# RESIDUE LEVELS AND RISK ASSESSMENT OF PERSISTENT HALOGENATED HYDROCARBONS IN SEAFOOD PRODUCTS FROM SOUTH CHINA

Guo JY[1, 2], Wu FC[2], Mai BX[1], Zeng EY[1]

[1]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China; [2]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

**Abstract**

A suite of persistent halogenated hydrocarbons (PHHs), including organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers (PBDEs), were determined in a wide variety of seafood products collected from South China in June and October 2005. The results suggested that PHHs in seafood products were predominated by DDTs, and were highly species-specific and location-dependent, probably due to different ecological characteristics for different aquatic species such as feeding habits and habitats and the presence of local input sources. DDTs presently found in the environment appeared to mainly originate from historical discharge, but new input sources could not be excluded. PBDEs were mostly derived from the usage of penta- and deca-BDE technical products. Risk assessment against various standards clearly showed that possible health risk via seafood consumption can not be excluded for DDTs but no significant health consequence for PBDEs was found based on the current toxicological knowledge.

**Introduction**

Persistent halogenated hydrocarbons (PHHs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), are ubiquitous in the environment and often reflect local anthropogenic impacts. They have the potential to bioaccumulate in humans through food chain. Historical use of DDT and HCH and the huge electronics manufacturing capacity and the world's largest electronics-waste recycling sites in South China could greatly subject the local environment to heavy PHH contamination.[1, 2] Several studies have revealed that the residues of DDTs in water and sediments collected in this area remain considerably abundant.[2, 3, 4]

Many previous investigations have suggested that the residual levels of DDTs in foodstuffs have been declined, but those in aquatic products are still increasing.[5] Dietary intake is the major route of human exposure to PHHs and aquatic products could be an important source of PHHs. Therefore, concerns have mostly focused on the health consequences via consumption of aquatic products. In the present study, a variety of seafood products collected from South China were analyzed for a suit of PHHs. The aims were to provide the occurrence of PHHs in different seafood products and to assess potential health risks associated with seafood consumption.

**Material and Methods**

Detailed sampling locations and sample preparation have been described elsewhere and only briefly presented here[6]. Selected seafood products ($n$ = 212), six species of shrimps, two species of crabs and thirteen species of

shellfish (oyster, mussel, ark shell, clam, razor clam and other mollusks), were randomly collected from local fishery markets of South China in June and October 2005. A portion (25–30 g wet weight) of homogenized sample spiked with surrogate standards 2,4,5,6-tetrachloro-*m*-xylene (TMX), PCB 67, PCB 191, $^{13}$C-PCB 141 and PCB 209 and Soxhlet extracted for 48 h. The concentrated extract was subject to gel permeation chromatography for lipid removal. The cleanup and fractionation of PHHs were performed on a silica/alumina column. After solvent exchange to hexane, internal standards (PCB 82, PCB 24, PCB 189 and $^{13}$C-PCB 208) were added to the extracts prior to GC/MS analysis.

Detailed QA/QC procedures have been described elsewhere.[6] The surrogate recoveries of TMX, PCB 67, PCB 191, $^{13}$C-PCB 141, and PCB 209 were 59.8±12.5%, 85.4±15.4%, 91.3±17.3%, 76.8±20.9% and 87.0±18.0%, respectively. Recoveries of 21 OCPs and 11 PBDEs in spiked samples ranged from 68.2±17.2% to 102.7±17.4% and from 82.6±20.0% to 100.7±7.7%, respectively. Reported concentrations were not surrogate recovery corrected.

**Results and Discussion**

*Preliminary Screening of PHHs*. Analyses of the 212 seafood samples indicated that PHHs were predominated by DDTs (sum of *o,p'*- and *p,p'*-DDT, DDD, and DDE) and to a less extent by PBDEs (sum of BDE-28, -47, -66, -99, -100, -138, -153, -154, and -209). The concentrations of other compounds were considerably low. Therefore, only the DDTs and PBDEs data are discussed below.

