

Distribution and Exposure Risk Assessment of Perfluorinated Alkyl Substances in Aquatic Products Along the Coastal Region of the South China Sea

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Research

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Abstract

Objective

The purpose of this investigation was to monitor the contamination characters and spatial and temporal distributions of 23 Perfluorinated alkyl substances (PFASs) in seafood along South China Coastal Regions. The exposure risks of PFOA and PFOS to human health in marine aquatic products were also evaluated.

Methods

A total of 844 samples including 359 fishes, 391 shellfishes and 94 crustaceans were collected from Guangdong, Guangxi and Hainan provinces. The samples were extracted and purified using a modified QuEChERS procedure and analyzed by UPLC-MS / MS. The statistical analysis was performed in view of the detection of different PFAS components in variety of fishes, shellfishes and crustaceans, respectively.

Results

Sixteen PFASs were detected in the survived samples and the total detection rates reached to 99.21 %. The highest \sum PFASs in each sample was 28.27 $\mu\text{g}/\text{kg}$, and the average and medium values of \sum PFAS were 1.83 $\mu\text{g}/\text{kg}$ and 1.18 $\mu\text{g}/\text{kg}$, respectively. PFOS and PFBA have been considered as predominant PFAS components with corresponding pollution contribution rates of 29.14% and 24.71%, respectively. However, it is noted that PFNA and PFBS were primarily enriched in the oyster and mussel. During the period of this investigation (2014-2016), \sum PFAS average concentrations turned out constantly rising trend and new pollution component PFHxS detected in 2016. \sum PFAS concentrations of Guangdong, Guangxi and Hainan provinces were approximately at similar level.

Conclusion

The contamination status of PFASs were getting worse in South China Coastal Regions. Safety and risk exposure assessments of PFOA and PFOS via daily diet intakes showed relatively low to local residents.

Introduction

Perfluorinated alkylated substances (PFASs) belong to a broad class of synthetic organic fluorides, which have been massively produced since 1950s and widely used in various industrial applications and daily consumer products, including food packaging materials, fire-fighting foams, textile, water-repellents painting coat on carpet, leather, oil, etc. [1-3]. PFASs contained in industrial wastewater and sewage wastewater will be disseminated to remote areas [4] such as the Arctic and Tibetan Plateau through atmospheric movement, rivers or ocean currents. PFASs are commonly distributed in abiotic environment [5, 6], wildlife [7-11], and even humans [12-14]. Due to public concerns of their potential carcinogenic risk, endocrine disruption effect [15] and other toxic effects on human health [16], PFASs have been classified as a new-type of persistent organic pollutants (POPs). Perfluorooctane sulfonic acid (PFOS) has been

listed as controlled POPs in the Stockholm Convention in 2009. Then, perfluorooctanoic acid (PFOA) and perfluorohexane sulfonate (PFNA), and their salts were subsequently listed as POP candidates by the European Chemical Agency (ECHA) from 2013 to 2015. Recently, PFOA was also listed in the Stockholm Convention and PFHxS was proposed to be listed. Moreover, the recommendation 2010/161/EU announced to urge member states to carry out monitoring of PFASs' contamination in foods of animal origin.

PFAS compounds are easily absorbed by suspended particles in water when entering rivers and lakes, and then they might be accumulated in sediments [4]. Bioaccumulation of PFASs were confirmed in aquatic animals, especially filter-feeding fish, such as silverfish and bighead carp, decapod crustacean larvae and shellfish [7, 9, 10, 17]. PFASs entering into the food chain would produce potential threats on human health [8, 18], as fish products are important sources of human exposure to PFASs [19]. Therefore, it is of great significance for human health to assess and monitor PFASs risks in aquatic animal-derived foods. At the present, most of the studies on PFASs pollution in the coastal region of the South China Sea have been focused on the environment, which included sediment, bottom water and surface water, *et al.* [20-22]. To our known, no comprehensive investigation on PFASs pollution analysis based on such large-scale datasets was reported in aquatic products collected from the coastal region of the South China Sea.

The object of the present study was to investigate the pollution characteristics and spatio-temporal distribution of 23 PFASs in aquatic products. A total of 844 samples were collected from 11 representative coastal cities of three provinces of South China in this study. Of which, 359 were fish, 391 shellfish and 94 crustacean samples. Targeted 23 PFASs were determined by using a modified sample pretreatment method based on QuEChERS extraction coupled with ultra-high liquid chromatography tandem mass spectrometry (UPLC-MS/MS). In addition, exposure risks of PFOA and PFOS to human health in aquatic products were also evaluated.

Materials And Methods

Sample collection

Aquatic samples, including variety of fishes (e.g., hairtail, perch, snapper, golden thread, bream and pomfret, etc.), shellfishes (e.g., mussels, clams, oysters, scallops and cockles, etc.) and crustaceans (e.g., shrimps, red shrimps, mantis shrimps, swimming crabs, green crabs and Charybdis, etc.), were collected from the aquatic products wholesale markets in three coastal provinces of South China (Guangdong, Hainan and Guangxi) during the study period (2014 to 2016). Sampling sites covered 11 major cities in the coastal region of the South China Sea—Additional file 1: Fig. S1. Specific sampling information of collecting sites, categories and quantity were listed in Table S1. The sampling was designed to have an appropriate representativeness to best reflect the pollution of PFASs in aquatic products in coastal cities of South China. Collected samples were kept at 4°C and during their transported to the laboratory within 48 h. Edible tissues from each sample were cut off, labeled, homogenized, and stored at -20 °C until use.

