Persistent Halogenated Hydrocarbons in Fish Feeds Manufactured in South China

YING GUO,[†,‡] HUAN-YUN YU,[†,‡] BAO-ZHONG ZHANG,[†,‡] AND EDDY Y. ZENG*,[†]

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China and [‡]Graduate School, Chinese Academy of Sciences, Beijing 100049, China

Persistent halogenated hydrocarbons (PHHs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), in fish feeds (including trash fish and compound feed) manufactured in South China, were analyzed. PHHs were ubiquitous in fish feeds, with the concentrations of OCPs, PBDEs, and PCBs at the upper, mid, and lower levels of the global range. Trash fish generally contained higher concentrations of DDXs (sum of *o,p'*- and *p,p'*-DDT, -DDD, and -DDE and *p,p'*-DDMU), especially *p,p'*-DDT and low-brominated PBDEs, while compound feeds had higher concentrations of highly brominated BDEs, e.g., BDE-209. In addition, no concentration difference of HCHs and PCBs was found between trash fish and compound feeds. The habit of direct use of trash fish as fish feeds has induced the accumulation of DDXs in aquatic species in China, and trash fish collected in South China seemed to be slightly hazardous to wildlife because of the concentrations of DDXs. The results from the present study suggest that the use pattern of fish feeds in China may have to be adjusted to minimize contamination of fishery products and wildlife by PHHs. Use of compound feeds produced with controlled procedures should be encouraged, whereas that of trash fish should be restricted, at least for now.

KEYWORDS: Fish feed; trash fish; persistent halogenated hydrocarbons; DDT; South China

INTRODUCTION

China is the world's largest fishery producer, with a total production of 47.5 million tons in 2004 (16.9 and 30.6 million tons of captured and aquacultured fisheries, respectively) (*1*). Organic contaminants, such as persistent halogenated hydrocarbons (PHHs), which are persistent, lipophilic, and liable to bioaccumulation and biomagnification, may have potential human health risk via fish consumption if sufficiently abundant in fish. Our previous study, on the basis of analyses of nearly 400 fish individuals, suggested that the PHHs, including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), in consumer fish of China were moderate, with the mean and upper bound values much lower than the action levels and tolerances developed by the United States Food and Drug Administration (*2*). On the other hand, PHHs were found to be more abundant in farmed fish than in wild fish and, particularly, the levels of PHHs in seawater farmed fish were high enough to raise concerns (*2, 3*). This finding was partly attributed to the discharge of contaminants from riverine runoff of the Pearl River Delta (PRD) to the adjacent bays and estuaries, where seawater fish are mostly raised (*4−6*). However, another potential source, i.e., fish feeds, was not adequately assessed. In fact, PHHs have been found ubiquitous in aquaculture feeds, fishmeal, and fish oil worldwide

(*7−9*). Some studies demonstrated that fish feeds were the main source of PHHs for farmed fish species (*10−13*).

Two types of fish feeds are currently used in China, i.e., trash fish and compound feed. Trash fish, mostly wild, various in species, and captured from deep sea, usually have low commercial value by virtue of low quality, small size, and low consumer preference and, therefore, are often used to directly feed fish in China. It was estimated that trash fish production amounted to over 5 million tons in China in 2001 (*1*), and almost all trash fish captured are exclusively applied to produce livestock and fish compound feeds in the form of fish powders or fish oil or used directly to feed fish. By 2013, China alone would require 4 million tons of trash fish to sustain marine cage aquaculture (*1*). On the other hand, compound feed was not widely used until recent years in China. The amount of aquaculture compound feeds produced was only 0.85 million tons in 1991 but increased rapidly in recent years. In 2004, the total production of aquaculture feeds amounted to about 9 million tons in China, yet the amount of compound feeds used in aquaculture was still less than one-third of the total fish feed need (*14*). The importance of trash fish and compound feeds in the aquaculture industry of China justifies a thorough investigation into the occurrence of PHHs in such products manufactured in China.

The present study measured PHHs in marine and freshwater fish feeds mostly manufactured in Guangdong Province and used by fish farms of the PRD. Because Guangdong Province is the largest producer of aquaculture

*To whom correspondence should be addressed. Telephone: 86-20-85291421. Fax: 86-20-85290706. E-mail: eddyzeng@gig.ac.cn.

Article

J. Agric. Food Chem., Vol. 57, No. 9, 2009 **3675**

feeds in China (*15*), accounting for ∼20% of the total production, the outcome of the present study should be reflective of the occurrence of PHHs in fish feeds throughout the entire country. Such information is significant in identifying potential sources of PHHs in fish-farming environments, which in turn will help to mitigate fish contamination with better quality control of aquaculture feed production.

MATERIALS AND METHODS

Sample Collection. Marine fish feeds, including 14 trash fish and 21 compound feeds of 13 brands (**Table 1**), were collected from aquaculture areas around Hailing Bay and Daya Bay, South China (Figure S1 in the Supporting Information). All but two brands were produced by local factories in Guangdong Province, and the two exceptions were manufactured in Fujian Province, also located in South China next to Guangdong. In addition, six compound feeds of three brands for freshwater fish farming were collected from the cities of Foshan and Dongguan (Figure S1 in the Supporting Information). One of the three brands was manufactured by a company headquartered in Sichuan Province of Southwest China, with factories in Guangdong Province, but it is unclear where the samples collected were produced.