In general, PHHs concentrations in seafood products were highly species and location dependent (Figure 1). The highest levels of PHHs were observed in oysters (with mean DDTs and PBDEs concentrations of 210.3 and 1.07 ng/g wet weight, respectively), while the lowest residual levels of PHHs were found in shrimps (with mean DDTs and PBDEs concentrations of 1.72 and 0.08 ng/g wet weight, respectively). Besides, PHHs concentrations in the same species also varied widely. For example, DDTs concentrations in crabs ranged from 0.49 to 56.3 ng/g wet weight. This was probably due to different ecological characteristics for different aquatic species, such as feeding habits and habitats, different local background PHHs levels and the presence of local input sources.

*Congener profiles of PHHs.* DDT compositions in seafood products varied considerably with individual samples (Figure 2). The DDT/(DDE+DDD) values ranged from 0 to 4.8 with an arithmetic mean of 0.7. This suggests that DDTs occurred in the study area were mainly originated from historical discharge. However, possible new input of DDT could not be excluded, because more than 20% of the samples had the ratios of DDT/(DDE+DDD) higher than one. As for PBDEs (Figure 3), congener patterns of low brominated BDE congeners were predominated by BDE-47 and BDE-99. Meanwhile, BDE-209 positively occurred in some samples. These indicate that PBDEs in local environments were mostly derived from the usage of penta- and deca-BDE technical products. Furthermore, some congeners (such as BDE-99) could biodegrade in certain organisms (crabs or mantis shrimps), though the mechanism of biodegradation remains unclear.

*Health risk assessment.* Human exposure to PHHs is associated with a wide array of adverse effects on human

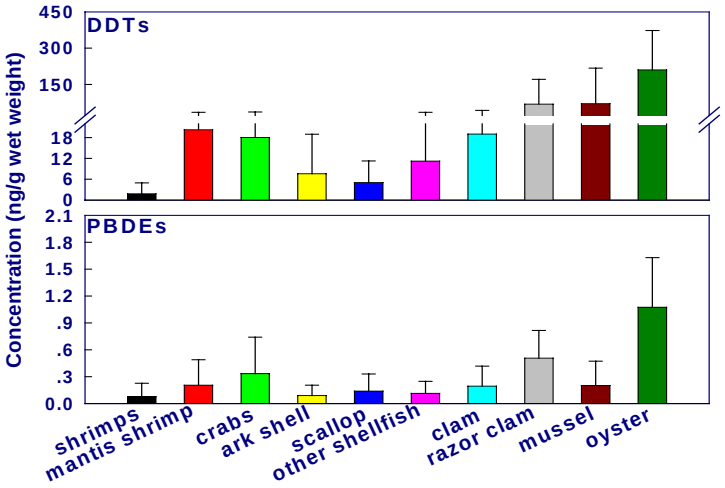


Figure 1. Concentrations of DDTs and PBDEs in seafood products.

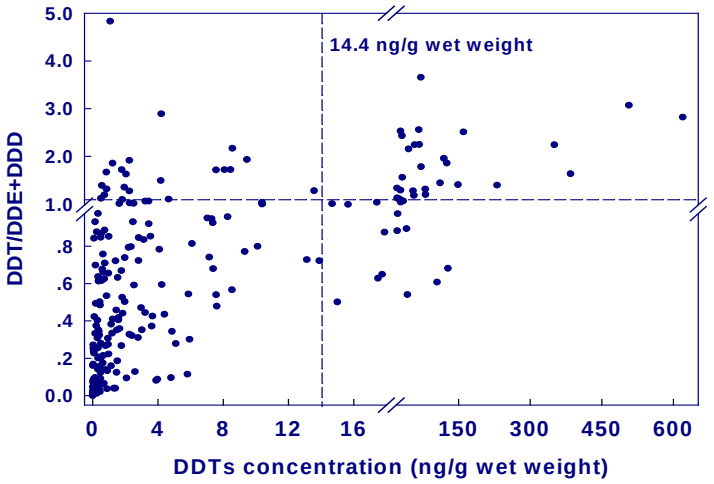


Figure 2. Concentrations and compositions of DDTs in seafood products.