Detection of PFASs

The materials including PFAS standards, acetonitrile, ammonium acetate, formic acid, deionized water, C₁₈ adsorbent, graphitized carbon black and others used were same as described in the previous studies[23]. The sample pre-treatment method based on the modified QuEChERS procedures as described by Guo *et al.* [24]. Homogenized samples (5 g) were extracted with 10 mL acetonitrile containing 2% formic acid and then purified by solid phase dispersion extraction using C₁₈ sorbent (100 mg), graphitized carbon black (50 mg) and magnesium sulfate (1.5 g). The prepared extracts were concentrated to dryness under a gentle nitrogen stream at 45 °C and the dried residues were reconstituted with 1 mL of acetonitrile-5 mM ammonium acetate solution (1:1, v:v), ultrasonicated to thoroughly dissolve and centrifuged at 18000×g for 10 min. The reconstituted solution was filtered through a 0.22- μ m filter prior to UPLC-MS/MS injection. Conditions of liquid chromatography/mass spectrometry were consistent with the previous studies [23].

Quality Control/Quality Assurance

Polypropylene centrifuge tubes and experimental containers used were washed with methanol before sample pretreatment routines. Pre-columns of the same length were placed tandem between post-column and pre-injector to eliminate the background interfaces sourced from the LC vessels. Equipment parts were modified, thus polytetrafluorethylene and fluoropolymer tubes were replaced by polyether ether ketone vessels or stainless steels. A procedural blank was prepared as each batch of 50 samples and no contamination values were found above the limit of detection (LOD) of 23 PFASs.

A seven-point standard calibration curve concentrations ranging from 0.05 to 50 μ g/L was prepared and injected, and excellent linearities ($r^2 > 0.99$) were obtained with each sample batch. To validate the method, blank samples were spiked at 0.2 μ g/kg with the accuracy in the range of 67.0%~112% and the precision 3.8%~11.7%. The LODs were 0.01 μ g/kg for the targeted PFASs.

Data statistics and analysis

The detection rate, average concentration and median concentration of each PFAS component, as well as the total detection rate of PFASs and \sum PFASs concentration in individual samples were computed, respectively, according to the original test data. Based on the statistical results, predominant PFAS components in all samples were identified. The \sum PFASs and pollution contribution rate of the predominant PFAS components were counted, and the overall pollution characteristics of PFASs in aquatic products collected from three provinces in the coastal region of the South China Sea were observed.

The statistical analysis was performed based on the detection of different PFAS components in fishes, shellfishes and crustaceans, respectively. Individual \sum PFASs concentrations, average and median concentrations of various categories of samples, detection rate of the predominant PFAS components, concentration range, pollution contribution rate, and the temporal-spatial variation characteristics of PFASs in all samples were also studied.

Safety and Risk Assessment

Health risks of human exposure to PFASs were estimated by using the following equations:

$$\text{Estimated Daily Intake (EDI) (ng/kg/day)} = C \cdot Q / BW \quad (1)$$

$$\text{Hazard Index (HR)} = \text{EDI} / \text{Reference Dose (RfD)} \quad (2)$$

Where, C was the mean PFAS concentrations (ng/g, wet weight) in aquatic samples, Q was the average daily consumption of aquatic products (g/day), and BW was the average body weight (kg) of the consumers. At this time, a recommended RfD is only available for PFOS and PFOA. According to the temporary minimum risk levels (MRLs) of PFOS and PFOA recommended by the United States Registry of Poisons and Diseases (ATSDR) [9], the potential risks of the two PFAS components to human health have been evaluated in the present study. If $HR > 1$, it indicates a potential exposure risk of PFAS components for human health; otherwise the risk was relatively lower.

Results And Discussion

Overall detection of PFASs in aquatic products

The purpose of this investigation was to monitor 23 PFASs in aquatic products captured from the South China Sea. The results showed that 16 PFAS components have been detected from the aquatic samples. If any PFAS was detected, it was a positive sample, and the detection rate of total 844 samples reached 99.21%. The maximum added concentrations of detected PFAS components (\sum PFASs) in a given sample was 28.27 $\mu\text{g}/\text{kg}$. The average and median concentrations of the \sum PFASs were 1.83 $\mu\text{g}/\text{kg}$ and 1.18 $\mu\text{g}/\text{kg}$ in individual samples, respectively. It meant that the PFASs pollution of aquatic products in the coastal region of the South China Sea was very common, which deserves an attention from public health perspective. The detection of PFASs in aquatic products from various countries and districts [7, 8, 11, 25-28] was listed in Table 1. It can be seen that the total amount of PFASs in aquatic products from the South China Sea was at an intermediate level but with a higher detection rate.

Table 1. Detection results of PFASs in aquatic products from various countries and districts

Sample sources	Sample categories	\sum PFAS detection range ($\mu\text{g}/\text{kg}$)	References
Northeast Pacific Ocean	Pacific cod	0.216~0.670	[8]
Korean waters		0.288~0.892	
Japanese coastal waters		0.819~1.710	
Lake Tana, Ethiopia	piscivorous fish	0~5.80	[25]
Miyun Reservoir in Beijing, China	freshwater fish	1.70~14.3	[26]
South China Sea	Seafood	0~28.27	This study
Charleston Harbor and tributaries, South Carolina, United States	five known dolphin, prey fish and southern flounder	12.7~33	[11]
Vaal River, South Africa	invertebrates and fish	0~34	[7]
Netherlands	marine fish, farmed fish, crustaceans, bivalves and European eel caught	0~172	[27]
Stockholm Arlanda Airport in Europe	European perch	Absolute systemic burden was 334 ± 80	[28]

Detection results of various PFAS components

The concentration (range, mean and medium values), frequency of individual PFAS in all detected samples and concentration percentage of individual PFAS concentration in \sum PFASs were showed in Fig. S2 and Table S2, respectively. Among the 16 PFAS components, the highest detection rate (72.40%) and concentration percentage (29.1%) were PFOS. The second highest detection rate (62.44%) and concentration percentage (24.71%) was PFBA. Though detection frequency of PFOSA and PFOA (67.95% and 65.86%) were slightly higher than frequency of PFBA, the concentration percentage were merely 7.18% and 3.14%, which were even less than concentration percentage of PFHxA and PFNA (10.66% and 9.19%). PFOS and PFBA represented for more than half of the concentration percentage of the \sum PFASs, indicating that PFOS and PFBA might be considered as the predominant PFAS components in aquatic products collected from the coastal region of the South China Sea. Previous studies showed that the total concentrations of PFASs in the surface water in the South China Sea were 0.195 ~ 4.925 ng/L, and the main PFAS components were PFOS (25%), PFOA (20%), PFBA (16%) and PFBS (10%) [29]. Another report showed that the concentrations of PFASs in surface seawater, bottom seawater and sediments in the South China Sea were 0.125~1.015 ng/L, 0.038~0.779 ng/L and 0.0075~0.0842 $\mu\text{g}/\text{kg}$, respectively.

