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Persistent Perfluorinated Acids in Seafood Collected from Two Cities of China

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As an initial survey of human exposure to perfluorinated acids through food consumption in China, seven types of seafood collected from fish markets in two coastal cities were analyzed. Nine perfluorinated compounds were determined using HPLC coupled with ESI-MS/MS. Perfluorooctane sulfonate (PFOS) was the predominant fluorochemical and was found in all 27 seafood samples, including fish, molluscs, crabs, shrimp, oysters, mussels, and clams. Concentrations of PFOS in seafood samples ranged from 0.3 to 13.9 ng/g wet weight, with the highest concentration in mantis shrimp. The hazard ratios of noncancer risk through seafood consumption based on PFOS and perfluorooctanoic acid concentrations were calculated and were less than unity.

Introduction

Perfluorinated compounds (PFCs) have been manufactured for more than 50 years and are used for a wide variety of industrial products, surfactants, and surface protectors for paper, food containers, leather, carpets, upholstery, and fabrics (*1*, *2*). Certain PFCs are also used in large volumes for the production of fire-fighting foams and in the chromium-plating industry (*3*).

Perfluorooctane sulfonate (PFOS) has recently attracted considerable attention because of its global distribution in fish, birds, and marine and terrestrial mammals, including humans, in North America, Europe, and Asia. PFOS and perfluorooctanoic acid (PFOA) have been detected in human serum and blood (*4*−*6*), surface water (*7*−*9*), freshwater and marine biota (*10*−*14*), and even in remote areas such as Alaska, Spitzbergen, and the Canadian Arctic (*15*−*17*). A recent study also reported the occurrence of significant concentrations of PFOS and related fluorochemicals in human blood samples collected from nine Chinese cities (*18*). The study reported that mean concentrations of PFOS ranged from 3.7 to 79 ng/mL and supposed that PFOS did not pose an intermediate risk to the Chinese population.

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The rapid urbanization and industrialization of China in the past 2 decades have put an enormous stress on its coastal environment (*19*). An increasing number of factories have been built close to major rivers and estuaries. Indeed, the Pearl River Delta (PRD) in southern China and the Yangtze River Delta (YRD) in central China have been the focus of a number of recent environmental investigations. These investigations have concentrated mainly on persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), and dichlorodiphenyltrichloroethane (DDTs) in biota, sediments, and water (*20*, *21*). Recently, concentrations of PFCs have been measured in coastal water and biota samples (*9*, *19*). Concentrations of PFOS and PFOA in water from the PRD ranged from 0.02 to 12 pg/mL and from 0.24 to 16 pg/mL, respectively (*9*). Although these concentrations were less than those that would be expected to have adverse effects on aquatic organisms or their predators, the presence of PFCs in coastal waters suggests their widespread distribution and potential release from adjacent industrialized coastal areas in China (*19*).

The consumption of contaminated food is an important route of human exposure to POPs (*22*). However, there is very little information about human exposure to PFCs through food consumption. To our knowledge, no study has reported PFC concentrations in seafood in China and its risks to the Chinese population. In coastal cities, the consumption of contaminated seafood is regarded as the main pathway of human exposure. Zhoushan Island is located on the coast in the YRD near Hangzhou, Ningbo, and Shanghai (*22*). The offshore area is an important fishing ground. The annual fish catch is about 800,000 tons, one-third of the national total. The PRD is located along the southern coastline of China and plays a pivotal role in the development of China's national economy (*9*, *20*, *21*). Guangzhou, the major city of the PRD, has many industries related to the manufacture of electronic products, garments, textile products, and plastic goods, which are potential sources of PFCs (*9*).

The objectives of this study were the measurement of PFCs in selected seafood that was collected from fish markets in two coastal cities of China and a preliminary risk evaluation of human exposure through seafood consumption.

