PERSISTENT HALOGENATED HYDROCARBONS IN CONSUMER FISH OF CHINA AND HUMAN EXPOSURE VIA FISH CONSUMPTION

Meng XZ[1, 2], Yu LP[1, 2], Guo Y[1, 2], Zeng EY[1]
[1]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China; [2]Graduate School, Chinese Academy of Sciences, Beijing, 100049, China

Abstract
The present study examined persistent halogenated hydrocarbons (PHHs), including organochlorine pesticides (including DDTs and hexachlorocyclohexane (HCHs)), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), in consumer fish of China. The results indicated that DDTs, HCHs, PCBs, and PBDEs were the predominant PHH residues in the fish samples. Moreover, the contributions of DDTs to the total PHHs ranged from 53.2% to 98.3% in all samples. Residual levels (mean values) of DDTs, HCHs, and PCBs in consumer fish of China were well below the respective maximum residual levels or maximum levels. Additionally, the human daily intakes of DDTs and HCHs were far below the provisional tolerable daily intakes and acceptable daily intakes recommended by the FAO/WHO. Fish consumption assessments indicated that consumption of freshwater farmed and wild marine fish generally does not subject consumers to significant health risk as far as PHHs are concerned, while limited consumption of seawater farmed fish is advised.

Introduction
Fish consumption is the main route for human exposure to persistent halogenated hydrocarbons (PHHs) such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). As a result, numerous investigations on residual levels of PHHs in consumer fish have been conducted in various countries during the past few decades.[1-4] On the other hand, China (mainland) is the largest fishery producer and exporter in the world.[5] Unfortunately, the state of fish contamination by PHHs and associated human health risk have not been systematically assessed in China. The present study aimed to determine the levels and distributions of PHHs, including OCPs, PCBs, and PBDEs, in consumer fish of China, assess the potential health risks associated with fish consumption, and provided preliminary advisories on consumption of fish from China.

Materials and Methods
Detailed sample collection, sample preparation, and instrumental analytical procedures of PHHs have been described previously.[6] Briefly, in November 2004 and January 2005, 13 fish species (seven freshwater farmed fish, three seawater farmed fish, and three wild marine fish) were randomly collected from fish markets and supermarkets in 11 coastal cities of Guangdong Province, China (Figure 1). Approximately 30 individuals were

Figure 1. Map of the general study area and sampling sites: Guangzhou, Dongguan, Zhuhai, Foshan, Zhongshan, Jiangmen, Yangjiang, Maoming, Zhanjiang, Shantou, and Shanwei.

collected for each species to ensure sufficient statistical power for data analysis. About 20 g fish muscle was Soxhlet extracted for 48 h after being spiked with surrogate standards TMX, PCB-67, PCB-191, ^{13}C-PCB-141 and PCB-209. Lipid contents were determined gravimetrically using 20% of each extract. The remaining extract was subject to a gel permeation chromatography column and a silica/alumina column for further purification. Finally, the internal standards (PCB-82 for OCPs, PCB-24 and PCB-189 for PCBs, and ^{13}C-PCB-208 for PBDEs) were added before instrumental analysis. Strict quality assurance/quality control program were followed.[6] Recoveries of 21 OCPs and 11 PBDEs in these spiked samples were 86.3 ± 18.4% and 87.2 ± 19.0%, respectively. The surrogate recoveries of TMX, PCB-67, PCB-191, ^{13}C-PCB-141, and PCB-209 were 55.3 ± 11.1%, 83.2 ± 12.5%, 89.8 ± 11.0%, 81.8 ± 17.3%, and 84.8 ± 18.4%, respectively. Blank values were not subtracted from the sample measurements. Reported concentrations were not surrogate recovery corrected.