PFBA and PFOA were the predominant PFAS component in seawater samples, while PFOS was the predominant PFAS component in sediment samples [30]. The detection results of PFASs in aquatic products in the present study were identical to the results of environmental samples, which indicated that fishes, shellfishes and crustaceans had a significant biological accumulation capacity of PFASs.

PFASs entered the environment continuously due to industrial emission. In the present study, in accordance with the average detection concentration of individual PFAS component in all aquatic samples, the concentration of PFOS was highest with an average value of 0.534 µg/kg. The principal source of PFOS in the Pearl River Delta region was industrial wastewater [20]. Similar findings were reported in Vietnam's sewage treatment plants [31]. Thus, we should pay more attention to the monitoring of PFASs pollution in industrial wastewater and municipal wastewater discharge.

Contribution percentage of individual PFAS component in various categories of samples

A total of 844 fishes, shellfishes and crustaceans was included in the study. At least one PFAS component was found in all fish and crustacean samples. Only 1.57% of the shellfish samples did not detect any PFAS component. For each category of samples, the concentration percentage of individual PFAS component to the \sum PFASs was calculated. As showed in Fig. 1, PFOS possessed the highest pollution contribution rate, accounting for 47.78% and 53.42% of the \sum PFASs in fish and crustacean samples, while barely 2.51% in shellfishes. However, PFBA contributed the maximal PFAS pollution at 54.26% in shellfish samples but merely contributed percentages of 2.60% and 1.49% in fish and crustacean samples, respectively.

As a POP, PFOS was difficult to hydrolyze, photolyze or biodegrade in the natural environment and could exist for a long time due to its extremely stable chemical properties [5]. It had been discovered in irrigation water, soil, vegetable, fruit [12] and aquatic products [10] in China, tap water in Korea [12] as well as surface water in Vietnam [31]. Except for water, sediment and other environmental samples, PFOS was also found in aquatic products [10, 11, 27, 32]. Concentrations of PFOS in fatty fish collected from 6 coastal cities in China were 0.0014~1.627 µg/kg [10]. It was surprising that the concentration of PFOS found in sharks was as high as 21.6 µg/kg. Without considering environmental pollution, sharks could accumulate more PFOS in the body because they were at the top of the food chain [27]. In the present study, the highest level of PFOS found in fish was 20.96 µg/kg, which almost approached the top predators.

PFBA was the primary PFAS component in shellfish samples. In the coastal areas of Bangladesh, the highest concentration of PFBA found in shellfish was 0.66 µg/kg [33], which was nearly one tenth of 6.07 µg/kg in this study. PFBA was often found in soil, sediment, irrigation water, tap water, seawater, crops, vegetables and fruit [12, 29, 30, 34, 35]. Considering that most shellfish had biological habits of benthic

and filter-feeding [36], it was not difficult to explain why the PFBA concentrations in shellfish were higher than that in fish and crustacean samples.

Furthermore, PFOSA was found in fishes, shellfishes and crustaceans in the present study, with corresponding pollution contribution rates of 6.12%, 7.22% and 9.84%, respectively. PFOSA, as a precursor substance of PFOS, could be degraded into PFOS [37]. The pollution contribution rate of PFOS in aquatic products was such high that the possibility of contribution from PFOSA should be considered.

Significant components in various categories of samples

We also determined the average concentration of each PFAS component in different aquatic samples, and the results were presented in Fig. 2. The average concentrations of PFOS in fish and crustacean samples were 0.889 $\mu\text{g}/\text{kg}$ and 1.47 $\mu\text{g}/\text{kg}$, respectively, which was significantly higher than the average concentration of 0.0405 $\mu\text{g}/\text{kg}$ in shellfish samples. However, the average concentration of PFBA in shellfish samples was 0.875 $\mu\text{g}/\text{kg}$, which was nearly 20 times higher than the corresponding average concentration in fish (0.0484 $\mu\text{g}/\text{kg}$) and crustacean (0.0409 $\mu\text{g}/\text{kg}$) samples. Obviously, PFBA was the predominant PFAS component in shellfish samples, while PFOS in crustaceans and fish samples.

The above finding was different from the previous reports. Previous researches pointed out that fishes and crustaceans tend to accumulate long-chain perfluoroalkyl carboxylic acid (PFCAs), and the concentration of PFOA in bivalve mollusks was higher than that of other PFASs [31]. Another study suggests that, among long-chain PFASs, the concentrations of PFOA in crabs and mollusks were higher than that of its homologue of PFOS. Except for fishes, the average concentration of PFCAs was higher than the average concentration of PFASs in all marine organisms [9].

Based on the statistics from 26 crab samples in this study, the \sum PFASs were 0.21 ~ 10.55 $\mu\text{g}/\text{kg}$, with the average and median concentrations of 2.96 $\mu\text{g}/\text{kg}$ and 2.52 $\mu\text{g}/\text{kg}$, respectively, which was basically consistent with the overall detection results from crustacean samples. As for the individual PFAS component, compared to the average (0.249 $\mu\text{g}/\text{kg}$) and median concentrations (0.11 $\mu\text{g}/\text{kg}$) of PFOA, the corresponding concentrations of PFOS were 1.12 $\mu\text{g}/\text{kg}$ and 0.78 $\mu\text{g}/\text{kg}$, respectively. Furthermore, the total detection concentration of PFOS was 4.5 times the amount of PFOA detected in crabs. Thus, it may conclude that the predominant PFAS component in crustaceans in the coastal region of the South China Sea was PFOS. Similar results were also reported in crustaceans and fishes [37].

