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Environ. Sci. Technol., **2009**, 43 (9), 3073-3079 • Publication Date (Web): 23 March 2009

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Occurrence and Fate of 1-Chloro-2,2-bis(4-chlorophenyl)ethene in the Environment of the Pearl River Delta, South China

YING GUO,^{†,‡} BAO-ZHONG ZHANG,^{†,‡} XIANG-ZHOU MENG,^{†,‡} HUAN-YUN YU,^{†,‡} YONG RAN,[†] SHAO-MENG LI,[§] AND EDDY Y. ZENG^{*,†}

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China, Graduate School, Chinese Academy of Sciences, Beijing 100049, China, and Meteorological Service of Canada, 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

Received November 21, 2008. Revised manuscript received February 6, 2009. Accepted February 16, 2009.

1-Chloro-2,2-bis(4-chlorophenyl)ethene (*p,p'*-DDMU), a metabolite of either 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDD) or 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (*p,p'*-DDE), which is degraded from 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDT), was detected in a variety of environmental matrices of the Pearl River Delta (PRD), South China, including fish, fish feeds, semidigested fish stomach contents, marine surface sediment, surface soil, atmospheric gaseous phase, and particulates, rainwater, and coastal rainwater. For fish species, the concentrations of *p,p'*-DDMU were significantly higher in farmed fish than in marine wild fish, with the highest value obtained in seawater farmed fish species (mean/median values of 262/173 ng/g lipid). The relative abundance of *p,p'*-DDMU to total DDTs (sum of *o,p'*- and *p,p'*-DDT, DDD, and DDE) was higher in samples of marine origin (~5%) than in those of terrestrial origin (~2%). Because *p,p'*-DDD was considerably abundant in all samples and a negative linear correlation was found between *p,p'*-DDD/(*p,p'*-DDD + *p,p'*-DDE) and *p,p'*-DDMU/DDTs in the marine sediments ($r^2 = 0.73$) and seawater farmed fish ($r^2 = 0.29$) under investigation, it is possible that DDMU was partially dehydrochlorinated from DDD in the environment of the PRD. A fugacity-based assessment suggested that *p,p'*-DDMU is likely to transport from sediment to seawater and then to air and from soil to air. The ubiquity of *p,p'*-DDMU in the PRD indicates that it may also be widespread worldwide particularly in countries with large amounts of DDT used currently and/or historically. Given the potential risk of *p,p'*-DDMU to human health, more efforts should be directed toward this previously overlooked contaminant.

Introduction

1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDT), which is persistent, lipophilic, and liable to bioaccumulation and biomagnification, had been widely used for pest control

and mosquito abatement prior to the global ban on its use around the 1970s and 1980s with limited use in disease vector control continuing in some low-latitude developing countries such as Vietnam (1, 2). It is a common notion that DDT is biodegraded to 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (*p,p'*-DDE) under aerobic conditions or to 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDD) under anaerobic conditions (3) (sum of *o,p'*- and *p,p'*-DDT, DDD, and DDE is designed as DDTs thereafter). 1-Chloro-2,2-bis(4-chlorophenyl)ethylene (*p,p'*-DDMU) is a secondary metabolite of *p,p'*-DDT, which can be generated by either reductive dechlorination from *p,p'*-DDE or dehydrochlorination from *p,p'*-DDD (4, 5).

DDMU is an endocrine disruptive chemical just like other DDT components and can increase the uterine glycogen content (6). Previous studies demonstrated that DDMU was the major component causing changes in hepatic microsomal enzyme systems in Japanese quail compared to DDTs (7). Recently, *p,p'*-DDMU was found to be biomagnified through the marine food chain (8, 9). However, research on *p,p'*-DDMU has been limited as compared to DDTs. Furthermore, only a few studies have been conducted on *p,p'*-DDMU in natural environments worldwide. In 1992, *p,p'*-DDMU was discovered for the first time in sediments of the Palos Verdes Shelf, California (10). Other previous studies on *p,p'*-DDMU also mostly focused on marine sediment (5, 8, 9, 11). Our recent study conducted in 2007 detected *p,p'*-DDMU in coastal seawater column (12). Reports on the toxicity and environmental levels and effects of *p,p'*-DDMU, as well as the mechanism for biotransformation of DDT to DDMU, are scarce around the world.

