

Residues and sources of HCHs and DDTs in the sediments of land-based sewage outlet to the Zhanjiang Bay, China

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Abstract

Due to the large usage of DDT-containing antifouling paints and lindane in China, heavy residuals of DDTs and HCHs have been found in many fishing harbors, but there is lack of studies on this issue for the Zhanjiang Bay which is an important fishing harbor and mariculture zone in South China. To evaluate the pollution status and sources of HCHs and DDTs in the Zhanjiang Bay, the concentrations, spatial distributions and sources in the sediments of 11 land-based sewage outlets to the Zhanjiang Bay were investigated. Since the 1980s, HCHs residuals had obviously decreased in studied areas, but DDTs had little change, even abnormally high levels were found in some sites. The content percentages and diagnostic ratios of HCHs isomers and DDTs showed that the source of HCHs was derived from soils around the bay and recent input of lindane, and DDTs were from historical residues of technical DDTs and fresh input of DDT-containing antifouling paints on fishing ships. Based on sediment quality guidelines, DDTs would be of more concern for the ecotoxicological risk on marine environment and adverse effects on benthonic organisms. This study indicated that lindane and DDT-containing products may be still used in some places of Zhanjiang City. It should be urgent to control their usage and clean the DDTs-contaminated sites by the local government.

Key words: Zhanjiang Bay, sediment, DDTs, HCHs

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1 Introduction

Dichlorodiphenyltrichloroethane (DDTs, including o, p'-DDT, p, p'-DDT, p, p'-DDE and p, p'-DDD) and hexachlorocyclohexane (HCHs, including α -HCH, β -HCH, γ -HCH and δ -HCH), were widely used in China as pesticides for agriculture, pest control and mosquito abatement between the 1950s and the 1980s. Although China officially prohibited HCHs and DDTs to use for agriculture in 1983 and fully banned in 2002 (except for special uses for hygiene purposes), DDTs were still allowed to use as biocide in antifouling paints and intermediate materials in dicofol production, and lindane as a substitute pesticide for technical HCHs for a long time, which possibly resulted in high residual levels of HCHs and DDTs in regional soil and sediment in China. Some reports have confirmed that the pollution of HCHs and DDTs is still serious in sediments of estuary, fishing port, marine aquaculture area, and shipyard, where DDTs' concentrations may be 1–2 orders of magnitude higher than those of the adjacent estuarine/marine sediments due to a strong local fresh input of DDT-containing antifouling paints (Lin et al., 2009; Yu et al., 2011b; Xin et al., 2011).

The Zhanjiang Bay is a traditional fishing harbor and famous aquaculture base of South China with about 25 000 (times) fishing boats in and out from the port every year, and several shipyards along the coastline. Yu et al. (2011a, b, c) indicated that

antifouling paints used in fishing boats might be an important source of DDTs to the mariculture zone of South China. The historical and current usage of antifouling paints may result in heavy pollution of DDTs in the Zhanjiang Bay. Surrounding the bay, Zhanjiang City is the major agricultural city of Guangdong Province. A large amount of HCHs and DDTs were used for agricultural and aquaculture in history, and even in 1984, the usage of HCHs was still up to 3 578.6 t. In the future, the city will focus on the development of harbor industry and marine economy around the Zhanjiang Bay. Large-scale land development and utilization may make residues of HCHs and DDTs in the soil into the sea (Zhang et al., 2002). Therefore, heavy pollution of HCHs and DDTs may be in the Zhanjiang Bay due to their historical residuals and potential fresh input.

Because HCHs and DDTs productions were still in use for some special purpose, even illegally in some areas of China, the pollution of HCHs and DDTs in fishing harbors has raised extensive concern in recent years. Early in the 1980s, there were a few reports on HCHs and DDTs in the Zhanjiang Bay (Chen, 1989), but recent studies have been scarce (Shi et al., 2010). In order to investigate current pollution status and fresh input of HCHs and DDTs in the Zhanjiang Bay, the present study was set to collect data of concentrations, spatial distributions and sources of HCHs and DDTs.

