



Legacy and alternative per- and polyfluoroalkyl substances in a subtropical marine food web from the Beibu Gulf, South China: Fate, trophic transfer and health risk assessment

Chang-Gui Pan^{a,b,c,d,1}, Shao-Ke Xiao^{a,b,c,1}, Ke-Fu Yu^{a,b,c,d,*}, Qi Wu^{a,b,c}, Ying-Hui Wang^{a,b,c,*}

^a Guangxi Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China

^b Coral Reef Research Center of China, Guangxi University, Nanning 530004, China

^c School of Marine Sciences, Guangxi University, Nanning 530004, China

^d Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), China

ARTICLE INFO

Editor: R Sara

Keywords:

PFASs

F-53B

Bioaccumulation

Trophic magnification

Hazard ratio

ABSTRACT

The usage of alternative per- and polyfluoroalkyl substances (PFASs) has been increasing due to the restriction and elimination of legacy PFASs. However, there is limited knowledge on bioaccumulation and trophic magnification of alternative PFASs, especially in subtropical ecosystems. In the present study, we performed a comprehensive survey to investigate the occurrence, bioaccumulation and trophic magnification of legacy and alternative PFASs in subtropical marine food webs in the Beibu Gulf, South China. Results showed that perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA) were the predominant PFASs in water phase, while perfluorooctane sulfonate (PFOS) contributed most to the sum of target PFASs in sediments and marine organisms. Of the investigated PFASs, PFOS and 6:2 chlorinated polyfluoroalkyl ether sulfonic acids (F-53B) exhibited the highest bioaccumulation factor with values > 5000, qualifying as very bioaccumulative chemicals. There was a significant positive correlation between log BSAF and the carbon chain length of perfluoroalkyl carboxylic acids (PFCAs). Trophic magnification (TMF) was observed for PFOS and F-53B, while the remaining PFASs were biodiluted through the present food web. The hazard ratios for PFOS and PFOA in all organisms were far less than unity, suggesting overall low PFAS risks for humans through consumption of marine organisms.

1. Introduction

The production and use of per- and polyfluoroalkyl substances (PFASs) have reportedly increased (Nøst et al., 2014; Zhou et al., 2014; Shi et al., 2015), and there are at least 3000 PFASs on the global market (Wang et al., 2017). Because of their thermal and chemical stability as well as surfactant properties, PFASs have been widely used in various industry and consumer products such as firefighting foams, metal plating, paper and textiles since the 1950s (Sun et al., 2016; Pan et al., 2019). Since Giesy and Kannan (2001) first reported the presence of PFOS with considerable concentrations in wild animals, PFASs have attracted great attention from the scientific community.

PFASs could not be removed efficiently by conventional wastewater treatment plants (WWTPs). Hence, most of them were released into the aquatic environment and distributed in various matrices including

water, sediment and biota samples (Pan et al., 2016; Kibambe et al., 2020). Due to their persistence, bioaccumulation and toxic effects, regulatory actions and voluntary phase-out plans have been implemented for some legacy PFASs (e.g., PFOS, PFOA, and PFOSF; Hlouskova et al., 2013; Shi et al., 2015). Following the global phase-out of legacy PFASs, a large number of alternative PFASs such as perfluorobutanoic acid (PFBA), perfluoro-1-butane-sulfonamide (FBSA) and chlorinated polyfluoroalkyl ether sulfonic acids (Cl-PFESAs) have gradually emerged and been used to meet the market demand (Wang et al., 2014; Gomis et al., 2015). Generally, these PFASs are designed by reducing the number of carbon atoms in legacy PFASs or the fluorine in legacy PFASs were replaced by other elements/functional groups to decrease their bioaccumulation capacities (Wang et al., 2013; Shi et al., 2015; Sun et al., 2016). However, these alternative PFASs are increasingly found in environmental samples at relatively high

* Corresponding author at: Guangxi Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China.

E-mail addresses: kfuyu@gxu.edu.cn (K.-F. Yu), wyh@gxu.edu.cn (Y.-H. Wang).

¹ These authors contributed equally to this work.

