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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Abstract
The purpose of the research was to monitor the contamination characters and spatial and temporal distributions of 23 Perfluorinated alkyl substances (PFASs) in seafood. Total of 844 samples, including 391 shellfish and 94 crustaceans, were collected from Guangdong, Guangxi, and Hainan provinces along South China Coastal Regions and analyzed by UPLC-MS/MS. Finally, 16 PFASs were detected in the survived samples and the total detection rates reached to 99.2%. The highest concentration of ∑PFASs in each sample was 28.3 μg/kg, and the average and medium values of ∑PFAS were 1.83 μg/kg and 1.18 μg/kg, respectively. Perfluorooctane sulfonic acid (PFOS) and perfluorobutyric acid (PFBA) have been considered as predominant PFAS components with the corresponding pollution contribution rates of 29.1% and 24.7%, respectively. However, it is noted that perfluorohexane sulfonate (PFNA) and perfluorobutanesulfonic acid (PFBS) were primarily enriched in the oyster and mussel. During the period of this investigation (2014–2016), ∑PFAS average concentrations turned out constantly rising trend and new pollution component perfluorohexanesulfonic acid (PFHxS) detected in 2016, indicating that the contamination status of PFASs was getting worse in South China Coastal Regions. ∑PFAS concentrations of Guangdong, Guangxi, and Hainan provinces were approximately at similar level (1.79 μg/kg, 1.91 μg/kg and 2.02 μg/kg), and the highest concentration sample contaminated with PFNA appeared in Guangxi province. The average and medium concentrations of ∑PFAS in samples collected from Guangzhou, Zhuhai, and Sanya were the top three. Safety and risk exposure assessments of perfluorooctanoic acid (PFOA) and PFOS via daily diet intakes showed relatively low potential to local residents.

Keywords Perfluorinated alkylated substances (PFASs) · Aquatic products · Pollution characteristic · Risk assessment · South China coastal region

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-repellent painting coat on carpet, leather, and oil (Yamashita et al. 2005; Nakata et al. 2006; Li et al. 2011). PFASs contained in industrial wastewater and sewage wastewater will be disseminated to remote areas (MacInnis et al. 2019), such as the Arctic and Tibetan Plateau through atmospheric movement, rivers, or ocean currents. PFASs are commonly distributed in abiotic environment (Kucharyzk et al. 2017; Nguyen et al. 2017), wildlife (Wu et al. 2012; Groffen et al. 2018; Fair et al. 2019; Fujii et al. 2019; Zhang et al. 2019), and even humans (Kim et al. 2011; Niu et al. 2019;
Pizzurro et al. 2019). Due to public concerns of their potential carcinogenic risk, endocrine disruption effect (Caron-Beaudoin et al. 2019), and other toxic effects on human health (Hu et al. 2019), PFASs have been classified as a new type of persistent organic pollutants (POPs). Perfluorooctanesulfonic 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 (MacInnis et al. 2019). Bioaccumulation of PFASs was confirmed in aquatic animals, especially filter-feeding fish, such as silverfish and bighead carp, decapod crustacean larvae, and shellfish (Wu et al. 2012; Groffen et al. 2018; Munoz et al. 2019; Zhang et al. 2019). PFASs entering into the food chain would produce potential threats on human health (Falk et al. 2019; Fujii et al. 2019), as fish products are important sources of human exposure to PFASs (Eun et al. 2020). 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 abiotic environment, which included sediment, bottom water, and surface water (Pan et al. 2014, 2019, 2020). 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 spatiotemporal 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), shellfishes (e.g., mussels, clams, oysters, scallops, and cockles), and crustaceans (e.g., shrimps, red shrimps, mantis shrimps, swimming crabs, green crabs, and Charybdis), 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 (Fig. S1). Sampling information of collecting sites, categories, and quantity are 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 transportation to the laboratory within 48 h. Edible tissues from each sample (i.e., flesh fillet and muscle tissue) 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 (Wang et al. 2018). The sample pre-treatment method based on the modified QuEChERS procedures as described by Guo et al. (Guo et al. 2019). 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 18,000×g for 10 min. The reconstituted solution was filtered through a 0.22-μm filter prior to UPLC-MS/MS injection. Conditions of liquid chromatography/mass spectrometry were consistent with the previous studies (Wang et al. 2018).

