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Inputs of antifouling paint-derived dichlorodiphenyltrichloroethanes (DDTs) to a typical mariculture zone (South China): Potential impact on aquafarming environment

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ABSTRACT

Existing evidence indicated that dichlorodiphenyltrichloroethane (DDT)-containing antifouling paints were an important source of DDT residues to mariculture zones. However, the magnitude of the impact on aquafarming environment has remained largely unknown. In the present study, the concentrations of DDT and its metabolites (designated as DDXs) were determined in harbor sediment and antifouling paint samples collected from a typical mariculture zone in South China. Compositional and concentration correlation analyses implicated the DDT-containing antifouling paints for fishing boat maintenance as an important source of DDT in the mariculture zone. The annual emission of DDXs to the study region was estimated at 0.58 tons/yr. Furthermore, a comparison of the expected DDT loadings in pelagic fish and field measurements indicated that fish feed especially trash fish was a major source of DDTs in the fish body. Nevertheless, the use of DDT-containing antifouling paints should be limited to prevent further deterioration in aquafarming environment.

1. Introduction

Dichlorodiphenyltrichloroethane (DDT)-containing antifouling paints have been the primary choice for ship maintenance since the 1950s (Cao and Zhang, 2009), because of the long-lasting superior antifouling effects and low cost. Approximately 250 tons of DDT were used for producing DDT-based antifouling paints annually from the 1950s to 2005 in China, resulting in a total amount of 11,000 tons of DDT used (Global Environment Facility, 2007). In 2004, the amount of DDT used in antifouling paints accounted for approximately 4% of the total DDT produced in China (The People's Republic of China, 2007). This gigantic amount of DDT, even if a small fraction is released to the marine environment, would lead to elevated contaminant loadings in the water, sediment and marine organisms. Consequently, this may affect the marine ecosystem and pose hazards to human health.

In a previous study (Meng et al., 2007), the concentrations of DDT and its primary metabolites (designated as DDTs; Supplemental Material) were found to be higher in seawater farmed fish than in wild marine fish or freshwater farmed fish. It was also demonstrated that the mariculture environment in South China was somewhat impaired by the occurrence of DDTs and consumption of seawater farmed fish might subject consumers to moderate cancer risk (Yu et al., 2011b,c). A recent study (Yu et al., 2011b) indicated that antifouling paints might be an important source of DDTs to the mariculture zones of South China. Despite the recent efforts in characterizing the levels and mass inventories of antifouling paints-derived DDTs in the coastal environment of China (Lin et al., 2009), studies on the concentrations and compositions of DDTs in antifouling paints have been scarce (Wang et al., 2007). The potential impact of antifouling paint-derived DDTs on aquafarming environment has also remained largely unknown.

Our recent study (Yu et al., 2011a) identified a large number of *o,p′*- and *p,p′*-isomers of DDT and their metabolites (sum of which designated as DDXs) in sediment samples collected from Hailing Bay, a typical mariculture zone of South China (Fig. S1 of the Supplemental Material; "S" indicates tables and figures in the Supplemental Material afterwards), and established probable degradation pathways of individual DDT components under field conditions. Building on these previous results, the present study was set out to collect data to verify that antifouling paint was an important source of DDT in the fishing harbor studied. The steps to

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achieve this objective included examining the concentration distribution of DDXs in sediment, comparing the DDT composition in various types of samples, analyzing the correlation between the concentrations of DDXs and Cu and estimating the sediment inventory of antifouling paint-derived DDTs in the mariculture zone of Hailing Bay. Most importantly, the impact from the use of DDT-containing antifouling paints on pelagic fish was assessed by comparing the expected fish loadings of DDTs, estimated from the DDT concentrations in water, with the field-measured DDT concentrations in fish (Yu et al., 2011c).

2. Materials and methods

2.1. Sample collection

Surface sediment and sediment core samples were collected from Hailing Bay of South China, which is embraced within the City of Yangjiang regarded as one of the most important fishery bases in Guangdong Province (Network of quaculture in China, 2010), in January 2010 (Fig. S1). Antifouling paint samples were purchased from a local store at the coast of Hailing Bay, a boat maintenance facility in Hailing Bay and Hong Kong, respectively. Water samples were also collected from Fengtou River, a major river discharging into Hailing Bay (Fig. S1). The procedures for collecting sediment samples were detailed elsewhere (Yu et al., 2011a).