Sample Preparation and Extraction. Upon transport to the laboratory, samples were stored at −20 °C if not processed immediately. For trash fish, each sample was cleaned with water and then homogenized with a blender. The compound feed or trash fish sample at ∼20 g wet weight (wet wt) was freeze-dried and ground into fine powders. After spiking with surrogate standards 2,4,5,6-tetrachloro-*m*-xylene (TMX), PCB-67, PCB-191, $^{13}C_{12}$-BDE-15, $^{13}C_{12}$-PCB-141, and PCB-209, the sample was processed with a previously described method (*2*). Briefly, each sample was Soxhlet-extracted with a 1:1 (v/v) acetone/hexane mixture for 48 h. Lipid was determined gravimetrically using 20% of the extract before gel permeation chromatography was conducted. The fraction was collected and concentrated to 4 mL. The 4 mL extract was divided into two aliquots, which were cleaned and fractionated with two different silica/alumina columns, respectively, and concentrated to 100 μL under a gentle stream of N_2. Finally, the internal standards (PCB-82 for OCPs, PCB-82 and PCB-189 for PCBs, and $^{13}C_{12}$-PCB-208 for PBDEs) were added before instrumental analysis.

Target Analytes and Instrumental Analysis. For OCPs, a total of 22 compounds were analyzed, including DDT and its metabolites (*o,p′*- and *p,p′*-DDT, -DDD, and -DDE and *p,p′*-DDMU, the sum of which is designated as DDXs), HCHs

Table 1. Background Information on the Compound Feed and Trash Fish Samples Manufactured in South China

code	date	location	lipid (%)	brand	factory location
A	July 18, 2007	Daya Bay	4.9	Dexing-655[a]	Guangdong
B	July 26, 2007	Hailing Bay	14	Wangxiangyu-235	Guangdong
C	July 26, 2007	Hailing Bay	9.9	Tianbang	Guangdong
D	July 26, 2007	Hailing Bay	9.3	Jiatai- —[b]	Guangdong
E	July 26, 2007	Hailing Bay	5.9	—	—
F	June 20, 2007	Hailing Bay	13	Shihai	Guangdong
G	December 25, 2007	Hailing Bay	9.4	Haixuan-7	Guangdong
H	December 25, 2007	Hailing Bay	6.1	Haixuan-6	Guangdong
I	December 25, 2007	Hailing Bay	6.9	Haixuan-5	Guangdong
K	December 25, 2007	Hailing Bay	8.4	Haixuan-2	Guangdong
M	July 18, 2007	Daya Bay	6.6	Jinchang-3	Fujiang
O	December 25, 2007	Hailing Bay	8.4	Jinchang-2	Fujiang
P	December 25, 2007	Hailing Bay	9.3	Yongsheng- —	Guangdong
R	December 25, 2007	Hailing Bay	3.1	Haiou	—
S	December 25, 2007	Hailing Bay	4.9	Bangni	—
T	December 25, 2007	Hailing Bay	8.5	Yongsheng-4	Guangdong
U	December 25, 2007	Hailing Bay	6.1	Dexing-656	Guangdong
V	December 25, 2007	Hailing Bay	6.3	Jiatai-684	Guangdong
X	December 25, 2007	Hailing Bay	9.8	Haima	Fujian
Y	December 25, 2007	Hailing Bay	6.7	Shuangxi-4	—
Z	December 25, 2007	Hailing Bay	7.7	Huijia-4	Fujiang
		Freshwater Compound Feed			
FF-1	May 21, 2007	Shunde	0.6	Hengxing-100A	Guangdong
FF-2	May 21, 2007	Shunde	0.6	Hengxing-107	Guangdong
FF-3	May 21, 2007	Shunde	0.6	Tongwei-103A	Sichuan
FF-4	May 21, 2007	Shunde	1.0	Tongwei-103B	Sichuan
FF-5	June 18, 2007	Dongguan	0.6	Dachuan-299	Guangdong
FF-6	June 18, 2007	Dongguan	1.2	Dachuan-616	Guangdong

Trash Fish

code	date	location	lipid (%)	code	date	location	lipid (%)
a	July 25, 2007	Daya Bay	3.5	i	January 10, 2008	Daya Bay	2.5
b	July 25, 2007	Daya Bay	2.1	j	December 25, 2007	Hailing Bay	3.6
c	July 26, 2007	Daya Bay	3.0	k	December 25, 2007	Hailing Bay	8.0
d	January 10, 2008	Daya Bay	2.3	l	December 25, 2007	Hailing Bay	2.3
e	January 10, 2008	Daya Bay	5.8	m	December 25, 2007	Hailing Bay	2.2
g	January 10, 2008	Daya Bay	4.5	n	January 10, 2008	Daya Bay	6.3
h	January 10, 2008	Daya Bay	1.7	o	January 10, 2008	Daya Bay	7.1

[a] Brand-type code, one brand may have several different types. [b] —, the information is not clear.