Quality Control/Quality Assurance

Polypropylene centrifuge tubes and experimental containers used were washed with methanol before sample pre-treatment 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, polytetrafluoroethylene 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 μg/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 μg/kg with the accuracy in the range of 67.0–112% and the precision 3.8–11.7%. The LODs were 0.01 μg/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 fish, shellfish, 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.

Exposure Safety and Risk Assessment

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

Estimated Daily Intake (EDI) (ng/kg/day) = \( C \times Q/BW \),

\[
\text{Hazard Index (HR)} = \frac{\text{EDI}}{\text{Reference Dose (RfD)}},
\]

where \( C \) is the mean PFAS concentrations (ng/g, wet weight) in aquatic samples, \( Q \) is the average daily consumption of aquatic products (g/day), and \( BW \) is 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) (Zhang et al. 2019), 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.

Result 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 99.2%. The maximum added concentrations of detected PFAS components (\( \sum \)PFASs) in a given sample was 28.3 μg/kg. The average and median concentrations of the \( \sum \)PFASs were 1.83 μg/kg and 1.18 μg/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 (Ahrens et al. 2015, 2016; Groffen et al. 2018; Fair et al. 2019; Fujii et al. 2019; Meng et al. 2019; Zafeiraki et al. 2019) is listed in Table 1. It can be observed that the total amount of PFASs in aquatic products from the South China Sea was at an intermediate level.

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 are shown in Fig. 1 and Table S2, respectively. Among the 16 PFAS components, the highest detection rate (72.4%) and concentration percentage (29.1%) were PFOS. PFBA possessed the second highest detection rate (62.4%) and concentration percentage (24.7%). Although detection frequency of PFOSA and PFOA (68.0% and 65.9%) were slightly Higher than frequency of PFBA, the concentration percentages were merely 7.2% and 3.1%, which were even less than concentration percentages of PFHxA and PFNA (10.7% and 9.2%). 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 0.195–4.92 ng/L, and the mean PFAS components were PFOS (25%), PFOA
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 (Pan et al. 2014). Similar findings were reported in Vietnam’s sewage treatment plants (Lam et al. 2017). 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 fish, shellfish, and crustaceans were included in this study. At least one PFAS component was found in all fish and crustacean samples. Only 1.6% 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 shown in Fig. 2, PFOS possessed the highest pollution contribution rate, accounting for 47.8% and 53.4% of the $\sum$PFASs in fish and crustacean samples, while barely 2.5% in shellfish. However, PFBA contributed the maximal PFAS pollution at 54.3% in shellfish samples but merely contributed percentages of 2.6% and 1.5% 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 (Kucharzyk et al. 2017). It had been discovered in irrigation water, soil, vegetable, fruit (Kim et al. 2011), and aquatic products (Wu et al. 2012) in China, tap water in Korea (Kim et al. 2011), as well as surface water in Vietnam (Lam et al. 2017). Except for water, sediment, and other environmental samples, PFOS was also found in

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

| Sample sources                        | Sample categories                                                                 | $\sum$PFAS detection range (μg/kg) | References                  |
|---------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------|-----------------------------|
| Northeast Pacific Ocean               | Pacific cod                                                                      | 0.216–0.670                       | Fujii et al. 2019           |
| Korean waters                         |                                                                                   | 0.288–0.892                       |                             |
| Japanese coastal waters               |                                                                                   | 0.819–1.71                        |                             |
| Lake Tana, Ethiopia                   |                                                                                   | 0–5.80                            | Ahrens et al. 2016          |
| Miyun Reservoir in Beijing, China     |                                                                                   | 1.70–14.3                         | Meng et al. 2019            |
| South China Sea                       |                                                                                   | 0–28.3                            |                             |
| Charleston Harbor and tributaries,    |                                                                                   | 12.7–33.0                         |                             |
| South Carolina, United States         | Piscivorous fish                                                                  | 0–34.0                            |                             |
| Vaa River, South Africa               | Invertebrates and fish                                                            | 0–172                             |                             |
| The Netherlands                       | Marine fish, farmed fish, crustaceans, bivalves and European eel caught           | 0–172                             |                             |
| Stockholm Arlanda Airport in Europe   | European perch                                                                    | Absolute systemic burden was 334  | Ahrens et al. 2015          |

