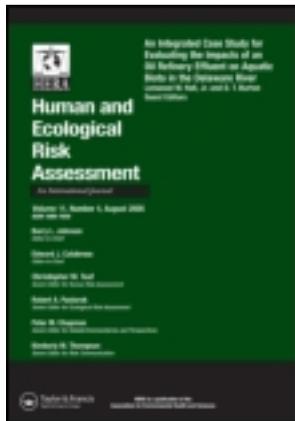


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Human and Ecological Risk Assessment: An International Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/bher20>

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Available online: 16 Nov 2011

To cite this article: Chunli Chen, Tieyu Wang, Jonathan E. Naile, Jing Li, Jing Geng, Cencen Bi, Wenyu Hu, Xiang Zhang, Jong Seong Khim, Yan Feng, John P. Giesy & Yonglong Lu (2011): Perfluorinated Compounds in Aquatic Products from Bohai Bay, Tianjin, China, *Human and Ecological Risk Assessment: An International Journal*, 17:6, 1279-1291

To link to this article: <http://dx.doi.org/10.1080/10807039.2011.618395>

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Perfluorinated Compounds in Aquatic Products from Bohai Bay, Tianjin, China

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ABSTRACT

To understand concentrations of perfluorinated compounds (PFCs) in aquatic products, and risks to human health, concentrations of 12 PFCs were measured in edible tissues of aquatic products collected from Tianjin, China, a typical industrial area on the western Bohai Sea. Perfluorooctane sulfonate (PFOS) was the predominant PFC. Concentrations of PFOS in aquatic products from Tianjin Binhai New Area (TBNA) ranged from <0.10 to 241 ng/g wet weight, with the greatest concentration observed in the edible portions of mullet (*Mugil so-iuy Basilewsky*). Concentrations of PFOS in mullet from the TBNA were greater than those in other species of lower trophic levels, which suggests biomagnification. Concentrations of PFOS in aquatic products from markets were greater than those of locally farmed or wild marine products. Relatively great concentrations of PFOS were not only observed in products from the rapidly growing industrial areas such as Tangu District (TG) and Hangu District (HG), but also in less industrialized areas like the Dagang District (DG). The results of the hazard assessment indicated that consumption of seawater-farmed fish and market fish posed a greater hazard than wild marine fish or freshwater-farmed fish, but the risk to human health was not great.

Key Words: PFOS, PFOA, seafood product, fish consumption, human exposure, health risk.

Received 9 July 2010; revised manuscript accepted 18 January 2011.

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INTRODUCTION

Perfluorinated compounds (PFCs) have attracted considerable scientific and public attention since they were found to be globally distributed, persistent, and toxic (Giesy and Kannan 2002; Giesy *et al.* 2010). In 2009, the Conference of the Parties 4 of the Stockholm Convention (COP-4) in Geneva placed perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonyl fluoride (PFOSF) into Annex B (UNEP 2009). The inclusion of PFOS into the list of Persistent Organic Pollutants (POPs) of Stockholm Convention makes it more important to investigate the source and risk to human health in addition to the distribution of PFCs. Monitoring the concentrations of PFCs in aquatic products is important for understanding the distribution and potential effects of these compounds in species of relevance to human health. It is also important to assess the potential sources by investigating the concentrations of PFCs in the species for diet that has direct contact with sources. Consumption of contaminated food is an important route of human exposure to POPs (Jiang *et al.* 2005), and fish consumption is considered to be a major source of dietary POPs exposure (Leng *et al.* 2009). Yet information about exposure of humans to PFCs through food consumption is relatively rare, especially in Asia (Dai *et al.* 2006; Gulkowska *et al.* 2006; So *et al.* 2006; Ye *et al.* 2008; Ostertag *et al.* 2009).

Residues of POPs, such as dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), chlordane, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), and polychlorinated biphenyls (PCBs) have been found in marine fish, mollusks, crabs, and shrimp in the coastal areas of China (Yang *et al.* 2006; Jiang *et al.* 2007; Liu *et al.* 2007; Miyake *et al.* 2008). Residents of coastal areas who have a habit of consuming sea fish are more exposed to POPs (Leng *et al.* 2009). PFCs differ from other POPs because they are more soluble in water and tend to become associated with proteins and not in lipids (Nakata *et al.* 2006; Paul *et al.* 2009).

The Tianjin Binhai New Area (TBNA) is along the eastern coast of China and near western Bohai Bay. The TBNA is composed of three administrative districts: Tanggu District (TG), Hangu District (HG), and Dagang District (DG) (Figure 1). In the last few decades, this area has been experiencing rapid urbanization and industrialization. There has been a long history of pollution from complex sources at TBNA, and this area has been reported to be polluted by organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) (Lu *et al.* 2007; Wang *et al.* 2009; Jiao *et al.* 2009). The purpose of this study was to determine the geographical pattern of concentrations of PFCs in aquatic food products from the TBNA, to examine associations between concentrations of PFCs in aquatic products and local consumption habits, and to identify potential sources of PFCs, and to perform a preliminary hazard assessment of local humans' exposure to PFOS.