(sum of α-, β-, γ-, and δ-HCH), heptachlor, aldrin, heptachlor epoxides I and II, endosulfans I and II, endrin, endrin aldehyde, endosulfan sulfate, endrin ketone, and methoxychlor. All OCPs were analyzed with a Varian 3800 gas chromatograph (GC) interfaced with a Saturn 2000 mass spectrometer (MS) in the selective ion monitoring mode, and the detailed analytical method is shown in a previous study (*16*). Briefly, a fused-silica capillary column (DB-5; 60 m × 0.25 mm inner diameter; 0.25 film thickness) was used for separation. The temperature of the injector was programmed from 60 °C and raised to 280 °C at 200 °C/min (held for 30 min). The oven temperature was programmed from 60 °C (held for 1.0 min), raised to 180 °C at 12 °C/min, increased to 220 °C at 4 °C/min, then increased to 245 °C at 1 °C/min, and finally ramped to 290 °C at 30 °C/min (held at 290 °C for 20 min). To minimize the breakdown of DDTs in the GC injector, *p,p′*-DDT and mixed OCP standard was injected every day to check whether the DDT breakdown occurred, in addition to the use of a temperature program for the injector. For PCBs, a total of 42 PCB congeners (PCB-1, -2, -3, -4, -6, -8, -9, -16, -18, -19, -22, -25, -28, -31, -44, -52, -56, -66, -71, -74, -87, -99, -101, -110, -118, -138, -146, -147, -149, -153, -170, -173, -174, -177, -179, -180, -187, -194, -195, -199/201, -203, and -206) were measured with a Shimadzu Model 2010 GC coupled with a Model QP2010 MS (Shimadzu, Japan). A fused-silica capillary column (Rxi-5 ms; 30 m × 0.25 mm inner diameter; 0.25 μm film thickness) was used for separation. High-purity helium was used as a carrier gas at a constant column flow at 1.1 mL/min. The oven temperature was programmed from 110 °C (held for 1.0 min), raised to 200 °C at 10 °C/min, increased to 220 °C at 1 °C/min, then increased to 310 °C at 50 °C/min (held for 20 min). For PBDEs, a total of 42 BDE congeners (BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -191, -183, -190, -196, -206, and -209) were measured and the detailed analytical method is shown in a previous study (*17*). Briefly, a DB-5 (30 m × 0.25 mm inner diameter, 0.25 μm film thickness) capillary column was used for the measurements from mono- to hepta-BDEs. The column temperature was initiated at 110 °C (held for 1 min) and increased to 180 °C at 8 °C/min (held for 1 min), 240 °C at 2 °C/min (held for 5 min), 280 °C at 2 °C/min (held for 25 min), and 290 °C at 5 °C/min (held for 15 min). For BDE-196, BDE-206, and BDE-209, a DB-5 (15 m × 0.25 mm inner diameter, 0.1 μm film thickness) capillary column was used. The oven temperature was programmed initiated at 110 °C (held for 5 min) and increased to 200 °C at a rate of 20 °C/min (held for 4.5 min) and 310 °C at a rate of 10 °C/min (held for 20 min). The reporting limits for OCPs, PCBs, from tri- to octa-BDEs, nona-BDEs, and BDE-209 were 2.5−5.0, 0.25, 0.05, 0.25, and 2.5 ng/g, respectively, for 1 g sample wet weight. In addition, all of the ^{13}C-labeled compounds referenced in the present study were acquired from Cambridge Isotope Laboratories (Andover, MA) and others were acquired from Accustandards (New Haven, CT).

Quality Assurance/Quality Control. For each batch of 20 field samples, a procedural blank, a spiked blank, a matrix-spiked sample, and a matrix-spiked sample duplicate were processed. Recoveries of the surrogate and spiking standards are listed in Table S1 in the Supporting Information. Low levels of DDXs and BDE-28, -47, -99, -116, -153, -183, and -190 were found in procedural blanks, which were either lower or only slightly higher than the reporting limits. For DDXs and BDE-28, -47, -99, and -153, the concentrations were much lower in procedural blanks than in the samples; hence, blank values were not subtracted from the sample measurements. On the other hand, the concentrations of BDE-116, -183, -190, -197, -206, and -209 in procedural blanks, which were higher than the reporting limits, were subtracted from the sample measurements. For PCBs, only PCB-153 at low levels (subtracted from the sample measurements) was found in procedural blanks. Reported concentrations were not surrogate-recovery-corrected.

Data Analysis. Among 42 PCB and 42 BDE congeners under investigation, 27 PCB congeners (PCB-25, -31/28, -52, -44, -56, -66, -71, -74, -87, -99, -101, -110, -118, -138, -146, -147, -153, -170, -174, -177, -179, -180, -187, -194, -201, and -203) and 23 BDE congeners (BDE-17, -25, -28, -35, -47, -49, -66, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -181, -183, -190, -196, -206, and -209) were quantified. All concentrations reported were normalized to lipid weight except where indicated. Data comparison among groups was performed using nonparametric tests (Kruskal−Wallis H and Mann−Whitney U). Statistical significance was defined at $p < 0.05$. All statistical analyses were conducted using SPSS version 13.0. In addition, all abbreviations used in the present study are displayed in Table S2 in the Supporting Information.

RESULTS AND DISCUSSION

Concentration Levels of PHHs. Preliminary analysis indicated that OCPs, PCBs, and PBDEs were found in all samples. Among OCPs, DDXs were detectable in all samples (at least one component was detected). Besides, HCHs were detected in 23 samples, and endosulfan I was detectable in eight samples. For other OCPs, they were found only in two or three samples (Table S3 in the Supporting Information). No heptachlor epoxide II, endosulfan II, and endrin ketone were detectable in any sample. Therefore, only DDXs and HCHs, along with PCBs and PBDEs, will be discussed in detail thereafter. The concentration ranges of OCPs, PCBs, and PBDEs were 16.2−7120, 1.93−59.3, and 4.18−278 ng/g in marine fish feeds (including trash fish and marine compound feed) and 91.0−348, 4.83−18.7, and 28.9−148 ng/g in freshwater compound feed (Table S3 in the Supporting Information).

DDXs and HCHs. Overall, DDXs were the most abundant components of PHHs, generally several times more abundant than PBDEs and PCBs (**Figure 1**), and accounted for 87 ± 10, 64 ± 27, and 68 ± 20% (all mean values ± standard deviations) of OCPs in trash fish, marine compound feed, and freshwater compound feed, respectively. The mean and median concentrations of DDXs in trash fish (417 and 343 ng/g) were significantly higher than those in marine compound feed (151 and 102 ng/g) and freshwater compound feed (97 and 101 ng/g), but no difference was found between the two compound feeds. In addition, the highest concentration of DDXs (7040 ng/g) was found in a trash fish sample collected from Daya Bay (not shown in **Figure 1**). The concentrations of DDXs in trash fish were consistent with those in marine wild fish (median values of 45.8−480 ng/g), reported in the study of Meng et al. (*2*), but were higher than those in aquaculture feeds (34−52 ng/g) and fish oil (11−218 ng/g) from Europe (*9*), fish feeds (mean value of 97.4 ng/g for total OCPs) from South America (*18*), and aquaculture feeds (6.9−47 ng/g) from Vietnam (*11*). On a wet weight basis, the concentrations of total DDTs (0.33− 40.8 ng/g) (DDXs minus *p,p′*-DDMU) from the present study were similar to those in commercial fish feed (0.05− 50 ng/g) used in the United States (*8, 19*). The generally higher concentrations of DDXs in fish feeds, especially trash fish, manufactured in South China compared to similar products from other regions of the world were apparently associated with the fact that the PRD region, where most compound feeds are manufactured (**Table 1**), has had the highest pesticide application in China (*20*). Numerous previous studies strongly suggested that the levels of DDTs in the environment of the PRD have remained considerably high despite China's official ban on the use of DDTs in 1983 (*21*). Besides, previous work also indicated that