Materials and Methods

Sample Collection and Preparation. Seven types of seafood (four species of marine fish, three species of shrimp, two species of crab, molluscs, clams, mussels, and one species of oyster) were purchased from local markets in Zhoushan and Guangzhou in 2004. Detailed information on the seafood samples is summarized in Table 1. The samples were wrapped in aluminum foil, placed in polyethylene bags, and stored frozen at −20 °C until analysis. The frozen samples were thawed and allowed to return to room temperature before extraction. Duplicate filleted muscle tissues were removed and pooled in a pre-washed glass jar. The samples were then homogenized by a mechanical homogenizer. All Teflon parts were removed from the homogenizer to avoid analytical interference. After duplicate samples from one location were homogenized, the homogenizer probe and laboratory ware were thoroughly washed in the sequence of tap water, distilled water, and methanol and were sonicated before the next set of samples were homogenized, to avoid cross contamination. Approximately 1 g of homogenized tissue was transferred to a 15 mL PP tube, into which 5 mL of Milli-Q water was added. The mixture was then shaken by hand. After dilution, 1 mL

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TABLE 1. Sample List of Seafood from Zhoushan and Guangzhou

category	species	location: Guangzhou	location: Zhoushan
fish	small yellow croaker (*Pseudosciaena plyacti*)	+	+
	silvery pomfret (*Pampus argenteus*)	+	+
	belt fish (*Trichiurus haumela*)	+	
	Japanese mackerel (*Pneumatophorus japonicus*)	+	
	white mouth croaker (*Argyrosomus argentatu*)		+
	conger pike (*Muraenesox cinereus*)		+
mollusc	cuttlefish (*Sepiidae*)	+	+
	squid (*Ommastrephidae*)	+	+
crab	swimming crab (*Portunus trituberculatus*)	+	+
	sand swimming crab (*Portunus pelogicus*)	+	+
shrimp	mantis shrimp (*Oratosquilla oratoria*)	+	+
	greasy-back shrimp (*Metapenaeus ensis*)	+	+
	Chinese spiny lobster (*Panulirus stimpsoni*)	+	
shellfish	oyster (*Ostrea*)	+	
	green mussel (*Perna viridis*)	+	+
	equilaterly venus (*Gomphinia aequilatera*)	+	+
	poker-chip venus (*Meretrix lusorua*)		+

of the water−tissue mixture was transferred to a new PP tube and then extracted for analysis.

Chemical Analysis. Nine PFCs were identified in the seafood samples and quantified by comparison to authentic standards. These included perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHS), PFOS, perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUnDA). Concentrations of PFCs were determined by using the ion-pairing liquid extraction method (*14*, *23*) with the following modifications. One milliliter of water−tissue mixture was spiked with ^{13}C-PFOA (10 ng/mL, 100 μL) as an internal standard to check the overall recovery. However, no corrections of values were made according to the internal standard. If the recovery of ^{13}C-PFOA or native PFCs in the recovery test for each experiment batch were below the acceptable level, all samples were discarded and the experiment was repeated. The particles in the final solution were removed by filtration using a 0.1 μm 13 mm nylon syringe filter. One hundred microliters of extract was transferred to an autosampler vial for instrumental analysis.

The separation of PFCs was performed using an Agilent 1100 high-performance liquid chromatograph (HPLC) (Agilent Technologies, Palo Alto, CA). A 10 μL aliquot of the sample extract was injected onto a guard column (Zorbax XDB-C8, 2.1 mm i.d. × 12.5 mm length, 5 μm; Agilent Technologies) that was connected sequentially to a Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 μm; Thermo Hypersil-Keystone, Bellefonte, PA). For quantitative analysis, the HPLC was interfaced with a Micromass (Beverly, MA) Quattro Ultima Pt tandem mass spectrometer (MS/MS). Detailed instrumental parameters followed those that Taniyasu et al. (*24*) reported.