Furthermore, it was noticed that oysters and mussels were the most likely to get accumulated PFNA and PFBS. In the present study, PFNA was found in 431 samples, of which 17.4% (75 samples) were oyster. The concentration of PFNA in oyster samples accounted for 80.13% of the \sum PFNA. Similarly, PFBS was found in 338 samples, and 25.4% (86 samples) of them were mussel, which contributed 85.75% of the \sum PFBS. Generally, researchers paid more attention to the overall pollution of PFASs, or a few hazardous

PFAS components, such as PFOS, PFOA or PFBA [9, 31]. There was less attention to why certain PFAS components tended to accumulate in some species. Higher concentration of PFNA has been found in gastropods and bivalves in the coastal areas of Vietnam [31]. Krista *et al.* found that consumption of oyster, scallop or shrimp was related to the increased serum concentrations of PFDE, PFOS, PFNA and PFUdA in humans [38]. From the findings of this study, it is possible that increased intake of oysters and mussels may also lead to the increase concentrations of PFNA and PFBS in humans.

Temporal variation characteristics of PFASs

The samples were obtained from offshore fishing, docks and aquatic product wholesale markets in the coastal cities of this study. However, the sample commodities were random and uncertain due to seasonality and marketing availability of aquatic products at the time. For instance, oysters were the fattest in autumn and winter, and they were mostly harvested during these periods with high marketing values. Samples were difficult to collect from May to August every year because of the imposed forbidden fishing period in China. Sampling time in each year was unevenly distributed, thus, statistical analysis was carried out on an annual basis rather based on seasons. Of all of the samples tested, 269, 305 and 270 samples were collected in 2014, 2015 and 2016, respectively, including fishes, shellfishes and crustaceans, which closely represented the actual consumption patterns of aquatic products in the coastal region of the South China Sea.

The average concentration variations of individual PFAS component in the three years of our study period were displayed in Fig. 3. The average value of \sum PFASs and some individual components, such as PFOS, PFBA and PFPeA, showed a significant yearly increase respectively, while the other components had a slight variation. Compared with previous studies on the temporal variation characteristics, the concentration of PFASs in sediments generally increased overtime [4, 39], and the concentration of PFOS found in the waters around Hong Kong in 2014 was doubled the level as detected nine years ago [29]. However, the tendency might not be observed in aquatic products. PFAS concentrations detected from cod in Hokkaido of Japan in 2016 were lower than the detection data of the previous four years in spite of the higher PFAS concentrations [8]. Monitoring results in finfish and shellfish samples in Bangladesh demonstrated that most PFAS components did not show obvious seasonal variation [33]. Temporal variation characteristics were closely related to the sampling time, site and sample variety of aquatic products.

It was remarkable that PFHxS was not found in the first two years (2014 and 2015) of our study period, but it had been found from fishes in 2016. PFHxS is a newly discovered PFAS component in aquatic products collected from the coastal region of the South China Sea, indicating a more serious PFAS pollution problem.

Spatial variation characteristics of PFASs

A total of 16 PFAS components was found in all tested samples, and total the detection rates in Guangdong, Guangxi and Hainan were 99.16, 99.49 and 100%, respectively. As we can see in Table S3, compared with Guangdong and Hainan, all PFAS detected components but PFHxS were also found in Guangxi. PFOS was the primary component with higher frequency (78.47% and 84.62%) and mean concentration (0.77 and 0.57 $\mu\text{g}/\text{kg}$) in Guangdong and Hainan, while PFBA was the predominant component in Guangxi with frequency of 70.72% and mean concentration of 0.76 $\mu\text{g}/\text{kg}$. The average and median values of \sum PFASs in Guangdong, Guangxi and Hainan were 1.79, 1.91, 2.02 $\mu\text{g}/\text{kg}$ and 1.09, 1.22, 1.75 $\mu\text{g}/\text{kg}$, respectively.

The concentration percentages of individual PFAS component in Guangdong, Guangxi and Hainan are presented in Fig. 4. Overall, the detection rates and pollution contribution rates of PFOS, PFBA, PFNA, PFOSA and PFHxA were significantly higher than the other PFAS components. The predominant PFAS components in Guangdong's samples were PFOS and PFBA, with corresponding pollution contribution rates at 33.77% and 23.56%. The predominant PFAS components in Hainan's samples were similar to Guangdong, except that PFOS and PFBA had almost equal pollution contribution rate of 23.75%, and 25.47% respectively. The PFASs pollution in Guangxi's samples was different from the other two provinces, and the predominant PFAS components were PFBA and PFNA with corresponding pollution contribution rates of 28.25% and 25.65%.

PFOS was the highest concentration of individual PFAS component among all tested samples at 20.96 $\mu\text{g}/\text{kg}$, which was found in *Ambassis gymnocephalus* sample. Previously, PFOS was found in shrimp samples collected from Holland with a concentration at 25.0 $\mu\text{g}/\text{kg}$ [32], which was slightly higher than the sample collected from the South China Sea in this study. Another individual component with relative high concentration was PFOSA. It was found in *Muscel* sample collected from Guangxi with a concentration of 15.84 $\mu\text{g}/\text{kg}$. Higher concentration of PFOSA may lead to more serious pollution of PFOS.

In this work, higher concentrations of PFNA were found in Guangxi samples with a pollution contribution rate of 25.65%. The average concentration of PFNA in Guangxi samples was 0.489 $\mu\text{g}/\text{kg}$, which was 6.04 times higher than Hainan samples and 5.47 times higher than Guangdong samples, respectively. The likely reason was that PFNA may be more easily accumulated in Oyster. PFNA was found in 101 samples collected from Guangxi, of which 54 samples were Oyster. Surprisingly, PFNA at a detection rate of 53.5% achieved 97.3% of its pollution contribution rate. In addition, PFNA was generally found in Beibu Gulf coastal waters and rivers, where the PFNA detection rate in water samples was 100% [22].