2.2. Sample preparation and extraction

Detailed sample preparation/extraction protocols were described previously (Yu et al., 2011a). Briefly, all sediment samples were freeze-dried, ground into powders and wrapped with clean filter paper. Each sample, spiked with the surrogate standards PCB-67 and PCB-191, was extracted with 200 mL of an acetone:-hexane mixture (1:1 in volume) for 48 h, and the extract was concentrated to 4 mL with a TurboVap II evaporator (Zymark, Hopkinton, MA). Half of the extract, used for measurements of DDXs, was purified with a neutral silica/alumina column and concentrated to 100 μL under a gentle stream of N_2. The internal standard PCB-82 was added to the extract before instrumental analysis.

The antifouling paint samples were first dissolved in dichloromethane, followed by addition of the surrogate standards PCB 67 and PCB 191 before a clean-up using concentrated sulfuric acid. The supernatant was collected, concentrated to 2 mL with the TurboVap II evaporator and purified on the silica/alumina column. Finally, the internal standard PCB-82 was added after the extract was concentrated to 100 μL under a gentle stream of N_2.

The water samples were filtered through 0.7 μm GF/F membranes (142 mm diameter, Whatman International, Maidstone, England) on a vermicular system. The suspended particulates were freeze-dried and Soxhlet-extracted. The dissolved organics in the filtrates were retained on a glass resin column and then eluted and extracted. All the extracts were purified using a silica/alumina column. Detailed sample preparation processes were described in a previous study (Guan et al., 2007).

2.3. Instrumental analysis

Concentrations of DDXs except for 2,2-bis(*p*-chlorophenyl)acetic acid (*p,p′*-DDA) were determined with a Shimadzu Model 2010 gas chromatograph coupled with a Model QP2010 mass spectrometer (Shimadzu, Japan). *p,p′*-DDA was quantified using an Agilent liquid chromatograph 1200 system equipped with an Agilent 6410 triple quadrupole mass spectrometer with electrospray ionization in the negative mode (Agilent, Palo Alto, CA). In addition, because commercial standards of 1-chloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p′*-DDMS), 2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-1-chloroethane (*o,p′*-DDMS) and 2,2-bis(*p*-chlorophenyl)ethane (*p,p′*-DDNS) were not available, their concentrations in field samples were determined based on the response factor of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (*p,p′*-DDD). Detailed instrumental analysis procedures were described previously (Yu et al., 2011a).

2.4. Quality assurance/quality control

A field blank, a procedural blank, a spiked blank, a matrix spiked sample and a matrix spiked sample duplicate were analyzed for each batch of 20 field samples, respectively. The recoveries of the target compounds were in the ranges of 41–68% with a relative standard deviation of 17% in spiked matrix samples and 50–78% with a relative standard deviation of 18% in spiked blank samples. The recoveries of the surrogate standards in all samples were 80 ± 31% for PCB-67 and 67 ± 26% for PCB-191, respectively.

2.5. Data analysis

Sediment inventory (I_{sed}; tons/yr) of total DDXs was estimated by

$$I_{sed} = 10^{-15} \times A \sum_{i=1}^{17} W_i C_i \rho r \quad (1)$$

where A is the area of Hailing Bay ($\sim 2.0 \times 10^8$ m^2) (Baidu Encyclopedia, 2010); W_i is the area weighting factor for each sample which were assumed to be 1/10 for sites 1, 2, 5, 6, 7, 8, 9 and 10, 1/20 for 3 and 4, and 1/70 for 11, 12, 13, 14, 15, 16 and 17 (Fig. S1); C_i is the concentration (ng/g dry wt) of DDXs in surface sediment sample i; ρ is the sediment density (1.5×10^{-6} g/m^3); and r is the average sedimentation rate (1.9×10^{-2} m/yr from ^{210}Pb activity measurements (Yu et al., 2011a)).

The expected concentrations of individual DDT components in pelagic fish were estimated from the concentrations in overlying water (Reuber et al., 1987; Mackay, 2001). The expected concentration (C_{pf}; ng/g) of an analyte in pelagic fish was estimated by

$$C_{pf} = C_w \times BCF_w / 1000 \quad (2)$$

where C_w is the chemical concentration (ng/L) in the overlying water determined in our previous study (Yu et al., 2011c) and BCF_w is the bioconcentration factor (L/kg) of the analyte for pelagic fish which can be estimated from

$$BCF_w = L_w \times K_{OW} \quad (3)$$

where L_w is the lipid content for pelagic fish (0.05 was assumed in the present study) and K_{OW} is the octanol-water partition coefficient for the analyte (Table S1). It should be noted that Eq. (3) is applicable at $\log K_{OW} < 7$ as suggested by previous studies (Meylan et al., 1999; Mackay, 2001).

