RESIDUAL LEVELS OF POLYBROMINATED DIPHENYL ETHERS (PBDEs), DICHLORODIPHENYLTRICHLOROETHANES (DDTs) AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN FRESHWATER AND MARINE FISH FROM HONG KONG MARKETS

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Introduction

The Pearl River Delta has undergone a rapid transition from a traditionally agricultural based economy to an industrial and technological based economy. These has resulted in increased industrial wastewater discharge[1], accompanied by increased risk of persistent organic pollutant (POP) contamination in the region. In South China, industrial products such as integrated circuits, computers, paint toys, textiles, furnishings, electronic appliances, and telecommunications may be the possible sources of BDE contamination. The use of dicofol (which contained DDT as impurities) has become an important source of DDT pollution in the environment. PAHs are by-products of incomplete combustion of organic materials.[35] There are several pathways of PAHs into the water body including petroleum contamination, fall-out from air pollution, and terrestrial runoff.[36]

Our recent study indicated that the levels of DDTs in pond fish samples collected from fish ponds around the Pearl River Delta ranged from 1.5 to 62 ng g^{-1} with 35% of the fish samples exceeded the limit of 14.4 ng g^{-1} for human consumption set by USEPA[2]. Tilapia (*Oreochromis mossambicus*), a freshwater fish purchased from the markets in Hong Kong (with fish supplied from the mainland) showed higher concentrations of PAHs (76.5 ng g^{-1} wet wt) than those collected from Hong Kong fish ponds (60.1 ng g^{-1} wet wt)[3]. A study indicated PBDEs contamination in blubber of male finless porpoises collected from the South China Sea ranged from 84 ng g^{-1} lipid wt sampled in 1990 to 980 ng g^{-1} lipid wt sampled in 2001, showing a significant increase during the investigation period[35]. According to the data of Hong Kong Government in 2004, the estimated local production of marine and freshwater fish and fishery products are 154,933 and 1977 tonnes, respectively and the amount of imported fish exceeded 175,622 tonnes. Therefore, consumption of fish containing elevated concentrations of PBDEs, DDT and PAHs is a public concern.

Henceforth, the major objective of the study was to examine the extent of bioaccumulation of PBDEs, DDTs and PAHs in freshwater and marine fish available in local markets of Hong Kong.

Materials and methods

Twenty species of marine and freshwater fish were purchased at local fish markets. The scientific and common names are listed in Table 1[33,34]. Three individuals of similar size for each species were collected, kept frozen in an ice box and transported immediately to the laboratory.

Fish samples were Soxhlet extracted according to EPA Standard Method 3540C using an acetone and dichloromethane mixture (1:1) for 18 h[4]. The proper clean-up procedures were established for the analyses of different pollutants in these samples. A series of chromatographic columns were applied for sample cleanup such as florisil cleanup (USEPA Standard Method 3620B)[5] and gel permeation cleanup (USEPA Standard Method 3640A)[6]. 22PBDEs (BDE-3, -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -184 and -191), 16PAHs [naphthalene (Nap), acenaphthylene (A), acenaphthene (Ace), fluorine (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenz[a,h]anthracene (DA) and benzo[g,h,i]perylene (BP)] and 3DDTs (*p,p*-DDE, *p,p*-DDD and *p,p*-DDT) will be analyzed by Gas Chromatography- Mass Spectrometry (GC/MS).

Results

Table 1 shows that residual levels of PBDEs, DDTs and PAHs in fish. Total PBDEs in different freshwater fish species ranged from 0.53 to 130 ng g^{-1} wet wt. Among PBDE congeners found in fish, BDE-47, -99 and -100 were commonly found in most fish muscles (Table 2). Spotted snakehead contained significantly higher levels of PBDEs in both ventral (130 ng g^{-1} wet wt.) and axial muscles (14.9 ng g^{-1} wet wt.) than other fish species investigated. The total PBDEs in different marine fish species ranged from 0.95 to 60.6 ng g^{-1} wet wt, with the highest PBDE found in bigeye.

