. The assessment of the ecological risk using sediment quality guidelines indicates that the OCPs in the sediments from XR probably have an adverse biological effect on organisms.

Table 2 Assessments of potential ecological risk of selected OCPs in the sediments of XR using sediment quality guidelines according to Long et al. (1995)

Chemical	Guidelines		Percentage (numbers) of samples above the corresponding levels	
	ER-L	ER-M	>ERL	>ERM
Dieldrin	0.02	8	84.2 % (16)	0
<i>p,p'</i> -DDE	2.2	27	47.4 % (9)	0
<i>p,p'</i> -DDD	2	20	0.8 % (1)	0
<i>p,p'</i> -DDT	1	7	29.4 % (5)	0
DDTs	1.58	46.1	100 % (19)	0
γ -HCH	0.32	0.99	31.6 % (6)	0

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