China had applied 0.4 million tons of DDTs for pest control and mosquito abatement between the 1950s and 1980s, accounting for 20% of the total world production (13). The Pearl River Delta (PRD) of South China, located in Guangdong Province and geographically embracing Hong Kong and Macau (Figure 1), has had the highest pesticide application in China (14). Numerous previous studies have strongly suggested that the levels of DDTs in the PRD environment have remained considerably high despite China's official ban on the use of DDTs in 1983 (15). In addition, previous research also suggested that new input sources of DDTs may be present in this region (16, 17). The special circumstances surrounding the evolution of the PRD offer a unique opportunity to comprehensively examine the occurrence and fate of *p,p'*-DDMU in natural environments, enhancing the knowledge base to deal with any potential adverse effects of *p,p'*-DDMU.

The present study measured *p,p'*-DDMU in various environment matrices of the PRD, including fish species, fish feeds (including compound feed and trash fish), semidigested fish stomach contents, marine surface sediment, surface soil, atmosphere, and rainwater, with the aim to demonstrate the ubiquity of *p,p'*-DDMU in the environment of the PRD and to stimulate more research efforts on this previously overlooked contaminant. It should be noted that trash fish are low in commercial value by virtue of low quality, small size, and low consumer preference and therefore are usually used to directly feed fish in China (18).

Materials and Methods

Sample Collection. Fish sampling procedures have been described in a previous study of Meng et al. (19). Briefly, a total of 13 fish species (30 individuals for each species) were collected from 11 coastal cities in the PRD between November 2004 and January 2005 (Figure 1a), including three seawater farmed fish species (red drum (*Sciaenops ocellatus*), snubnose

* Corresponding author phone: 86-20-85291421; fax: 86-20-85290706; e-mail: eddyzeng@gig.ac.cn.

[†] Guangzhou Institute of Geochemistry.

[‡] Graduate School, Chinese Academy of Sciences.

[§] Meteorological Service of Canada.



FIGURE 1. Map showing the sampling locality around the Pearl River Delta, South China. (a) Fish: Guangzhou, Dongguan, Zhuhai, Foshan, Zhongshan, Jiangmen, Yangjiang, Maoming, Zhanjiang, Shantou, and Shanwei. Fish feeds: fish ponds in Foshan and Dongguan; seawater fish farms in Hailing Bay and Daya Bay. Atmosphere and rainwater: Dongguan and Foshan. (b) Surface marine sediment from Hailing Bay: HL-1 (12.8 m in water depth), HL-2 (13.1 m), and HL-3 (9.5 m). (c) Surface soil: Guangzhou, Dongguan, Foshan, and Qingyuan.

pompano (*Trachinotus blochii*), and crimson snapper (*Lutjanus erythropterus*), three seawater wild fish (hairtail (*Trichiurus lepturus*), golden threadfin (*Nemipterus virgatus*), and common mullet (*Mugil cephalus*)), and seven freshwater farmed fish (tilapia (*Oreochromis*), grass carp (*Ctenopharyngodon idellus*), bighead carp (*Aristichthys nobilis*), blunt snout bream (*Megalobrama amblycephala*), largemouth bass (*Micropterus salmoides*), mandarin fish (*Siniperca chuatsi*), and northern snakehead (*Ophicephalus argus*)). Among the 13 species, tilapia and common mullet are detritivorous, grass carp, bighead carp, and blunt snout bream are herbivorous, and all other species are carnivorous. The main characteristics of fish samples are listed in Table S1 of the Supporting Information. Besides, a total of 44 fish feeds, including 28 compound feed (6 for freshwater and 22 for seawater fish) and 16 trash fish, were collected from seawater fishery farms

in Hailing Bay and Daya Bay and from freshwater fish farms in Dongguan and Foshan between 2006 and 2007 (Figure 1 and Table S2 of the Supporting Information). At the same time, 19 samples of semidigested stomach contents in 2 seawater farmed fish species (12 snubnose pompano and 7 crimson snapper individuals) from Hailing Bay and Daya Bay were collected. In addition, nine marine surface sediments (using a stainless steel grab sampler) were collected from three locations designated as HL-1, HL-2, and HL-3 (three samples were collected around each location) in Hailing Bay in July 2007 (Figure 1b). Twenty-three surface soil (0–20 cm) samples were collected from Guangzhou (12), Dongguan (5), Foshan (2), and Qingyuan (4) (Figure 1c) in 2002 and 2005 (20), where various kinds of vegetables are grown along the river watershed basin. Finally, between June 2006 and September 2007, atmosphere and rainwater samples