Total DDTs in different freshwater and marine fish species ranged 1.10-127 and 2.30-1018 (ng g^{-1} wet wt).

p,p-DDE was detected in most of the fish muscles (Table 2). In general, ventral muscles of all fish species showed comparatively higher levels of DDTs than the axial muscles. Rice field eel showed significantly higher levels of DDTs in both ventral and axial muscle than the other fish species investigated.

Total PAHs were detected in all fish muscles, ranging from 1.57 to 26.4 ng g^{-1} wet wt for freshwater fish and from 15.5 to 118 ng g^{-1} wet wt for marine fish. Nearly all the 16 PAHs except Bbf, Bkf, BaP and DA were detected in the fish samples. Besides, Nap, F and Phe were found in all fish species (Table 2). In addition, there were large variations of total PAHs among different species of freshwater fish. Catfish and Tongue sole exhibited the highest concentrations of total PAHs in ventral muscle among 10 freshwater and 10 marine fish species, respectively. Grass carp, mud crap and bighead carp had relatively lower concentrations of PAHs than the other species. The results indicated that all potency equivalent concentrations of total PAHs in ventral and axial muscles were below the screening value of 0.67 ng g^{-1} (wet wt) for human consumption set by USEPA.[22]

Discussion

Table 3 compares the concentrations of PBDEs, DDTs and PAHs detected in fish from different parts of the world. Most of PBDE levels detected in fish exceeded the upper range of 3–4 ng g^{-1} wet wt. in wild salmon (*Ptyochromis salmon*) investigated in a global assessment[7]. A European survey indicated the highest concentration in trout (*Salvelinus fontinalis*) collected from mountain lakes was 1.20 ng g^{-1} wet wt.[8] and whitefish (*Salangichthys microdon*) from Swiss lakes contained up to 7.4 ng g^{-1} wet wt.[9]. Elevated levels of PBDEs were also found in finless porpoises (*Neophocaena phocaenoides*)[10]. In comparison with other market fish, the present higher values were comparable to fish from Spain which ranged from 0.088 to 1.02 ng g^{-1} wet wt.[11]and those from USA from 0.011 to 3.73 ng g^{-1} wet wt.[12] A food market-basket study conducted in Belgium reported that the highest total concentration of PBDEs (2.36 ng g^{-1} wet wt.) was found in one fresh salmon fillet[13]. In general, the total PBDE concentrations in fish investigated in our study were comparable to or higher than those from other countries.

Concentrations of DDTs in marine fish were higher than those in freshwater fish and the results were in line with those reported by Nakata[15]. The present study showed that concentrations of DDTs in fish (1.1– 1018 ng g^{-1} wet wt) collected from local markets were higher than those fish collected from East China Sea (0.94– 8.62 ng g^{-1})[14] and Shanghai (9.1 ng g^{-1})[15], but lower than those sampled in Taihu Lake (3700–23500 ng g^{-1}). Taihu Lake is one of the most polluted freshwater bodies in the whole of China[16]. Due to the surface water run off and soil particle erosion, DDT residues are transported from agricultural soils to the lake. Organic matter containing DDTs in the soil is eaten and digested by fish, resulted in elevated concentrations of DDTs in their muscles.

Among the twenty fish species such as golden threadfin bream and catfish exhibited higher concentrations of PAHs than the other species. Bioconcentration from water via the gills, skin, and ingestion of contaminated food or sediment are possible routes for PAHs to accumulate in fish tissues, and the rate of bioaccumulation depends mainly on their feeding preference, general behavior, and trophic level of fish[17, 18]. Marine fish living in contact with sediment, which is a sink for PAHs, can be enriched with these compounds[19]. Production of PAHs during anthropogenic combustion will eventually deposit on remote sites via atmospheric particulate transport[20]. If these particles settled on ocean surface, they can be incorporated onto larger fecal pellets or suspended matter, and will then result in relatively rapid deposition into marine sediments[21]. The present results of total concentrations of PAHs (1.57–118 ng g^{-1} wet wt) are in line with our previous results: tilapia (15.1–92.5 ng g^{-1} wet wt) collected from fishponds and local fish markets in Hong Kong[2], bighead carp, grass carp, crucian carp, tilapia and mandarin fish (25.8–77.1 ng g^{-1} wet wt) from different fishponds in the Pearl River Delta[3].