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2 Materials and methods

2.1 Sampling

Previous investigation showed that there were 11 main rivers, drainage canals and sewage pipes into the Zhanjiang Bay (collectively called drainage river). Their functions and locations were shown in Fig. 1. The upper (0–10 cm) surface sediment sample was collected at river estuary or sewage pipe outlet (named as drainage outlet) in December, 2012. Due to the tidal flat environment around sampling sites, the sediment samples were black mud on the west side and grey mixtures of mud and sand on the east and south sides.

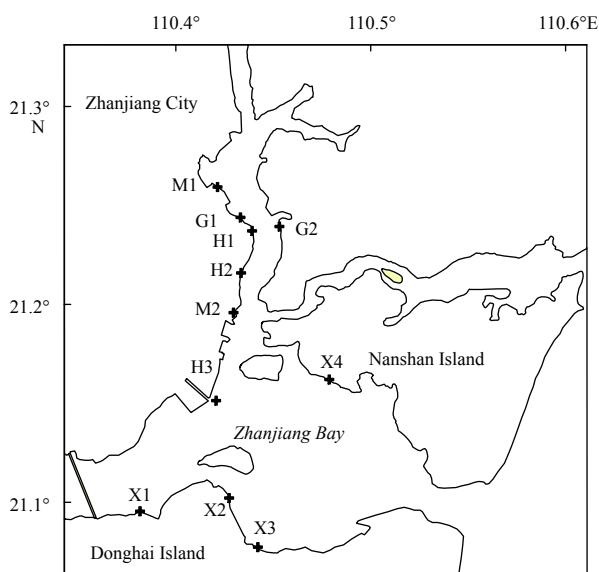


Fig. 1. The map of sampling sites in the Zhanjiang Bay, China. G1 and G2 represent outlets of municipal sewage in coastal park; M1 and M2 outlets of municipal sewage in wharf; H1, H2 and H3 the mouth of rivers in urban area; and X1, X2, X3 and X4 the mouth of rivers or canals in rural.

2.2 Materials and methods

The standard solution of HCHs and DDTs was purchased from the o2si Smart Solutions Inc. (USA). Before use, all solvents were redistilled, anhydrous sodium sulfate (Na_2SO_4) was Soxhlet-extracted for 48 h with dichloromethane, and then baked for 4 h at 450°C.

In the laboratory, sediment samples were freeze-dried, pulverized, and sieved through 80-mesh stainless steel. According to USEPA Method 3546, about 10 g sample with 10 g Na_2SO_4 was extracted by microwave extraction apparatus (CEM MARS, USA) with a mixed solvent of (1:1) hexane and acetone. 2, 4, 5, 6-tetrachloro-*m*-xylene was added to each of the samples as surrogate standards, and activated copper sheets were added for desulphurization in extracted liquid. The extract was concentrated and solvent-exchanged to hexane, and then further to concentrate to 0.5 mL. A quantity of pentachloronitrobenzene was added as an internal standard prior to analysis.

The eight target compounds including α -HCH, β -HCH, γ -HCH, δ -HCH, *p*, *p'*-DDD, *p*, *p'*-DDE, *o*, *p'*-DDT and *p*, *p'*-DDT were quantitatively analyzed by gas chromatograph (GC) coupled with triple-quadrupole mass spectrometry detector (GC-MS/MS, Trace GC Ultra & TSQ Quantum XLS, Thermo Fisher, USA) and a HP-5MS capillary column (30 m×0.25 mm×0.25 μm).

The mass spectrometry mode is selective reaction monitoring (SRM). The oven temperature was programmed from 60°C for 1 min to 250°C at a rate of 4°C/min, held for 10 min. Injector and detector temperatures were 260°C, and helium and argon were respectively the carrier gas and collision gas.

2.3 Quality assurance/quality control (QA/QC)

All data were subject to strict quality control procedures, including the analysis of method blanks (solvent), duplicate samples and spiked blanks (standards spiked into solvent). The surrogate recoveries ranged from 74% to 113%, and method detection limit (MDL) from 0.01 ng/g to 0.10 ng/g. Actual detection limits were adjusted based on the sample size used. The reported concentrations of HCHs and DDTs were corrected for surrogate recoveries.

In this study, the source and fate of HCHs and DDTs were discussed mainly by their compositions and diagnostic ratios: (1) content percentages of HCHs and DDTs: to identify historical residues and fresh input of HCHs and DDTs; (2) α -/ γ -HCH, β -/ $(\alpha+\gamma)$ -HCH and (DDE+DDD)/DDTs: to indicate if there was recent input of lindane and DDTs; (3) DDD/DDE: to determine if DDTs were degraded under aerobic or anaerobic conditions; and (4) *o*, *p'*-/*p*, *p'*- DDT: to discuss if DDTs were from dicofol.

