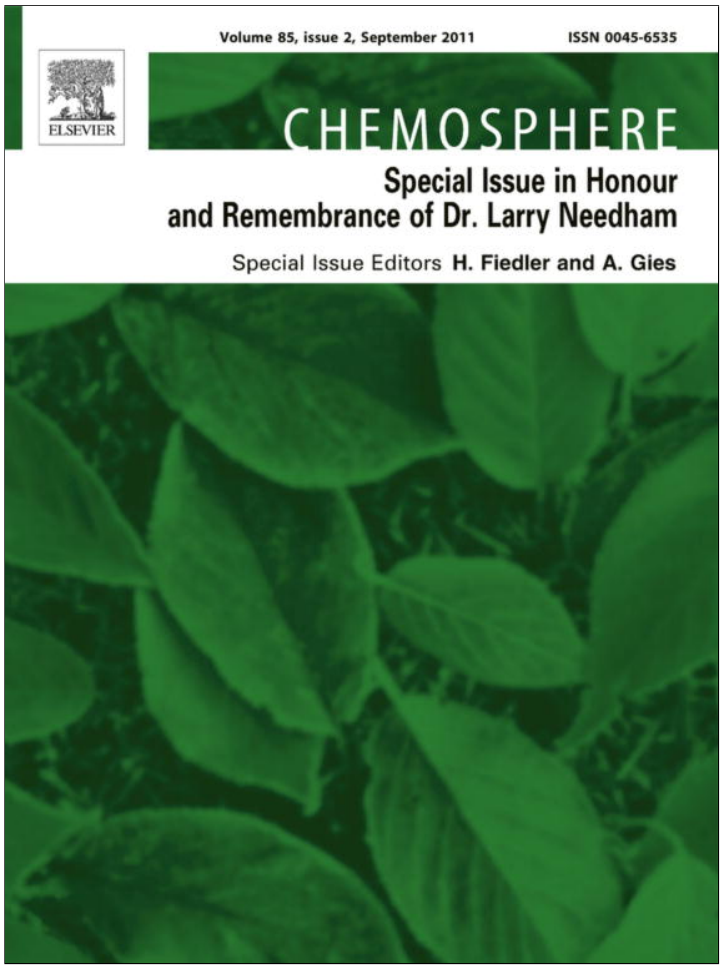

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Risk assessment for human consumption of perfluorinated compound-contaminated freshwater and marine fish from Hong Kong and Xiamen

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ABSTRACT

Perfluorinated compounds (PFCs) are man-made fluoro-surfactants that are identified as global pollutants and can pose health risks to humans and wildlife. Two aspects of risk assessment were conducted in this study, including exposure and response. Exposure was estimated by using the concentrations of PFCs in fish and applying standard exposure factors. Among different PFCs, PFOS, PFOA, PFNA, PFDA, PFUdA and PFTrDA were detected. Total concentrations of PFC in fish ranged from 0.27–8.4 ng g^{-1} to 0.37–8.7 ng g^{-1} respectively in Hong Kong and Xiamen. The calculated hazard ratio (HR) of PFOS for all fish was less than 1.0. However, the HR for mandarin fish in Hong Kong and bighead carp, grass carp and tilapia in Xiamen, had HR values of approximately 0.5, indicating that frequent consumption of these 4 more contaminated fish species might pose an unacceptable risk to human health. Our data support the notion that the released/disposed chemical pollutants into water systems make fish a source of environmental toxicants to humans. The risks and potential effects of PFCs to health of coastal population in the Pearl River Delta are of concern.

1. Introduction

Perfluorinated compounds (PFCs) are man-made fluorinated hydrocarbons that have been manufactured since the late 1940s (Paul et al., 2009). The family of PFC includes perfluoroalkyl sulfonates (PFASs) and carboxylates (PFCAs), that can be synthesized directly or formed indirectly through degradation of fluorotelomer alcohols (FTOHs) or fluoroalkyl sulfonamides (FOSAs) (Loewen et al., 2008). PFCs have unique chemical stability and inertness that allow their extensive applications in surface protecting agents, such as textiles, paper products and carpets. In addition their surface-active properties make them useful as lubricants, coating formulations and fire-fighting foams (Paul et al., 2009). Moreover these unique chemical properties also make PFCs ubiquitous in the environments (Giesy and Kannan, 2001, 2002) as other persistent organic pollutants (POPs) (Mak et al., 2009; Paul et al., 2009). The residues of PFCs, including perfluorooctanesulfonate (PFOS) can be found in the environment, including marine and terrestrial animals at ng g^{-1} level (Kannan et al., 2005b; Dai et al., 2006; Gulkowska et al., 2006; Shi et al., 2010), surface fresh and seawater at ng L^{-1} levels (Taniyasu et al., 2003; So et al., 2004; Ju et al., 2008; Mak et al., 2009). Even in humans, PFCs were detectable in breast milk (So et al., 2006a,b) and blood plasma at ng mL^{-1} levels (Yeung et al., 2008). From 1949 to 2002, approximately 3665 t of PFOS had been produced (Paul et al., 2009). With the increasing concern of PFOS-related toxicities reported in animals (Newsted et al., 2005; Beach et al., 2006; Betts, 2007; Giesy et al., 2009; Liu et al., 2010), the production and the use of PFOS and PFOS-related products has been discontinued since year 2000 (3M, 2008).