Conclusion

The PBDE concentrations in fish ranged between 0.53 and 130 ng g^{-1} wet wt. Concentrations of PBDEs in fish were comparable to or higher than those reported from other countries. The results of PBDE levels found in fish commonly consumed in South China raised a concern about PBDE contamination of fishery products.

The compositions and residue concentrations of DDTs observed in this study indicated the past agricultural usage of DDTs is the main source. DDT levels in more than 70% of the marine fish and 45% of the freshwater fish investigated were higher than the guideline of 14.4 ng g^{-1} wet wt set by USEPA[22], suggesting that consumption of this fish in large amounts might pose a human health risk. Nevertheless, the levels of DDTs in fish muscles were lower than China's National Environmental Protection Agency maximum permissible limits set for foodstuffs. In the case of PAHs, the levels of different fish species were similar. The levels of PAHs in all the fish samples were still far below the guideline recommended by USEPA for human consumption.

Due to the increasing concern about POPs and their hazardous impact on environmental and human health

recently, especially on the possible linkage between fish consumption and their human loadings, it is necessary to improve and update information on different POPs in market fish in order to establish a framework for their proper management and control in future. It is also suggested to use ventral muscle as an indicator tissue due to its high fat content, and hence POPs contents, when using fish as a biological indicator for monitoring POPs.

Acknowledgements
Financial support from the Faculty Research Grant, Science Faculty, Hong Kong Baptist University and Group Research, Central Allocation Fund from the Research Grant Council of Hong Kong (HKBU1/03C), Environment and Conservation Fund (ECF/04-05/04) is gratefully acknowledged.