MATERIALS AND METHODS

Sampling Collection and Preparation

Samples of farmed and wild-caught freshwater and marine fishes, as well as fish and crabs, and shrimp purchased in local markets in three districts of the TBNA

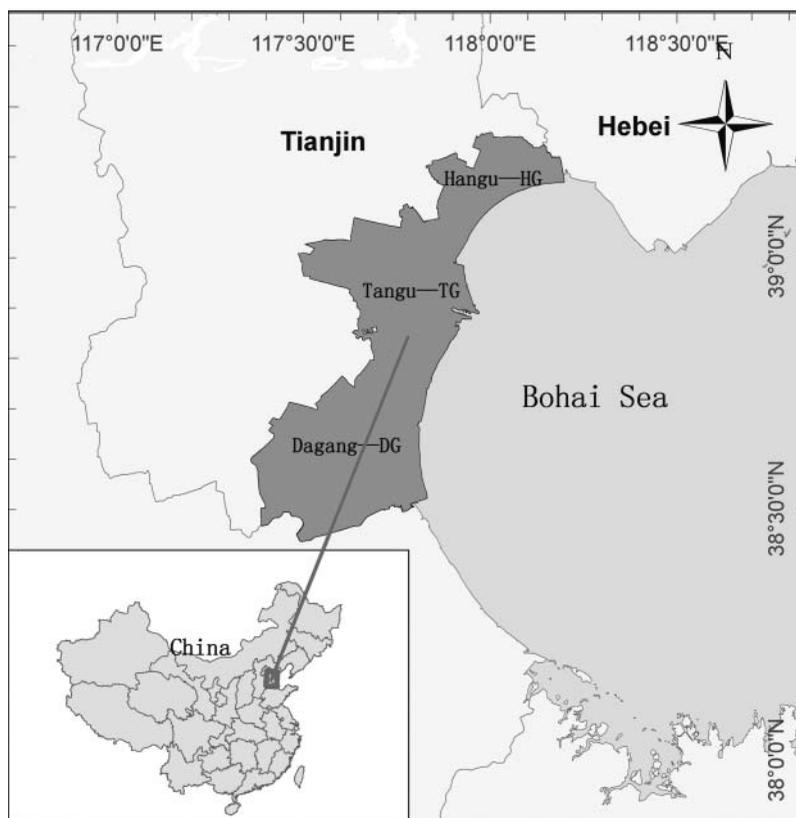


Figure 1. Sampling locations. HG: Hangu District; TG: Tangu District; DG: Dagang District (color figure available online).

were collected in October 2008 (Figure 1). Samples were stored in polyethylene bags and transported on ice to the laboratory. All laboratory equipment was thoroughly washed sequentially with tap water, nano-pure water, and methanol before sample extraction and clean-up to avoid possible contamination. Edible tissues were collected after removing the shell from all the samples and then were ground and homogenized by mortar and pestle. Samples were stored at -20°C until extraction.

The extraction method was a slight modification of a previously described method (So *et al.* 2006). Prior to extraction, samples were thawed to room temperature. Approximately 1 g of homogenized tissue was added to a 50 ml polypropylene (PP) tube, and then 30 ml of 0.01 N KOH/Methanol was added to the PP tube. The mixture was shaken at 250 rpm at room temperature for 16 h and then sonicated for 5 min. After digestion, 5 ml of the soft tissue solution mixture with 0.5 ml of internal standard solution containing 5 ng/ml each of PFOS [$^{18}\text{O}_2$] and PFOA [1,2,3,4- ^{13}C] (RTI International) were added to a 250 ml PP bottle containing 100 ml nano-pure water and shaken thoroughly.

Standards and Reagents

A mixture of perfluorinated compounds (PFCs-mix, >98%, Wellington Laboratories) including PFOS, perfluorooctanoic acid (PFOA), perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and perfluorodecane sulfonate (PFDS), each at a concentration of 6.0 ng/ml was used as an external standard, whereas 0.5 ml of PFOS [$^{18}\text{O}_2$] and PFOA [$1,2,3,4\text{-}^{13}\text{C}$] (RTI International) at 5.0 ng/ml were used as internal standards. Methanol (HPLC grade), acetonitrile (Li Chrosolv for HPLC), acetic acid (analytical grade), and Nitrogen gas (>99.9995% purity) were used. Milli-Q water was obtained from a Milli-Q Gradient A-10 (Millipore, Bedford, MA, USA).

Sample Extraction

Spiked samples were extracted by use of an Oasis HLB cartridge (Oasis HLB: 0.2 g, 6 ml; Waters Corp., Milford, Massachusetts) (So *et al.* 2004). Extraction cartridges were preconditioned by eluting 10 ml of methanol followed by 10 ml of nano-pure water at a rate of 1 drops/s. The tissue mixture was loaded onto the cartridge at a rate of 1 drop/s and the eluate was discarded and the column was allowed to run dry for at least 2 h prior to elution. The column was eluted with 15 ml of 100% methanol at a rate of 1 drop/s into a new, cleaned 15 ml PP tube. The collected volume was reduced to 1 ml under a gentle stream of high-purity nitrogen. After volume reduction, the eluates were passed through separate prewashed 0.1 μm nylon filters and then collected in a new 15 ml PP tube. Any eluates that remained on the filter were washed through the filter with a small volume of 100% methanol then reduced the volume to 1.0 ml. Extracts were transferred to a glass vial after passing through a nylon membrane Millex filter unit (pore diameter 0.2 μm , Whatman, Maidstone, United Kingdom) and stored at 4°C until analysis.