Food consumption is the most important route for human exposure to many chemical contaminants (Brustad et al., 2008; Dovydaitis, 2008; Genuis, 2008), contributing over 90% of total lifetime exposure. In coastal areas with industrial activities, the released/disposed chemical pollutants into water systems make fish a source of various environmental toxicants to humans (Li et al., 2010), including PFCs (Naile et al., 2010). In Pearl River Delta (PRD) of China, consumption of contaminated fish is one of the main pathways of human exposure to organic pollutants (Kannan et al., 1997). Hong Kong was ranked 6th in global fish consumption

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(WWF, 1999; ECP, 2000), where the amount of fish consumption was about 60 kg per person per year (Dickman and Leung, 1998). Thus there is an increasing concern of health effects of PFC exposure via fish consumption (So et al., 2004, 2006a,b). In the present study, concentrations of PFCs were measured in 20 species of freshwater and marine fish collected from Hong Kong and Xiamen, China. Risk assessment of local people exposure to PFCs through fish consumption was assessed.

2. Materials and methods

2.1. Samples, chemicals and instrumentation

2.1.1. Sample collection

A total of 20 fish species, including 10 species of freshwater and 10 species of marine fish, were purchased in 2009 from local markets in Hong Kong, China. A total of 16 species of eight freshwater fish and eight marine fish were collected from local markets in Xiamen, China at the same year (Fig. S1 and Table S1). The sources of each fish species and the number of replicates for them are listed in Table S1.

2.1.2. Sample preparation

All the muscle from a single fish was scraped from skin, head, tail and bones, mixed thoroughly using a homogenizer (Polytron®, Capitol Scientific, Inc., Austin, United States. The homogenate was then wrapped in an aluminum foil and was stored at −20 °C. To avoid cross contamination among different samples, knives, chopping boards and some parts of the homogenizer were washed in Milli-Q water (Millipore, Billerica, United States) and then in methanol for every preparation.

2.1.3. Chemical materials for instrumental analysis

A mixture of standard solution of perfluoroalkylcarboxylic acids (PFCAs) [i.e. perflurotoheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluoroononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA)] and perfluoroalkylsulfonates (PFASs) [i.e. sodium perfluorohexanesulfonate (PFHxS) and sodium perfluorooctanesulfonate (PFOS)] as well as a mass-labeled standard solution (used as the internal standard, including perfluoro-(1,2,3,4-$^{13}C_4$)octanoic acid (MPFOA), perfluoro-(1,2,3,4,5-$^{13}C_5$)nonanoic acid (MPFNA), perfluoro-(1,2-$^{13}C_2$)decanoic acid (MPFDA), perfluoro-(1,2-$^{13}C_2$)undecanoic acid (MPFUdA), perfluoro-(1,2-$^{13}C_2$)dodecanoic acid (MPFDoA) and sodium perfluoro-1-(1,2,3,4-$^{13}C_4$)octanesulfonate (MPFOS)) were purchased from Wellington Laboratories (Ontario, Canada). Purities of the analytical standards were greater than 98%. Methyl tert-butyl ether (MTBE), methanol and acetonitrile were purchased from Tedia Company Inc. Tetrabutylammonium hydroxide solution (TBA), sodium carbonate and sodium hydrogen carbonate were from Sigma–Aldrich (Missouri, United States).

2.1.4. Sample extraction

The procedure used was the ion pairing method (Wang et al., 2008), followed by using solid phase extraction (SPE)-Oasis HLB cartridge (Waters, Milford, United States) for cleanup (So et al., 2004). Briefly, the volume of 0.2 g of homogenized fish muscle was adjusted to 1 mL with Milli-Q water before the extraction. The sample was then mixed with the internal standard (1 ng), 1 mL of 0.5 M TBA, 2 mL of 0.25 M sodium carbonate buffer and 5 mL of MTBE, followed by mixing in a reciprocating shaker (HS 501 digital shaker, Janke & Kunkel IKA-Labortechnik) at 250 rpm for 20 min. Organic and aqueous layers were separated by centrifugation at 3000 rpm for 15 min. Four milliliter of the organic phase was collected and was transferred into a new 15 mL PP tube. The extraction procedure was repeated twice. All three organic phases were pooled and mixed with 2 mL of methanol. The mixed solution was then concentrated to 1 mL under high purity grade nitrogen gas ($N_2 \geqslant 99.995\%$, Hong Kong oxygen) in a nitrogen evaporator (N-EVAP112, Organomation Associates, Inc. Massachusetts, USA). The 1 mL extracts was cleaned by SPE using Oasis HLB cartridges. The eluate was blow-dried using N_2 gas and redissolved in 1 mL of 40% acetonitrile/60% 10 mM of ammonium acetate in Milli-Q water.

2.1.5. Instrumental analysis

The detection of PFCs was performed using an Agilent 1200 high-performance liquid chromatograph coupled with tandem mass spectrometry (HPLC–MS/MS, Agilent 1200 series, Agilent Technologies, California, USA). A 30 μL aliquot of the extract was injected into a guard column (Zorbax Eclipse Plus-C8, 2.1 mm i.d. × 12.5 mm length, 5-μm; Agilent Technologies), which was connected to a Zorbax Eclipse Plus C8 column (2.1 mm i.d. × 100 mm length, 3.5-μm; Agilent Technologies). The instrumental parameters for PFC analysis were listed in Table S2.