<https://doi.org/10.1016/j.jhazmat.2020.123618>

Received 19 May 2020; Received in revised form 24 July 2020; Accepted 25 July 2020

Available online 9 August 2020

0304-3894/© 2020 Elsevier B.V. All rights reserved.

concentrations. For example, FBSA concentrations as high as 80.12 ng/g wet weight (ww) were detected in *Platichthys flesus* muscle from the Netherlands (Chu et al., 2016). FBSA was also detected at high detection frequencies in drinking water samples collected worldwide, suggesting potential for global human exposure (Kaboré et al., 2018). Likewise, 6:2 chlorinated polyfluorinated ether sulfonate (F-53B, PFOS alternative) was widely detected in Chinese rivers and lakes with levels ranging from 1.1–7.8 ng/L (Pan et al., 2018b). Particularly, F-53B concentration up to 7600 ng/L was measured in drain outlets from the Bohai Sea of China (Chen et al., 2017). A recent review has compiled the levels of F-53B in surface waters (0.01–77 ng/L) and biota worldwide (< 0.016–0.580 ng/g ww) (Munoz et al., 2019). A previous study reported the occurrence of F-53B in polar bears from Greenland, Arctic region, suggesting its widespread distribution and long-range transport potential (Gebbinck et al., 2016).

The bioaccumulation and biomagnification of legacy PFASs were previously investigated in aquatic food webs, especially PFOS and some long-chain PFCAs. Results demonstrated that the bioaccumulation of perfluoroalkyl acids (PFAAs) varied greatly with carbon chain length and trophic levels (Loi et al., 2011; Xu et al., 2014; Liu et al., 2018). For instance, PFAAs with chain length greater than 8 carbons can generally be bioaccumulated and biomagnified along the food chains/webs (Conder et al., 2008). The assessment of bioaccumulative substances relies on examination of biota accumulation factors (bioaccumulative BAF > 2000 and very bioaccumulative BAF > 5000) and trophic magnification factors (TMF > 1) (European Regulation EC/1907/2006; Franklin, 2016). TMF values of 2.92 and 3.94 have been reported for PFOS in the Arctic marine food web from the Fildes Peninsula at King George Island and in the temperate marine food web from the Bohai Sea of China, respectively (Chen et al., 2018; Gao et al., 2019). In temperate ecosystems the TMF values for PFOS were also in the range of 2.6–4.1 and 0.41–1.70 in southeastern France and the Yadkin-Pee Dee River of USA, respectively (Simmonet-Laprade et al., 2019; Penland et al., 2020). To date, there is only one research investigating the biomagnification of PFASs in subtropical marine food webs, which focused on a suite of legacy PFASs and extractable organic fluorine (Loi et al., 2011). Due to the similar structure between PFASs and alternative PFASs (e.g. PFOS and F-53B), it is hypothesized that some of these alternative PFASs may also be biomagnified through food webs (Munoz et al., 2019). Previous studies have reported the trophic magnification of F-53B in food webs from the Bohai Sea of China, with TMF values of 3.37 and 3.43–4.32 (Liu et al., 2017b; Chen et al., 2018). However, there is limited information on bioaccumulation and trophic magnification for alternative PFASs, and in particular no data is available in subtropical marine food webs.

Beibu Gulf is a semi-closed bay, surrounded by the land of China, Vietnam and the South China Sea Island. Coastal water quality in the Beibu Gulf is gradually deteriorating due to the rapid urbanization, industrialization and aquaculture over the past decade (Lao et al., 2019; Pan et al., 2019). As one of the four major fishing grounds in China, Beibu Gulf provides high-yield and diversified seafood to China and its surrounding countries (Pan et al., 2019; Zhang et al., 2020). However, it is not clear whether the continuous release of pollutants (e.g. PFASs) into the Beibu Gulf affects the food safety and human health. Moreover, different from temperate and Arctic regions, Beibu Gulf is a subtropical region with higher temperature, abundant rainfall and larger biomass, which may influence the bioaccumulation and trophic magnification of PFASs.

Therefore, the objectives of the present study were to: (i) investigate the occurrence and levels of legacy and emerging PFASs in water, sediments and marine organisms with various trophic levels from the Beibu Gulf; (ii) evaluate the bioaccumulation and biomagnification of legacy and alternative PFASs in subtropical marine food webs; and (iii) assess the potential human health risks of PFOS and PFOA associated with the consumption of seafood from the Beibu Gulf. To the best of our knowledge, this is the first study to report the trophic magnification of F-

53B (6:2 Cl-PFESA) in a subtropical marine food web.