3 Results

3.1 The concentration levels and spatial distributions of HCHs and DDTs

In this work, all of studied compounds had 100% of detection frequencies except β -HCH with 64% and more than 100% variation coefficients of concentration (Table 1), indicating a wide occurrence of these compounds but significant difference of their contents in different regions. As shown in Fig. 2, Site G1 had the highest concentration of total HCHs (sum of α -, β -, γ - and δ -HCH) with the value of 11.32 ng/g, and other sites were ranged from 0.23 ng/g to 3.45 ng/g. In the studied areas, concentrations of total DDTs (sum of *o*, *p'*-DDT, *p*, *p'*-DDT, *p*, *p'*-DDE and *p*, *p'*-DDD) varied in the range of 1.98–871.66 ng/g. However, if the two maxima were excluded with the values of 871.66 ng/g and 760.96 ng/g at Sites M2 and X2, the levels of total DDTs were fell in the range of 1.98–51.84 ng/g. These two abnormally high DDTs levels were found in samples collected adjacent to fishery wharf and mariculture zone where many fishing vessels were mooring and maintenance. It implied that the high concentration levels of DDTs may be linked to the release of DDTs from antifouling paints used in fishing boats (Xin et al., 2011; Lin et al., 2009).

Table 1. The concentrations of HCHs and DDTs in 11 sediment samples

Compounds	Concentration range/ng·g ⁻¹	Variation coefficient of concentration/%	Detection frequency ratios/%
α -HH	0.05–5.95	187	100
β -HH	ND–1.39	194	64
γ -HH	0.03–2.66	129	100
δ -HH	0.08–1.31	93	100
<i>p</i> , <i>p'</i> -DDE	0.67–54.19	164	100
<i>p</i> , <i>p'</i> -DDD	0.83–313.17	213	100
<i>o</i> , <i>p'</i> -DDT	0.12–95.17	197	100
<i>p</i> , <i>p'</i> -DDT	0.36–554.82	211	100
Σ HCHs	0.23–11.32	150	
Σ DDTs	1.98–871.66	199	

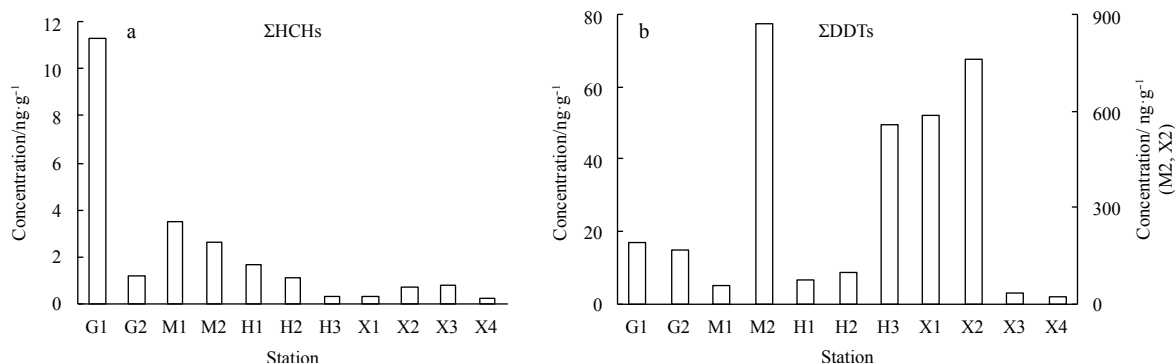


Fig. 2. Concentrations of Σ HCHs and Σ DDTs in sediments.

At 11 sampling sites around the Zhanjiang Bay, concentrations of HCHs were higher on the west than the east and south, and their values were declined from north to south, which was consistent with the spatial distributions of HCHs in soils around the bay. In Zhanjiang City, the soils around the Zhanjiang Bay, especially on the northeast (just on the top of the bay), were the most heavily polluted areas of HCHs (Ma et al., 2010), higher than those in adjacent sediments. It implied that HCHs in this study may be derived from the input of HCHs in soils around the bay. On the contrary, slight pollution of DDTs was found in soils, and DDTs concentrations were relatively low compared with sediments. It can be explained that there may be other input of DDTs from marine environment or long-term accumulation of DDTs from the soils.