Quality Assurance and Quality Control. Concentrations of quality control standards were measured after every 10 injections to check for instrumental drift. Analysis was stopped and a new calibration curve was constructed if the quality control standard was not measured within ±20% of its theoretical value. To minimize background contamination, all known sources of instrumental and procedural contamination described in Yamashita et al. (*7*) were eliminated (*24*). For instance, all fluoropolymer materials such as poly(tetrafluoroethylene) (PTFE) were removed from laboratory products and instruments. The limit of quantification (LOQ) was estimated at the lowest concentration point on the calibration curve that could be accurately measured within ±30% of its theoretical value. The LOQ in this study was 0.25 ng/g (wet weight) for all analytes that were measured in the seafood samples. Procedural blanks, procedural recovery, and matrix-spiked recovery tests were conducted with each set of samples that were extracted to determine the precision and accuracy of the extraction and analytical procedures. All target compounds that were detected in the procedural blanks were less than the LOQ. The results of the whole procedural recovery (%, $n = 3$) of PFOS, PFHS, PFBS, PFUnDA, PFDA, PFNA, PFOA, PFHpA, and PFHxA were 94, 102, 67, 79, 72, 55, 105, 67, and 77, respectively. Matrix spikes were performed for each seafood type. Ten nanograms of each target analyte was spiked into tissue samples and subjected to the whole analytical procedure in duplicate. In general, the average values of matrix recoveries were 88% (77−113), 74% (59−83) and 62% (49−77) for PFOS, PFOA, and PFUnDA, respectively. We mainly focus our discussion on PFOS, PFOA, and PFUnDA because of the significant residues in seafood compared to the rest of the chemicals. The reliability of the aforementioned method was validated for nine chemicals in seafood samples at 0.25 ng/g of LOQ level and further verified through participation in the First International Laboratory Calibration Study (*25*). The results of this interlaboratory calibration study show the limited reliability of the ion-pairing method but the results were comparable among participants, and thus the data are used in the present initial risk evaluation of PFCs residue in seafood in China.

Dietary Survey and Risk Assessment. A questionnaire-based dietary survey of 160 healthy adults from the general population was conducted in Zhoushan in 2001. The estimated daily consumption (g per person, wet weight) of various kinds of food in the Zhoushan population was as follows: 38 g of pork, 105 g of fish, 3.4 g of molluscs, 54 g of shrimp, 76 g of bivalves (mussels, oysters, and clams), 17 g of crabs, 0.2 g of seaweed, 7 g of eggs, 67 g of beans, 241 g of vegetables, 527 g of rice, 14 g of oil, and 25 g of creamery. Consumption of seafood accounted for 22% of the total intake (1172 g) and was the main source of animal protein. As both Zhoushan and Guangzhou are both coastal cities, consumption data collected at Zhoushan were applied to the Guangzhou population for risk assessment.

To assess potential public health risks, exposure concentrations were compared to benchmark doses of PFOS and PFOA, which were statistically derived values used in setting a Reference Dose (RfD) for noncancer health effects

TABLE 2. PFCs Concentrations (ng/g wet weight) in Soft Tissue of Chinese Seafood Samples from Guangzhou and Zhoushan[a]

type of food	location[b]	PFOS	PFHS	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
				Fish					
small yellow croaker	G	2.93	-[c]	0.35	-	-	-	-	-
	Z	0.92	-	-	-	-	-	-	-
silvery pomfret	G	0.67	-	-	-	-	-	-	-
	Z	0.38	-	-	-	-	-	-	-
belt fish	G	0.91	-	-	-	-	-	-	-
Japanese mackerel	G	2.18	-	0.65	-	-	-	0.41	-
white mouth croaker	Z	0.86	-	0.46	-	-	-	-	-
conger pike	Z	1.77	-	0.48	-	-	-	-	-
				Mollusc					
cuttlefish	G	0.87	-	0.38	-	-	0.31	-	-
	Z	0.96	-	0.34	-	-	0.31	-	-
squid	G	1.07	-	-	-	-	0.43	-	-
	Z	1.32	0.28	0.52	-	-	0.35	-	-
				Crab					
swimming crab	G	2.02	-	0.59	-	0.61	1.67	-	0.29
	Z	0.94	-	0.52	-	-	0.34	-	-
sand swimming crab	G	4.59	-	0.49	-	0.28	0.42	-	-
	Z	2.80	-	0.72	0.27	0.28	0.87	-	-
				Shrimp					
mantis shrimp	G	13.9	-	0.93	-	-	0.45	-	-
	Z	1.80	-	-	-	-	-	-	-
greasy-back shrimp	G	0.58	-	-	-	-	0.42	-	-
	Z	1.28	-	0.42	-	-	-	-	-
Chinese spiny lobster	G	1.83	-	-	0.30	-	-	-	-
				Shellfish					
oyster	G	0.54	-	0.41	-	-	-	-	-
green mussel	G	0.42	-	-	-	-	0.34	-	-
	Z	0.42	-	0.77	-	-	0.48	-	-
equilaterly venus	G	0.42	-	-	-	-	0.27	-	-
	Z	0.51	-	0.27	-	-	0.29	-	-
poker-chip venus	G	0.33	-	-	-	-	0.27	-	-