2.1.6. Quality assurance and quality control

To achieve lesser detection limits, all accessible PTFE and fluoropolymer tubes/parts were replaced by PEEK (polyether ether ketone) materials to minimize background signals (Yamashita et al., 2004). All auto-sampler vials and septa used were made of PP materials (Grace Davison Discovery Science, Deerfield, United States). Matrix spike recovery ($n = 2$) were determined by spiking 1 ng of mixed target standards into the fish muscle samples, followed by the extraction and analysis as described in the previous section. The values of matrix recoveries were 79%, 92%, 114%, 87%, 110%, 98%, 111%, 89%, 87%, 108% for PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFHxS and PFOS, respectively. Procedural blanks were tested every 10–15 samples to check for possible laboratory contaminations and interferences. The concentrations of PFC in the sample extracts were quantified using five- to seven-point calibration curves constructed with the analysis of the external standards in the concentration ranged from 0.25 to 10 ng mL^{-1}. The regression coefficients (r^2) of the calibration curves for all target analytes were higher than 0.994. The limit of quantification (LOQ) (S/N > 10) was estimated at the lowest concentration point of the calibration curve, which was at least five times greater than the procedural blank. In this study, the LOQ was 0.25 ng g^{-1}, wet weight (ww) for PFHxS, PFOS, PFUdA, PFDoA, PFTrDA and PFTeDA. The LOQ for PFHpA, PFNA and PFDA was 0.5 ng g^{-1}, ww while the LOQ for PFOA was 1 ng g^{-1} ww. After the analysis of every 10 samples, duplicated sample inspection were conducted to check the instrumental consistency.

2.2. Statistical analysis

Statistical evaluation was conducted using SPSS16. Data normality was checked by Shapiro–Wilk and Q–Q plot. The Spearman's correlation analysis was used to examine the possible correlation among PFOS, PFUdA and PFTrDA in the samples, and with body lipid content. The data are presented as the mean ± SD. Groups are considered significantly different if $p < 0.05$.

3. Results and discussion

3.1. PFC contamination in the fish samples from Hong Kong and Xiamen

In this study, PFCs were detectable in 70–80% of the freshwater and marine fish species collected from Hong Kong. In Xiamen, 100%

and 75% of the freshwater and marine fish species contained detectable PFCs. The concentrations of PFHpA, PFDoA, PFTeDA and PFHxS were less than the LOQs while PFOS, PFOA, PFNA, PFDA, PFUdA and PFTrDA were detected in 16 Hong Kong fish species and the 14 Xiamen fish species (Table 1).

3.1.1. PFOS concentrations in the fish from Hong Kong and Xiamen

PFOS was the predominant PFAS detected in the fish. In Hong Kong samples, there were seven marine and eight freshwater fish species that contained detectable concentration of PFOS. The concentrations ranged from 0.27 ± 0.15 to 4.5 ± 0.38 ng PFOS g^{-1}, wet weight (ww). The greatest concentration of PFOS was found in mandarin fish (4.5 ± 0.38 ng PFOS g^{-1}, ww), followed by yellow croaker (1.5 ± 0.65 ng PFOS g^{-1}, ww) and bartail flathead (1.1 ± 0.36 ng PFOS g^{-1}, ww). The concentrations of PFOS in the other 12 fish species were less than 1.0 ng g^{-1}. The mean concentration of PFOS in the marine fish (0.71 ± 0.47 ng g^{-1}, ww) was comparable with the concentration observed in the freshwater fish (1.0 ± 1.4 ng PFOS g^{-1}, ww). PFOS was detected in six species of marine fish and eight species of freshwater fish from Xiamen. The concentrations ranged from 0.37 ± 0.12 to 5.98 ± 0.91 ng PFOS g^{-1}, ww (Table 1). The greatest concentration of PFOS was found in the tilapia (5.98 ± 0.91 ng PFOS g^{-1}, ww), followed by grass carp (4.4 ± 1.1 ng PFOS g^{-1}, ww) and bighead carp (3.9 ± 1.2 ng PFOS g^{-1}, ww). The mean PFOS concentration in the marine fish was 0.91 ± 0.74 ng PFOS g^{-1}, ww while in the freshwater fish it was 2.6 ± 1.9 ng PFOS g^{-1}, ww.

In this study, we observed that the freshwater fish was more commonly contaminated with PFOS than the marine fish. Approximately 80% and 100% of the freshwater fish samples collected respectively from Hong Kong and Xiamen contained detectable concentrations of PFOS. In the marine fish, PFOS was detected in 70% and 75% of the fish from Hong Kong and Xiamen. The ratio of PFOS concentration measured in Hong Kong freshwater/marine fish was 1.5, while in Xiamen the ratio was 2.8. Since the calculated ratio was greater than 1.0, this supports the assumption that the freshwater fish contained greater concentrations of PFOS. This is probably due to the fact that the solubility of PFOS is 40 times greater in freshwater than that in seawater (Moore, 2003). Water sample analysis from the river of the PRD region (12 pg mL^{-1}) indicated greater concentration of PFOS than in the South China Sea (3.1 pg mL^{-1}) (So et al., 2004). Nevertheless the average PFOS concentration in Hong Kong freshwater fish (1.0 ± 1.4 ng PFOS g^{-1}, ww) was less than that in the freshwater fish from Xiamen (2.6 ± 1.9 ng PFOS g^{-1}, ww). This observation may indicate that freshwater aquaculture systems in Xiamen were more contaminated with PFOS than those in the areas around Hong Kong.