Article

*J. Agric. Food Chem.,* Vol. 57, No. 9, **2009** **3677**
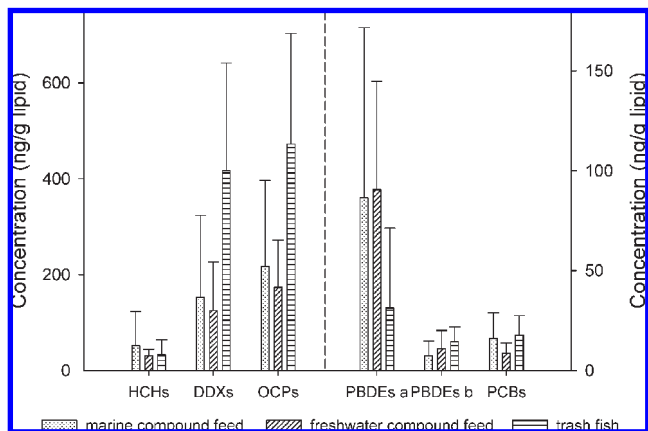
Figure 1. Concentrations of persistent halogenated hydrocarbons (ng/g lipid) in trash fish and compound feeds sampled from the Pearl River Delta, South China. The bars are the mean values with standard deviations. DDXs is the sum of DDT and its metabolites (o,p'- and p,p'-DDT, -DDD, and -DDE and p,p'-DDMU). HCHs is the sum of α-, β-, γ-, and δ-HCH. OCPs is the sum of total OCP target compounds. PBDEs a is the sum of 23 BDE congeners quantified. PBDEs b is PBDEs a minus BDE-196, -206, and -209. PCBs is the sum of 27 PCB congeners quantified.

new input sources of DDTs may be present in this region (*22−24*).

The concentrations of HCHs accounted for ∼10% of total OCPs in trash fish and ∼20% in both marine and freshwater compound feeds. No difference was found between the HCH levels in trash fish and compound feeds, with a mean value of ∼28 ng/g in all samples. This value was slightly higher than those in aquaculture feeds (2.4−46.8 ng/g) and fish oil (2.8−20.5 ng/g) from Europe (*9*) and aquaculture feeds (0.46−25 ng/g) from Vietnam (*11*). This result indicates that the levels of HCHs in aquaculture feeds manufactured in South China are at the high end of the global range.

PCBs. Generally, PCBs were the lowest abundant PHHs in fish feeds under investigation, especially for freshwater compound feed (**Figure 1**). No difference was found between the PCB levels in trash fish and marine compound feed, with levels ranging from 1.92 to 59.3 ng/g (mean/median values of 16.5/12.5 ng/g) in all marine fish feed samples. These values were significantly lower than those in aquaculture feeds from Europe (75.6−1153 ng/g) (*9*) and Canada (mean value of 270 ng/g) (*25*) and fish feeds from South America (mean value of 84.8 ng/g) (*18*) and within the same order of magnitude of those in aquaculture feeds (3.3−25 ng/g) from Vietnam (*11*). These results indicated that fish feeds are not highly contaminated by PCBs in China, which are consistent with the suggestion (*26*) that production and/or usage of PCBs has been relatively low in China.

PBDEs. Higher levels of total PBDEs were found in compound feeds (4.18−230 and 28.9−148 ng/g, respectively, in marine and freshwater compound feeds) than those in trash fish (7.15−156 ng/g) (**Figure 1**). The values in trash fish were within the range of < 0.1−53 ng/g in the muscle of skipjack tuna (*Katsuwonus pelamis*), collected from offshore waters of various regions in the world (*27*). In comparison to compound feeds from other countries, the levels of PBDEs from the present study were slightly higher than those in aquaculture feeds (0.35−7.0 ng/g) from Vietnam (*11*). These values, on a wet weight basis (0.18−137 ng/g), were mostly in the same range with fish feeds purchased from various global suppliers (0.50−10.9 ng/g) (*28*). Some high values reported in the present study were directly associated with
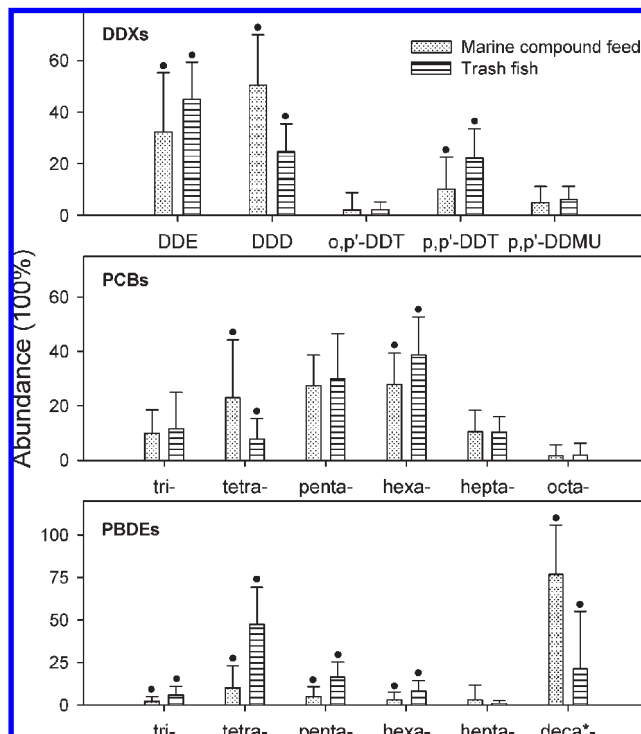
Figure 2. Compositional profiles of PHHs in trash fish and marine compound feed sampled from the Pearl River Delta, South China. The bars are the mean values with standard deviations. Bars with dots on top indicate that there is a significant difference of concentrations ($p < 0.05$) between trash fish and marine compound feed. DDD is the sum of o,p'- and p,p'-DDD, and DDE is the sum of o,p'- and p,p'-DDE. For PCBs, tri- is the sum of PCB-25, -31, and -28; tetra- is the sum of PCB-44, -52, -56, -66, -71, and -74; penta- is the sum of PCB-87, -99, -101, -110, and -118; hexa- is the sum of PCB-138, -146, -147, and -153; hepta- is the sum of PCB-170, -174, -177, -179, -180, and -187; and octa- is the sum of PCB-194, -201, and -203. For PBDEs, tri- is the sum of BDE-17, -25, -28, and -35; tetra- is the sum of BDE-47, -49, and -66; penta- is the sum of BDE-85, -99, -100, -116, -118, -119, and -126; hexa- is the sum of BDE-138, -153, and -154; hepta- is the sum of BDE-181, -183, and -190; and deca*- is the sum of BDE-196, -206, and -209.