Results and Discussion

Levles of PHHs Contamination. Preliminary analysis indicated that DDTs (sum of *o,p*'-DDT, *o,p*'-DDE, *o,p*'-DDD, *p,p*'-DDT, *p,p*'-DDE, and *p,p*'-DDD), HCHs (sum of α-HCH, β-HCH, γ-HCH, and δ-HCH), PCBs, and PBDEs (sum of BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183) were the predominant PHH residues in the fish samples (Figure 2). The occurrence frequencies for other OCP compounds, such as heptachlor, heptachlor epoxide, aldrin, dieldrin, endosulfan (I), endosulfan sulfate, endrin, endrin aldehyde, and methoxychlor, were 1%, 9%, 2%, 3%, 4%, 2%, 2%, 26%, and 5%, respectively. No endosulfan (II) and endrin ketone were detected. Therefore, only the data of DDTs, HCHs, PCBs, and PBDEs were discussed herein.

Of all 390 fish samples, the concentration ranges of DDTs, HCHs, PCBs, and PBDEs were 0.14–698.9 ng/g, 0.13–24.06 ng/g, <0.02–7.65 ng/g, and <0.0012–3.85 ng/g (all normalized to wet weight except where indicated), respectively (Figure 2). Overall, the concentrations of DDTs were 1–2 orders of magnitude higher than those of HCHs, PCBs, and PBDEs. The contributions of DDTs to the total PHHs residues (sum of DDTs, HCHs, PCBs, and PBDEs ranged from 53.2% in grass carp (a freshwater farmed fish) to 98.3% in snubnose pompano (a seawater farmed fish), which reflected their usage in China and their characteristics (Figure 3). During 1950s to 1983, the total production of DDT was 0.4 million tons in China, which accounted for 20% of the total world production[7]. Moreover, DDT mixtures may still be produced to satisfy export demand and usage, and dicofol technical products known to contain a large amount of DDT residues have been used in recent years.[8] On the other hand, DDTs levels have declined slowly in foodstuffs and biota over the past two decades because of the high persistency and low biodegradability with DDTs compared to HCHs, another OCPs largely used in China.[9]

In addition, despite the relative low percentage of other PHHs in consumer fish of China (ranges of 0.7–38.9%, 0.5–6.9%, and 0.3–6.4% for HCHs, PCBs, and PBDEs, respectively), impact of these compounds should not be ignored because some of them are still used in China, such as PBDEs. The domestic demand for brominated

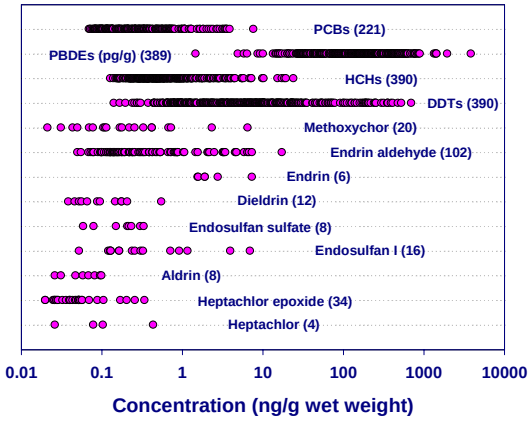

Figure 2. Concentrations (ng/g; pg/g for PBDEs) of 13 PHHs determined in fish samples of China. The numbers in parentheses are the numbers of samples containing detectable analytes.

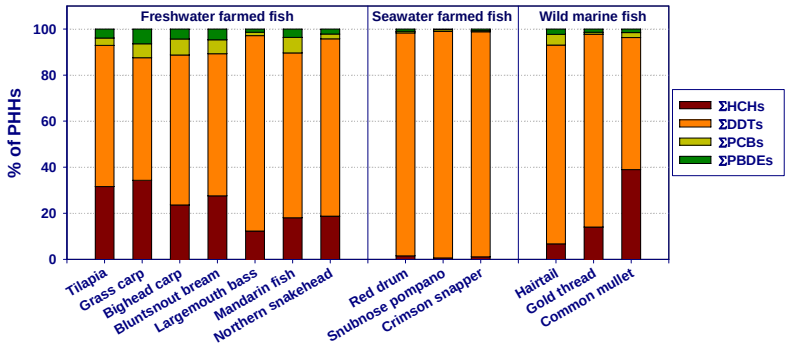

Figure 3. Compositions of main persistent halogenated hydrocarbons in consumer fish of China