were collected from Dongguan and Foshan. For the atmospheric sample, 170–880 m³ of air was drawn at 0.13–0.62 m³/min for 24 h through 20.3 cm × 25.4 cm glass fiber filters and subsequently through 6.5 cm (in diameter) × 7.5 cm polyurethane foam plugs using a high-volume sampler. A total of 33 pairs of atmospheric samples were collected, with 18 from Dongguan and 15 from Foshan, respectively. Rainwater was collected by big salvers with hole and pipes and drained into glass bottles underneath the salvers. A total of 11 samples with volume of 20–120 L were collected in November 2006 and from April to August 2007, with 7 from Dongguan and 4 from Foshan, respectively.

Sample Preparation and Instrumental Analysis. For fish samples, muscle off the skin from the fish back was taken and processed by the method of Meng et al. (19). Briefly, samples were freeze-dried and ground into fine powders. After spiking with surrogate standards of 2,4,5,6-tetrachloro-*m*-xylene (TMX), PCB-67, and PCB-191, each sample was Soxhlet extracted with a 1:1 (v/v) acetone and hexane mixture for 48 h. Lipid was determined gravimetrically using 20% of the extract. The remaining extract was cleaned and fractionated with a gel permeation column and a silica/alumina column, respectively, and concentrated to 100 µL under a gentle stream of N₂. Finally, the internal standard (PCB-82) was added to the extract before instrumental analysis. For samples of fish feeds, semidigested stomach contents, sediment, glass fiber filters, and polyurethane foam, the extraction method was similar to that used for fish samples with minor alterations; that is, the lipid was not determined and removed for sediment and atmospheric samples. For samples of soil and rainwater, the procedures were described in detail by Zou et al. (20) and Guan et al. (21) and are presented in the Supporting Information.

The detailed instrumental methods for DDTs have been described by Meng et al. (19). For *p,p'*-DDMU, all samples were analyzed with a Varian 3800 GC interfaced with a Saturn 2000 MS in the selective ion monitoring mode and quantified using *m/z* 212 (12). Detailed procedures are provided in the Supporting Information. The reporting limits of all target analytes are listed in Table S3 of the Supporting Information.

Quality Assurance/Quality Control. For each batch of 20 samples, a procedural blank, a spiked blank, and a pair of matrix spiked sample/duplicate were processed. All the recovery results are provided in Table S4 of the Supporting Information. Only low concentrations of individual DDT components (always lower than half of the reporting limits) were detected in procedural blanks; hence, blank values were not subtracted from the sample measurements. Reported concentrations were not surrogated recovery corrected. All concentrations were normalized to lipid sample weight except where indicated.

Data Analysis. Zero values were used for relative abundance and model calculation when measured concentrations were below the reporting limits. For soil samples, the concentrations of *p,p'*-DDMU could be underestimated because the silica/alumina column was packed with acid silica gel, which may have destroyed unknown amounts of DDTs and *p,p'*-DDMU in the extracts. Therefore, soil measurement results should be considered to be qualitative. Comparison among different sample types was conducted using nonparametric tests (Kruskal–Wallis H and Mann–Whitney U, SPSS v 13.0). Statistical significance was defined as *p* < 0.05.

Results and Discussion

Detection Frequency of *p,p'*-DDMU in Various Environmental Matrices. Preliminary analyses indicated that *p,p'*-DDMU was ubiquitous in the various environmental media of the PRD. The detection frequency of *p,p'*-DDMU was 83, 66, 90, 70, 55, and 46%, respectively, in samples of fish, fish

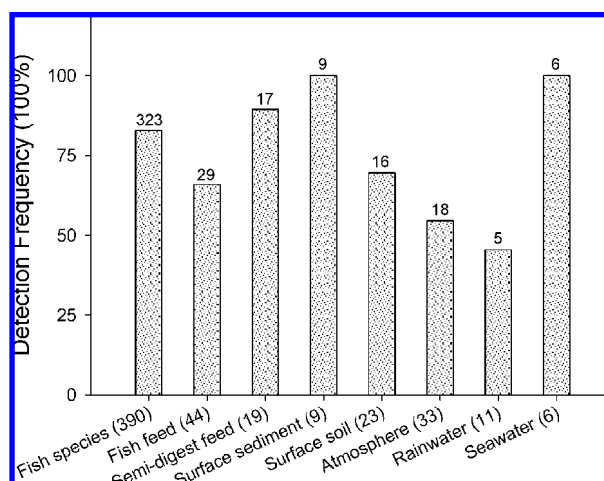


FIGURE 2. Detection frequency of *p,p'*-DDMU in various environmental matrices of the Pearl River Delta, South China. The number of samples for each matrix is in the parentheses, and the number of samples containing detectable *p,p'*-DDMU is placed above each bar.