the occurrence of BDE-209, which was detected in 25 of the 27 compound feed samples and 4 of the 14 trash fish samples, with the concentrations ranging from none detectable to 271 ng/g (Table S3 in the Supporting Information). Excluding BDE-209, -206, and -196, the total mean and median PBDE concentrations were significantly higher in trash fish (14.5 and 12.2 ng/g) than in compound feeds (7.21 and 4.18 ng/g for marine feed and 11.0 and 8.05 ng/g for freshwater feed, respectively).

Compositional Profiles. Only the compositional profiles of PHHs in trash fish and marine compound feed (**Figure 2**) are discussed in this section, while those in freshwater compound feed will be discussed in the next section. For DDXs, DDD (sum of p,p'- and o,p'-DDD) and DDE (sum of p,p'- and o,p'-DDE) were the predominant congeners, followed by DDT (sum of p,p'- and o,p'-DDT), and p,p'-DDMU was the least abundant. Trash fish contained significantly higher DDE and p,p'-DDT and lower DDD concentrations than marine compound feed. In addition, the ratios of DDT/(DDD + DDE) were higher in trash fish (mean/median values of 0.38/0.28) than in marine compound feed (0.25/0.10), with an abruptly high value of 3.0 in one compound feed sample. In combination with the fact that DDT accounts for more than 80% of the technical DDT formulation (*29*),

the abruptly high value may indicate potential fresh DDT input sources. All of these results suggest that marine fish feeds manufactured in South China are contaminated with DDTs of both current and historical origins. The mean value of o,p'-DDT/p,p'-DDT was close to 7 (*22*) for dicofol, a pesticide containing abundant o,p'-DDT and low-level p,p'-DDT, while it is close to ~0.2 in a technical DDT mixture (*ref29*). The average o,p'-DDT/p,p'-DDT value in marine fish feeds from the present study was ~0.1, suggesting minimal effects of dicofol.

For PCBs, penta- and hexa-PCBs were the most abundant, with hexa-PCBs more abundant in trash fish than in marine compound feed (mostly as PCB-153 and PCB-138). The concentrations of other PCBs in trash fish and marine compound feed were not significantly different, except for a significantly higher level of tetra-PCBs in marine compound feed than in trash fish. For PBDEs, excluding BDE-196, -206, and -209, tetra-BDEs were the predominant congeners (mostly as BDE-47 and BDE-49), followed by penta-BDEs (mostly as BDE-99, -100, and -126) and hepta-BDEs (mostly BDE-153 and BDE-154). It is interesting to note that marine compound feed usually had higher levels of heavily brominated BDE congeners, such as BDE-196, -206, and -209, while trash fish contained higher abundances of low-brominated BDEs, i.e., tri-, tetra-, penta-, and hexa-BDEs (**Figure 2** and Table S3 in the Supporting Information). The results with trash fish supported the previously reached conclusion that the uptake of PHHs with high log K_{ow} (> 7) was relatively inefficient in fish species (*30, 31*). Another explanation for this result is that highly brominated BDEs may be debrominated *in vivo* of fish that have already been demonstrated by an experimental fish study (*32−34*).

**Fish Feeds as Potential Sources of PHHs to Farmed Fish.** The results presented above indicate that PHHs were ubiquitous in fish feeds manufactured in South China, with the levels of DDXs, PBDEs, and PCBs within the upper, mid, and lower portions of the global range. The previous studies of Meng et al. (*2*) and Guo et al. (*35*) obtained considerably higher concentrations of DDTs in seawater farmed fish than in freshwater farmed fish. In the present study, no significant difference was detected between the concentrations of DDXs in 21 marine and 6 freshwater compound feed samples, but significantly higher levels of DDXs were found in trash fish than in both marine and freshwater compound feeds. Because large amounts of trash fish are directly used as feeds for fish farming in China, trash fish is obviously an important source to explain the higher concentrations of DDXs in marine farmed fish than in freshwater farmed fish. In addition, Meng et al. and Guo et al. (*2, 35*) also found different relative abundances of DDTs between two farmed fish types. For example, seawater farmed fish contained higher relative abundances of DDD (~30%) and p,p'-DDT (~30%) and lower abundances of DDE (10−20%) and o,p'-DDT (< 10%) than freshwater farmed fish (~20% for DDD, ~10% for p,p'-DDT, ~50% for DDE, and > 10% for o,p'-DDT) (*35*). Nevertheless, marine compound feed did contain significantly higher relative abundances of DDD (median of 50%) and lower abundance of o,p'-DDT (zero) than freshwater compound feed (27 and 62% for DDD and o,p'-DDT, respectively), which was similar to the results obtained by the fish study of Guo et al. (*35*). Although the abundances of DDE and p,p'-DDT were not significantly different between the two compound feeds, seawater farmed fish feeding mainly on trash fish are still expected to contain higher abundances of DDD and DDT than freshwater

farmed fish because trash fish contained higher relative abundances of p,p'-DDT than compound feeds and p,p'-DDT may be partly biotransformed to p,p'-DDD in fish liver (*ref35*).