[a] Values reported as mean concentration ($n = 2$). [b] G, Guangzhou; Z, Zhoushan. [c] "-"; below LOQ (<0.25 ng/g wet weight).

(*22*). RfD values for PFCs have not been established by any government agency. However, provisional RfDs for PFOS and PFOA have been estimated based on a rat chronic carcinogenicity study and a rat multigenerational study, respectively. On this basis, the provisional RfD that was derived for PFOS was 0.025 μg/kg/d and that for PFOA was 0.333 μg/kg/d (*26*). Risk assessment was conducted based on the average concentrations of PFCs in fish, molluscs, shrimps, oysters, clams, mussels, and crabs. The health risks of Zhoushan and Guangzhou residents through the consumption of seafood were assessed by estimating relevant hazard ratios (HRs). These HRs were calculated by dividing the average daily intake (ADI) by the benchmark dose (eq 1). The average body weight for Asian people is 60 kg. A hazard ratio (HR) that is greater than unity indicates that the average exposure level exceeds the benchmark concentration (*27*). For each PFC, the ADI

$$\text{HR} = \text{ADI}/\text{benchmark dose} \quad (1)$$

level for a population was calculated by

$$\text{ADI } (\mu\text{g/kg/d}) = \text{fish consumption (g/kg/d, wet weight basis)} \times \text{PFC concentration } (\mu\text{g/g, wet weight basis}) \quad (2)$$

Results and Discussion

PFC Concentrations in Seafood. Twenty-seven seafood samples were collected from fish markets in two Chinese coastal cities and analyzed for nine PFCs (Table 2, Figure 1 and Figure 2). In agreement with other published work on the monitoring of perfluorinated acids in biota, PFOS was the predominant compound. All of the food samples contained concentrations of PFOS that were above the LOQ, ranging from 0.3 to 13.9 ng/g. The mean concentration for all samples analyzed was 1.8 ± 2.6 ng/g. In general, concentrations of PFOS in food from Zhoushan and Guangzhou were low. A notable exception to this observation was from mantis shrimp samples collected in Guangzhou, which contained 13.9 ng/g PFOS, the highest level of PFC measured in this study. The greatest concentration of PFOS (from 0.6 to 13.9 ng/g) in seafood was observed in shrimp tissue and is slightly higher than that reported in shrimp from Greenland (*17*). The PFOS concentrations were slightly lower in crabs (0.9−4.6 ng/g), fish (0.38−2.9 ng/g), and molluscs (0.87−1.3 ng/g). The lowest concentrations were reported for oysters, green mussels, and clams. The PFOS concentration in oysters (0.54 ng/g) was similar to that reported earlier in oysters from Tokyo Bay and slightly higher than that reported in mussels from southern China (*9*). Clam and mussel tissues had similar concentrations of PFOS and were comparable with clams from Frobisher Bay, Nunavut (*17*), and mussels from southern China (*9*). These concentrations were lower than the PFOS concentrations that were observed in zebra mussel in the Great Lakes (*28*). The PFOS concentrations recorded in six species of fish harvested off the Chinese coast were the lowest among all reported data for fish. The concentrations of PFOS in fish that were measured in this study were less than those in fish from the Italian Mediterranean coast (*29*), Greenland (*17*), the Canadian Arctic (*15*), and the Great Lakes (*13*, *28*) and were far lower than the highest concentration (72900 ng/g) detected in fish tissue samples from Etobicoke Creek following the accidental release of fire-fighting foam (*30*). The concentrations of PFOS in seafood from China conformed to the following trend: mussel < mollusc < fish < crab < shrimp (Figure 1).