HPLC-MS/MS Conditions

Perfluorinated compounds were analyzed by use of high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). Analytical methods were optimized to allow for simultaneous detection of target analytes. Analyte separation was accomplished by use of an Agilent 1200 HPLC fitted with a Thermo Scientific Betasil C18 (100 \times 2.1 mm, 5 μm particle size) analytical column operated at 35°C. Gradient conditions were a flow rate of 300 $\mu\text{l}/\text{min}$, starting with 60% (A; 2 mM ammonium acetate) and 40% (B; 100% methanol). Initial conditions were held for 2 min and then ramped to 20% A over 18 min, held 20 min, decreased to 0% A after 21 min, increased to 100% A after 22 min, held until 22.5 min, returned to initial condition at 23 min, and finally held constant for 26 min.

Mass spectra were collected using an Applied Bioscience SCIEX 3000 (Foster City, California) tandem mass spectrometer, fitted with an electro-spray ionization source, operated in negative ionization mode. Chromatograms were recorded using MRM mode, and when possible at least two transition ions were monitored for each

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analyte. The following instrument parameters were used: desolvation temperature (450°C), desolvation (curtain) gas 6.0 arbitrary units (AU); nebulizer gas flow 5 AU; ion spray voltage=3500 V; collision gas 12 AU; and a residence time of 40 ms. Optimal collision energies and declustering potentials were determined for each analyte's transitions. Quantification using these transitions was performed using Analyst 1.4.1 software provided by SCIEX (Applied Bioscience, Foster City, California).

Quality Assurance and Control

To minimize interferences from the instrument, a guard column was placed just ahead of the injection port to isolate the peaks for the background contamination from the analytical peaks of interest. The limit of quantification (LOQ) was defined as five times the background. The accuracy (% recovery) and precision (pooled coefficient of variation) were estimated by replicate analysis of three concentrations. The accuracy was determined to be within 20% while the precision, expressed as the coefficient of variation, was also less than 20%. The detection limits and recoveries for compounds analyzed are summarized in Table 1. The recoveries of PFCs spiked into aquatic products ranged from 68.3% to 123%.

RESULTS AND DISCUSSION

Concentrations of PFCs in Aquatic Products

Mean concentrations of the 12 target PFCs are given in Table 2. Of the 12 target PFCs, PFOS was the predominant compound while PFDA and PFTrDA were observed in some samples of biota from the TBNA. These results are consistent with the results of other studies of PFCs in edible fish muscle that have found PFOS to be the predominant PFC (Giesy and Kannan 2001; Kannan *et al.* 2005; Gulkowska *et al.* 2006; Tittlemier *et al.* 2007; Ericson *et al.* 2008). Concentrations of PFOS in aquatic products ranged from <0.10 to 241 ng/g wet weight (ww), with the

Table 1. The limit of quantification (LOQ) and recovery of PFCs.

| Analyte | Chemical | LOQ (ng/g) | Recovery (%) |
|---------------------------|----------|------------|--------------|
| Perfluorobutane sulfonate | PFBS | 1.0 | 97.4 |
| Perfluorohexane sulfonate | PFHxS | 1.0 | 113 |
| Perfluorooctanesulfonate | PFOS | 0.1 | 85.0 |
| Perfluorodecane sulfonate | PFDS | 0.1 | 68.3 |
| perfluorobutyric acid | PFPeA | 1.0 | NA |
| Perfluorohexanoic acid | PFHxA | 0.1 | 73.3 |
| Perfluoroheptanoic acid | PFHpA | 0.1 | 104 |
| Perfluorooctanoic acid | PFOA | 0.5 | 85.0 |
| Perfluorononanoic acid | PFNA | 1.0 | 123 |
| Perfluorodecanoic acid | PFDA | 0.1 | 71.2 |
| Perfluoroundecanoic acid | PFUnA | 1.0 | 86.3 |
| perfluorotridecanoic acid | PFTrDA | 1.0 | NA |

NA means no standard was spiked.

Table 2. PFCs concentrations in edible tissues of aquatic products from TBNA (ng/g wet weight)

| Location | Species | Source | N | PFOS | PFDA | PFTTrDA |
|----------|---------------|--------|----|------|------|---------|
| TG | Crab | R | 2 | <0.1 | <0.1 | 1.57 |
| TG | Crab | W | 4 | <0.1 | 1.09 | <1.0 |
| TG | Crab | M | 2 | 10.7 | 0.70 | <1.0 |
| TG | Prawn | M | 12 | 2.84 | <0.1 | <1.0 |
| TG | Prawn | W | 9 | <0.1 | <0.1 | <1.0 |
| TG | Mantis shrimp | W | 10 | <0.1 | <0.1 | <1.0 |
| TG | Crucian carp | M | 1 | 148 | <0.1 | <1.0 |
| TG | Crucian carp | S | 5 | 59.4 | 1.27 | <1.0 |
| TG | Mullet | S | 3 | 241 | <0.1 | <1.0 |
| HG | Crucian carp | R | 3 | 64.7 | 2.80 | <1.0 |
| HG | Crucian carp | M | 4 | 49.6 | 1.06 | <1.0 |
| HG | Prawn | M | 10 | <0.1 | 0.26 | <1.0 |
| HG | Prawn | W | 10 | <0.1 | <0.1 | <1.0 |
| HG | Prawn | F | 13 | <0.1 | <0.1 | <1.0 |
| HG | Mantis shrimp | M | 15 | 37.6 | <0.1 | <1.0 |
| HG | Crab | M | 2 | 82.2 | 1.80 | <1.0 |
| HG | Swimming crab | W | 3 | 1.78 | 1.26 | <1.0 |
| DG | Crucian carp | R | 5 | 34.2 | 1.69 | <1.0 |