In this study, samples obtained from 11 cities were selected to analyze the distribution characteristics of PFASs. The average concentrations of PFASs in these cities were shown in Fig. 5. Guangzhou's samples were found the highest average concentration at 3.69 $\mu\text{g}/\text{kg}$. In cities with high PFASs concentrations in aquatic products, Guangzhou and Zhuhai belong to the Pearl River Delta region, and the higher detection rate of PFASs was consistent with the previous research [29, 30]. Sanya was an international tourist city and it had the third highest PFASs concentration in aquatic products among all cities, which deserves

attention to the risks of PFASs from local seafood to humans. Previous study showed that PFBA and PFOS were the predominant PFAS components in seawater in the South China Sea [22, 29, 30], and the higher detection rate and pollution contribution rate of PFOS and PFBA in the aquatic products were consistent with the environmental investigation. Results from this study confirmed the bioaccumulation theory.

Exposure and Risk Assessment

According to the data from China's report network, the average consumption of aquatic products by urban households in China from 2013 to 2017 was 14.54 kg per year. This statistical data included household consumption, dining out and other consumption. The average weight of Asians was 60 kg, the RfD of PFOS and PFOA were 0.002 $\mu\text{g}/\text{kg}/\text{day}$ and 0.003 $\mu\text{g}/\text{kg}/\text{day}$, respectively [9]. Based on the average concentration of PFOS and PFOA in each category of samples, the *HR* values of PFOS were 2.95×10^{-1} , 1.34×10^{-2} and 4.86×10^{-1} in fishes, shellfishes and crustaceans, respectively, and the corresponding *HR* values of PFOA were 7.39×10^{-3} , 1.21×10^{-2} and 3.65×10^{-2} for fishes, shellfishes and crustaceans, respectively. Thus, it can be concluded that the potential exposure risks of PFOA and PFOS in aquatic products in the coastal region of South China Sea is considered low, as the *HR* values were all less than 1.

Nevertheless, as the ultimate receptor of PFASs, humans are exposed to more pollution sources [12, 35]. For example, the *HR* of PFASs in PM_{10} in Bohai area were $1.80 \times 10^{-7} \sim 4.04 \times 10^{-5}$ [40], and *HRs* of PFASs in soil, groundwater and tap water was lower than the risk value [41]. The *EDI* values of PFOS and PFOA in fatty fishes and shellfish in six coastal cities in China were no more than 0.001 $\mu\text{g}/\text{kg}/\text{day}$, which is considerably lower than the acceptable daily intake values of 0.15 $\mu\text{g}/\text{kg}/\text{day}$ and 1.5 $\mu\text{g}/\text{kg}/\text{day}$ for PFOS and PFOA, respectively [10]. These assessments were evaluated based on a single risk factor. According to the estimation from pharmacokinetic model, PFOA exposure from tap water accounted for 8.6%~10.1% of the total daily intake exposure, but the contribution of PFOS to total exposure is less than 10%, indicating that other food-derived potential exposure sources were ignored [12]. The assessment outcomes may be more reasonable if other influencing factors were taken into account. For example, in the assessment of PFASs risk index in the environment, the potential comprehensive risks of milk and dairy products, drinking water, cereals, seafood, eggs and egg products, meat and meat products and other foods were considered [35], and the *HR* was higher than 1.

Conclusions

Briefly, a total of 16 PFAS components were found in the study. PFOS and PFBA were considered to be the dominant PFAS components due to their higher pollution contribution rates. Little difference was observed in PFAS components identified among the three provinces. The predominant component in shellfish was PFBA, while in crustaceans and fishes were PFOS. The detection rate of PFASs was 99.2%. The highest concentration of \sum PFASs in a single sample was 28.27 $\mu\text{g}/\text{kg}$, and the average

concentration and the median value for all samples were 1.83 $\mu\text{g}/\text{kg}$ and 1.18 $\mu\text{g}/\text{kg}$, respectively. PFHxS component was found for the first time in 2016, indicating an aggravation tendency of PFASs pollution in aquatic products in the coastal region of South China Sea. The *HR* of PFOS and PFOA in the samples was $7.39 \times 10^{-3} \sim 4.86 \times 10^{-1}$, indicating low risks for them in the aquatic products.

This study comprehensively monitored the pollution of PFASs in aquatic products in the coastal region of South China Sea and provided important basic data for the supervision of administrative departments. Although the risk was relatively low at this time, pollution of PFASs in aquatic products remain a continuous concern due to the increasingly serious pollution in the environment.

Declarations

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Author's contributions

Xu-Feng Wang: Methodology, Writing-original draft, Data analysis. Mong-Song MO: Writing-review & editing, Data analysis, Investigation. Hai-Gang Chen: Investigation. Qiang Wang: Supervision. Jin-Lan Yang: Supervision. Dong-Hao Zhao: Conceptualization, Methodology, Investigation, Formal analysis, Writing-review & editing, Funding acquisition.

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Consent for publication

Not applicable.

Competing interests

The authors declare that there is no conflict of interest.

Availability of data and materials

The datasets used in the current study are available from the corresponding authors on reasonable request.

Ethics approval and consent to participate

Not applicable.