3. Results and discussion

3.1. Occurrence of DDT components in costal sediment

Concentration levels of DDXs in all surface sediment samples varied in the range of 0.70–4800 ng/g dry wt (Fig. 1 and Table S2). However, if two abnormally high concentration values were excluded, the concentration levels fell in the range of 0.7–94 ng/g dry wt., similar to we observed at the same general area in 2007 (3.7–180 ng/g dry wt) (Yu et al., 2011c). The two abnormally high concentration values (1200 and 4800 ng/g dry wt.) were comparable to the highest level (7400 ng/g dry wt.) of DDTs detected in sediment collected from Hong Kong fishing harbors of South China (Lin et al., 2009) and a level (1600 ng/g dry wt.) detected in sediment from Macau Harbor (Mai et al., 2002). It is noted that these two abnormally high DDX levels were found in samples collected from within Zhapo Fishing Harbor where many fishing boats are

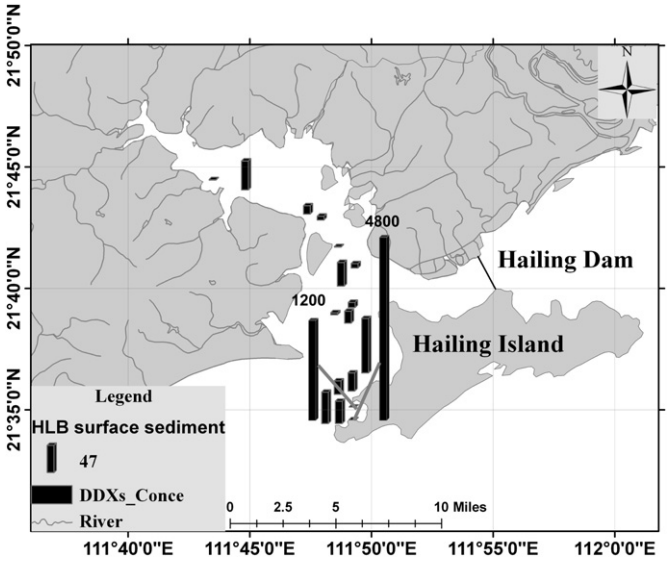

Fig. 1. Concentrations (ng/g dry wt.) of the sum of DDT and all its metabolites (designated as DDXs; Supplemental Material) in surface sediment collected from a typical marine aquaculture zone (Hailing Bay in Guangdong Province) of South China (Fig. S1).

often mooring. As expected, levels of DDXs declined sharply with increasing distance from the inner fishing harbor (Fig. 1). Concentrations of DDXs in sediment cores were in the range of 0.03–3800 ng/g dry wt and the highest level was also found in upper sediment layer within the fishing harbor (Fig. 2). The concentrations of total DDXs in all surface sediment samples located within the fishing harbor were approximately 40 times those outside the fishing harbor areas. These results suggested that heavy DDT pollution was mainly derived from the use of antifouling paints around the fishing harbor. Similar results have been reported previously (Lee et al., 2001; Barakat et al., 2002; Hong et al., 2006, 2008; Lin et al., 2009) that concentrations of DDTs in coastal harbor sediments decreased from the harbor centers to the outside locations.

3.2. Occurrence of DDT components in antifouling paints and source diagnostics

In the present study, seven types of antifouling paints used locally in Hailing Bay and three antifouling paint products purchased from Hong Kong were analyzed for DDT components (Table 1 and Table S3). The concentrations of DDTs in the antifouling paint samples collected from Hailing Bay varied from 0.15 to 40,000 μg/g wet wt, whereas those in three antifouling paint samples collected from Hong Kong were 0.33, 0.37 and 0.22 μg/g wet wt., respectively (Table 1). A previous study (Wang et al., 2007) also obtained concentrations of DDTs at 2400 and 520 μg/g, respectively, in two antifouling paint samples collected from the Pearl River Delta. These results suggested that there was significant difference between mainland China and Hong Kong in terms of DDT content in the antifouling paint products.