Previous study reported that the contents of total HCHs and DDTs were respectively 0.009 2–0.203 0 mg/kg and 0.002 2–0.012 3 mg/kg in the Zhanjiang Harbor (Chen, 1989). Combined with results of this work, it can be estimated that pollution levels of HCHs were obviously dropped in studied areas, but DDTs do not show much change, even their concentrations were still very high in some sites. China is the only country of continuously using DDT based antifouling paints on ship, and DDT-containing antifouling paint for fishing boat maintenance has been an important source of DDT in the mariculture zone and fish harbor (Yu et al., 2011b; Lin et al., 2009), which could be respond for the current DDTs pollution in this study.

The reduction of HCHs in sediments may be attributed to the degradation of historical HCHs and little fresh input. Before 1983, production and usage of technical HCHs had large quantities, but over more than 30 years, the residues in the soil and sedi-

ment may be mostly degraded due to their short half-life. After technical HCHs were banned in 1983, lindane was allowed to use in China, but its production and usage were limited, e.g., in 1999, lindane production of two particular factories was 1 335 t, among which 1 307 t for exports.

3.2 Composition and sources of HCHs

In China, technical HCH mixture and lindane were the two kinds of HCH products most widely used respectively before 1983 and after 1991. Usually, technical HCHs contain 60%–70% of α -HCH, 5%–12% of β -HCH, 10%–12% of γ -HCH and 6%–10% of δ -HCH (Willett et al., 1998; Breivik et al., 1999), while lindane contains almost pure γ -HCH (Ma et al., 2003). In this study, the isomers α -, β -, γ - and δ -HCH respectively accounted for from 18.2% to 57.4% (mean of 33.4%), 0% to 36.7% (mean of 9.6%), 11.2% to 52.6% (mean of 27.5%), and 11.6% to 51.0% (mean of 29.4%) of total HCHs (Fig. 3). Compared with original components of technical HCHs and lindane, the percentages of HCH isomers changed obviously, which could be attributed to their different physical-chemical properties and sources (Hu et al., 2009).

Amongst the isomers of HCH, β -HCH was the more stable and relatively resistant to microbial degradation due to its low vapor pressure and less degradable property, and other HCHs can be transformed to β -HCH in the aged environmental samples (Willett et al., 1998; Walker et al., 1999). Therefore, the longer retention of HCHs was in environment, the more β -HCH content was, β -HCH was often the most abundant isomer of HCH in soils and sediments, which can be used for exploring the source of historical usage of HCHs (Law et al., 2001; Luo et al., 2005). In this study, low percentage and concentration of β -HCH were found,

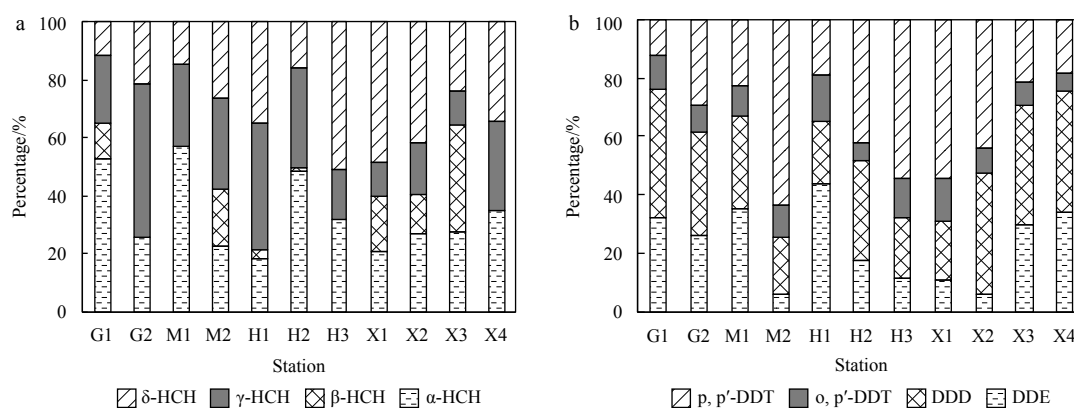


Fig. 3. Composition percentages of HCHs and DDTs in sediments.

meaning that HCHs were from fresh input, or most of β -HCH was in soils while little into the marine environment because high concentration level of β -HCH was found in the soils around the bay (Ma et al., 2010).