2. Materials and methods

2.1. Chemicals and reagents

Twenty-one legacy and alternative PFASs were selected as target compounds, including 11 PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFTTeDA), 5 perfluoroalkane sulfonates (PFSAs) (PFBS, PFHxS, PFHpS, PFOS, PFDS), F-53B, GenX, 6:2 FTSA, FBSA and FOSA. Six stable isotope standards (MPFBA, MPFHxA, MPFOA, MPFDA, MPFHxS and MPFOS) were used as internal standards. Detailed information on the standards, chemicals and reagents are summarized in the Text S1 and Table S1 in Supporting Information.

2.2. Sampling campaign and sample pretreatment

Marine organisms were sampled at three sites from the inshore area of the Beibu Gulf, South China in November, 2018 (Fig. S1). Zooplankton was collected using a 113- μ m mesh net. The sampled zooplankton was transferred into a 50 mL polypropylene centrifuge tube, freeze-dried at -50°C for 72 h, and stored at -18°C until extraction (Houde et al., 2006; Ma et al., 2014). Samples of other marine organisms, including 8 crustacean species, 5 cephalopod species and 20 fish species, were caught with a bottom trawl by fishermen. All collected samples were stored in cooler box and transported to laboratory immediately. Upon arrival at the laboratory, the body length and weight of individual organisms were measured. Soft tissue and muscle tissue were dissected and freeze-dried at -50°C for 72 h. After that, all samples were ground to powder by mortar and pestle, and stored at -18°C until extraction. Seawater (including surface and bottom water samples) and sediment samples were collected at each site simultaneously with the biota samples. The total organic carbon contents (TOC) of sediment samples were measured by an Elemental Analyser (Elementar in Germany, Variomacro cube). The lipid content of biota samples was extracted by Soxhlet extraction and determined gravimetrically (Ewald et al., 1998). Detailed information on the sampling sites and biota samples are shown in Table S2.

2.3. Sample extraction and instrumental analysis

The extraction methods of PFASs in various samples (water, sediment and biota) have been reported in our previous studies (Pan et al., 2014a, 2014b). Internal standards were used by spiking them to the different matrices prior to the start of extraction. Briefly, water samples were extracted by Waters Oasis WAX Cartridges (150 mg, 6 mL). Freeze-dried sediments were extracted by ion-pair extraction method. Biota samples were extracted using alkaline digestion followed by solid phase extraction for purification. Detailed extraction and cleanup protocols for water, sediment and biota sample are presented in Text S2.

The concentrations of PFASs in the extracts were analyzed by Agilent 1290 ultra-performance liquid chromatography coupled to a 6460 triple quadrupole mass spectrometer (UPLC-MS/MS, Agilent Technologies, Santa Clara, CA) equipped with an electrospray ionization source under negative ionization mode. The gradient elution of the mobile phase, 2 mM ammonium acetate (A) and methanol (B), are shown in Table S3. Specific instrumental parameters are provided in Text S3.

2.4. Stable isotope analysis and trophic level determination

The carbon stable-isotope ratio ($\delta^{13}\text{C}$) and nitrogen stable-isotope ratio ($\delta^{15}\text{N}$) were analyzed by an elemental analyzer (Flash EA1112, Thermo Electron, Milan, Italy) combined with a continuous-flow isotope ratio mass spectrometer (Delta V Advantages; Thermo Fisher Scientific, Bremen, Germany). $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ were calculated based on

atmospheric N₂ and Vienna PeeDee Belemnite (vPDB), respectively. To account for lipid effects, $\delta^{13}\text{C}$ values were adjusted by C/N ratio (Liu et al., 2017a). The trophic level (TL) was estimated according to the following equation (Liu et al., 2017b; Chen et al., 2018):

$$\text{TL}_{\text{sample}} = 2 + (\delta^{15}\text{N}_{\text{sample}} - \delta^{15}\text{N}_{\text{baseline}})/3.8 \quad (1)$$

where $\text{TL}_{\text{sample}}$ and $\delta^{15}\text{N}_{\text{sample}}$ represent the trophic level of organism and stable nitrogen isotope abundance, respectively; $\delta^{15}\text{N}_{\text{baseline}}$ is the stable nitrogen isotope abundance of the mussels with an average of 10.112‰ (Ding et al., 2019).