In China, current input sources of DDT mainly include dicofol (Qiu et al., 2005; Liu et al., 2009), antifouling paints (Lin et al., 2009) and hygiene products (Wang et al., 2007; United Nations Development Programme (UNDP), 2008). Yet, previous studies demonstrated that antifouling paints most likely served as a significant source of DDTs in the study area, due to the high levels of DDTs detected in the harbor sediments along the coastal line of China (Hu et al., 2009; Lin et al., 2009). The present study supported the previous finding that boat maintenance and/or fishing boat traffics may have served as important sources of DDT. In particular, among the seven antifouling paint samples, substantial levels of *p,p′*-DDT and *o,p′*-DDT were detected in two samples, and the *o,p′*-DDT/*p,p′*-DDT values ranged between 0.2 and 0.33 (average: 0.25) in five samples containing detectable *o,p′*-DDT (Table 1). The average *o,p′*-DDT/*p,p′*-DDT value was 0.20 in all the sediment core samples, but ranged between 0.12 and 0.19 in the associated water samples (with detectable *o,p′* and *p,p′*-DDT) in our previous study (Yu et al., 2011c). In order to account for the effects of metabolism, all related metabolites were included in the sum of *p,p′*-DDT (labeled as *p,p′*-DDXs-S) in sediment core C which has relatively high DDX concentrations compared to the other cores (Yu et al., 2011a). Similarly, all primary metabolites were included in the sum of *p,p′*-DDT in antifouling paints (designated as *p,p′*-DDTs-A) and water samples (designated as *p,p′*-DDTs-W). The comparison revealed that the relative abundance of *p,p′*-DDXs or *o,p′*-DDXs (sum of the relative abundances of *p,p′*-DDXs and *o,p′*-DDXs is equal to 1) among sediment, antifouling paints and water showed no significant difference (Fig. 3). This strongly supported that antifouling paints are an important source of DDT in the fishing harbor studied. Furthermore, a good relationship ($R = 0.6$) was also found between the concentrations of DDXs and Cu, which is an active component in antifouling paints (Lin et al., 2009) in surface sediment (Fig. S2), further corroborating the above-mentioned conclusion.

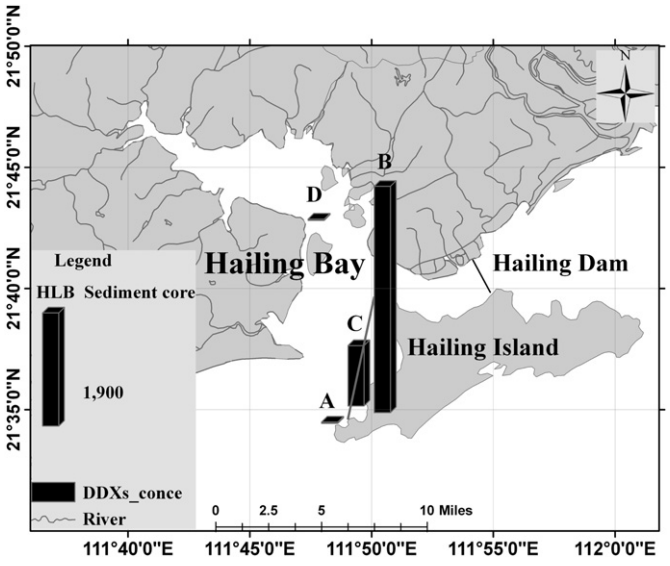

Fig. 2. Concentrations (ng/g dry wt.) of the sum of DDT and all its metabolites (designated as DDXs; Supplemental Material) in the top 3 cm sediment layer samples of four sediment cores A, B, C and D collected from a typical marine aquaculture zone (Hailing Bay in Guangdong Province) of South China (Fig. S1).