γ -HCH is the least persistent HCH isomer in environment because it is most ready to be degraded or transformed into other isomers (Jagnow et al. 1977; Quintero et al., 2005). Then, relatively high percentages of γ -HCH, especially at Sites G2 (52.6%) and H1 (43.5%) compared to composition of technical HCHs, provided another evidence of the fresh input of lindane in this study. As reported previously, the high δ -HCH fraction in sediment samples was also observed in Zhanjiang coastal sediments. The reason may be that δ -HCH has the longest half-life among HCH isomers (Satpathy et al., 1997; Hu et al., 2009).

Diagnostic ratios of HCH isomers in the environment generally indicate varied sources of contaminants, and ratios of α -/ γ -HCH between 3 and 7 represent the technical HCH mixture, while ratios close to 1 indicate the recent use of lindane (Law et al., 2001; Willett et al., 1998). Ratios of α -/ γ -HCH in 11 sediment samples ranged from 2.3 to 0.4, suggesting that α -HCH, the major component of technical HCHs, were mostly degraded, or lindane is replacing technical HCHs to be the main source of HCH in the environment (Mu et al., 2012). At Sites G2, M2, H1, H2 and X4, the diagnostic ratios were closed to 1, which means that there was fresh input of lindane, even its recent usage in Zhanjiang City. This observation was supported by the fact that the percentages of γ -HCH were above 30% in these sites, far more than the values in technical HCH mixture (6%–10%). Ratio of β -/(α + γ)-HCH was also used to determine whether the HCHs in the environment were the residue or fresh input, and β -/(α + γ)-HCH > 0.5 indicates that HCHs are mainly from the residuals in the environment, otherwise, from recent input or atmospheric deposition (dry and wet) (Chen et al., 2014; Zheng et al., 2009). In this study, the ratios of β -/(α + γ)-HCH were less than 0.5 except Sites X1 and X3 with the values of 0.6 and 0.9, indicating that HCHs were mainly from recent input but Sites X1 and X3 from residuals of technical HCHs.

3.3 Composition and sources of DDTs

Technical DDT mixtures, widely used in China as major DDT product, contained 75% p, p'-DDT, 15% o, p'-DDT, 5% p, p'-DDE, and less than 5% p, p'-DDD and other materials, respectively. Figure 3b showed the content percentages of DDTs. At Sites M1 and H1, the most abundance compound was DDE with the concentration percentages of 35.4% and 44.0% respectively; at Sites G1, G2, X3 and X4, DDD was the major compound, accounting for 44.2%, 35.2%, 40.7% and 41.8% of total DDTs. In other sites, p, p'-DDT has the highest percentages of 41.9%–63.7% but lower than those in technical DDTs. It is reported that DDT was likely to be biodegraded into DDE under aerobic conditions, whereas to DDD in an anaerobic setting, so the composition difference of DDT and its metabolites have been used to identify the aerobic/anaerobic conditions and the possible sources of DDT in the environment (Hitch and Day, 1992; Metcalf, 1973; Tao et al., 2007). In this study, DDD/DDE ratios were more than 1 except at Sites M1 (0.89) and H1 (0.48) (Fig. 4), indicating anaerobic conditions in these sediments. This was supported that pristane/phytane ratios ranged from 0.66 to 0.96 (Fig. 4) which indicated the reduction condition in studied areas (Didyk et al., 1978).

The ratio of (p, p'-DDE + p, p'-DDD)/p, p'-DDTs was also the common indicative indices (Barakat et al., 2013; Hong et al., 1999), even used to indicate the possibility of the continuous illegal use of DDT in some lake areas of China (Peng et al., 2005).

The (p, p'-DDE + p, p'-DDD)/p, p'-DDTs ratios greater than 0.5 indicate historical input of DDT, while those less than 0.5 imply recent input. In this study, (DDE+DDD)/DDTs ratios at Sites M2 (0.29), H3 (0.37) and X1 (0.36) suggested little attenuation or recent input of DDT, even with illegal use of DDT at these sites. At other sites, the ratios ranged from 0.52 to 0.86, implying that DDTs were from early input of technical DDTs and degradation of the parent DDT had occurred significantly.