2.5. Bioaccumulation factor (BAF), biota-sediment accumulation factor (BSAF) and TMF calculation

BAF (L/kg ww) was calculated according to the equation below (Wilkinson et al., 2018):

$$\text{BAF}_{\text{organism}} = C_{\text{organism}}/C_{\text{average}} \quad (2)$$

where C_{organism} is the concentration (ng/g ww) of PFAS in the biota sample, and C_{average} is the mean concentration (ng/L) of PFAS in the surface and bottom water at corresponding site.

BSAF (kg_L/kg_{OC}) was calculated according to the following equation (Prosser et al., 2016; Lee et al., 2020):

$$\text{BSAF}_{\text{organism}} = (C_{\text{organism}}/\varphi\text{L})/(C_{\text{sediments}}/\varphi\text{OC}) \quad (3)$$

where C_{organism} is the concentration (ng/g ww) of PFAS in biota sample; $C_{\text{sediments}}$ is the concentration of PFAS in the sediments (ng/g dw); φL is the lipid fraction of organisms (g/g), and φOC is the organic carbon (OC) fraction of sediments (g/g).

TMFs were calculated according to relationship between TLs and PFAS concentrations as equations 4 and 5 (Liu et al., 2017b; Chen et al., 2018):

$$\text{Log } C = a \times \text{TL} + b \quad (4)$$

$$\text{TMF} = 10^a \quad (5)$$

where C represents the concentration of the target PFAS, a and b stand for the slope (constant), respectively.

2.6. Human health risk assessment

The human health risk of PFASs through seafood consumption was assessed by hazard ratio (HR), which is derived from the ratio between estimated daily intake (EDI, ng/kg/d) and oral reference dose (RfD, ng/kg/d). EDI was calculated by the following equation:

$$\text{EDI} = C_{\text{PFASs}} \times \text{DC}_{\text{organism}}/\text{BW} \quad (6)$$

where C_{PFASs} represents the concentration of PFASs in biota sample (ng/g ww). $\text{DC}_{\text{organism}}$ is the average daily consumption of seafood (g/d), which is derived by a questionnaire-based dietary survey (Guo et al., 2010). BW is the average body weight of human (kg), and the average body weight of different age groups was based on recent surveys (Yang et al., 2005). The hazard ratio (HR) was calculated using the following equation:

$$\text{HR} = \text{EDI}/\text{RfD} \quad (7)$$

The RfDs are 20 ng/kg/day for both PFOS and PFOA, which was based on U.S. Environmental Protection Agency (US EPA, 2016a, 2016b). HR greater than 1.0 indicates a high risk, whereas HR value below 1.0 suggests a low risk.

2.7. Quality assurance/quality control (QA/QC)

QA/QC procedures were strictly followed throughout the whole sampling and indoor experiments. Three replicates were performed for each sample. Glassware and Teflon coated lab equipment were avoided. Blank samples, control samples and recovery tests were run each batch to check for any residue, background contamination and stability of the instrument. Limit of detection (LOD) and limit of quantification (LOQ) were defined as the 3 and 10 times of the signal to noise ratio (S/N), which were derived from the Agilent Masshunter qualitative software. The LODs, LOQs and recoveries of individual PFASs are listed in Table S4.

2.8. Statistical analysis

PFASs concentrations below LOD were treated as zero, levels between LOD and LOQ were given a value of LOQ/2. Normality was tested using Shapiro-Wilk. Accordingly, Spearman rank correlation analysis was performed to evaluate the correlations between individual PFASs. Mann-Whitney U test and t-test were utilized to evaluate interspecies differences in the concentration of PFASs depending on the normality and homogeneity of the data. Linear regression was used to evaluate the relationship between concentration of PFASs and trophic level. The statistical significance was set at $p < 0.05$. All the statistical analyses were performed in IBM SPSS Statistics 25.