3.3. Inputs of DDT to sediment of the mariculture zone

It was reported that 5000 tons of DDTs-containing antifouling paints were annually used in China (Global Environment Facility, 2007) and the amount used in the coastal environment of Guangdong Province accounted for 1/5 of the national total (Wang et al., 2007). There were 6700 marine motored fishing boats in the City of Yangjiang, accounting for approximately 1/10 of the total number (~60,000) in Guangdong Province (Rural Statistical Yearbook of Guangdong Province Editorial Board, 2009). Assuming the amounts of DDT-containing antifouling paints used are proportional to the number of fishing boats, the annual input of DDTs-containing antifouling paint to Hailing Bay was 100 tons/yr. Combined with the concentrations of DDTs (mean: 7100 ug/g) in antifouling paints determined in the present study, the annual amount of antifouling paints-derived DDTs inputted to Hailing Bay was estimated at 0.7 tons. On the other hand, the annual amount of DDTs emitted to surface sediment of Hailing Bay estimated with Eq. (1) was approximately 0.58 tons. This indicates that the majority of DDTs inputted to the mariculture zone via the use of antifouling paints may have been sequestered in sediment. In addition, close correlation was observed between the sedimentary fluxes in sediment core C estimated from our previous study (Yu et al., 2011a) and the amounts of marine fishery catch since the 1950s (Rural Statistical Yearbook of Guangdong Province Editorial Board, 2009) (Fig. 4). This suggests that increased marine fishery catch may result from increased fishing effort such as an increase in the use of fishing boats, which may be closely associated with more antifouling paint applications for maintaining the boats.

China has begun to limit DDT usage for all purposes since 2002, and a downward trend of the amounts of DDT used for antifouling paints production was observed from 2002 to 2005 (Global Environment Facility, 2007). The sedimentary flux of DDXs in sediment core C peaked around 2004 (Fig. 4), probably reflecting the restricted use of DDT. However, the sedimentary flux showed an increasing trend again after 2005, indicating the continuous use of DDT-containing antifouling paints in the study region. Previous studies also suggested that there were fresh inputs of DDT in China

Table 1
Measured concentrations (μg/g wet weight) of DDT and its metabolites in antifouling paint products. Samples coded 1–7 were collected from a boat maintenance facility and purchased from a local store right along the coast of Hailing Bay (Fig. S1). Samples coded 8–10 were collected from Hong Kong. Detailed sample information is presented in Table S3.

Target analyte[a]	1	2	3	4	5	6	7	8	9	10
p,p′-DDT	0.15	1.2	7.9	30000	5800	0.38	0.21	0.33	0.30	0.19
o,p′-DDT	<RL[b]	0.26	1.6	7900	1900	0.099	<RL	<RL	0.066	0.030
p,p′-DDD	<RL	0.041	0.24	1100	1400	0.065	<RL	<RL	<RL	<RL
o,p′-DDD	<RL	<RL	<RL	616	766	<RL	<RL	<RL	<RL	<RL
p,p′-DDE	<RL	<RL	<RL	99	27.1	<RL	<RL	<RL	<RL	<RL
o,p′-DDE	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
o,p′-DDT/*p,p′*-DDT		0.22	0.2	0.26	0.33	0.26			0.22	0.15

[a] Definitions of individual DDT components are given in the Supplemental Material.
[b] RL is an abbreviation of the reporting limit at 0.001 μg/g for 1 g wet weight of antifouling paints.

(Qiu et al., 2005; Guo et al., 2009a). Obviously, China still needs to overcome numerous hurdles in completely banning the uncontrolled use of DDT, e.g., lack of viable alternative technologies and products, poor public awareness of environmental protection, and most importantly, enforcement of laws and regulations (Global Environment Facility, 2007).

3.4. Expected loading of DDTs in fish body

The input fluxes of DDTs to the typical aquaculture zones in South China via antifouling paints were one to several orders of magnitude greater than those through atmospheric wet and dry deposition, air–water exchange and fish feeding estimated by our previous study (Yu et al., 2011b). In addition, the riverine input flux of DDTs to Hailing Bay estimated with the average concentration (5.5 ng/L) of DDTs in Fengtou River (Fig. S1) and its annual runoff (1.6 billion m^3) (Ren et al., 2001) was 0.0088 tons/yr, much lower than the annual amount of antifouling paint-derived DDTs inputted to Hailing Bay (0.7 tons/yr). All these findings suggested that antifouling paints were the most dominant input source of DDTs in the mariculture zone. Combined with the sediment inventory mentioned above, it can be deduced that the majority of DDT originated from antifouling paints may initially be sorbed to suspended particles in the water column and then deposited with suspended particles into sediment. Apparently, the portions of DDTs in overlying water may alter fish loading via bioconcentration.