The concentrations of PFOS in the fish studied in Hong Kong and Xiamen, were comparable with those reported from other cities in China. The concentrations of PFOS in marine fish from Guangzhou (2.2 ± 3.4 ng g^{-1}), Zhoushan (1.2 ± 0.70 ng g^{-1}) and Qinghai-Tibetan Plateau (1.6 ± 1.5 ng g^{-1}) (Gulkowska et al., 2006; Shi et al., 2010), were similar to or greater than the mean concentrations of PFOS in the fish from Hong Kong (0.88 ± 1.1 ng g^{-1}) and Xiamen (1.9 ± 1.7 ng g^{-1}) (Fig. 1). The concentration of PFOS detected in Chinese sturgeon (0.09 ng g^{-1}) from Yangtze River (Peng et al., 2010), however was considerably lesser than the present study. This is probably due to the fact that the Chinese sturgeons spend most of their adult life in the open sea. Besides, it may also result

Table 1
PFC concentrations (ng g^{-1} ww) in Hong Kong and Xiamen fish species.

Sample source	Fish name	PFOS Mean ± SD	PFOA Mean ± SD	PFNA Mean ± SD	PFDA Mean ± SD	PFUdA Mean ± SD	PFTrDA Mean ± SD	Total PFCs
Hong Kong freshwater fish	Big head carp	0.73 ± 0.31	1.4 ± 0.62	0.69 ± 0.29	–	0.51 ± 0.14	–	3.3
	Grey Mullet	–	–	–	–	–	–	–
	Mandarin fish	4.5 ± 0.38	1.1 ± 0.43	0.89 ± 0.14	1.0 ± 0.06	0.55 ± 0.09	0.39 ± 0.03	8.4
	Grass carp	0.55 ± 0.14	–	–	–	–	–	0.55
	Mud fish	–	–	–	–	–	–	–
	Spotted snakehead	0.47 ± 0.09	–	–	–	0.33 ± 0.03	0.30 ± 0.09	1.1
	Rice field eel	0.27 ± 0.12	–	–	–	–	–	0.27
	Snakehead	0.58 ± 0.24	–	–	–	–	–	0.58
	Catfish	0.51 ± 0.05	–	–	–	–	–	0.51
	Tilapia	0.64 ± 0.12	–	–	–	–	–	0.64
Hong Kong marine fish	Tongue sole	0.84 ± 0.18	–	0.65 ± 0.07	–	0.50 ± 0.19	0.46 ± 0.09	2.5
	Bartail flathead	1.1 ± 0.36	–	–	–	–	0.29 ± 0.06	1.4
	Orange-spotted grouper	0.57 ± 0.26	–	–	–	–	–	0.57
	Yellow croaker	1.5 ± 0.65	–	–	–	0.71 ± 0.05	0.75 ± 0.06	3.0
	Yellow seafin	0.37 ± 0.02	–	–	–	–	–	0.37
	Snubnose pompano	–	–	–	–	–	–	–
	Bigeye	–	–	–	–	0.39 ± 0.05	0.37 ± 0.08	0.76
	Goldspotted rabbitifish	0.27 ± 0.15	–	–	–	–	–	0.27
	Golden threadfin bream	0.31 ± 0.23	–	–	–	–	–	0.31
	Bleeker's grouper	–	–	–	–	–	–	–
Xiamen freshwater fish	Big head carp	3.9 ± 1.2	1.2 ± 0.57	0.87 ± 0.27	0.82 ± 0.01	0.81 ± 0.24	1.1 ± 0.55	8.7
	Grey Mullet	1.2 ± 0.36	–	–	–	0.54 ± 0.14	0.42 ± 0.28	2.1
	Mandarin fish	1.2 ± 0.32	–	–	–	0.58 ± 0.29	0.36 ± 0.09	2.2
	Grass carp	4.4 ± 1.05	–	0.82 ± 0.17	–	0.28 ± 0.13	–	5.5
	Spotted snakehead	1.9 ± 0.45	–	–	–	–	–	1.9
	Rice field eel	1.0 ± 0.44	–	–	–	–	–	1.5
	Catfish	0.49 ± 0.05	–	–	–	–	–	0.49
	Tilapia	5.98 ± 0.91	–	0.65 ± 0.10	–	0.27 ± 0.01	–	6.9
Xiamen marine fish marine	Tongue sole	0.65 ± 0.16	–	0.61 ± 0.04	–	–	–	1.3
	Bartail flathead	0.76 ± 0.19	–	–	–	–	–	0.76
	Orange-spotted grouper	0.75 ± 0.09	–	–	–	–	–	0.75
	Yellow croaker	2.39 ± 0.61	1.0 ± 0.62	0.86 ± 0.15	0.60 ± 0.04	0.59 ± 0.02	–	5.5
	Yellow seafin	0.53 ± 0.02	–	–	–	–	–	0.53
	Snubnose pompano	–	–	–	–	–	–	–
	Bigeye	–	–	–	–	–	–	–
	Goldspotted rabbitifish	0.37 ± 0.12	–	–	–	–	–	0.37

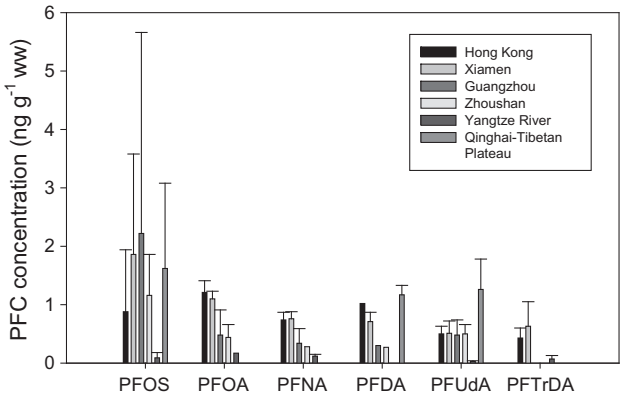

Fig. 1. The comparison of PFC concentrations (ng g^{-1}) in the fish samples collected from Hong Kong, Xiamen (the present study) and other areas in China: Guangzhou and Zhoushan (Gulkowska et al., 2006), Yangtze River (Peng et al., 2010) and Qinhai-Tibetan Plateau (Shi et al., 2010).

from that Chinese sturgeon accumulate much more PFOS in their egg and liver than muscle (Peng et al., 2010).