3. Results and discussion

3.1. PFAS concentrations in water and sediment samples

In the water samples, 10 out of 21 target PFASs (PFBA, PFPeA, PFBS, PFHxA, FBSA, PFHxS, PFHpA, PFOA, PFNA, PFOS, and F-53B) were detected (Table S5). The total PFASs concentrations were in the range of 1.53-2.11 ng/L with the mean value of 1.84 ng/L. The total PFASs concentrations in surface seawater (1.81-2.11 ng/L) were higher than that in bottom seawater (1.53-1.86 ng/L). This could be due to the sewage effluent discharged in the studied area as effluent of sewage has a greater influence on the surface water than the seawater due to their different density (Wang et al., 2020). PFBA was the predominant PFAS in the water phase, followed by PFOA and PFPeA, their concentrations being 0.29-0.53 ng/L, 0.33-0.41 ng/L and 0.22-0.33 ng/L, which accounted for 21.4%, 19.7% and 14.7% of the total PFASs, respectively. Not surprisingly, short-chain PFASs such as PFBA and PFPeA were frequently detected with relatively higher levels, while long-chain PFASs (e.g. PFDA, PFUnDA, PFDoDA and PFTrDA) were seldom detected. This could be attributed to the lower K_{oc} , higher solubility, and relatively larger-scale use of short-chain than the long-chain PFASs (Pan et al., 2014b, 2019). Additionally, the higher mobility of PFBA and PFPeA relative to long chained analogs could result in their easier transport from land to ocean. Several studies have found that the concentrations and detection frequencies of short-chain PFASs were much higher than those of long-chain PFASs in aqueous phase (Pan et al., 2019; Lee et al., 2020; Wang et al., 2020).

In the sediment samples, seven PFASs (PFOA, PFNA, PFOS, PFDA, PFUnDA, PFDoDA and PFTrDA) were detected (Table S5). The total PFASs concentrations ranged from 0.25 ng/g to 0.28 ng/g (dw). PFOS was the dominant PFAS in the sediment phase with the highest concentration of 0.09 ng/g (dw). In contrast to the water samples, only long-chain PFASs were detected in the sediments. Lee et al. (2020) reported that long-chain PFASs were more easily adsorbed onto sediments as compared to short-chain PFASs. In general, PFASs in the Beibu Gulf were at relatively low levels compared to previous studies worldwide, which could be due in part to the lower level of economic development in this region (e.g., lower GDP and less PFASs-related industrial facilities) in the Beibu Gulf (Pan et al., 2019). Indeed, a previous study suggested that PFASs contamination was positively correlated with economic

development and industry types (Kwok et al., 2015).

3.2. PFAS concentrations in marine organisms

PFAS concentrations in marine organism samples from the Beibu Gulf are presented in Fig. 1 and Table S6. Eleven out of 21 PFASs analyzed (PFPeA, PFOA, PFNA, PFOS, F-53B, PFDA, PFUnDA, FOSA, PFDoDA, PFTrDA, and PFTeDA) were detected. The highest detection frequency was found for PFOS (97%), followed by PFUnDA (94%) and PFTrDA (91%) (Table 1). The total PFASs concentrations ranged from 0.2 ng/g (ww) to 3.4 ng/g (ww), with the mean value of 1.2 ng/g (ww). The highest and lowest PFAS concentration were respectively detected in *Trachypenaeus sedili* (a crustacean) and *Argyrops bleekeri* (a fish), most likely due to their different feeding habit, exposure environment and physiology of organisms. The low PFAS levels observed in organisms agree with the relatively low exposure levels in the water and sediments in this coastal area. Multixenobiotic resistance transporter proteins can also play a role in PFAS elimination (Stevenson et al., 2006). The total PFASs concentration in the crustaceans, cephalopods and fish species were in the range of 1.45-3.40 ng/g (ww), 0.84-2.36 ng/g (ww) and 0.20-2.7 ng/g (ww), respectively (Fig. S2). The total PFASs concentrations were significantly higher in the crustaceans than in the fish ($p < 0.05$), which suggests that ingesting sediment constituted additional exposure route for PFAS in crustaceans. These results may also suggest that proteins in the chitinous exoskeletons of crustaceans might be important binding sites for PFASs, as it has been demonstrated that PFASs have affinity for proteins (Prosser et al., 2016; Princz et al., 2018).

PFOS was the dominant PFAS in most of the biota samples with levels ranging from < LOD to 1.53 ng/g ww (found in *Johnius fasciatus*, a fish), which accounted for 36% of the total PFASs (Fig. 2). The mean PFOS concentration was slightly lower in the fish (0.49 ng/g ww) than in the crustaceans (0.65 ng/g ww) and cephalopods (0.67 ng/g ww). Compared to other areas, marine organisms from the Beibu Gulf (< LOD-1.53 ng/g ww) had lower PFOS levels than those from Hong Kong (0.50-8.20 ng/g ww, Loi et al., 2011), and Bohai Gulf of China (< LOD-6.10

Table 1

Detection frequency, mean, median, range, and percentage to total PFASs of individual PFASs in biotic samples from the Beibu Gulf (South China).