In general, the reported PFC concentrations were in ranges similar to those of PCBs, chlordanes (CHLs), and hexachlo-

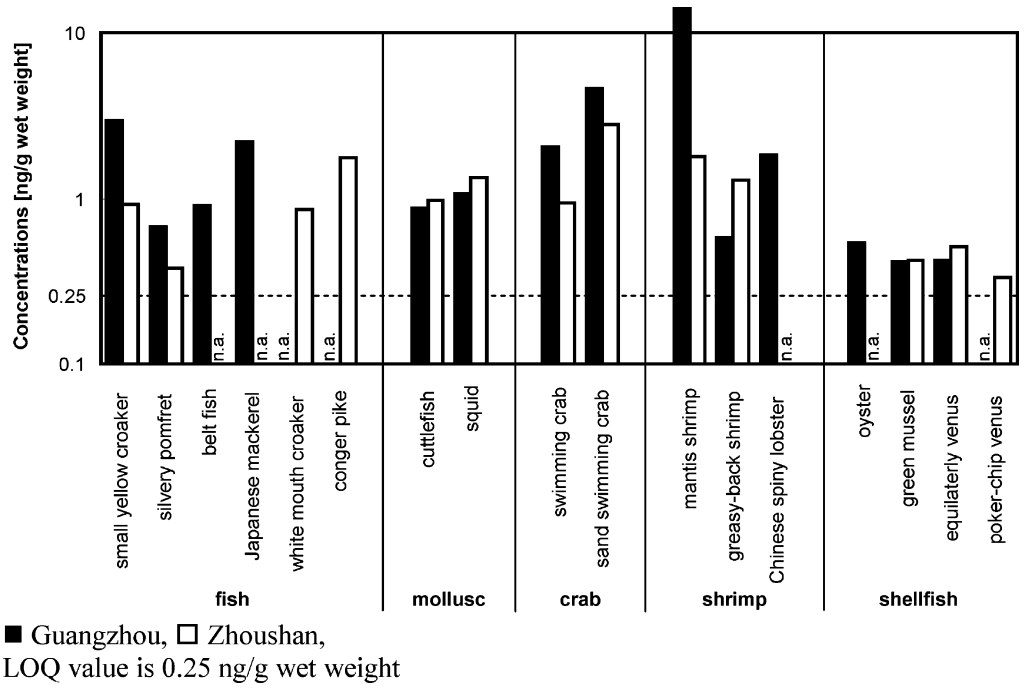

FIGURE 1. PFOS concentrations in seafood samples from Guangzhou and Zhoushan cities.