The concentrations of PFOS in the fish from Hong Kong and Xiamen were greater than those in fish from some European and Asian countries, such as Netherlands, Norway, Denmark, Turkey, Vietnam, Indonisia and Bangladesh, where concentration ranged from 0.01 to 0.60 ng PFOS g^{-1}, ww (van Leeuwen et al., 2009). However the concentration observed in this study was considerably less than those in fish from Lake Ontario where the concentration ranged from (6.0 to 96 ng PFOS g^{-1}, ww) (Furdui et al., 2008), and much less than the concentration (2000 ng PFOS g^{-1}, ww) detected in Minnesota Lakes and Rivers near the major PFC manufacturing plants (Delinsky et al., 2010).

3.1.2. PFCA concentrations in the fish from Hong Kong and Xiamen

The predominant PFCA compounds found in Hong Kong and Xiamen fish were: PFDA, PFNA, PFOA, PFTrDA and PFUdA (Table 1). PFUdA was detected in the three marine and three freshwater fish species from Hong Kong. The concentration ranged from 0.33 ± 0.03 to 0.71 ± 0.05 ng g^{-1}, ww. The greatest concentration of PFUdA was measured in the marine fish yellow croaker (0.71 ± 0.05 ng g^{-1}, ww). PFTrDA was found in four marine and two freshwater fish species, with the concentration ranging from 0.29 ± 0.06 to 0.75 ± 0.06 ng g^{-1}, ww. PFOA was detected in the two freshwater fish (big head carp: 1.4 ± 0.62 ng g^{-1}, ww and mandarin fish: 1.1 ± 0.43 ng g^{-1}, ww). PFNA was found in the two freshwater fish (mandarin fish: 0.89 ± 0.14 ng g^{-1}, ww and big head carp: 0.69 ± 0.29 ng g^{-1}, ww) and one marine fish (Tongue sole: 0.65 ± 0.07 ng g^{-1}, ww). PFDA was only detected in the mandarin fish at a concentration of 1.0 ± 0.06 ng g^{-1}, ww. In Xiamen, PFUdA was detected in the five species of freshwater and one species of marine fish, with concentration ranging from 0.27 ± 0.01 to 0.81 ± 0.24 ng g^{-1}, ww (Table 1). The greatest concentration of PFUdA was found in bighead carp (0.81 ± 0.24 ng g^{-1}, ww). PFTrDA was only detected in freshwater fish species with concentration ranging from 0.36 ± 0.09 to 1.1 ± 0.55 ng g^{-1}, ww. PFNA was found in the three freshwater and two marine fish species, ranging from 0.61 ± 0.10 to 0.87 ± 0.27 ng g^{-1} and 0.61 ± 0.04 to 0.86 ± 0.15 ng g^{-1}, respectively. PFOA and PFDA were detected in big head carp (1.2 ± 0.57 and 0.82 ± 0.01 ng g^{-1}, ww) and yellow croaker (1.0 ± 0.62 and 0.60 ± 0.04 ng g^{-1}, ww). Both big head carp and yellow croaker were contaminated with the greatest concentrations of most PFCAs.

The mean concentrations of PFUdA in the fish from Hong Kong and Xiamen were comparable to the fish collected from Guangzhou and Zhoushan and the Qinghai-Tibetan Plateau of China, but nearly 17-fold greater than those detected in the Chinese Sturgeon collected from the Yangtze River (Fig. 1). The mean concentrations of PFTrDA in the fish from Hong Kong and Xiamen were 0.43 ± 0.17 and 0.63 ± 0.42 ng g^{-1} ww, respectively. These values are at least 6-fold greater than those detected in Chinese Sturgeon collected from the Yangtze River (0.07 ± 0.06 ng g^{-1}, ww) (Peng et al., 2010). The mean concentrations of PFOA, PFNA and PFDA in the fish from Hong Kong and Xiamen were significantly greater than those in the fish from Guangzhou, Zhoushan, the Yangtze River and the Qinghai-Tibetan Plateau (Fig. 1).

3.2. Relationship among PFC concentrations and fish body weights

It was previously reported that predators at higher trophic-level accumulated more PFOS than did organisms at lower trophic-level (Kannan et al., 2005a). In this study carnivorous fish, such as the mandarin fish from Hong Kong and the omnivorous tilapia from Xiamen contained the greatest concentrations of PFOS. This result is consistent with the fact that these two fish species are fed with fingerlings, shrimp and small fish. The concentrations of PFOS in the mandarin fish from Hong Kong (4.5 ng g^{-1}, ww) were significantly greater than those collected from Xiamen (1.2 ng g^{-1}, ww). This difference was probably due to the different supplies of feed and/or the dissimilar fish body size sold in the markets of the two cities. In Hong Kong the average body size of mandarin fish (body mass, 1519 g) was larger than those from Xiamen (body mass, 288 g) (Table S1). This general observation is consistently observed in the herbivorous fish (bighead carp and grass carp), that were sold in the markets also were of greater body mass and length than other fish species. These fish were thus older and had a higher opportunity to accumulate PFOS. In this study, no significant correlation between the concentration of PFC and the fish lipid content was noted (data not shown). This is consistent with the fact that PFOS tends to bind preferentially to proteins in liver and blood plasma than lipid (Jones et al., 2003). A significant correlation was observed between the concentrations of PFUdA and PFTrDA ($p < 0.05$) (Fig. S2). There were no other significant correlations among other PFCs.