feeds, semidigested fish stomach contents, surface soil, atmosphere, and rainwater. In addition, all surface sediment samples contained detectable *p,p'*-DDMU (Figure 2). In a previous study, which employed a solid-phase microextraction (SPME)-based sampler for in situ field sampling, *p,p'*-DDMU was detected in coastal seawater of all six deployment locations in Hailing Bay of South China (12).

In fish species, *p,p'*-DDMU was detected in 93% of the freshwater farmed fish, in all seawater farmed fish, and in 75% of the marine wild fish (Figure S1 of the Supporting Information). For fish feeds, *p,p'*-DDMU was detected in 14 of 28 compound feeds and 12 of 16 trash fish. Finally, *p,p'*-DDMU was detected in 18 gaseous and only one particulate sample of 33 atmospheric sample pairs, respectively. To our best knowledge, this is the first report of detecting *p,p'*-DDMU in the atmosphere, rainwater, and surface soil around the world. All these results indicate that *p,p'*-DDMU is highly ubiquitous in the environment of the PRD, probably because of the large amount of historically used DDT and the likelihood of new DDT inputs in the PRD region that have created the opportunity for transformation of DDT to DDMU.

Concentration Levels of *p,p'*-DDMU in Various Environmental Matrices. In fish species, significant linear correlations (*p* < 0.001) were found between the concentrations of total DDTs and *p,p'*-DDMU (*r*² = 0.90, 0.91, and 0.43 in seawater farmed, marine wild, and freshwater farmed fish, respectively) (Figure S2 of the Supporting Information). As a result, the distribution of *p,p'*-DDMU in fish species (Figure 3 and Table 1) is similar to that of total DDTs obtained by Meng et al. (19), with the *p,p'*-DDMU concentrations significantly (*p* < 0.001) higher in farmed fish (freshwater and seawater farmed fish combined) than in marine wild fish. This result is also consistent with the patterns of total DDTs in farmed and wild marine fish obtained by Hites et al. (22), further underscoring the impact of anthropogenic activities on fish farming conditions. Fish can bioconcentrate contaminants both from water and fish feeds. Among the fish feeds measured in the present study, the concentrations of *p,p'*-DDMU were significantly higher in trash fish (mean/median values of 49.6/17.8 ng/g) than in all compound feed (8.69/1.50 ng/g) (*p* < 0.001), while no differences were found between seawater (10.4/none detectable (ND) ng/g) and freshwater compound feed (2.28/1.67 ng/g) (*p* > 0.76) and between semidigested fish stomach contents of snubnose pompano (51.7/23.3 ng/g) and crimson snapper (958.5/38.2 ng/g) (*p* > 0.59). Therefore, the higher concentrations of *p,p'*-

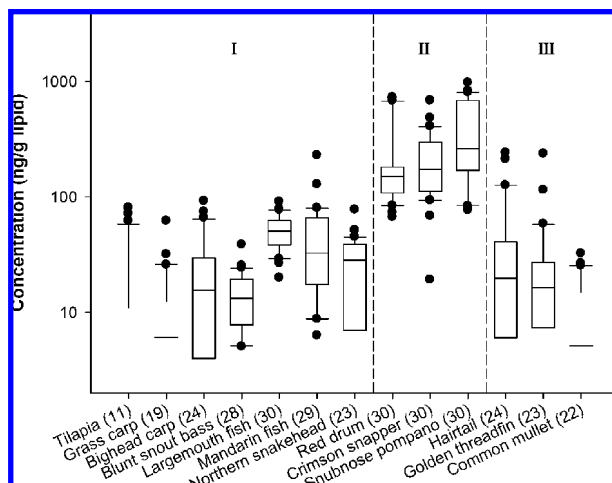


FIGURE 3. Concentrations (ng/g, dry weight) of p,p' -DDMU in (I) seven freshwater farmed fish species, (II) three seawater farmed fish species, and (III) three seawater wild marine fish species. The numbers of detectable p,p' -DDMU in fish individuals for each species are given in parentheses. The horizontal lines represent 10th, 50th, and 90th percentiles, and the boxes represent 25th and 75th percentiles. Outliers are shown as individual points.