S: seawater farmed; F: freshwater farmed; W: wild marine; R: River; M: market. HG: Hangu District; TG: Tanggu District; DG: Dagang District.

greatest concentration of PFOS observed in edible parts of mullet (*Mugil so-iuy Basilewsky*). Concentrations of PFDA ranged from <0.10 to 2.80 ng/g ww, with the greatest concentration of PFDA observed in crucian carp collected from HG. PFTTrDA was occasionally detected only in crab collected from TG. Concentrations of PFOA were all less than the LOQ. Concentrations observed were similar to those reported for other aquatic products (Bossi *et al.* 2008; Ericson *et al.* 2008; Berger *et al.* 2009), due to the relatively small bioconcentration potential of PFOA (Gulkowska *et al.* 2006). Concentrations of PFPeA, PFHpA, PFNA, PFUnA, PFBS, and PFDS were generally not observed greater than their respective LOQs.

Comparison of PFOS Concentrations among Species

The greatest concentration of PFOS in aquatic products was observed in fishes (34.2–241 ng/g, ww), while PFOS concentrations were slightly less in crustaceans, such as crab (<0.1–82.2 ng/g, ww), mantis shrimp (<0.1–37.6 ng/g, ww), and prawn (<0.1–2.84 ng/g, ww). PFOS concentrations can vary among species and sampling locations (Giesy and Kannan 2001; Kannan *et al.* 2005; Gulkowska *et al.* 2006; Tittlemier *et al.* 2007; Ericson *et al.* 2008). The statistic analysis showed that mean concentrations of PFOS varied among species collected from the TBNA (Kruskal-Wallis test $p = .031$). PFOS has bioconcentration properties, and highly elevated PFOS levels have been observed in top predators in food chains containing fish (UNEP 2006). Concentrations of PFOS in aquatic products from TBNA in decreasing order were: fish > crab > prawn, a result that was consistent with their trophic levels. The

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greater concentrations of PFOS observed in fish from the TBNA could be due to aqueous exposure to PFOS, since laboratory studies suggest that the primary route of accumulation into fish was from aqueous exposure to PFOS (Beach *et al.* 2006). Moreover, the greater concentrations in higher trophic-level organisms suggest the biomagnification of PFOS through the aquatic food chain (Nakata *et al.* 2006).

Bohai Bay is one of the main oil processing and transport areas in China, and two major oil refineries as well as several petrochemical industries are located in Tianjin. The survey also showed that the Bohai Sea had been polluted by petroleum hydrocarbons (Wang *et al.* 2004). The relatively great concentrations of PFOS in fish in the TBNA could be related to use of PFOS-based light water, fire-fighting foams (Moody and Field 1999; Moody *et al.* 2003) or their possible use as an emulsifier in petrochemical processes (Olivero-Verbel *et al.* 2006; Vecitis *et al.* 2010). Other sources could include releases of untreated sewage from nearby land or industrial discharge from production of pesticide or plastics.

Since concentrations of PFOS in mantis shrimp from the HG market were greater than that in prawns, and as great as those in some fishes, the potential bioaccumulation of PFOS in mantis shrimp was suspected. This is similar to the results of other studies where mantis shrimp in Zhoushan and Guangzhou were found to have greater concentrations of PFOS (Gulkowska *et al.* 2006).

Spatial Differences

Since PFOS was the predominant PFC detected in the three districts, mean concentrations of PFOS were compared among the districts (Figure 2). Mean concentrations of PFOS in crucian carp (*Carassius carassius*) from TG (104 ng/g, ww) and HG (57.2 ng/g, ww) were greater than those from DG (34.2 ng/g, ww). DG is a relatively less industrialized area compared with HG or TG, but concentrations of PFOS in crucian carp from DG were 34.2 ng/g, ww. Thus, relatively great concentrations of PFOS were not only found in locations proximate to the more industrialized areas (Gulkowska *et al.* 2006). In the Dagang District (DG), there are one major oil refinery and one of the largest oil and gas exploration and development industry. Since fluorosurfactants have been widely used in the petrochemical industry, the relatively great concentrations of PFOS observed in crucian carp from the DG region could be related to oil-related activities. Mean concentrations of PFOS in edible tissue of crab (42.0 ng/g, ww) and mantis shrimp from HG (37.6 ng/g, ww) were greater than those in mantis shrimp from TG.

Comparison of Concentrations of PFOS in Aquatic Products of Different Origin

Although there were previous reports on concentrations of PFCs in edible fish muscle (Giesy and Kannan 2001; Kannan *et al.* 2005; Gulkowska *et al.* 2006; Tittlemier *et al.* 2007; Ericson *et al.* 2008), little was known about concentrations of PFCs among market aquatic products and other farmed or wild marine aquatic products in China. The greatest concentration of PFOS in the TBNA was observed in mullet, which was a special product in TG and seawater farmed. Previous studies have shown that pollutants in some species of farmed fish can be greater than that in wild marine fish (Meng *et al.* 2007). Seawater-farmed fish are cultured in intertidal zones, small bays, or shallow seas. These areas have less self-purification capacities than the open ocean