3.3. Risk assessment of fish consumption

Since benchmark doses for PFUdA, PFTrDA, PFNA and PFDA are not available, in this study the hazard ratio (HR) was calculated on the basis of PFOS and PFOA concentrations measured in the fish. The hazard ratio (HR) was calculated by dividing the average daily intake (ADI) by the RfD. The ADI level was calculated [ADI μg kg^{-1} d^{-1} (d^{-1}) = fish consumption (g kg^{-1} d^{-1}, wet weight basis) × PFOS/PFOA concentration (μg g^{-1}, wet weight basis)], with an assumption that the average body weight for Asian people is 60 kg (Table 2). The amount of fish consumption was about 60 kg per person per year in Hong Kong (Dickman and Leung, 1998). Since there is no data of Xiamen people's fish consumption, the same fish consumption rate was used for the calculation. The RfD of PFOS and PFOA were 0.025 μg g^{-1} d^{-1} and 0.33 μg g^{-1} d^{-1} respectively. The values were established on the basis of the rat chronic carcinogenicity studies and rat multigenerational studies, respectively (Thayer, 2002).

The average daily intakes (ADI) of PFOS and PFOA were 2.4 ± 2.9 and 3.3 ± 0.54 ng kg^{-1} bw d^{-1} for Hong Kong population. In Xiamen the corresponding values were 5.1 ± 4.7 and 3.0 ± 0.35 ng kg^{-1}, bw d^{-1}. These values are greater than that reported in Guangzhou (2.8 and 0.19 ng kg^{-1}, bw d^{-1}), Zhoushan (1.7 and 0.19 ng kg^{-1}, bw d^{-1}) (Gulkowska et al., 2006), and Norway, with the mean (range) ADI of PFOS and PFOA of 0.78 (0.02–5.9) and 0.09 (0.01–0.60) ng kg^{-1}, bw d^{-1} (Haug et al., 2010). More-

Table 2
Average daily intakes (ADI) and hazard ratio (HR) values for Hong Kong and Xiamen residents to PFC exposure via fish consumption.

Sample source	Fish name	Concentration ($\mu g\ g^{-1}$)			ADI ($\mu g\ kg^{-1}\ d^{-1}$)			Hazard ratio (HR)			Total HR
		PFOS	PFOA	Other PFCs	PFOS	PFOA	Other PFCs	PFOS	PFOA	Other PFCs	
Hong Kong freshwater fish	Big head carp	7.3×10^{-4}	1.4×10^{-3}	1.2×10^{-3}	0.002	0.0037	0.0033	0.08	0.011	0.13	0.22
	Mandarin fish	4.5×10^{-3}	1.1×10^{-3}	2.9×10^{-3}	0.012	0.0029	0.0078	0.49	0.009	0.31	0.81
	Grass carp	5.5×10^{-4}	–	–	0.0015	–	–	0.06	–	–	0.06
	Spotted snakehead	4.7×10^{-4}	–	6.3×10^{-4}	0.0013	–	0.0017	0.052	–	0.07	0.12
	Rice field eel	2.7×10^{-4}	–	–	0.0007	–	–	0.03	–	–	0.03
	Snakehead	5.8×10^{-4}	–	–	0.0016	–	–	0.064	–	–	0.064
	Catfish	5.1×10^{-4}	–	–	0.0014	–	–	0.056	–	–	0.056
	Tilapia	6.4×10^{-4}	–	–	0.0018	–	–	0.07	–	–	0.07
Hong Kong seawater fish	Tongue sole	8.4×10^{-4}	–	1.6×10^{-3}	0.0023	–	0.0044	0.09	–	0.18	0.27
	Bartail flathead	1.1×10^{-3}	–	2.9×10^{-4}	0.003	–	0.0008	0.12	–	0.03	0.15
	Orange-spotted grouper	5.7×10^{-4}	–	–	0.0016	–	–	0.062	–	–	0.062
	Yellow croaker	1.5×10^{-3}	–	1.5×10^{-3}	0.0041	–	0.004	0.16	–	0.16	0.32
	Yellow seafin	3.7×10^{-4}	–	–	0.001	–	–	0.04	–	–	0.04
	Bigeye	–	–	7.6×10^{-4}	–	–	0.0021	–	–	0.08	0.08
	Goldspotted rabbitifish	2.7×10^{-4}	–	–	0.0007	–	–	0.03	–	–	0.03
	Golden threadfin bream	3.1×10^{-4}	–	–	0.0008	–	–	0.034	–	–	0.034
Xiamen freshwater fish	Big head carp	3.9×10^{-3}	1.2×10^{-3}	3.6×10^{-3}	0.0107	0.0033	0.0099	0.43	0.01	0.40	0.84
	Grey Mullet	1.2×10^{-3}	–	9.6×10^{-4}	0.0033	–	0.0026	0.13	–	0.11	0.24
	Mandarin fish	1.2×10^{-3}	–	9.4×10^{-4}	0.0033	–	0.0026	0.13	–	0.10	0.23
	Grass carp	4.4×10^{-3}	–	1.1×10^{-3}	0.0121	–	0.003	0.48	–	0.12	0.6
	Spotted snakehead	1.9×10^{-3}	–	–	0.0052	–	–	0.21	–	–	0.21
	Rice field eel	1.5×10^{-3}	–	–	0.0041	–	–	0.16	–	–	0.16
	Catfish	4.9×10^{-4}	–	–	0.0013	–	–	0.054	–	–	0.054
	Tilapia	6.0×10^{-3}	–	9.2×10^{-4}	0.016	–	0.0025	0.66	–	0.10	0.76
Xiamen seawater fish	Tongue sole	6.5×10^{-4}	–	6.1×10^{-4}	0.0018	–	0.0017	0.071	–	0.07 0.14	
	Bartail flathead	7.6×10^{-4}	–	–	0.0021	–	–	0.083	–	–	0.083
	Orange-spotted grouper	7.5×10^{-4}	–	–	0.0021	–	–	0.082	–	–	0.082
	Yellow croaker	2.4×10^{-3}	1.0×10^{-3}	2.1×10^{-3}	0.0066	0.0028	0.0056	0.26	0.008	0.22	0.49
	Yellow seafin	5.3×10^{-4}	–	–	0.0015	–	–	0.058	–	–	0.058
	Goldspotted rabbitifish	3.7×10^{-4}	–	–	0.001	–	–	0.041	–	–	0.041