It is reported that the production and application of dicofol, DDT-containing antifouling paints and hygiene products could be respond for current DDTs pollution in China (Wan et al., 2005; Qiu et al., 2005; Liu et al., 2009; Wang et al., 2007). Due to high o, p'-DDT content in dicofol, o, p'-/p, p'-DDT ratio was used to determine the source of DDT from technical DDTs or dicofol, the ratio between 0.2 and 0.3 represent technical DDTs, while 7.0 ± 2.2 indicate dicofol (Qiu et al., 2005; Qiu and Zhu, 2010). In this work, o, p'-/p, p'-DDT ratios (0.94–0.15, mean of 0.39; Fig. 4) were much lower than that of dicofol, indicating that dicofol may be not significant to the fresh input and high levels of DDTs at several sites, which should linked to the historical/current usage of antifouling paints for ships in Zhanjiang City. Some reports also have identified technical DDTs were still used as an additive for the production of antifouling paints used in fishing ships and a main source of DDT found in marine environment (Hu et al., 2009; Xin et al., 2011).

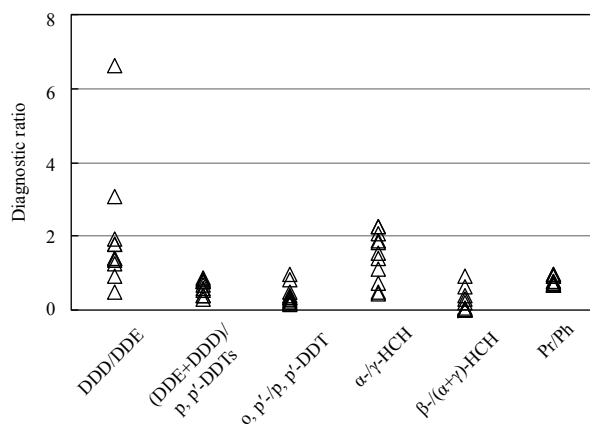


Fig. 4. Characteristic ratios of HCHs, DDTs and Pr/Ph.

3.4 The relationship of HCHs, DDTs and TOC

Studies reported that organic matter played an important role in affecting the fate and distribution of organochlorine pesticides (OCPs), total organic carbon (TOC) was in good correlation with OCPs due to their similar sources, post-depositional sorption and co-emission; meanwhile, poor relationship was also found in some areas, implying that there existed localized or new input of OCPs and TOC was not the governing factor (Hu et al., 2009; Hong et al., 2008; Hung et al., 2007). In this study, the linear regression of log-normalized HCHs, DDTs and TOC concentrations was conducted to evaluate the relationship among TOC and HCHs, DDTs (Fig. 5). In general, TOC content was positively correlated with HCHs and DDTs, TOC was strongly related with HCHs ($R^2=0.70$) but weakly with DDTs ($R^2=0.04$). This was also reported in some other studies on marine sediments in China, such as the Bohai Sea (Hu et al., 2009), and the Jiaozhou Bay (Liu et al., 2013).

In this study, HCHs were derived from the input of HCHs in soils around the Zhanjiang Bay which was also the important source of organic matter in sediments. The good relationship

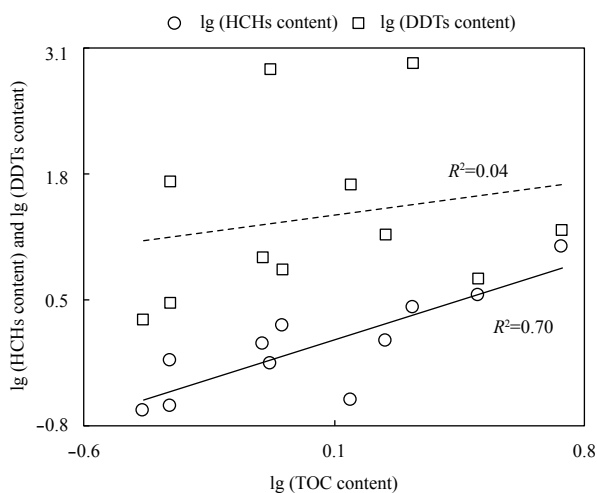


Fig. 5. Linear regression of normalized logarithms of HCHs, DDTs and TOC concentrations, respectively.