#### Fig. 1 Concentration profiles of individual PFAS components in all samples

(20%), PFBA (16%), and PFBS (10%) (Kwok et al. 2015). Another report showed that the concentrations of PFASs in surface seawater, bottom seawater, and sediments in the South China Sea were 0.125–1.02 ng/L, 0.038–0.779 ng/L, and 0.0075–0.0842 μg/kg, respectively. PFBA and PFOA were the predominant PFAS component in seawater samples, while PFOS was the predominant PFAS component in sediment samples (Wang et al. 2019). The detection results of PFASs in aquatic products in the present study were identical to the results of environmental samples, which indicated that fish, shellfish, 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 (Pan et al. 2014). Similar findings were reported in Vietnam’s sewage treatment plants (Lam et al. 2017). Thus, we should pay more attention to the monitoring of PFASs pollution in industrial wastewater and municipal wastewater discharge.
aquatic products (Wu et al. 2012; Fair et al. 2019; Zafeiraki et al. 2019a, b; Zafeiraki et al. 2019). Concentrations of PFOS in fatty fish collected from 6 coastal cities in China were 0.0014–1.63 μg/kg (Wu et al. 2012). 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 (Zafeiraki et al. 2019). In the present study, the highest level of PFOS found in fish was 21.0 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 (Habibullah-Al-Mamun et al. 2017), 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 (Kim et al. 2011; Kwok et al. 2015; Li et al. 2019; Wang et al. 2019; Zhou et al. 2019). Considering that most shellfish had biological habits of benthic and filter feeding (Naile et al. 2013), 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 fish, shellfish, and crustaceans in the present study, with the corresponding pollution contribution rates of 6.1%, 7.2%, and 9.8%, respectively. PFOSA, as a precursor substance of PFOS, could be degraded into PFOS (Taylor et al. 2018). 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**

The concentration variations of each PFAS component in different aquatic samples are presented in Fig. 3. The average concentrations of PFOS in fish and crustacean samples were 0.889 μg/kg and 1.47 μg/kg, respectively, which were significantly higher than the average concentration of 0.0405 μg/kg in shellfish samples. However, the average concentration of PFBA in shellfish samples was 0.875 μg/kg, which was nearly 20 times higher than the corresponding average concentration in fish (0.0484 μg/kg) and crustacean (0.0409 μg/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 fish and crustaceans tend to accumulate long-chain perfluorooalkyl carboxylic acid (PFCAs), and the concentration of PFOA in bivalve mollusks was higher than that of other PFASs (Lam et al. 2017). Another study suggests that, among long-chain PFASs, the concentrations of PFOA in crabs and mollusks were higher than those of its homolog of PFOS. Except for fish, the average concentration of PFCAs was higher than the average concentration of PFSAs in all marine organisms (Zhang et al. 2019).
Based on the statistics from 26 crab samples in this study, the ∑PFASs were 0.21–10.6 μg/kg, with the average and median concentrations of 2.96 μg/kg and 2.52 μg/kg, respectively, which were basically consistent with the overall detection results from crustacean samples. As for the individual PFSA component, compared to the average (0.249 μg/kg) and median concentrations (0.11 μg/kg) of PFOA, the corresponding concentrations of PFOS were 1.12 μg/kg and 0.78 μg/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 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 fish (Taylor et al. 2018).

Furthermore, it was noticed that oysters were the most likely to get accumulated PFNA and mussels were trended to be accumulated 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 80.1% of the ∑PFNA. Similarly, PFBS was found in 338 samples, and 25.4% (86 samples) of them were mussel, which contributed 85.8% of the ∑PFBS. Generally, researchers paid more attention to the overall pollution of PFASs, or a few hazardous PFAS components, such as PFOS, PFOA, or PFBA (Lam et al. 2017; Zhang et al. 2019). 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 (Lam et al. 2017). 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 (Christensen et al. 2017). From the findings of this study, it is possible that increased intake of oysters and mussels may also lead to the increased 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 fish, shellfish, and crustaceans, which closely represented the actual consumption patterns of aquatic products in the coastal region of the South China Sea.