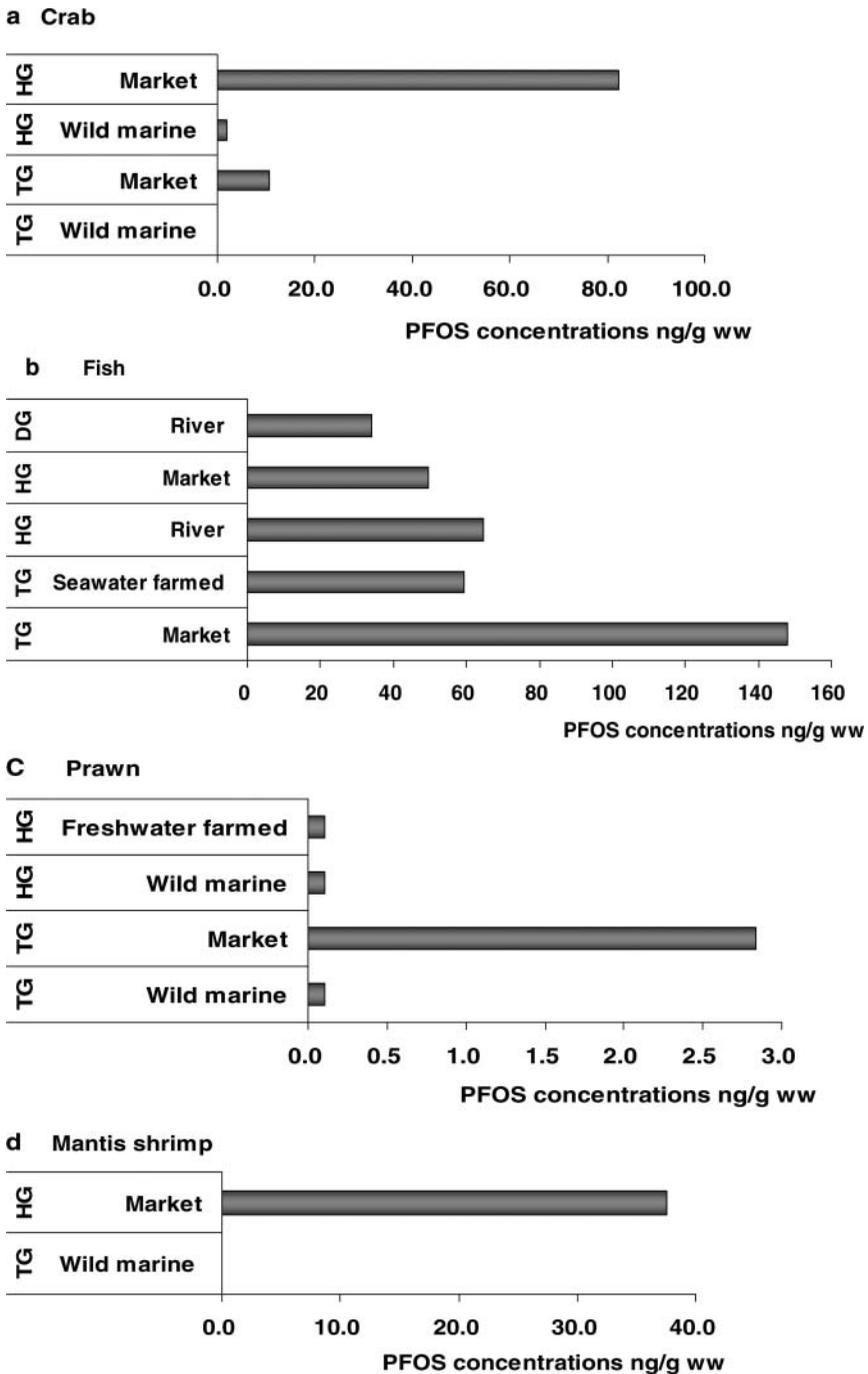


Figure 2. Comparison of mean concentrations of PFOS in aquatic products among districts. HG: Hangu District; TG: Tanggu District; DG: Dagang District (color figure available online).

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and thus these areas are more easily influenced by human activities. The results of this study are in agreement with those reported by Meng *et al.* (2007). Since diet would not be a major route of PFOS exposure for fish (Beach *et al.* 2006), the results of this study probably reflect the relatively contaminated coastal environment where most seawater-farmed fish were raised in TBNA, as water-borne PFOS have been identified to be an important uptake route for fish (Beach *et al.* 2006).

Mean concentrations of PFOS in edible tissue of aquatic products within the same species collected from markets were greater than those in local farmed or wild aquatic products from TBNA (Figure 2). Ninety percent of the market aquatic products originated locally and most of them were either seawater farmed or freshwater farmed. With the rapid development of the fishery in Tianjin, seawater- and freshwater-farmed fish account for 75% of the total fish products in Tianjin. However, the farmlands and fish ponds in Tianjin have become polluted due to the limited exchange volume of water (Tianjin Environmental Protection Bureau 1991). Concentrations of certain POPs in freshwater fish in some areas of China were two-fold greater than those of wild-caught marine fish (Zhang *et al.* 2005). Therefore, the greater concentrations of PFOS in aquatic products in markets for TBNA were directly related with concentrations of PFOS in seawater-farmed aquatic products and freshwater-farmed aquatic products. There was no obvious difference in concentrations of PFOS between wild-caught (<0.1 ng/g, ww) and farmed (<0.1 ng/g, ww) marine prawn.