For PBDEs, Meng et al. (*2, 36*) reported higher levels in marine farmed fish than in freshwater farmed fish and ascribed atmospheric deposition as the main source of PHHs in freshwater farmed fish and wastewater effluent from the PRD as an additional source in seawater farmed fish in the absence of any PHH data in fish feeds of China. Conversely, the present study has found no significant difference in the concentrations of PBDEs between marine and freshwater compound feeds, which suggests that the high levels of PBDEs in seawater farmed fish may also have been partly attributed to the use of trash fish as farming feeds. For example, trash fish contained significantly higher concentrations of low-brominated BDEs than the two compound feeds (**Figure 1**), and low-brominated BDEs are usually easy to bioaccumulate in fish species (*30, 31*). Several previous studies have also attributed aquaculture feeds as an important source of PHHs in farmed fish (*10, 11, 28, 37*).

Eco-environmental Effects Because of the Occurrence of DDTs in Trash Fish. High levels of DDXs in trash fish not only induce fish contamination but may also affect marine wildlife predators. The screening value for wildlife consumption of aquatic biota, such as fish species, established by the Government of Canada, is 14.0 ng/g wet wt for total DDTs (*ref38*), which is intended to address the questions of whether fish are safe to eat and whether fish resources are being adequately protected. In the present study, the mean DDTs concentration of 16.2 ng/g wet wt in 13 trash fish (not including the abnormal high concentration of 421 ng/g wet wt in one sample from Daya Bay) or the concentrations in 5 of the 14 samples were higher than the screening value (**Figure 3**). Apparently, trash fish may be somewhat hazardous to wildlife because of the occurrence of DDTs. Previous surveys on DDTs in eggs of fish-eating ardeids suggested that DDTs in eggs were associated with adverse effects on the survival of the ardeid young in Hong Kong (*39, 40*).

Direct use of trash fish as fish feeds may partially explain why the concentrations of DDTs in aquatic species of China,
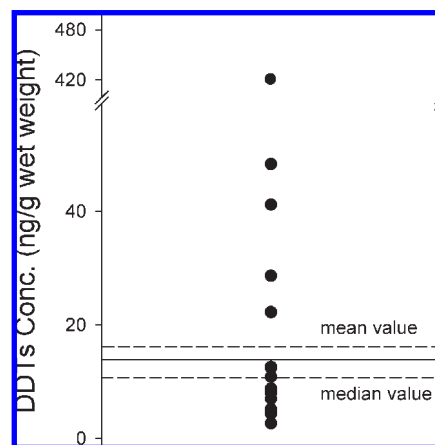
Figure 3. Concentrations of DDTs in trash fish sampled from the Pearl River Delta, South China. The solid black line represents the screening value (14.0 ng/g wet weight) for wildlife consumption of fish established by the Government of Canada (http://www.riverinstitute.ca/envtech/Documents/WQA/CEQG%20aquatic%20life.pdf). The highest concentration (421 ng/g wet weight) of DDTs detected in one trash fish sampled from Daya Bay was not included in the mean and median calculation.

Article

J. Agric. Food Chem., Vol. 57, No. 9, 2009 **3679**

especially in coastal regions, were at the high end of the global range. Meng et al. (*2*) estimated that the outflow of DDTs from China via fishery product exportation was ~15 kg in 2005. On the other hand, the total inflow of DDTs via trash fish required to sustain aquaculture is ~60 kg, estimated using the median value of DDTs in trash fish (12 ng/g wet wt) and the amount (5 million metric tons) of trash fish captured in China in 2001 (*1*). Therefore, DDTs can be accumulated in fishery products of China through the use of captured trash fish as feeds. In addition, trash fish directly used as fish feed also induce many environmental problems. For examples, marine cage fish culture is partly responsible for the eutrophication and organic enrichment that have occurred along the coast area (*41*, *42*). A recent study (*43*) reported that approximately 10 mg of nitrogen and phosphorus was excreted as fish fed for trash fish, which grew by every gram. It is obvious that the use of trash fish as fish-farming feeds has to be restricted in China to mitigate contamination of fishery products and wildlife by PHHs. On the other hand, compound feeds produced under better controlled conditions should be used more widely to meet the growing need of aquaculture.

Supporting Information Available: Additional tables and figure containing detailed information about the QA/QC results, abbreviations for the study region (including locality) and target analytes, and detailed concentrations of PHHs in all samples. This material is available free of charge via the Internet at http://pubs.acs.org.

LITERATURE CITED

(1) Food and Agriculture Organization of the United Nation. The state of world fisheries and aquaculture 2006. http://www.illegal-fishing.info/uploads/FAO-state-of-world-fisheries-and-aquaculture-2006.pdf (accessed on Dec 2008).

(2) Meng, X.-Z.; Zeng, E. Y.; Yu, L.-P.; Mai, B.-X.; Luo, X.-J.; Ran, Y. Persistent halogenated hydrocarbons in consumer fish of China: Regional and global implications for human exposure. *Environ. Sci. Technol*. **2007**, *41*, 1821–1827.