The concentration variations of individual PFAS component in the three years of our study period are displayed in Fig. 4. The average value of ∑PFASs and some individual components, such as PFOS, PFBA, and PFPeA, showed...
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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 (Chen et al. 2017; MacInnis et al. 2019), and the concentration of PFOS found in the waters around Hong Kong in 2014 was doubled as detected nine years ago (Kwok et al. 2015). 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 (Fujii et al. 2019). Monitoring results in finfish and shellfish samples in Bangladesh demonstrated that most PFAS components did not show obvious seasonal variation (Habibullah-Al-Mamun et al. 2017). 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 fish 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 were found in all tested samples, and total detection rates in Guangdong, Guangxi, and Hainan were 99.2%, 99.5%, and 100%, respectively. As we can observed 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 (78.5% and 84.6%) and mean concentration (0.77 and 0.57 μg/kg) in Guangdong and Hainan, while PFBA was the predominant component in Guangxi with frequency of 70.7% and mean concentration of 0.76 μg/kg. The average and median values of ∑PFASs in Guangdong, Guangxi, and Hainan were 1.79, 1.91, and 2.02 μg/kg and 1.09, 1.22, and 1.75 μg/kg, respectively.

The concentration percentages of individual PFAS component in Guangdong, Guangxi, and Hainan are presented in Fig. 5. 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 the corresponding pollution contribution rates at 33.8% and 23.6%. The predominant PFAS components in Hainan’s samples were similar to Guangdong, except that PFOS and PFBA had almost equal pollution contribution rate of 23.7%, and 25.5%, 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 28.2% and 25.6%.

PFOS was the highest concentration of individual PFAS component among all tested samples at 21.0 μg/kg, which was found in Ambassis gymnocephalus sample. Previously, PFOS was found in shrimp samples collected from Holland with a concentration at 25.0 μg/kg (Zafeiraki et al. 2019a, 

Fig. 4 Concentration variations of individual PFAS components during 2014–2016
b), 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 Mussel sample collected from Guangxi with a concentration of 15.8 μg/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 25.6%. The average concentration of PFNA in Guangxi samples was 0.489 μg/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% (Pan et al. 2019).

In this study, samples obtained from 11 cities were selected to analyze the distribution characteristics of PFASs. The concentrations of PFASs in the samples collected from the selected cities are shown in Fig. 6. Guangzhou’s samples were found the highest average concentration at 3.69 μg/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 (Kwok et al. 2015; Wang et al. 2019). 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 (Kwok et al. 2015; Pan et al. 2019; Wang et al. 2019), 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 Safety 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 14.5 kg per year (CBG 2019). These 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 μg/kg/day and 0.003 μg/kg/day, respectively (Zhang et al. 2019). Based on the average concentration of PFOS and PFOA in each category of samples, the HR values of PFOS were 2.94 × 10⁻¹, 1.34 × 10⁻² and 4.85 × 10⁻² in fish, shellfish, and crustaceans, respectively, and the corresponding HR values of PFOA were 7.37 × 10⁻³, 1.21 × 10⁻², and 3.64 × 10⁻² for fish, shellfish, 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 are 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 (Kim et al. 2011; Li et al. 2019). For example, the HR of PFASs in PM₁₀ in Bohai area were 1.80 × 10⁻²–4.04 × 10⁻² (Liu et al. 2019), and HRs of PFASs in soil, groundwater, and tap water were lower than the risk value (Gao et al. 2019). The EDI values of PFOS and PFOA in fatty fish and shellfish in six coastal cities in China were no more than 0.001 μg/kg/day, which are considerably lower than the acceptable daily intake values of 0.15 μg/kg/day and 1.5 μg/kg/day for PFOS and PFOA, respectively (Wu et al. 2012). 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 (Kim et al. 2011). 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 (Li et al. 2019), 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 fish were PFOS. The detection rate of PFASs was 99.2%. The highest concentration of ∑PFASs in a single sample was 28.3 μg/kg, and the average concentration and the median value for all samples were 1.83 μg/kg and 1.18 μg/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 7.37 × 10⁻³–4.85 × 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 remains a continuous concern due to the increasingly serious pollution in the environment.

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

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

Consent for Publication All participants signed an informed consent before any procedure was performed.

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