Hazard Assessment of Dietary PFOS Exposure to Humans

Consumer products are an uptake route of PFOS and PFOA, but the greatest portion of the chronic exposure to PFOS and PFOA is likely to result from the intake of contaminated foods (Trudel *et al.* 2008). Non-food sources generally contribute <2% of accumulated PFOS (EFSA 2008). A major route for PFOS into local food chains is generally through fish (UNEP 2006), and the significance of dietary fish in PFOS accumulation in the food chain has been highlighted (Sinclair *et al.* 2006). Consumption of contaminated fish has been suggested to contribute significantly to elevated PFOS levels in human blood. For instance, a population that consumed more fish had 2.6-fold more PFOS in their blood than the population that ate less fish (Falandysz *et al.* 2006).

The residents in the TBNA consume more fish than the general Chinese population. Fish grown locally within Tianjin constitute the primary source of protein, and Tianjin residents eat both freshwater and marine fish (Wang *et al.* 2005). To investigate how different consumption behaviors would affect the estimated dietary intake of PFOS, several scenarios were investigated (Figure 3). Consumption of fish was assumed to be 9.11 kg/year/person, while that of shrimp and crabs was assumed to be 5.48 kg/year/person (Tianjin Statistic Yearbook 2007). The average adult body mass for Beijing residents in year 2005 (60.4 kg) was used to calculate the average daily intake (ADI) (Eq. (1)) (Gulkowska *et al.* 2006). A hazard ratio (HR) was calculated (Figure 4) by dividing the ADI by the reference dose (RfD) (Eq. (2)). RfD values for PFCs have not yet been established by any government agency. However, potential RfDs for PFOS and PFOA have been estimated based on rat chronic carcinogenicity studies and rat multigenerational studies, respectively,

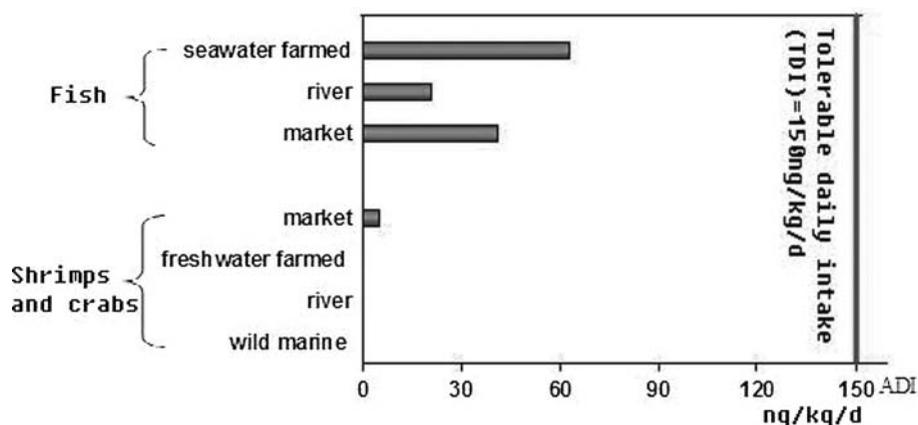


Figure 3. Average Daily Intake (ADI) of PFOS (color figure available online).

whereas RfDs for the other PFCs are not available at this time. On this basis, the RfD derived for PFOS was estimated to be 25 ng/kg/d (Thayer 2002).

$$ADI(\text{ng/kg/d}) = \text{fish consumption}(\text{g/kg/d, wet weight basis}) \times \text{PFC concentration}(\text{ng/g, wet weight basis}) \quad (1)$$

$$HR = ADI/RfD \quad (2)$$

Guidance values such as tolerable daily intake (TDI) have been proposed by health authorities in the United Kingdom and Germany as well as the European Food Authorities (COT 2006; German Federal Institute for Risk Assessment 2006; EFSA 2008). The UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment recommended a TDI of 300 ng PFOS/kg bw (COT 2006). The German Federal Institute for Risk Assessment (2006) derived a provisional TDI of 100 ng PFOS/kg bw and the German Drinking Water Commission (2006) also established a provisional TDI of 100 ng/kg bw for both PFOS and PFOA. This TDI was applicable to infants and pregnant women as well as the general population. Subsequently, the Scientific Panel on Contaminants in the Food Chain (CONTAM Panel) established a TDI for PFOS of 150 ng/kg bw/d by applying an overall uncertainty factor (UF) of 200 to the No Observable Effect Level (NOAEL) of 0.03 mg/kg bw (EFSA 2008). Even the largest PFOS intake from fish by local residents with a high consumption of seawater-farmed fish was less than the proposed TDIs. The estimated PFOS exposure to fish consumers in the TBNA ranged from

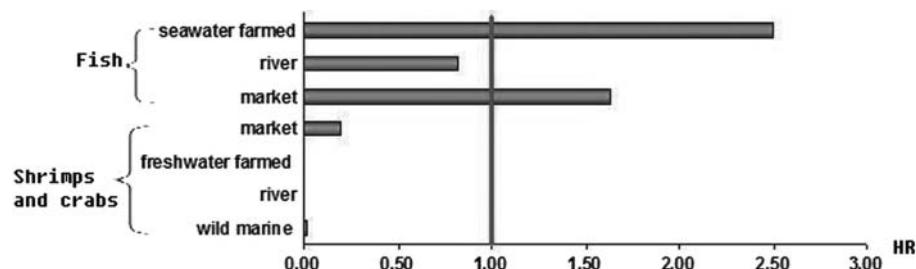


Figure 4. Hazard ratios (color figure available online).