DDMU in farmed fish than in wild fish should partly be attributed to the occurrence of p,p' -DDMU in their fish feeds. The high concentrations of p,p' -DDMU detected in trash fish suggested that trash fish as fish feeds should be restricted and compound feeds should be used more widely to meet the growing need of aquaculture. Furthermore, the concentrations of p,p' -DDMU were significantly ($p < 0.001$) higher in seawater farmed fish than in freshwater farmed and marine wild fish and significantly higher in carnivorous fish than in detritivorous fish and herbivorous fish, respectively (Table 1 and Figure S3 of the Supporting Information). The results may partly be attributed to the direct use of trash fish as fish feed, since the high concentrations of p,p' -DDMU were detected in trash fish and large amount of trash fish are directly used to feed fish in China (18). In addition, discharge of contaminants from riverine runoff of the PRD may have also contributed to the difference between freshwater and seawater fish species.

The concentrations of p,p' -DDMU ranged from none detectable (ND) to 40.4 pg/m³ in atmospheric pair samples (median value of 2.96 pg/m³), with 9.0 pg/m³ in one particulate sample from Dongguan. No difference was found between the atmospheric samples from Dongguan and Foshan. For surface vegetable soil along the river watershed basin, the concentrations of p,p' -DDMU were ND–28.3 ng/g, with median values of ND, 4.06, 2.30, and 1.58 ng/g for samples from Qingyuan, Guangzhou, Dongguan, and Foshan, respectively. For marine surface sediment, the concentrations of p,p' -DDMU ranged from 0.67 to 2.95 ng/g, and no difference was found among all samples ($p > 0.73$). The p,p' -DDMU levels in sediment in the present study were similar to those found in sediments of Haihe Basin in North China (ND–5.8 ng/g) (23) and of the Baltic South Coast (0.6–3.1 ng/g) (9) but were much lower than those in sediment near a point source in San Francisco Bay, California (11–23 330 ng/g) (5). For rainwater samples, the p,p' -DDMU levels ranged from ND to 52.7 pg/L (median and mean values of ND and 17.6 pg/L), much lower than those (99.3 and 72.5 pg/L) in seawater of Hailing Bay detected in our previous study (12) which ranged from 0.047 to 0.21 ng/L. By comparison, a previous study conducted in Haihe Basin of North China obtained a range of p,p' -DDMU concentrations in seawater samples from ND to 10.4 ng/L (23).

Relative Abundance of p,p' -DDMU to DDTs and Implications for Source Diagnostics. The relative abundance of p,p' -DDMU to total DDTs ranged from 0 to 41% with a mean value of ~5% in the environment of the PRD (Table 1 and Figure S4 of the Supporting Information). In fish species, this ratio varied from 0 to 41% with a mean value of 6.9%, which was higher than that in fish collected from the Baltic South Coast (3.8% calculated from the data provided) (9). The mean/median relative abundances of p,p' -DDMU in seawater (7.0%/6.7%) and freshwater farmed fish (7.7%/6.3%) were not significantly ($p > 0.22$) different from each other but were significantly ($p < 0.001$) higher than those in wild marine fish (5.0%/4.9%) (Figure S5 of the Supporting Information). Obviously, farmed fish contained higher relative abundances of p,p' -DDMU than wild marine fish. In addition, the p,p' -DDMU relative abundances were not significantly ($p > 0.05$) different among detritivorous, herbivorous, and carnivorous fish species (Figure S4 of the Supporting Information).