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Figures

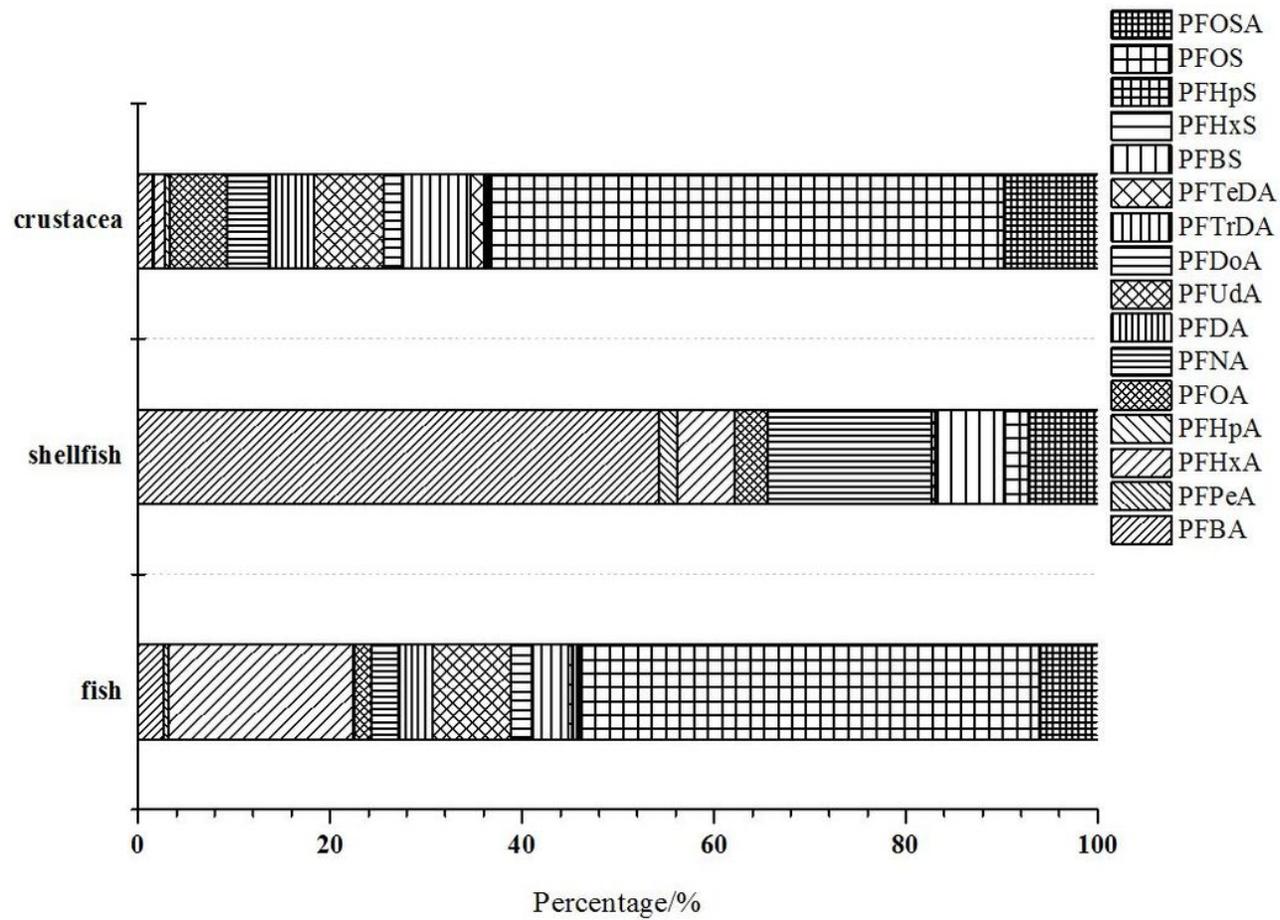


Figure 1

Pollution contribution rate of individual PFAS component in various aquatic samples

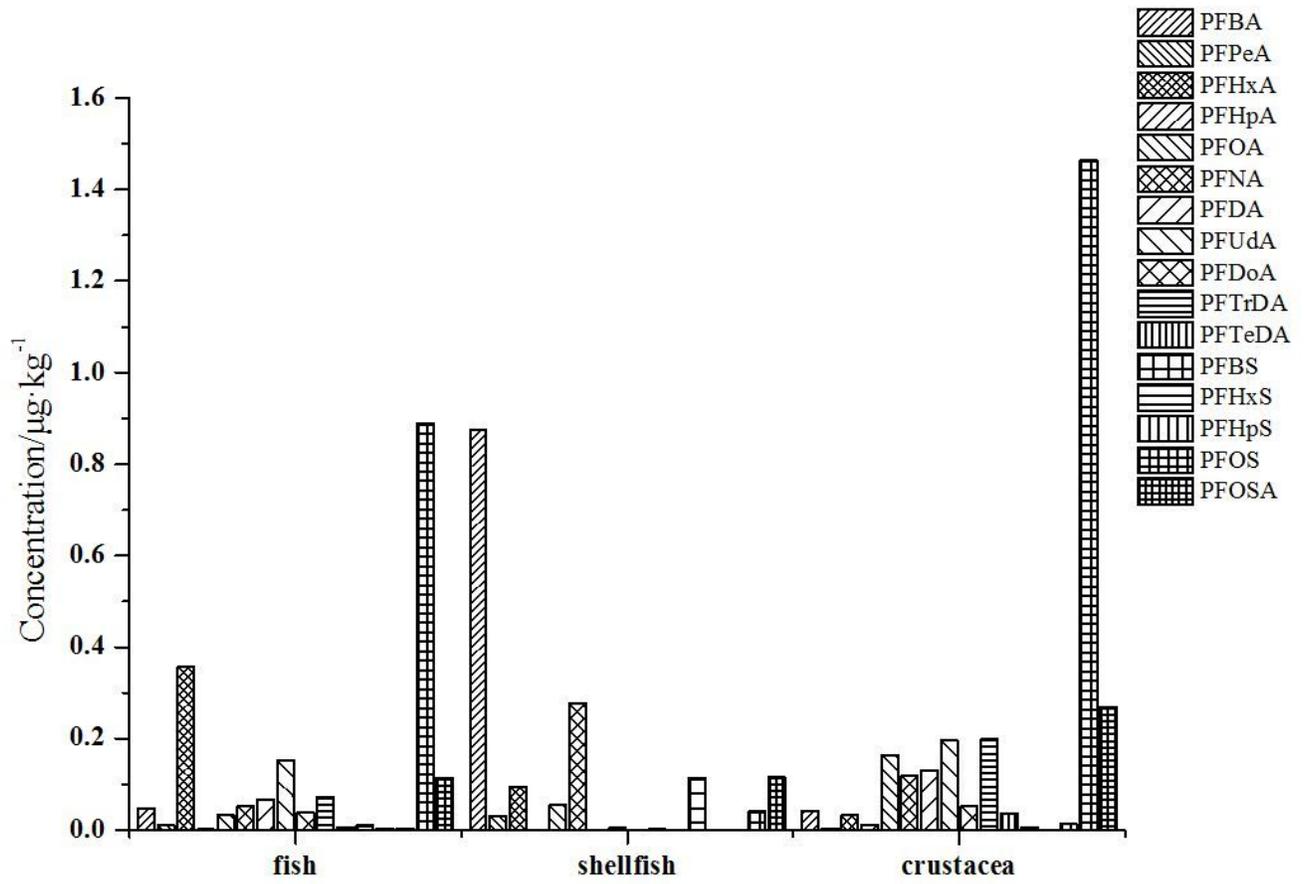


Figure 2

Average concentrations of each PFAS component in fishes, shellfishes and crustaceans

