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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

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

where A is the area of Hailing Bay (~2.0×10^8 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

$$C_{\text{pf}} = C_{\text{w}} \times \text{BCF}_{\text{w}}/1000 \quad (2)$$

where C_{w} is the chemical concentration (ng/L) in the overlying water determined in our previous study (Yu et al., 2011c) and BCF$_{\text{w}}$ is the bioconcentration factor (L/kg) of the analyte for pelagic fish which can be estimated from

$$\text{BCF}_{\text{w}} = L_{\text{w}} \times K_{\text{OW}} \quad (3)$$

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 $K_{\text{OW}} < 7$ 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

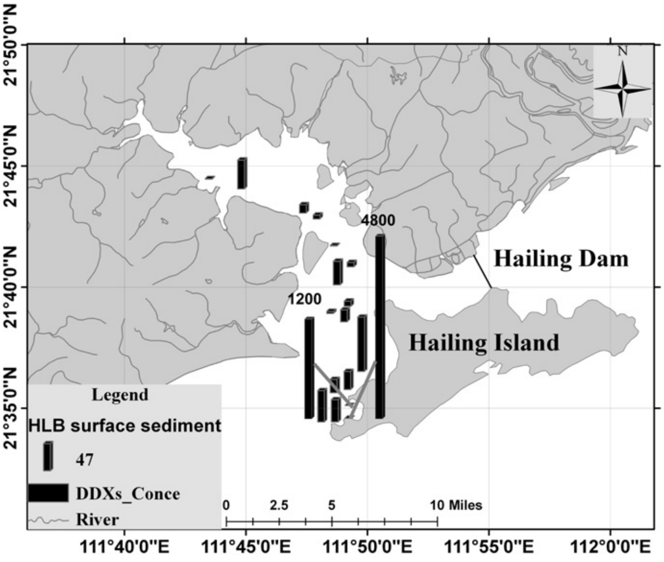

Fig. 1. Concentrations (ng/g dry wt.) of the sum of DDT and all its metabolites (designated as DDXs; Supplemental Material) in surface sediment collected from a typical marine aquaculture zone (Hailing Bay in Guangdong Province) of South China (Fig. S1).