over the HR for PFOS in the fish from Hong Kong and Xiamen were less than 1.0, with the range of 0.030 to 0.49 and 0.041 to 0.66, respectively. This indicates that the average PFOS exposure is less than the benchmark concentration (Dougherty et al., 2000). The HR values for PFOA are less than 0.01 for all the studied fish. Therefore in the present study, the concentrations of PFOS and PFOA detected in the fish are unlikely to cause immediate harm to the residents of Hong Kong or Xiamen. However fish is not the only source for human exposure to PFOS/PFOA. Although the HR was less than 1.0, fish in the diet still contributes to PFOS accumulation in humans. In particular, the HR for PFOS in the mandarin fish in Hong Kong and the tilapia, grass carp and big head carp in Xiamen, were approximately half of the threshold for adverse effects with values of 0.49, 0.66, 0.48 and 0.43, respectively.

There is no RfD available for PFUdA, PFTrDA, PFNA and PFDA, and the hazard ratio (HR) of them cannot be calculated. However the risk of these PFCs is needed to be taken into account. Here we make an assumption that if the toxic potencies of other detectable PFCs (PFUdA, PFTrDA, PFNA and PFDA) were the same as PFOS, the HR of these PFCs can be calculated based on the RfD of PFOS. After the calculation, the HR of total PFCs in all Hong Kong and Xiamen fish species were still less than 1 (Table 2), ranged from 0.03–0.81 (Hong Kong fish species) and 0.041–0.84 (Xiamen fish species). These data indicate even if the toxicities of PFUdA, PFTrDA, PFNA and PFDA were the same as PFOS, the total PFCs exposure may not have adverse effects on the local population. However, PFC would be more toxic as the chain length is increased (Hagenaars et al., 2011). Therefore the potential RfD of other PFCs with longer carbon chain is theoretically lower than PFOS. Even if we considered the other PFCs as twice toxic as PFOS, the HR for most samples was less than 1. The exceptions were the mandarin fish from Hong Kong and the big head carp from Xiaman, with the HR of 1.119, 1.21 respectively. Nevertheless the toxic potencies of other PFCs are still not known, the potential threats of total PFC exposure to Hong Kong and Xiamen residents are still exist.

4. Conclusion

This study reveals that frequent consumption of some fish species, such as the mandarin fish in Hong Kong and the bighead carp, grass carp and tilapia in Xiamen may impose potential risk of PFC exposure to human health. The exposure risk is particularly critical for developing fetus and infants due to the potential effects of PFCs on brain development (Johansson et al., 2009). While the current concentrations detected in the different fish species are unlikely to cause adverse effects, however people are simultaneously exposed to other contaminants such as methylmercury, pesticides and flame retardants found in fish (Hansen and Gilman, 2005; Dorea and Donangelo, 2006; Cheung et al., 2007; Gao et al., 2007; Cheung et al., 2008). Hence a more refined assessment of exposures and more scrutiny of internal doses, by measuring concentrations in adult and fetal blood seem warranted. It would be prudent to weigh the relative risks of eating large quantities of fish produced in the PRD during pregnancy. However, it needs to be considered that fish is an important source of protein in the diet of many people in Coastal China. Fish is also an excellent source of omega-3 fatty acids (Innis, 2008; Fotuhi et al., 2009; Cederholm and Palmblad, 2010) and provide protection against cardio-vascular diseases (de Leiris et al., 2009; Galli and Risé, 2009; Rudkowska, 2010).

Thus, while PFC in fish sold in Hong Kong and Xiamen is a potential issue, the relative risks posed by these compounds needs to be weighed against the known benefits of eating fish, especially marine fish (Bushkin-Bedient and Carpenter, 2010; Yu et al., 2010).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.06.002.

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Supplementary data

Fig. S1


Zhejiang
Jinjiang
Zhangzhou
Xiamen
Guangxi
Shunde
Hong Kong
South China Sea
Hainan

Fig. S2.