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20.6 to 62.5 ng PFOS/kg/d. This value was similar to the estimated dietary intake of 60 ng PFOS/kg/d estimated for Europeans who consumed average amounts of fish, but less than the estimate for Europeans who consumed larger amounts of fish, with the estimated daily intake of 200 ng PFOS/kg/d.

Hazard ratios (HRs) based on non-cancer risk posed by PFOS concentrations in shrimp and crabs were less than 1.0, which indicated that prevalent concentrations of PFOS in shrimp and crabs were unlikely to cause immediate harm to the local population. But HRs for non-cancer risk based on PFOS concentrations in market fish and seawater-farmed fish were greater than 1.0. Thus, consumers of seawater-farmed fish and market fish were more at risk for health concerns than those who consumed wild-caught marine fish or freshwater-farmed fish.

Even though the greater concentrations of PFOS in fish resulted in HR values greater than 1.0, intake of PFOS through fish consumption as part of an average diet was still less than the proposed TDI. Since aquatic products are the best source of protein and calcium, nutritional value of fish likely outweighs the risk posed by contamination with PFOS, but limited consumption of seawater-farmed fish is advised. This is a preliminary health risk assessment, and investigations should be promoted by performing with larger numbers of species with different origins, and gender, age, occupation and eating habit of the consumers need to be taken into consideration. In addition, since the seawater-farmed fish was more contaminated by PFOS in the TBNA, great attention should be paid to the marine environment quality in the rapidly industrialized area, with more studies on the route of PFOS transportation into the water and the countermeasures to improve the water environment.

ACKNOWLEDGMENTS

This study was supported by National Natural Science Foundation of China with Grant No.41071355, the National Basic Research Program of China ("973" Research Program) with Grant No.2007CB407307, the External Cooperation Program of the Chinese Academy of Sciences with Grant No.GJHZ0948, and the State Key Laboratory Project with Grant No.SKLURE2008-1-4. Portions of the research were supported by a Discovery Grant from the National Science and Engineering Research Council of Canada (Project Nos. 326415-07). Prof. Giesy's participation in the project was supported by the Einstein Professorship Program of the Chinese Academy of Sciences.

REFERENCES

- Beach SA, Newsted JL, Coady K, *et al.* 2006. Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS). *Rev Environ Contam T* 186:133–74
- Berger U, Glynn A, Holmstrom KE, *et al.* 2009. Fish consumption as a source of human exposure to perfluorinated alkyl substances in Sweden-analysis of edible fish from Lake Vattern and the Baltic Sea. *Chemosphere* 76:799–804
- Bossi R, Strand J, Sortkjaer O, *et al.* 2008. Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. *Environ Internat* 34:443–50
- COT (Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment). 2006. Statement on the Tolerable Daily Intake for Perfluorooctanoic Acid, statement 2006/10; COT, London, UK
- Dai JY, Li M, Jin YH, *et al.* 2006. Perfluorooctanesulfonate and perfluorooctanoate in red panda and giant panda from China. *Environ Sci Technol* 40:5647–52

- EFSA (European Food Safety Authority). 2008. Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts, Scientific Opinion of the Panel on Contaminants in the Food chain. *EFSA J* 653:2–131
- Ericson I, Martí-Cid R, Nadal M, *et al.* 2008. Human exposure to perfluorinated chemicals through the diet: Intake of perfluorinated compounds in foods from the Catalan (Spain) market. *J Agr Food Chem* 56:1787–94
- Falandysz J, Taniyasu S, Gulkowska A, *et al.* 2006. Is fish a major source of fluorinated surfactants and repellents in humans living on the Baltic coast? *Environ Sci Technol* 40:748–51
- German Federal Institute for Risk Assessment. 2006. High Levels of Perfluorinated Organic Surfactants in Fish are Likely to be Harmful to Human Health. Statement no. 021/2006; 7/28/2006. Berlin, Germany
- Giesy JP and Kannan K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ Sci Technol* 35:1339–42
- Giesy JP and Kannan K. 2002. Perfluorochemical surfactants in the environment. *Environ Sci Technol* 36:146A–152A
- Giesy JP, Naile JE, Khim JS, *et al.* 2010. Aquatic toxicology of perfluorinated chemicals. *Rev Environ Contam T* 202:1–52
- Gulkowska A, Jiang QT, So MK, *et al.* 2006. Persistent perfluorinated acids in seafood collected from two cities of China. *Environ Sci Technol* 40:3736–41
- Jiang Q, Lee T, Chen K, *et al.* 2005. Human health risk assessment of organochlorines associated with fish consumption in a coastal city in China. *Environ Pollut* 136:155–65
- Jiang QT, Hanari N, Miyake Y, *et al.* 2007. Health risk assessment for polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans, and polychlorinated naphthalenes in seafood from Guangzhou and Zhoushan, China. *Environ Pollut* 148:31–9
- Jiao WT, Lu YL, Li J, *et al.* 2009. Identification of sources of elevated concentrations of polycyclic aromatic hydrocarbons in an industrial area in Tianjin, China. *Environ Monit Assess* 158:581–92
- Kannan K, Tao L, Sinclair E, *et al.* 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Arch Environ Con Toxicol* 48:559–66
- Leng JH, Kayam F, Wang PY, *et al.* 2009. Levels of persistent organic pollutants in human milk in two Chinese coastal cities, Tianjin and Yantai: Influence of fish consumption. *Chemosphere* 75:634–9
- Liu WX, Chen JL, Lin XM, *et al.* 2007. Residual concentrations of micropollutants in benthic mussels in the coastal areas of Bohai Sea, North China. *Environ Pollut* 146:470–7
- Lu JX, Wang YW, Zhang QH, *et al.* 2007. Contamination trends of polybrominated diphenyl ethers, organochlorine pesticides and heavy metals in sediments from Dagu Drainage River estuary, Tianjin. *Chinese Sci Bull* 52:1320–6
- Meng XZ, Zeng EY, Yu LP, *et al.* 2007. Persistent halogenated hydrocarbons in consumer fish of China: Regional and global implications for human exposure. *Environ Sci Technol* 41:1821–7
- Miyake Y, Jiang Q, Yuan W, *et al.* 2008. Preliminary health risk assessment for polybrominated diphenyl ethers and polybrominated dibenzo-p-dioxins/furans in seafood from Guangzhou and Zhoushan, China. *Mar Pollut Bull* 57:357–64
- Moody CA and Field JA. 1999. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ Sci Technol* 33:2800–6
- Moody CA, Hebert G.N, Strauss SH, *et al.* 2003. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *J Environ Monit* 5:341–5
- Nakata H, Kannan K, Nasu T, *et al.* 2006. Perfluorinated contaminants in sediments and aquatic organisms collected from shallow water and tidal flat areas of the Ariake Sea, Japan: Environmental fate of perfluorooctane sulfonate in aquatic ecosystems. *Environ Sci Technol* 40:4916–21