flame retardants (containing largely PBDEs) in China has increased at an annual rate of 8%.[10] Furthermore, China has been the destination for massive amounts of recycled electrical and electronic components from developed countries. These wastes are often processed in small workshops using simple methods such as manual disassembly, acid-washing, and open burning to extract valuable metals.[11] Therefore, PBDEs may be released into the environment accompanying the usage and disassembly process, which would inevitably result in continuously rising PBDE levels in the environmental media.

Human Exposure. The mean concentrations of DDTs (32.2 ng/g), HCHs (1.2 ng/g), and PCBs (0.33 ng/g) in consumer fish of China much lower than the corresponding maximum residueal limits (MRLs, 0.5 and 0.1 mg/kg wet weight for DDTs and HCHs, respectively) or maximum levels (MLs, 2.0 mg/kg wet weight for PCBs) established by the Chinese government.[12, 13] Also no fish samples contained higher contaminant levels than the action levels and tolerances for DDTs (5.0 mg/kg) and PCBs (2.0 mg/kg) developed by the U.S. Food and Drug Administration (USFDA).[14] However, 0.5% and 13.8%, respectively, of the fish samples containing DDTs levels exceeded the advisory limits for human consumption recommended by the Chinese government and the Europe Union (0.05 mg/kg wet weight).[15] Currently no MRL is available for PBDEs.

In addition, estimated daily intakes (EDIs) of PHHs via fish consumption were calculated by multiplying the mean concentrations of PHHs from the present study with the per capita fish consumption values of Chinese population.[16] The mean values of EDIs (EDI_{50}) of DDTs for urban and rural residents of China were 3.66 and 1.27 ng/kg bw/d, respectively. All these values were far below the provisional tolerable daily intakes for DDTs (10000 ng/kg bw/d) recommended by the Food and Agriculture Organization and World Health Organization.[17] EDI_{50} of HCHs were 0.30 and 0.11 ng/kg bw/d, respectively, for urban and rural residents, also well below the acceptable daily intakes (ADIs) for γ-HCH (5000 ng/kg bw/d) [17]. No ADIs were available for PCBs and PBDEs. EDI_{50} were 0.06 and 0.02 ng/kg bw/d for PCBs, whereas EDI_{50} for PBDEs were 0.09 and 0.03 ng/kg bw/d.

Advisories on Fish Consumption. We used approach developed by U.S. Environmental Protection Agency to derive consumption advisories for consumer fish of China (assuming an acceptable risk level as 1 in 100,000).[14] The mean concentrations of DDTs, HCHs, and PCBs in this study and the corresponding cancer slope factor for carcinogenic effects were used to calculate species-specific consumption limits expressed as number of fish meals per month. The risk-based meal consumption limits for the fish species and PHHs under consideration (Figure 4) suggested that consumption of seawater farmed fish was more likely to raise health concern than that of seawater wild fish or freshwater farmed fish. If the mean concentrations of PHHs were used, no restrictive limits should be imposed for freshwater framed fish and seawater wild fish (i.e., more than 16 meals per month allowed). Consumption of bighead carp (freshwater farmed) and golden thread (wild marine) would not result in health concern even if the upper-bound concentrations of PHHs were used in the calculation. On the other hand, less than 13 meals (mean) and 4 meals (upper-bound) per month were allowed for seawater farmed fish. The worst case occurred with snubnose pompano, a cage-cultured seawater fish, where no more than one meal per month should be allowed (Figure 4).