The expected loadings in pelagic fish were 63 ng/g for *p,p′*-DDT, 4.5 ng/g for *o,p′*-DDT, 44 ng/g for *p,p′*-DDD, 2.4 ng/g for *o,p′*-DDD, 13 ng/g for *p,p′*-DDE and 2.9 ng/g for *o,p′*-DDE normalized to lipid weight, much lower than the mean lipid-normalized concentrations (470 ng/g for *p,p′*-DDT; 100 ng/g for *o,p′*-DDT; 720 ng/g for *p,p′*-DDD; 51 ng/g for *o,p′*-DDD; 460 ng/g for *p,p′*-DDE and 18 ng/g for *o,p′*-DDE) determined in crimson snapper (*Lutjanus erythopterus*) and snubnose pompano (*Trachinotus blochii*) in our previous study (Yu et al., 2011c) conducted in the same general area. This suggests that input sources other than antifouling paints in water also contributed to the DDT loadings in fish. Another previous study (Yu et al., 2011b) estimated that input fluxes of DDTs via fish feeding were one to several orders of magnitude greater

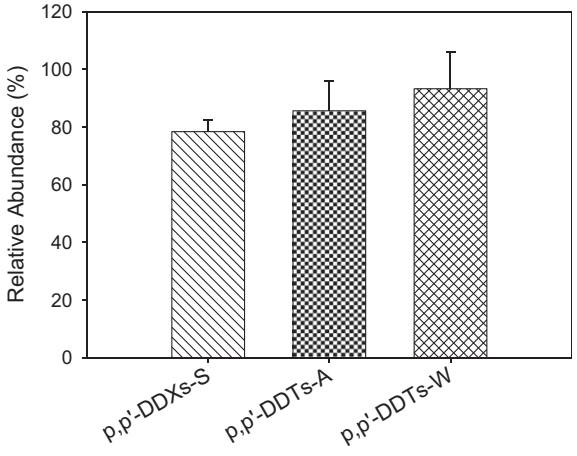

Fig. 3. Relative abundances of the sum of *p,p′*-isomers of DDT and its metabolites (designated as *p,p′*-DDXs; Supplemental Material) normalized to the sum of DDT and all its metabolites (designated as DDXs; Supplemental Material) in sediment core C (labeled as *p,p′*-DDXs-S) and relative abundances of the sum of *p,p′*-isomers of DDT and its primary metabolites (designated as *p,p′*-DDTs; Supplemental Material) normalized to the sum of DDT and its primary metabolites (designated as DDTs; Supplemental Material) in antifouling paints (labeled as *p,p′*-DDTs-A) collected from a boat maintenance facility and purchased from a local store right along the coast of Hailing Bay and water (labeled as *p,p′*-DDTs-W) collected from Hailing Bay (Yu et al., 2011c).

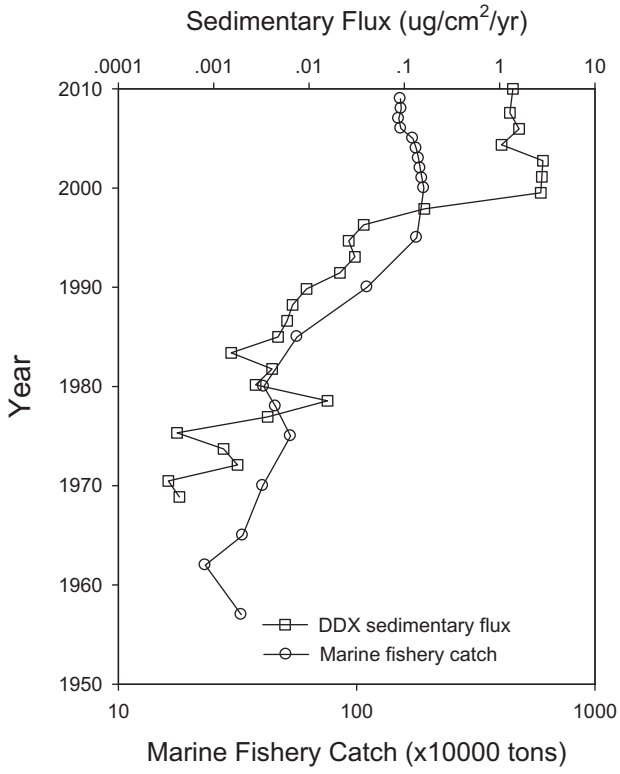

Fig. 4. Estimated sedimentary fluxes (Yu et al., 2011a) of the sum of DDT and all its metabolites (designated as DDXs; Supplemental Material) in sediment cores C collected from a typical marine aquaculture zone (Hailing Bay in Guangdong Province) of South China (Fig. 2) and the marine fishery catch in Guangdong Province (Rural Statistical Yearbook of Guangdong Province Editorial Board, 2009).