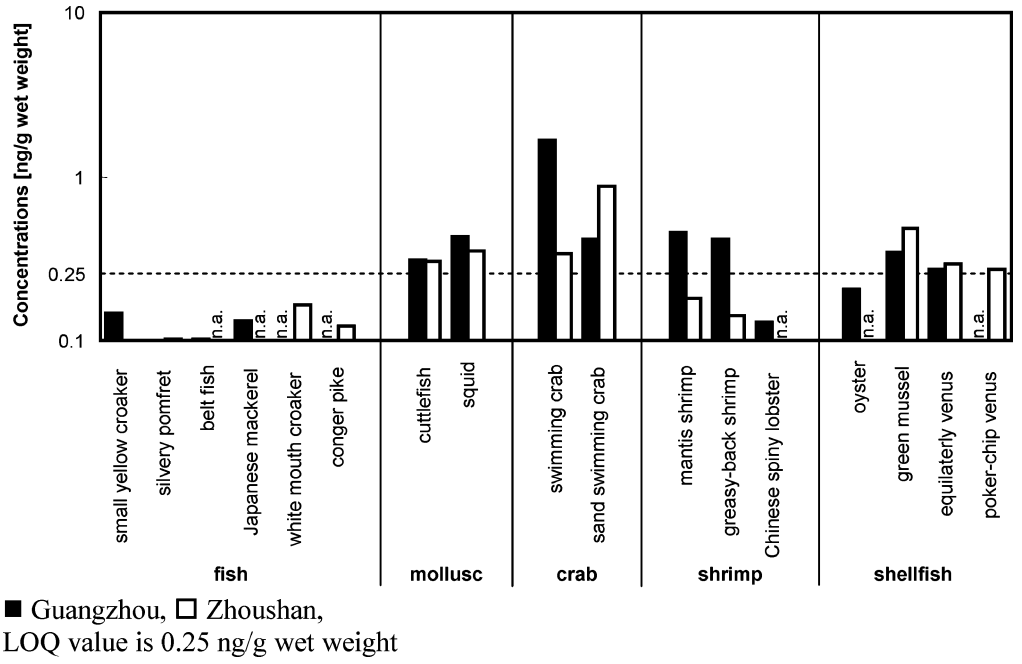

FIGURE 2. PFOA concentrations in seafood samples from Guangzhou and Zhoushan cities.

rocyclohexanes, but less than that of DDTs, in mussels that were collected along the coast of China. In a recent study, the same fish species were examined, and the results indicated that the concentrations of dioxin-like compounds in fish collected from the East China Sea were below detection (*22*). The greatest concentrations of DDT, CHLs, and OC pesticides were observed in a location close to Zhoushan. There were no significant differences among different fish species and sampling locations. However, relatively greater average concentrations of HCB (2.0 ng/g) and PCBs (1.4 ng/g) were detected in conger pike (*22*). Again, these concentrations were observed in a location close to Zhoushan, and they were similar to the PFOS concentrations in conger pike (1.8 ng/g) that were detected in the present study. Conger pike was expected to accumulate greater amounts of lipophilic compounds, e.g., organochlorine compounds, because of its greater fat content and habit of feeding on sediment (*31*).

Unlike with lipophilic organic pollutants such as PCB, the possible covalent binding of PFOS to proteins in liver and blood plasma has been reported (*32*). Therefore, the accumulation of PFOS in higher trophic predators seems to be controlled by a dynamic equilibrium between uptake and elimination and/or is related to protein turnover. These results provide a better understanding of PFC bioaccumulation in lower trophic organisms (*33*).

Among perfluorocarboxylic acids (PFCAs), PFOA and PFUnDA were the prominent compounds found in seafood. The mean concentrations of individual PFCAs homologues ranged from <LOQ (0.25) to 1.7 ng/g. Despite the occurrence of PFOA in Chinese coastal waters (*9*), concentrations of this compound were below LOQs in the fish tissue samples

analyzed. This may be due to a low bioconcentration potential of PFOA. The bioconcentration factor (BCF) reported for PFOA in rainbow trout exposed under laboratory conditions ranged between 4 and 27; this range is 1000-fold lower than that reported for PFOS (*34*). Quantifiable concentrations of PFOA were found in all crab and mollusc tissues (most of the clam and mussel tissues, except oyster) and two shrimp species at a mean concentration of 0.48 ng/g. PFUnDA was found at a slightly greater mean concentration of 0.52 ng/g. This trend is contrary to the bioaccumulation potential of PFCAs, whereby bioaccumulation increases with increasing perfluoroalkyl chain length (*34*). Correspondingly, the dominant PFCA in northern fulmars, common loons, and all fish from the Canadian Arctic is PFUnDA, and lower concentrations have been recorded for both longer and shorter homologues (*13*).