In fish feeds and semidigested fish stomach contents, the relative abundances of p,p' -DDMU ranged from 0 to 31.5% with no significant ($p > 0.17$) difference between each other. The p,p' -DDMU relative abundance in atmospheric samples was ~2%. In water samples, p,p' -DDMU relative abundances were much higher in seawater (a mean of ~5%) than in rainwater (~2%). In soil samples, the mean/median p,p' -DDMU relative abundances were 2.6%/1.4%, which were the lowest among all sample types. In sediment samples, it is interesting to notice that the p,p' -DDMU relative abundance was almost the same at HL-1 and HL-2 (~6%) but much low at HL-3 (~2%). At the same time, the concentrations of DDTs were higher in HL-3 (~100 ng/g) than in HL-1 and HL-2 (~20 ng/g), and the levels of p,p' -DDMU concentrations were nearly the same at all three locations. These results indicate that more recent inputs of DDT may have occurred near the HL-3 sampling point because HL-3 might be a high depositional zone due to its particular geographical setting (Figure 1b). Another plausible explanation is that there are more fish-farming cages near this region than HL-1 and HL-2; therefore, the use of fish feeds (trash fish and compound feed) and antifouling paint, which contains technical DDT (17), may also have contributed to the high abundance of DDTs in HL-3. Nevertheless, the p,p' -DDMU relative abundances in marine surface sediments of the PRD were much lower than those (14–25%) in sediment of the Palos Verdes Shelf, California (11). This also demonstrates that higher relative abundance of p,p' -DDMU may occur in older DDT-contaminated sediments, an obvious consequence of the biotransformation of DDT (via DDE and/or DDD) to DDMU.

In the technical DDT formulation, DDT (sum of p,p' -DDT and o,p' -DDT) accounts for more than 80% of the total content (3). As a result, the ratio of DDT/(DDE + DDD) has often been used to determine whether there is any fresh technical DDT input (24). The present study has demonstrated that the relative abundance of p,p' -DDMU to DDTs is more than 5% in most marine environmental media of the PRD. Combined with the fact that DDMU may degrade from both DDE and DDD, which reduces the denominator of DDT/(DDE + DDD), the results presented herein indicate that, although the impact may be low, the ratio of DDT/(DDE + DDD) in the marine environment of the PRD is likely to be overestimated when used for source diagnostics.

Possible Routes for Transformation of DDT to DDMU.

The sample types investigated in the present study are divided into two groups (i.e., marine group, including seawater farmed and marine wild fish, trash fish, seawater compound feed, semidigested fish stomach content, and surface sediment, and terrestrial group, including freshwater farmed fish, freshwater compound feed, rainwater, atmosphere, and surface soil) (Table 1). To proceed, p,p' -DDD/(p,p' -DDD +

TABLE 1. Mean/Median (Range) Concentrations and Compositional Indices of DDTs (Sum of *o,p'*- and *p,p'*-DDT, DDD, and DDE) and *p,p'*-DDMU in the Pearl River Delta, South China

	<i>p,p'</i> -DDMU ^a	DDTs ^a	<i>p,p'</i> -DDMU/DDTs (%)	DDD/(DDD+DDE) ^b
marine group				
seawater farmed fish	262/173 (19.3–978)	3984/2547 (332–18002)	7.0/6.7 (4.2–11)	0.62/0.58 (0.39–0.83)
seawater wild fish	25.5/14.5 (ND ^c –242)	538/236 (18.2–5862)	5.0/4.9 (0–21)	0.36/0.34 (0.16–0.61)
trash fish	49.6/17.8 (ND–324)	789/325 (114–6715)	7.4/5.4 (0–32)	0.33/0.34 (0.13–0.65)
seawater compound feed	10.4/ND (ND–63.4)	138/89.3 (3.95–631)	5.4/0 (0–28)	0.58/0.58 (0–1.0)
semidigested fish stomach contents				
crimson snapper	58.5/39.2 (4.58–206)	1547/1030 (203–6219)	4.1/4.0 (2.2–7.3)	0.44/0.45 (0.22–0.57)
snubnose pompano	51.7/23.3 (ND–167)	531/406 (83.3–1103)	7.6/8.5 (0–18)	0.62/0.62 (0.57–0.68)
sediment				
HL-1	1.04/1.14 (0.77–1.20)	17.9/18.1 (16.6–19.1)	5.8/6.3 (4.7–6.3)	0.64/0.65 (0.62–0.65)
HL-2	1.03/0.92 (0.70–1.47)	15.2/14.1 (11.4–20.1)	6.7/6.7 (6.1–7.3)	0.69/0.70 (0.67–0.71)
HL-3	1.86/1.97 (0.67–2.95)	113/131 (27.9–180)	1.8/1.6 (1.5–2.4)	0.82/0.82 (0.78–0.84)
seawater	99.3/72.5 (47.0–213)	1883/1892 (840–3290)	5.1/5.6 (2.4–6.5)	0.95/0.95 (0.93–0.97)
terrestrial group				
freshwater farmed fish	25.3/16.9 (ND–230)	382/206 (8.70–2042)	7.7/6.3 (0–41)	0.29/0.25 (0–0.79)
freshwater compound feed	2.28/1.67 (ND–6.17)	123/95.3 (43.1–316)	1.5/1.8 (0–3.2)	0.30/0.37 (0–0.52)
atmosphere	5.19/2.96 (ND–40.4)	194/182 (20.7–473)	2.1/1.1 (0–15)	0.31/0.29 (0.02–0.71)
soil	4.37/2.30 (ND–28.3)	219/93.3 (2.38–1550)	2.6/1.4 (0–10)	0.14/0.09 (0–0.39)
rainwater	17.6/ND (ND–70.6)	681/527 (377–1613)	2.0/0 (0–5.3)	0.38/0.39 (0.13–0.56)