References

1. Chen, H.M., Zheng, C.R., Tu, C. and Zhu, Y.G. *Ambio* 1999; 28: 130–134.
2. Kong, K.Y., Cheung, K.C., Wong, C.R.C. and Wong, M.H. *Water Res.* 2005; 39: 1831–1843.
3. Kong, K.Y., Cheung, K.C., Wong, C.R.C. and Wong, M.H., *J. Environ. Sci. Heal.* 2005; 40: 1–11.
4. USEPA, Method 3540C. US Environmental Protection Agency, Washington, DC. 1996.
5. USEPA, Method 3620B. US Environmental Protection Agency, Washington, DC. 1996.
6. USEPA, Method 3640A. US Environmental Protection Agency, Washington, DC. 1994.
7. Hites, R.A., Foran, J.A., Schwager, S.J., Knuth, B.A., Hamilton, M.C. and Carpenter, D.O. *Environ. Sci. Technol.* 2004; 38: 4945-4949.
8. Vives, I., Grimalt, J.O., Lacorte, S., Guillamon, M. and Barcelo, D. *Environ. Sci. Technol.* 2004; 38: 2338–2344.
9. Zennegg, M., Kohler, M., Gerecke, A.C. and Schmid, P. *Chemosphere* 2003; 51: 545–553.
10. Ramu, K., Kajiwara, N., Lam, P.K.S., Jefferson, T.A., Zhou, K., Tanabe, S. *Environ. Pollut* 2006; 144: 516–523.
11. Bocio, A., Llobet, J.M., Domingo, J.L., Corbella, J., Teixido, A., and Casas, C. *J. Agric. Food Chem.* 2003; 51: 3191–3195.
12. Schecter, A., Papke, O., Harris, T.R., Tung, K.C., Musumba, A., Olson, J. and Birnbaum, L. *Environ. Health Perspect.* 2006; 114: 1515–1520.
13. Voorspoels, S., Covaci, A., Neels, H. and Schepens, P. *Environ. Int.* 2007; 33: 93–97.
14. Jiang, Q.T., Lee, T.K.M., Chen, K., Wong, H.L., Zheng, J.S., Giesy, J.P., Lo, K.K.W., Yamashita, N. and Lam, P.K.S. *Environ. Pollut.* 2005; 136: 155–165.
15. Nakata, H., Kawazoe, M., Arizono, K., Abe, S., Kitano, T., Shimada, H., Li, W. and Ding, X. *Arch. Environ. Con. Toxicol.* 2002; 43: 473–480.
16. Feng, K., Yu, B.Y., Ge, D.M., Wong, M.H., Wang, X.C. and Cao, Z.H. *Chemosphere* 2003; 50: 683–687.
17. Fisher, S.W., 1995; In: Ware, G.W. (Ed.), *Rev. Environ. Contam. T,* 142, Springer, New York, pp. 87–118.
18. Lake, J.L., Mckinney, R., Lake, C.A., Osterman, F.A. and Heltshe, J. *Arch. Environ. Con. Tox.*. 1995; 29: 207–220.
19. Tolosa, I., Bayona, J.M. and Albige´s, J. *Environ. Sci. Technol.* 1996; 30: 2495–2503.
20. Lipiatou, E. and Saliot, A. *Mar. Chem.* 1991; 32: 51–75.
21. Parhl, F.G. and Carpenter, R. *Geochim. Cosmochim. Ac.* 1979; 43: 1959–1972.
22. USEPA, 2000; Guidance for assessing chemical contaminant, data for use in fish advisories, vol. 1: fish sampling and analysis, third ed. EPA 823-R-95-007. Office of Water, Washington, DC.
23. Hajslova, J., Pulkrabova, J., Poustka, J., et al. *Chemosphere* 2007; 69: 1195-1203
24. Thomsen, C., Knutsen, H. K., Liane, V. H., et al. *Mol. Nutri. Food Res.* 2008; 52: 228-237.
25. Bakker, M. I., de Winter-Sorkina, R., de Mul, A., et al. *Mol. Nutri. Food Res.* 2008: 52, 204-216.
26. Leeuwen, S. P. J. and Boer, I. *Mol. Nutri. Food Res.* 2008; 52: 194-203
27. Hayward, D., Wong, J. and Krynitsky, A. J. *Environ Res.* 2007; 103: 46-54.
28. Domingo, J. L., Marti-Cid, R., Castell, V. and Llobet, J. M. *Toxicology* 2008. In press.
29. Mariussen, E., Fjeld, E., Breivik, K., et al. *Sci. Tot. Environ.* 2008; 390: 132-141.
30. Li, X., Gan, Y. P., Yang, X. P., Zhou, J., Dai, J. and Xu, M. *Food Chem.* 2008; 109: 348-354.
31. Erdogrul, O., Covaci, A. and Schepens, P. *Environ. Int.* 2005; 31: 703-711.
32. Dong, J., et al. *Ecology and Environment* 2006; 4, 101-105. (in Chinese).
33. Cheung, K. C., Leung, H. M., Kong, K. Y. and Wong, M. H. *Chemosphere* 2007; 66: 460-468.
34. Cheung, K. C., Zheng, J. S., Leung, H. M. and Wong, M. H. *Chemosphere* 2008; 70: 1707-1720.
35. Qiu, X. H., Zhu, T., Yao, B., Hu, J. X. and Hu, S. W. *Environ. Sci. Technol.* 2005; 39: 4386-4390.
36. Yang, G. P. *Environ. Pollut.* 2000; 108: 163-171.