(3) Engelhaupt, E. Mixed news on Chinese farmed fish. http://pubs.acs.org/subscribe/journals/esthag-w/2007/feb/science/ee_chinesefish.html (accessed on Feb 2007).

(4) Chau, K. W. Characterization of transboundary POP contamination in aquatic ecosystems of Pearl River Delta. *Mar*. *Pollut*. *Bull*. **2005**, *51*, 960–965.

(5) Chen, S.-J.; Luo, X.-J.; Mai, B.-X.; Fu, J.-M.; Sheng, G.-Y.; Zeng, E. Y. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the northern South China Sea. *Environ. Sci. Technol*. **2006**, *40*, 709–714.

(6) Guan, Y.-F.; Wang, J.-Z.; Ni, H.-G.; Zeng, E. Y. Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: Assessment of mass loading, input source and environmental fate. *Environ. Pollut*. **2009**, *157*, 618–624.

(7) Karl, H.; Lehmann, I.; Oetjen, K. Levels of chlordane compounds in fish muscle, -meal, -oil and -feed. *Chemosphere* **1998**, *36*, 2819–2832.

(8) Easton, M. D. L.; Luszniak, D.; Von der Geest, E. Preliminary examination of contaminant loadings in framed salmon, wild salmon and commercial salmon feed. *Chemosphere* **2002**, *46*, 1053–1074.

(9) Jacobs, M. N.; Covaci, A.; Schepens, P. Investigation of selected persistent organic pollutants in farmed Atlantic Salmon (*Salmo salar*), salmon aquaculture feed, and fish oil components of the feed. *Environ. Sci. Technol*. **2002**, *36*, 2797–2805.

(10) Montory, M.; Barra, R. Preliminary data on polybrominated diphenyl ethers (PBDEs) in farmed fish tissues (*Salmo salar*) and fish feed in southern Chile. *Chemosphere* **2006**, *63*, 1252–1260.

(11) Minh, N. H.; Minh, T. B.; Kajiwara, N.; Kunisue, K.; IIwata, H.; Viet, P. H.; Tu, N. P. C.; Tuyen, B. C.; Tanabe, S. Contamination by polybrominated diphenyl ethers and persistent organochlorines in catfish and feed from Mekong River Delta, Vietnam. *Environ. Toxicol. Chem*. **2006**, *25*, 2700–2709.

(12) Hites, R. A.; Foran, J. A.; Carpenter, D. O.; Hamilton, M. C.; Knuth, B. A.; Schwager, S. J. Global assessment of organic contaminants in farmed salmon. *Science* **2004**, *303*, 226–229.

(13) Carlson, D. L.; Hites, R. A. Polychlorinated biphenyls in salmon and salmon feed: Global differences and bioaccumulation. *Environ. Sci. Technol*. **2005**, *39*, 7389–7395.

(14) Journal of China Aquaculture. The development, challenge and suggestion for aquaculture feeds in China (in Chinese). http://www.cnfm.gov.cn/info/display.asp?sortid = 40&id = 11022 (accessed on Dec 2008).

(15) Zhang, L.-Y. China feedstuff market analysis. In *The Feedstuff Economy and Manage Research in China*; China Economy Press: China, 2007; p 23 (in Chinese).

(16) Xing, Y.-N.; Guo, Y.; Xie, M.; Shen, R.-L.; Zeng, E. Y. Detection of DDT and its metabolites in two estuaries of South China using a SPME-based device: First report of *p,p'*-DDMU in water. *Environ. Pollut*. **2009**, *157*, 1382−1387.

(17) Mai, B. X.; Chen, S. J.; Luo, X. J.; Chen, L. G.; Yang, Q. S.; Sheng, G. Y.; Peng, P. A.; Fu, J. M.; Zeng, E. Y. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol*. **2005**, *39*, 3521–3527.

(18) Serrano, R.; Barreda, M.; Blanes, M. A. Investigating the presence of organochlorine pesticides and polychlorinated biphenyls in wild and farmed gilthead sea bream (*Sparus aurata*) from the Western Mediterranean sea. *Mar*. *Pollut*. *Bull*. **2008**, *56*, 963–972.

(19) Maule, A. G.; Gannam, A. L.; Davis, J. W. Chemical contaminants in fish feeds used in federal salmonid hatcheries in the USA. *Chemosphere* **2007**, *67*, 1308–1315.

(20) Hua, X.; Shan, Z. The production and application of pesticides and factor analysis of their pollution in environment in China. *Adv. Environ. Sci*. **1996**, *4*, 33–45 (in Chinese).

(21) Fu, J. M.; Mai, B. X.; Sheng, G. Y.; Zhang, G.; Wang, X. M.; Peng, P. A.; Xiao, X. M.; Ran, R.; Cheng, F. Z.; Peng, X. Z.; Wang, Z. S.; Tang, U. W. Persistent organic pollutants in environment of the Pearl River Delta, China: An overview. *Chemosphere* **2003**, *52*, 1411–1422.

(22) Qiu, X.; Zhu, T.; Yao, B.; Hu, J.; Hu, S. Contribution of dicofol to the current DDT pollution in China. *Environ. Sci. Technol*. **2005**, *39*, 4385–4390.

(23) Wang, J.; Guo, L.-L.; Li, J.; Zhang, G.; Lee, C. S. L.; Li, X.-D.; Jones, K. C.; Xiong, Y.-R.; Zhong, L.-J. Passive air sampling of DDT, chlordane and HCB in the Pearl River Delta, South China: Implications to regional sources. *J. Environ. Monit*. **2007**, *9*, 582–588.

(24) Mai, B. X.; Fu, J. M.; Sheng, G. Y.; Kang, Y. H.; Lin, Z.; Zhang, G.; Min, Y. S.; Zeng, E. Y. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environ. Pollut*. **2002**, *117*, 457–474.