^a The units of the concentrations are pg/L in rainwater and seawater, pg/m³ in atmosphere, ng/g dry wt in marine surface sediment and surface soil, and ng/g lipid in other sample types. ^b Equal to *p,p'*-DDD/(*p,p'*-DDD + *p,p'*-DDE). ^c ND = none detectable.

p,p'-DDE) in all sample matrices is calculated to compare the relative abundances of *p,p'*-DDD and *p,p'*-DDE, which are the most probable precursors of *p,p'*-DDMU. It is interesting to note that the concentrations of *p,p'*-DDD in the samples of the marine group, except for wild marine fish and trash fish that were probably caught in deep seas, were higher than or at least similar to those of *p,p'*-DDE. A previous study also indicated that DDD was more abundant than DDE in sediments of the Pearl River Estuary and the northern South China Sea, but the ratio of DDD/DDE became smaller than 1 in deeper areas (25). In contrast to the results noted above for the marine group, the levels of *p,p'*-DDE were significantly higher than those of *p,p'*-DDD in the terrestrial group, consistent with the findings of several previous studies on soil and atmosphere of the PRD (26–28).

Quensen et al. (4) conducted a marine microcosm study on sediment from the Palos Verdes Shelf and concluded that DDE was the main precursor of DDMU and the contribution of DDD was negligible under anaerobic conditions. On the other hand, DDMU was believed to be partially dehydrochlorinated from DDD in sediment of San Francisco Bay, California, where DDD was more abundant than DDE (5). In the PRD marine environment, *p,p'*-DDD was more abundant than *p,p'*-DDE, sharply different from what has been observed in sediment of the Palos Verdes Shelf (sediment samples were collected from the deep sea where oxygen was extremely depleted); that is, *p,p'*-DDE was the dominant component of all individual DDTs (11, 29, 30) but similar to the results obtained from San Francisco Bay, California (5). Therefore, transformation of DDD to DDMU may also occur meaningfully in the coastal marine environment off the PRD. Supporting this conclusion is the negative linear correlation ($r^2 = 0.73$) between p,p' -DDD/(*p,p'*-DDD + *p,p'*-DDE) and *p,p'*-DDMU/DDTs in the marine surface sediment samples (Figure 4). With a less significant level ($r^2 = 0.29$), the same linear correlation was also found in seawater farmed fish species (Figure 4).

Intercompartmental Transport of *p,p'*-DDMU in the Pearl River Delta. Given the ubiquity of *p,p'*-DDMU in the environment of the PRD, it is possible to conduct a fugacity-based assessment of the intercompartmental transport of *p,p'*-DDMU across the interfaces of seawater–air and soil–air. The difference in fugacities can be regarded as the “escaping tendency” of a chemical substance to move from

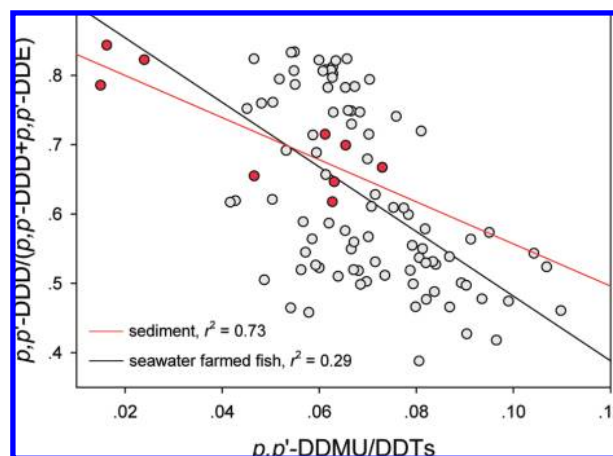


FIGURE 4. Correlations between the compositional indices of DDTs and *p,p'*-DDMU in the coastal surface sediment and seawater farmed fish species (both are considered to be of marine origin) from the Pearl River Delta, South China.