Table 1. PBDEs, DDTs and PAHs (ng g^{-1} wet weight) in Hong Kong market fish (n=3) [33,34]

Common name	Scientific name	Concentrations (ng g^{-1} wet wt.)					
Pollutants		PBDEs		DDTs		PAHs	
Muscle type		ventral	axial	ventral	axial	ventral	axial
Freshwater fish							
Bighead Carp	*Aristichthys nobilis*	8.10±2.05	1.49±1.01	26.3±5.10	11.2±1.83	2.84±2.91	3.90±2.86
Catfish	*Clarias fuscus*	7.65±5.74	19.5±28.2	40.7±12.1	25.0±11.2	24.8±9.43	9.10±6.47
Grass Carp	*Ctenopharyngodon idellus*	3.51±0.50	1.83±1.10	9.86±0.42	5.51±3.56	3.96±1.06	4.09±1.15
Grey Mullet	*Mulgil cephalus*	20.3±20.7	9.06±7.24	27.1±19.5	11.7±2.78	12.3±6.08	4.77±2.43
Mandarin Fish	*Siniperca kneri*	7.15±3.01	0.38±0.29	82.2±40.5	8.71±4.71	12.8±13.6	1.57±0.53
Mud Carp	*Cirrhina molitorella*	2.29±2.29	3.53±3.57	13.1±2.34	2.38±0.68	8.18±5.25	3.63±1.94
Rice Field Eel	*Monopterus albus*	3.52±0.21	5.49±7.92	125±163	127±159	11.3±6.68	8.31±3.87
Snakehead	*Channa asiatiea*	1.66±2.63	5.60±4.37	13.9±20.0	2.48±3.34	14.6±16.1	7.84±6.16
Spotted Snakehead	*Channa maculate*	130±92.6	14.9±20.6	28.4±7.02	15.8±3.08	13.0±15.5	10.6±6.44
Tilapia	*Oreochromis mossambicus*	2.72±1.97	12.8±6.21	8.90±2.76	1.10±0.60	5.28±1.47	5.47±4.60
Marine fish							
Bartail Flathead	*Platycephalus indicus*	15.4±19.0	2.71±2.39	43.2±30.3	34.1±9.73	38.5±22.5	35.6±17.9
Bigeye	*Priacanthus macracanthus*	60.6±83.7	2.75±1.98	5.67±2.01	2.30±0.75	68.3±16.4	15.5±3.80
Bleeker's Grouper	*Epinephelus bleekeri*	0.76±0.29	3.31±2.62	163±79.1	89.1±38.0	45.8±41.7	37.6±27.7
Goldspotted rabbitfish	*Siganus punctatus*	4.22±0.95	2.59±2.51	12.3±3.24	7.12±1.76	18.1±5.70	24.8±13.3
Golden Threadfin Bream	*Nemipterus virgatus*	9.74±6.84	2.98±2.38	97.0±53.2	27.5±16.0	118±99.6	40.6±31.7
Orange-spotted Grouper	*Epinephelus coioides*	1.61±0.31	2.62±2.20	5.43±7.27	4.18±7.10	50.2±56.3	30.2±20.0
Snubnose Pompano	*Trachinotus blochii*	6.57±1.95	3.29±0.39	1018±703	409±386	67.2±29.1	48.7±23.9
Tongue Sole	*Cynoglossus robustus*	5.07±2.45	2.65±2.32	36.2±4.92	15.5±3.31	145±171	37.7±44.6
Yellow Croaker	*Pseudosciaena crocea*	1.56±1.13	2.55±1.81	142±86.6	64.6±40.5	115±108	53.5±9.00
Yellow Seafin	*Acanthopagrus latus*	7.77±6.27	4.42±4.06	45.6±19.9	23.7±6.51	67.1±18.6	57.0±20.8

Table 2. Concentration range (ng g^{-1} wet weight) of PBDEs, PAHs and DDTs congeners in freshwater and marine fish[33,34]

	Congeners																				
PBDE	-3	-7	-15	-17	-28	-47	-49	-66	-71	-77	-85	-99	-100	-119	-126	-138	-153	-154	-156	-183	-184	-191
Freshwater fish	nd-1.74	nd-0.38	nd-0.14	nd-0.09	nd-1.31	0.26-41.1	nd-1.29	nd-0.74	nd-0.54	nd	nd-0.23	0.05-60.9	0.12-12.1	nd	nd-0.08	nd-0.18	nd-4.63	nd-2.72	nd-0.93	nd	nd	nd-0.27
Marine fish	nd-0.42	nd-0.29	nd-0.05	nd	nd-0.23	0.26-9.21	nd-0.38	nd-0.88	nd-0.35	nd-0.06	nd-0.56	0.10-39.2	0.14-3.72	nd-0.09	nd-0.07	nd-0.11	nd-3.22	nd-2.48	nd-0.08	nd	nd	nd