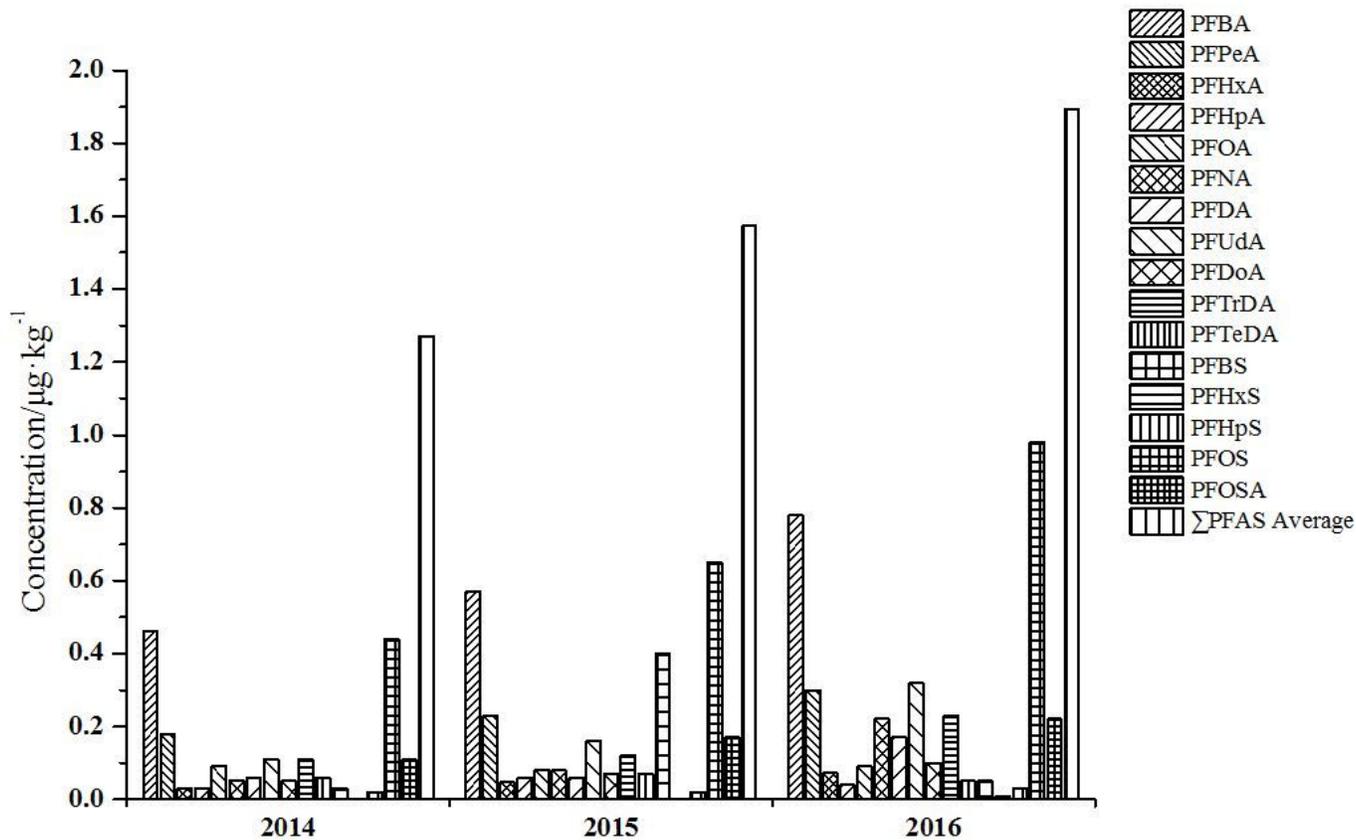


Figure 3

Average concentration variations of individual PFAS components during 2014 - 2016