one phase or matrix to another. A practical parameter to characterize this driving force is fugacity ratio (FR) defined as the ratio of the fugacities of the chemical in two interacting phases or matrices. A value of FR equal to unity indicates an equilibrium state for the chemical between two phases. The fugacities of *p,p'*-DDMU in water (f_w), atmosphere (f_a), and soil (f_{soil}) can be calculated from the following equations (31–33):

$$f_w = C_w H \quad (1)$$

$$f_a = C_a RT \quad (2)$$

$$f_{soil} = C_{soil} RT / 0.411 \Phi_{om} K_{oa} \quad (3)$$

$$K_{oa} = K_{ow} RT / H \quad (4)$$

where C_w , C_a , and C_{soil} are the concentrations of *p,p'*-DDMU in water, atmosphere, and soil (mol/m³), H is the Henry's law constant (Pa m³/mol), R is the ideal gas constant (8.314 Pa m³/mol K), T is the absolute temperature (K), Φ_{om} is the fraction of total organic matter in soil estimated through

total organic carbon (TOC) multiplied by 1.7 (33), K_{oa} is the temperature-dependent octanol–air partition coefficient of p,p' -DDMU, and K_{ow} is the octanol–water partition coefficient of p,p' -DDMU at 298 K (32). The factor 0.411 (34) improves the correlation between the soil–air partition coefficient and K_{oa} (35, 36).

For the sediment–seawater system, because we did not measure the concentrations of p,p' -DDMU in sediment porewater, the assumptive porewater concentration at equilibrium ($C_{w,e}$), calculated from $C_{w,e} = C_{\text{sediment}} / (\text{TOC})K_{oc}$ where C_{sediment} is the concentration of p,p' -DDMU in surface sediment, TOC is the sediment organic carbon content, and K_{oc} is the sediment organic carbon–water partition coefficient of p,p' -DDMU, was used to compare with the seawater concentration (C_w) of p,p' -DDMU measured in our previous study based on a SPME approach (12). If the ratio of $C_{w,e} / C_w$ is higher than unity, a net flux of p,p' -DDMU from sediment (porewater) to seawater can occur thermodynamically. All the parameters used for calculation are listed in Table S5 of the Supporting Information.

The results (Figure S6 of the Supporting Information) show that the FRs of p,p' -DDMU in for the seawater–air interface are all greater than 1 even if the lowest concentration (47 pg/L; Table 1) of p,p' -DDMU in seawater is used, which suggests that p,p' -DDMU tends to move from seawater to air. The FRs of p,p' -DDMU the soil–air interface are also considerably higher than 1, even though unknown amounts of p,p' -DDMU may have been destroyed during the cleanup/fractionation step as discussed previously in the Materials and Methods section. Clearly, p,p' -DDMU is likely to diffuse from soil to air. For the sediment–seawater interface, the concentration ratios (Figure S6 of the Supporting Information), calculated using the highest concentration of p,p' -DDMU in seawater (213 pg/L) and sediment porewater concentrations estimated from the sediment data associated with Hailing Bay (Table 1), indicate that there is a net flux of p,p' -DDMU from sediment (porewater) to seawater. Furthermore, the tendency for p,p' -DDMU to diffuse from both seawater and soil to the air indicates that the PRD may be a source of p,p' -DDMU to the global environment.

The ubiquity of p,p' -DDMU in the environment of the PRD points to the possibility that it may also be widespread globally, especially in countries with large amounts of DDT used currently and/or historically. Unfortunately, little attention has been paid to p,p' -DDMU in the past. Because of the potential risk of p,p' -DDMU to human health and the likelihood for generation of p,p' -DDMU from DDE and/or DDD, enhanced research work is desirable to better understand the fate of p,p' -DDMU in the global environment and its toxicity to the ecosystem and humans.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. U0633005, 40588001, and 40821003) and the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (SKLOG2008A05). This is contribution NO. IS-1049 from GIGCAS.

Note Added after ASAP Publication

The Acknowledgments section was modified in the version of this paper that published ASAP March 23, 2009; the corrected version published ASAP March 25, 2009.

Supporting Information Available

Additional tables and figures containing detailed information about sample collection and physicochemical parameters, QA/QC results, and concentration data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES803294W