In general, concentrations of PFCs are expected to be low in lower trophic-level organisms such as amphipods and mussels and relatively higher in higher trophic level organisms. This has been observed in the Great Lakes food chain (*28*). However, higher concentrations of perfluoroalkyl contaminants were reported in lower trophic levels in the present study. A similar observation has also been reported in the food chain of Lake Ontario (*13*). Martin et al. hypothesize that sediments must be a major source of all detected perfluoroalkyl contaminants. This may be a result of the sorption of perfluorinated acids or neutral perfluoroalkyl substances to organic matter, followed by sedimentation and subsequent uptake by benthic invertebrates such as shrimp, molluscs, and crabs (*13*). However, PFCs concentrations were greater in zooplankton samples compared to clams and shrimp in the eastern Arctic marine food web. The fact that clams and shrimp have a greater benthic association and lower PFC concentrations than zooplankton suggests that concentrations of and exposure to PFOS and PFOA may be greater in the water column (*17*).

Spatial Differences. Slightly higher PFOS concentrations were observed in fish and crabs from Guangzhou. Among other species, PFCs concentrations were comparable between the two cities, with the exception of a higher level measured in mantis shrimp from Guangzhou. The Zhujiang River receives industrial and domestic contaminants mainly from Guangzhou, the capital of Guangdong Province, which is a highly urbanized city with intense industrial and commercial activities. Discharges from this river enter the PRD and may account for high concentrations of PFCs in the surrounding waters (*9*). Zhoushan is located in the YRD, near the East China Sea. The PFOS concentrations in seafood showed that high concentrations are not only found in locations in proximity to the fastest growing industrial areas, as is the case of Guangzhou, but might also occur in less industrialized areas. This is clearly the case for seafood samples from Zhoushan. It should be noted, however, that Zhoushan Island is located near Hangzhou, Ningbo, and Shanghai, which are some of the most developed industrial cities in the YRD.

Hazard Assessment of PFCs Exposure to Humans. Public health risk through seafood consumption was assessed by estimating the HR. According to the dietary survey, a healthy adult in the Zhoushan population ate 105 ± 182 g of fish each day. Daily fish consumption in the coastal city of Zhoushan was greater than the average rate of consumption of marine products in China as a whole (23 g/kg/d) (*35*). In this survey, 17 species of seafood were examined for individual dietary consumption (Table 2). Marine fish accounted for about 98% of the total fish consumption in the coastal cities, and among the top species consumed were white mouth croaker and small yellow croaker. Only fish fillets were included in this survey, along with whole shrimp, clams, and crabs. Shrimp, clams, and crabs accounted for <13% of the total dietary intake. The average daily intake and HR values are summarized in Table 3. The HRs of noncancer risk based on PFOS and PFOA concentrations were less than unity. This is due to the relatively small concentrations of these PFCs in the seafood (Table 2). Similarly, the health risk assessment of mussels in coastal cities in China also indicated that the noncancer risk quotients for DDTs, CHLs, and PCBs were all less than 1.0. These findings suggest that prevalent concentrations of PFCs and other persistent organic pollutants in seafood are unlikely to cause immediate harm to the Chinese coastal population.

TABLE 3. Average Daily Intake (ADI) of PFOS and PFOA to Chinese Citizens and Hazard Ratio Values

		ADI μg/kg/day		hazard ratio	
food	city	PFOS	PFOA	PFOS	PFOA
fish	Guangzhou	0.0028	0.00019	0.11	0.00056
	Zhoushan	0.0017	0.00019	0.066	0.00057
crab	Guangzhou	0.00095	0.0003	0.038	0.0009
	Zhoushan	0.00054	0.0001	0.022	0.0003
mollusc	Guangzhou	0.00005	0.00002	0.0022	0.00006
	Zhoushan	0.00006	0.00001	0.0026	0.00003
shrimp	Guangzhou	0.0049	0.0003	0.2	0.0009
	Zhoushan	0.0014	0.0002	0.056	0.00044
bivalve[a]	Guangzhou	0.00058	0.00035	0.023	0.0011
	Zhoushan	0.00054	0.00044	0.021	0.0013

[a] Bivalve includes mussel, oyster, and clam.

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Supporting Information Available

(1) Sampling locations (Zhoushan and Guangzhou) in China. (2) Literature survey of PFCs in seafood in February 2006. This material is available free of charge via the Internet at http://pubs.acs.org.

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