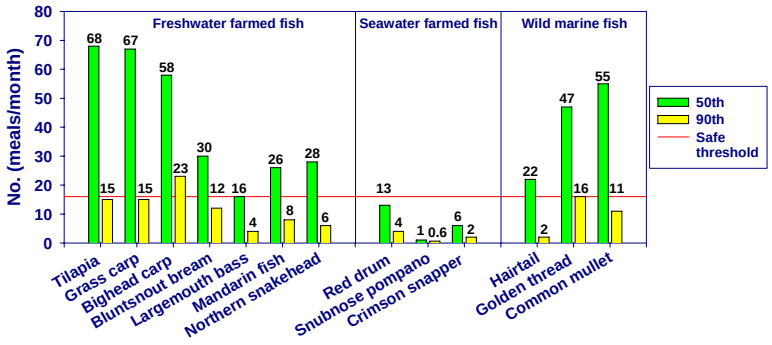

Figure 4. Risk-based consumption advisories using the concentration data of DDTs, HCHs, and PCBs in consumer fish of China. The solid red line is a safe fish consumption threshold, suggesting that the consumption of this species does not require restriction based on the PHHs evaluated (16 meals/month). The numbers on the green bars are calculated with the 50th percentile concentrations, while the numbers on the yellow bars are calculated with the 90th percentile concentrations.

Acknowledgements
This work was financially supported by the National Natural Science Foundation of China (40532013 and U0633005) and the "One Hundred Talents Program" of the Chinese Academy of Sciences.

References

1. Hites RA, Foran JA, Carpenter DO, Hamilton MC, Knuth BA, Schwager SJ. *Science* 2004; 303:226.
2. Tittlemier SA, Forsyth D, Breakell K, Verigin V, Ryan JJ, Hayward S. *J Agric Food Chem* 2004; 52:7740.
3. Domingo JL, Bocio A, Falcó G, Llobet JM. *Environ Sci Technol* 2006; 40:4394.
4. Schecter A, Papke O, Harris TR, Tung KC, Musumba A, Olson J, Birnbaum L. *Environ Heal Perspect* 2006; 114:1515.
5. Food and Agriculture Organization of the United Nation. www.fao.org/DOCREP/007/y5600e/y5600e00.htm (accessed December 2006).
6. Meng XZ, Zeng EY, Yu LP, Mai BX, Luo XJ, Ran Y. *Environ Sci Technol* 2007; 41:1821.
7. Zhang G, Parker A, House A, Mai B, Li X, Kang Y, Wang Z. *Environ Sci Technol* 2002; 36:3671.
8. Qiu X, Zhu T, Yao B, Hu J, Hu S. *Environ Sci Technol* 2005; 39:4385.
9. Nakata H, Kawazoe M, Arizono K, Abe S, Kitano T, Shimada H, Li W, Ding X. *Arch Environ Contam Toxicol* 2002; 43:473.
10. Mai BX, Chen SJ, Luo XJ, Chen LG, Yang QS, Sheng GY, Peng PA, Fu JM, Zeng EY. *Environ Sci Technol* 2005; 39:3521.
11. Ueno D, Kajiwara N, Tanaka H, Subramanian A, Fillmann G, Lam PKS, Zheng GJ, Muchitar M, Razak H, Prudente M, Chung K-H, Tanabe S. *Environ Sci Technol* 2004; 38:2312.
12. Ministry of Health of the People's Republic of China. www.instrument.com.cn/show/download/shtml/014500.shtml (accessed September 2006).
13. Ministry of Health of the People's Republic of China. www.instrument.com.cn/show/download/shtml/020604.shtml (accessed September 2006).
14. U.S. Environmental Protection Agency. www.epa.gov/ost/fishadvice/volume2/index.html (accessed September 2006).
15. Binelli A, Provini A. *Mar Pollut Bull* 2003; 46:879.
16. National Bureau of Statistics of China. www.stats.gov.cn/tjsj/ndsj/2005/indexch.htm (accessed September 2006).
17. The International Programme on Chemical Safety (IPCS). http://www.who.int/ipcs/publications/jmpr/jmpr_pesticide/en/index.html (accessed November 2006).