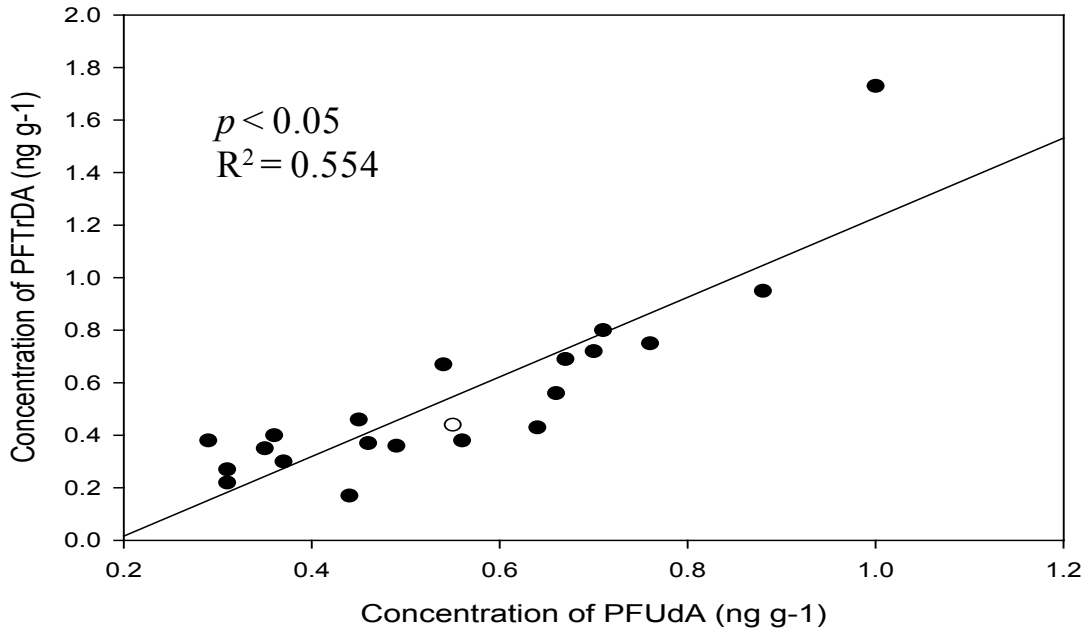
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Concentration of PFTrDA (ng g-1)
p < 0.05
R2 = 0.554
0.2
0.4
0.6
0.8
1.0
1.2
Concentration of PFUdA (ng g-1)

TABLE S1. Information of the different fish species collected from Hong Kong and Xiamen

	Fish Species	Location		Body Weight		Body Length		N		Original Source	
		Hong Kong	Xiamen	Hong Kong (g)	Xiamen (g)	Hong Kong (cm)	Xiamen (cm)	Hong Kong	Xiamen	Hong Kong	Xiamen
Seawater Fish	Tongue Sole	+	+	202±36	73±6	32±2	25±1	27	6	South China Sea	Zhejiang
	Bartail Flathead	+	+	489±407	339±19	40±17	41±1	6	3	South China Sea	Hainan
	Orange-spotted grouper	+	+	432±17	325±47	30±1	29±1	9	3	South China Sea	Zhejiang
	Yellow Croaker	+	+	352±65	97±10	30±2	22±1	15	6	Hong Kong Island	Guangdong
	Yellow Seafin	+	+	417±33	105±10	26±1	19±1	9	6	South China Sea	Guangxi
	Snubnose Pompano	+	+	409±37	386±42	27±1	29±1	9	3	Hong Kong Island	Zhejiang
	Bigeye	+	+	202±56	104±16	24±2	22±2	33	4	Hainan	Zhejiang
	Goldspotted rabbitifish	+	+	122±33	82±14	20±2	20±1	15	6	Hong Kong Island	Zhejiang
	Golden Threadfin Bream	+	-	175±63	-	22±2	-	36	-	South China Sea	-
	Bleeker's Grouper	+	-	358±151	-	30±5	-	10	-	Hainan	-
Freshwater Fish	Big head Carp	+	+	1977±141	1798±42	-	-	6	3	New Territories	Zhangzhou
	Grey Mullet	+	+	379±28	131±11	31±1	26±1	18	5	Shunde	Jinjiang
	Mandarin Fish	+	+	1519±43	288±25	43±2	27±1	3	3	Shunde	Jinjiang
	Grass Carp	+	+	1841±156	2025	-	-	6	3	New Territories	Zhangzhou
	Mud Fish	+	-	414±132	-	28±3	-	15	-	New Territories	-
	Spotted Snakehead	+	+	450±68	339±38	32±1	34±3	10	3	Shunde	Zhangzhou
	Rice Field Eel	+	+	288±27	256±15	60±4	42±3	14	6	Shunde	Jinjiang
	Snakehead	+	-	254±18	-	29±1	-	10	-	Shunde	-
	Catfish	+	+	316±37	106±10	31±1	22±1	21	4	New Territories	Jinjiang
	Tilapia	+	+	437±28	368±17	26±1	26±1	10	3	Shunde	Zhangzhou

TABLE S2. Multiple Reaction Monitoring (MRM) Transitions of Perfluorinated Compounds (PFCs)

Compound	Acryonym	Precursor Ion	Product Ion	Fragmentor	Collision Energy
Perfluoroheptanoic	PFHpA	363	319	75	3
Perfluorooctanoic acid	PFOA	413	369	90	5
Perfluorononanoic acid	PFNA	463	419	85	3
Perfluorodecanoic acid	PFDA	513	469	100	3
Perfluoroundecanoic acid	PFUdA	563	519	100	5
Perfluorododecanoic acid	PFDoA	613	569	110	5
Perfluorotridecanoic acid	PFTrDA	663	619	110	7
perfluorotetradecanoic acid	PFTeDA	713	669	125	7
perfluorohexanesulfonate	PFHxS	399	99	120	45
Perfluorooctanesulfonate	PFOS	499	99	200	65