PAHs	Nap	A	Ace	F	Phe	Ant	Flu	Pyr	BaA	Chr	BbF	Bkf	Bap	Ip	DA	BP
Freshwater fish	0.61-6.92	nd-0.91	nd-1.41	0.07-2.00	0.28-4.36	nd-2.00	nd-1.74	nd-2.23	nd-0.36	0.06-0.92	nd	nd	nd	nd-0.39	nd	nd-0.2
Marine fish	9.07-39.2	nd-2.21	0.11-6.36	0.11-5.38	1.83-33.7	nd-7.80	nd-23.8	nd-17.8	0.16-63.9	nd-25.2	nd	nd	nd	nd	nd	nd

DDTs	*pp*-DDE	*pp*-DDD	*pp*-DDT
Freshwater fish	0.68-75.2	0.31-19.7	n.d.-3.50
Marine fish	2.58-244	n.d.-641	n.d.-133

Table 3. Concentrations of persistent organic pollutants in fish tissues

Species	Locations	Concentration (ng g^{-1} ww)			Reference
		PBDEs	PAHs	DDTs	
Anchovy	Spain	0.610			28
Bartail flathead	Hong Kong	9.05	37.1	38.7	33, 34
Bigeye	Hong Kong	31.7	1.90	3.99	33, 34
Bighead carp	Hong Kong	4.80	3.37	18.8	33, 34
	Pearl River, China		30.9-410	5.47-125	32
Bleeker's grouper	Hong Kong	2.04	41.7	126	33, 34
Bluefish	United States	0.7-38.0			27
Brown trout	Norway	0.30-342			29
Burbot	Norway	135-781			29
Carp	Turkey	0.02-1.30		4.50-170	31
	Turkey	nd-1.50		8.4-246	31
	Hong Kong	2.91	5.90	7.75	33, 34
Catfish	Hong Kong	13.6	17.0	32.9	33, 34
Eel	Hong Kong	4.51	9.80	126	33, 34
	Dutch	<0.40-230			26
	Netherlands	4.16			25
Golden thread-fin bream	Hong Kong	6.35	79.0	62.5	33, 34
	Czech	9.80			23
Goldfish	Beijing, China			7.54-25.4	30
Goldspotted rabbitfish	Hong Kong	3.41	21.5	9.70	33, 34
Grass carp	Hong Kong	2.67	4.03	7.70	33, 34
Grey mullet	Hong Kong	14.7	8.55	19.4	33, 34
Guillemot	Norway	192			29
Hake	Spain	0.221			28
Mackerel	Spain	1.12			28
Mandarin fish	Hong Kong	3.77	7.20	45.5	33, 34
Orange spotted grouper	Hong Kong	2.12	40.2	4.81	33, 34
Perch	Czech	3.80			23
Red mullet	Spain	0.769			28
Rockfish	United States	1.70-12.0			27
Salmon	Spain	2.02			28
Smelt	Norway	6.20			29
Snakehead	Hong Kong	3.63	11.2	8.20	33, 34
Snubnose poampano	Hong Kong	4.93	58.0	714	33, 34
Sole	Spain	0.242			28
Spotted snakehead	Hong Kong	36.3	5.90	15.2	33, 34
Swordfish	Spain	0.977			28
Tilapia	Hong Kong	7.60	5.40	5.00	33, 34
Tongue sole	Hong Kong	3.86	91.4	25.9	33, 34
Trout	United States	70.8-344			24
Weather loach	Beijing, China			15.4-44.2	30
Wels	Turkey	0.06-6.70		22.1-960	31
Yellow croaker	Hong Kong	2.06	84.3	103	33, 34
Yellow seafin	Hong Kong	6.10	62.1	34.7	33, 34