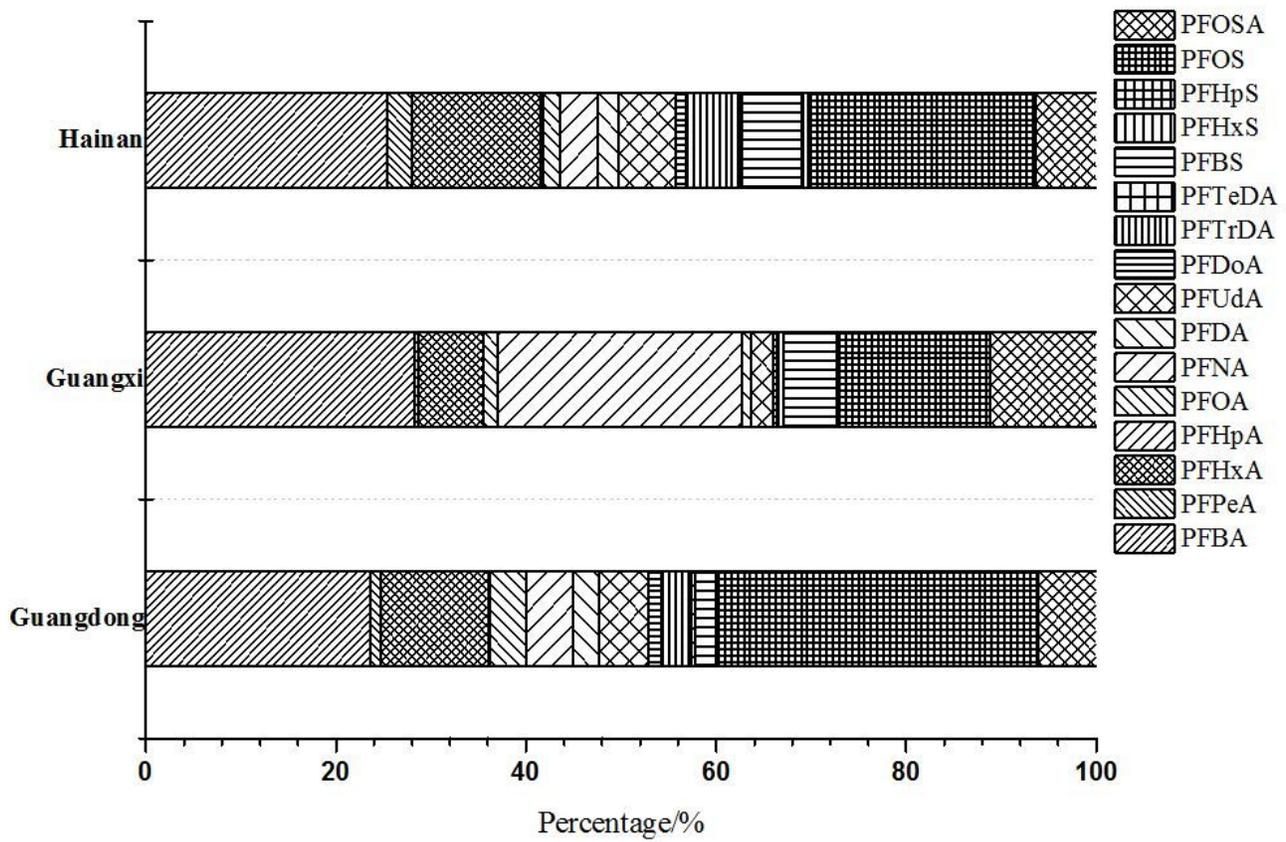


Figure 4

Concentration percentages of individual PFAS components in aquatic samples collected from the three provinces

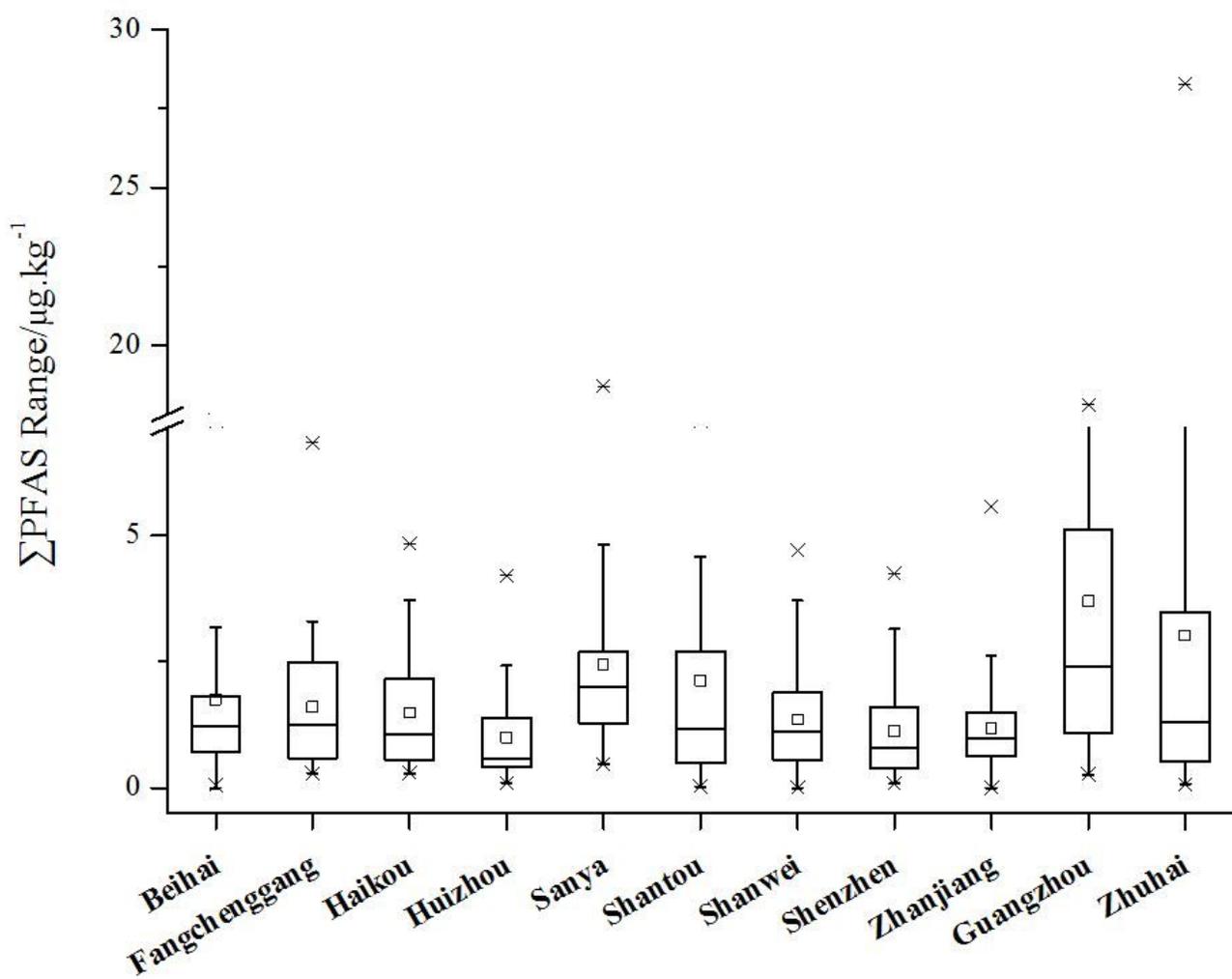


Figure 5

Average concentrations of PFASs in the samples collected from 11 selected cities

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