than those through other pathways except for antifouling paints in typical mariculture zones of South China. The relative uptake abundances of *p,p′*- and *o,p′*-DDT, -DDD and -DDE accumulated in fish were also much higher through fish feeding than via uptake of phytoplankton and gill diffusion (Yu et al., 2011b). Apparently, fish feed may have been a major source of DDTs in fish compared to antifouling paints in the mariculture environment of South China.

3.5. Fish feed as the potential source of fish contamination

The above discussions justified the need to examine the sources of contaminants in fish feed. Currently, there are two important types of fish feed used in China, i.e. trash fish and compound feed, with compound feed constituting less than one-third of the total (China Fisheries Government Network, 2006). Our previous study found higher concentration levels of DDTs in seawater farmed fish than those in wild marine fish or freshwater farmed fish (Meng et al., 2007). To explain for this difference, our previous study (Guo et al., 2009b) determined the levels of DDTs in trash fish, freshwater compound feed and marine compound feed collected from the typical aquaculture zones of South China, and DDTs were ubiquitous in all types of fish feed. Furthermore, the levels of DDTs in trash fish were higher than those in compound feed, while there was no difference between the DDT levels in freshwater compound feed and marine compound feed. Therefore, it may be concluded that high DDTs levels in trash fish fed to seawater farmed fish are the main cause of the difference in DDTs levels between seawater and freshwater farmed fish. Furthermore, a risk assessment (Meng et al., 2007) indicated that there was little health risk for consumption of freshwater farmed fish, whereas consumption of seawater farmed fish should be limited.

Clearly, attention should be paid to the prevailing use of trash fish as main fish feed in China. It was reported that the amount of trash fish used directly to feed fish in aquaculture of China was approximately 4–5 million tons per year (China Fisheries Government Network, 2006). Use of trash fish in large amounts in aquaculture of China not only poses threat to the marine ecological environment, but also causes serious pollution of fish with contaminants such as DDT (China Fisheries Government Network, 2006; Yu et al., 2011c). Therefore, use of compound feed instead of trash fish in aquaculture should be encouraged in China. Besides, it should be noted that trash fish are comprised of various species of small wild fish by-caught through capture fishery (Food and Agriculture Organization of the United Nation, 2009); hence high DDT levels in trash fish may also be ascribed to the use of antifouling paint in mariculture zones. However, this hypothesis needs to be verified with further investigations.

Finally, it is worthwhile to note that the concentrations of selected target analytes in sediment porewater (21 ng/L for *p,p′*-DDT, 68 ng/L for *p,p′*-DDD and 17 ng/L for *p,p′*-DDE) (Bao et al., unpublished results) were much higher than those in overlying water (0.16 ng/L for *p,p′*-DDT, 0.28 ng/L for *p,p′*-DDD and 0.029 ng/L for *p,p′*-DDE) (Yu et al., 2011c); both studies were conducted in the same general area targeted in the present study. Therefore, there is tendency for DDTs sequestered in sediment to release into overlying water. The impact of this process on aquafarming environment, though minor presently, may become significant as contamination of fish feed will be mitigated gradually. As a result, contaminated sediment will become a main source of DDXs to the mariculture environment.

4. Conclusions

The sharp decline in the levels of DDXs with increasing distance from the inner fishing harbor indicated that the heavy DDT pollution in the fishing harbor mainly derived from the use of antifouling paints. The similarity between the DDT composition in sediment samples and antifouling paints and the good relationship between the concentrations of DDXs and heavy metal Cu in surface sediment confirmed the use of DDT-containing antifouling paints as an important source of DDT in the mariculture zone. The estimated sediment DDT inventory suggested that the majority of DDTs derived from the use of antifouling paints may have been sequestered in sediment. The levels of DDTs in fish samples determined from our previous study were much higher than the expected loadings in pelagic fish estimated in the present study, indicating that fish feed may have been a major source of DDTs in fish body.

Acknowledgments

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.07.010.

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