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- Olivero-Verbel J, Tao L, Johnson-Restrepo B, *et al.* 2006. Perfluorooctanesulfonate and related fluorochemicals in biological samples from the north coast of Colombia. *Environ Pollut* 142:367–72
- Ostertag SK, Tague BA, Humphries MM, *et al.* 2009. Estimated dietary exposure to fluorinated compounds from traditional foods among Inuit in Nunavut, Canada. *Chemosphere* 75:1165–72
- Paul AG, Jones KC, and Sweetman AJ. 2009. A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate. *Environ Sci Technol* 43:386–92
- Sinclair E, Mayack DT, Roblee K, *et al.* 2006. Occurrence of perfluoroalkyl surfactants in water, fish, and birds from New York State. *Arch Environ Con Tox* 50:398–410
- So MK, Taniyasu S, Yamashita N, *et al.* 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. *Environ Sci Technol* 38:4056–63
- So MK, Taniyasu S, Lam PKS, *et al.* 2006. Alkaline digestion and solid phase extraction method for perfluorinated compounds in mussels and oysters from south China and Japan. *Arch Environ Con Tox* 50:240–8
- Thayer K. 2002. Perfluorinated chemicals: Justification for Inclusion of this Chemical Class in the National Report on Human Exposure to Environmental Chemicals. Environmental Working Group, Washington, DC, USA
- Tianjin Bureau of Statistics. 2007. Tianjin Statistic Yearbook, China Statistical Publishing House, Tianjin, China
- Tianjin Environmental Protection Bureau. 1991. Environmental Quality Report of Tianjin, Tianjin Environmental Protection Bureau, Tianjin, China
- Tittlemier SA, Pepper K, Seymour C, *et al.* 2007. Dietary exposure of Canadians to perfluorinated carboxylates and perfluorooctane sulfonate via consumption of meat, fish, fast foods, and food items prepared in their packaging. *J Agr Food Chem* 55:3203–10
- Trudel D, Horowitz L, Wormuth M, *et al.* 2008. Estimating consumer exposure to PFOS and PFOA. *Risk Anal* 28:251–69
- UNEP (United Nations Environment Programme). 2006. Draft Risk Profile: Perfluorooctane Sulfonate (PFOS). Stockholm Convention on Persistent Organic Pollutants. UNEP/POPS/POPRC.2/11. 2006/7:COP.2. Geneva, Switzerland
- UNEP. 2009. Listing of Perfluorooctane Sulfonic Acid, Its Salts and Perfluorooctane Sulfonyl Fluoride. Stockholm Convention on Persistent Organic Pollutants. UNEP/POPS/COP.4/SC.4/17.2009/5:COP.4. Geneva, Switzerland
- Vecitis CD, Wang YJ, Cheng J, *et al.* 2010. Sonochemical degradation of perfluorooctanesulfonate in aqueous film-forming foams. *Environ Sci Technol* 44:432–8
- Wang G, Lu YL, Li J, *et al.* 2009. Regional differences and sources of organochlorine pesticides in soils surrounding chemical industrial parks. *Environ Monit Assess* 152:259–69
- Wang XL, Deng NN, Li KQ, *et al.* 2004. Petroleum pollution condition and estimation of its environmental capacities summer in Bohai Sea. *Mar Environ Sc* 23(4):14–8
- Wang XL, Sato T, Xing BS, *et al.* 2005. Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *Sci Total Environ* 350:28–37
- Yang NQ, Matsuda M, Kawano M, *et al.* 2006. PCBs and organochlorine pesticides (OCPs) in edible fish and shellfish from China. *Chemosphere* 63:1342–52
- Ye X, Strynar MJ, Nakayama SF, *et al.* 2008. Perfluorinated compounds in whole fish homogenates from the Ohio, Missouri, and Upper Mississippi Rivers, USA. *Environ Pollut* 156:1227–32
- Zhang JQ, Jiang YS, Zhou J, *et al.* 2005. Comparison of PCDD/Fs content and profile in fish between marine and fresh water in a typical Chinese area. *J. Hyg. Res.* 34:463–5