health. According to our recent survey, the estimated dietary intakes (EDIs) of DDTs and PBDEs were 33.0 and 0.25 ng/kg bw/day, respectively. With respect to DDTs, the EDI via seafood consumption in the present work was far below the acceptable daily intake (ADI) (20 g/kg bw/day) recommended by FAO/WHO[7]. However, possible health risk caused by DDT via seafood consumption can not be excluded, because DDTs widely occurred in the samples and 32.1% of the total samples exceeded the maximum residue level (MRL) established by the U.S. Environmental Protection Agency[8] (Figure 2). Furthermore, the EDI of DDTs (33.0 ng/kg bw/day) is much higher than the cancer benchmark concentration of DDTs (1.7 ng/kg day) derived from U.S. EPA's Integrated Risk Information System (IRIS),[9] which suggests that a lifetime cancer risk remains a possibility. As with the potential health risk derived from PBDEs, it should be note that the toxicological and epidemiologic data are extremely limited. Presently, only a lowest observed adverse effect of levels (LOAEL) value of 1 mg/kg/day has been suggested for compounds or mixtures belonging to the PBDE group.[10] The current

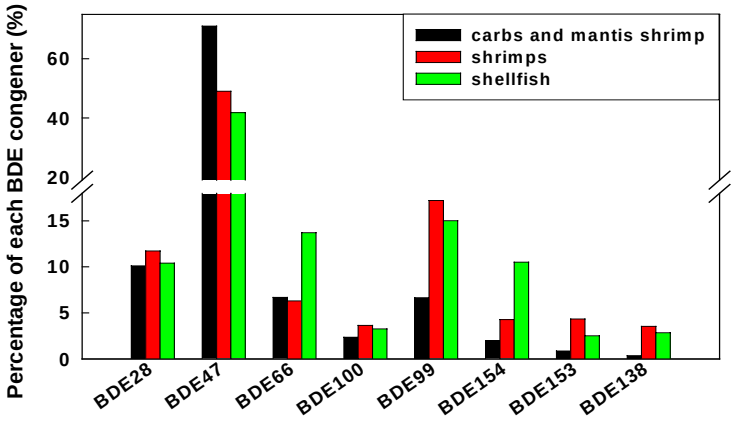


Figure 3. Congener patterns of low brominated BDE congeners in seafood products.

dietary intake (0.25 ng/kg bw/day) was several orders of magnitude lower than the suggested LOAEL, and it seems that consumption of seafood products is safe as far as PBDEs concerned based on the current toxicological knowledge. Nevertheless, it is advisable to continue monitoring DDTs and PBDE in seafood products from South China, because DDTs residues in seafood products remain considerably high and the demand for PBDEs-containing products is still increasing in South China.

**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. Fu J, Mai B, Sheng G, Zhang G, Wang X, Peng PA, Xiao X, Ran R, Cheng F, Peng X, Wang Z, Tang UW. *Chemosphere* 2003; 52:1411.
2. Mai BX, Chen SJ, Luo XJ, Chen LG, Yang QS, Sheng GY, Peng PA, Fu JM, Zeng EY. *Environ Sci Technol* 2005; 39:3521.
3. Zhang G, Parker A, House A, Mai BX, Li XD, Kang YH, Wang ZS. *Environ Sci Technol* 2002; 36:3671.
4. Luo X, Mai B, Yang Q, Fu J, Sheng G, Wang Z. *Mar Pollut Bull* 2004; 48:1102.
5. Nakata H, Kawazoe M, Arizono K, Abe S, Kitano T, Shimada M, Li W, Ding X. *Arch Environ Contam Toxicol* 2002; 43:473.
6. Meng XZ, Zeng EY, Yu LP, Wu FC, Mai BX, Luo XJ, Ran R. *Environ Sci Technol* 2007; 41:1821.
7. Sun F, Wong SS, Li GC, Chen SN. *Chemosphere* 2006; 62:674.
8. US EPA 823-B-94-008. Washington, DC: United States Environmental Protection Agency, 2000.
9. Jiang QT, Lee TK, Chen K, Wong HL, Zheng JS, Giesy JP, Lo KK, Yamashita N, Lam PK. *Environ Pollut* 2005; 136:155.
10. Bocio A, Llobet JM, Domingo JL, Corbella J, Teixido A, Casas C. *J Agric Food Chem* 2003; 51:3191.