between TOC and HCHs provided the evidence that they were likely from similar sources, and organic matter may be the dominated factor on the fate and distribution of HCHs during migration and deposition in marine environment as carrier. For DDTs, its poor correlation with TOC can be explained as that DDTs cannot be controlled by organic matter and they may be the current input from localized source. As discussed above, antifouling paints used in maintenance and repair of boats were the important contributors to the content of DDTs in the Zhanjiang Bay, which should be responsible for the abnormally content of DDTs at some sampling sites. In a short time, the DDTs from the local-

ized source cannot reach equilibration status in marine environment. The different sources may be also the reason of poor correlation between DDTs and HCHs ($R^2=0.00$).

3.5 Potential biological effects of OCPs

Considering that most of studied sites are in mariculture zone, it needs to conduct an ecological risk assessment to evaluate the possible ecotoxicological risks of selected OCPs to aquatic organisms and marine environment using two sediment quality guidelines (Long et al., 1995, 1998; MacDonald et al., 1996; CCME, 2002) (Table 2). In studied areas, 82% (p, p'-DDT), 64% (DDE and DDD) and 100% (DDTs) of sampling sites had higher concentration levels than their effect range-low values (ERL), and 73% (p, p'-DDT), 64% (DDE), 82% (DDD and DDTs) and 55% (γ -HCH) were higher than threshold effect levels (TEL). At the four sites (M2, H3, X1 and X2), concentration levels of p, p'-DDT and DDTs were above the effect range-medium (ERM), the maximum concentration of p, p'-DDT and DDTs were 79 times and 19 times their ERM values. Meanwhile, p, p'-DDT, DDD and DDTs also exceeded the probable effect level (PEL) at the same sites (DDTs except Site H3). The results showed that large amount of DDTs and lindane was enriched in the sediments, which may cause a high potential ecological risk on the neighboring benthic organisms and marine environment (Hu et al., 2009).

All the time, mariculture is the main form of aquaculture in Zhanjiang City, and its production was 1 million tons in 2012, accounting for 87.5% of total aquaculture production. DDT pollution may affect the quality and production of aquatic products in studied areas. Based on the previous results of HCHs and DDTs sources, it is recommended to concern on DDTs and γ -HCH more, and minimize their sources, e.g., reducing or replacing the usage of lindane and DDT-based antifouling paints.

Table 2. Assessments of potential biological risks of HCH and DDT using two sediment quality guidelines (SQG)

Chemical	ERL ¹⁾ /ng·g ⁻¹	ERM ²⁾ /ng·g ⁻¹	TEL ³⁾ /ng·g ⁻¹	PEL ⁴⁾ /ng·g ⁻¹	<ERL ⁵⁾ /%	ERL-ERM ⁵⁾ /%	>ERM ⁵⁾ /%	<TEL ⁵⁾ /%	TEL-PEL ⁵⁾ /%	>PEL ⁵⁾ /%
p, p'-DDT	1	7	1.19	4.77	18	45	36	27	36	36
p, p'-DDE	2.2	27	2.07	374	36	45	18	36	64	0
p, p'-DDD	2	20	1.22	7.81	36	45	18	18	45	36
DDTs	1.58	46.1	3.89	51.7	0	64	36	18	55	27
γ -HCH	0	-	0.32	0.99				45	45	9

Note: ¹⁾ Effect range-low value; ²⁾ effect range-median value; ³⁾ threshold effect level; ⁴⁾ probable effect level; ⁵⁾ percentage of samples above the corresponding levels.

4 Conclusions

Over 30 years since OCPs were banned in China, HCHs contents were relatively lower than those reported in previous studies but DDTs were still high in this study. Although technical HCHs and DDTs had degraded significantly, fresh inputs of DDTs and HCHs have been identified and attributed to local usage of lindane and DDT-containing antifouling paints which was responsible for the abnormally high DDTs content in some areas. These results showed that HCH and DDT pollution still needs to be concerned due to the usage of lindane and DDT-containing antifouling paints in Zhanjiang City. The phasing out of lindane and elimination of DDT-containing anti-fouling paints are of urgent need for the protection of the marine environment and associated biota.

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