(25) Kelly, B. C.; Fernandez, M. P.; Ikonomou, M. G.; Knapp, W. Persistent organic pollutants in aquafeed and Pacific salmon smolts from fish hatcheries in British Columbia, Canada. *Aquaculture* **2008**, *285*, 224–233.

(26) Mai, B. X.; Zeng, E. Y.; Luo, X. J.; Yang, Q. S.; Zhang, G.; Li, X. D.; Sheng, G. Y.; Fu, J. M. Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China. *Environ. Sci. Technol*. **2005**, *39*, 49–56.

(27) Ueno, D.; Kajiwara, N.; Tanaka, H.; Subramanian, A.; Fillmann, G.; Lam, P. K. S.; Zheng, G. J.; Muchitar, M.; Razak, H.; Prudente, M.; Chung, K. H.; Tanabe, S. Global pollution monitoring of polybrominated diphenyl ethers using skipjack tuna as a bioindicator. *Environ. Sci. Technol*. **2004**, *38*, 2312–2316.

3680 *J. Agric. Food Chem.,* Vol. 57, No. 9, 2009

Guo et al.

(28) Hites, R. A.; Foran, J. A.; Schwager, S. J.; Knuth, B. A.; Hamilton, M. C.; Carpenter, D. O. Global assessment of polybrominated diphenyl ethers in farmed and wild salmon. *Environ. Sci. Technol.* **2004**, *38*, 4945–4949.

(29) Metcalf, R. L. A century of DDT. *J. Agric. Food Chem.* **1973**, *21*, 511–519.

(30) Burreau, S.; Axelman, J.; Broman, D.; Jakobsson, E. Dietary uptake in pike (*Esox lucius*) of some polychlorinated biphenyls, polychlorinated naphthalenes and polybrominated diphenyl ethers administered in natural diet. *Environ. Toxicol. Chem.* **1997**, *16*, 2508–2513.

(31) Konwick, B. J.; Garrison, A. W.; Black, M. C.; Avants, J. K.; Fisk, A., T. Bioaccumulation biotransformation, and metabolite formation of fipronil and chiral legacy pesticides in rainbow trout. *Environ. Sci. Technol.* **2006**, *40*, 2930–2936.

(32) Stapleton, H. M.; Brazil, B.; Holbrook, R. D.; Mitchelmore, C. L.; Benedict, R.; Konstantinov, A.; Potter, D. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. *Environ. Sci. Technol.* **2006**, *40*, 4653–4658.

(33) Tomy, G. T.; Palace, V. P.; Halldorson, T.; Braekevelt, E.; Danell, R.; Wautier, K.; Evans, B.; Brinkworth, L.; Fisk, A. T. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (*Salvelinus namaycush*). *Environ. Sci. Technol.* **2004**, *38*, 1496–1504.

(34) Kierkegaard, A.; Balk, L.; Tjarnlund, U.; De Wit, C. A.; Jansson, B. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (*Oncorhynchus mykiss*). *Environ. Sci. Technol.* **1999**, *33*, 1612–1617.

(35) Guo, Y.; Meng, X.-Z.; Tang, H.-L.; Zeng, E. Y. Tissue distribution of organochlorine pesticides in fish collected from the Pearl River Delta, China: Implications for fishery input source and bioaccumulation. *Environ. Pollut.* **2008**, *155*, 150–156.

(36) Meng, X.-Z.; Yu, L.-P.; Guo, Y.; Mai, B.-X.; Zeng, E. Y. Congener-specific distribution of polybrominated diphenyl ethers in fish of China: Implication for input sources. *Environ. Toxicol. Chem.* **2008**, *27*, 67–72.

(37) van Beusekom, O. C.; Eljarrat, E.; Barceló, D.; Koelmans, A. A. Dynamic modeling of food-chain accumulation of brominated flame retardants in fish from the Ebro River Basin, Spain. *Environ. Toxicol. Chem.* **2006**, *25*, 2553–2560.

(38) Canadian Environmental Quality Guidelines. http://www.riverinstitute.ca/envtech/Documents/WQA/CEQG%20aquatic%20life.pdf (accessed on Feb 2009).

(39) Connell, D. W.; Fung, C. N.; Minh, T. B.; Tanabe, S.; Lam, P. K. S.; Wong, B. S. F.; Lam, M. H. W.; Wong, L. C.; Wu, R. S. S.; Richardson, B. J. Risk to breeding success of fish-eating ardeids due to persistent organic contaminants in Hong Kong: Evidence from organochlorine compounds in eggs. *Wat. Res.* **2003**, *37*, 459–467.

(40) De Luca-Abbott, S. B.; Wong, B. S. F.; Peakall, D. B.; Lam, P. K. S.; Young, L.; Lam, M. H. W.; Richardson, B. J. Review of effects of water pollution on the breeding success of waterbirds, with particular reference to ardeids in Hong Kong. *Ecotoxicology* **2001**, *10*, 327–349.

(41) Karakassis, I.; Tsapakis, M.; Hatziyanni, E.; Papadopoulou, K. N.; Plaiti, W. Impact of cage farming of fish on the seabed in three Mediterranean coastal areas. *ICES J. Mar. Sci.* **2000**, *57*, 1462–1471.

(42) Alongi, D. M.; Chong, V. C.; Dixon, P.; Sasekumar, A.; Tirendi, F. The influence of fish cage aquaculture on pelagic carbon flow and water chemistry in tidally dominated mangrove estuaries of peninsular Malaysia. *Mar. Environ. Res.* **2003**, *55*, 313–333.

(43) Xu, Z. N.; Lin, X. T.; Lin, Q.; Yang, Y. F.; Wang, Y. X. Nitrogen, phosphorus, and energy waste outputs of four marine cage-cultured fish fed with trash fish. *Aquaculture* **2007**, *263*, 130–141.