Compounds	Detection frequency (%)	Mean (ng/g ww)	Median (ng/g ww)	Range (ng/g ww)	Percentage to total PFASs (%)
PFBA	0	<LOD	<LOD	<LOD	0
PFPeA	88	0.31	0.20	<LOD-0.89	18
PFHxA	0	<LOD	<LOD	<LOD	0
PFHpA	0	<LOD	<LOD	<LOD	0
PFOA	68	0.15	0.12	<LOD-0.61	7
PFNA	59	0.10	0.07	<LOD-0.26	4
PFDA	74	0.09	0.07	<LOD-0.21	4
PFUnDA	94	0.14	0.12	<LOD-0.38	9
PFDoDA	62	0.06	0.05	<LOD-0.13	3
PFTrDA	91	0.14	0.12	<LOD-0.40	9
PFTeDA	38	0.05	0.04	<LOD-0.09	1
PFBS	0	<LOD	<LOD	<LOD	0
PFHxS	0	<LOD	<LOD	<LOD	0
PFHpS	0	<LOD	<LOD	<LOD	0
PFOS	97	0.56	0.42	<LOD-1.53	36
PFDS	0	<LOD	<LOD	<LOD	0
FBSA	0	<LOD	<LOD	<LOD	0
GenX	0	<LOD	<LOD	<LOD	0
6:2FTSA	0	<LOD	<LOD	<LOD	0
F-53B	44	0.05	0.04	<LOD-0.10	2
FOSA	79	0.13	0.07	<LOD-0.71	7

LOD: limit of detection

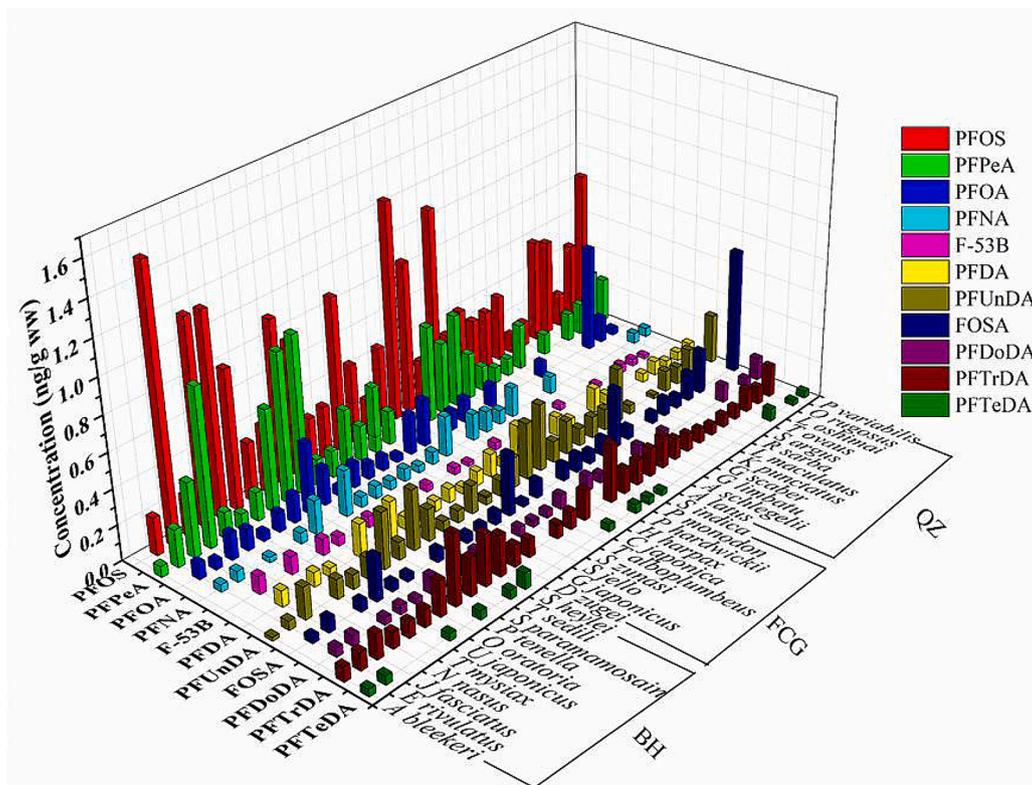


Fig. 1. Concentrations (ng/g ww) of detected PFASs detected in marine organisms from the Beibu Gulf (South China).

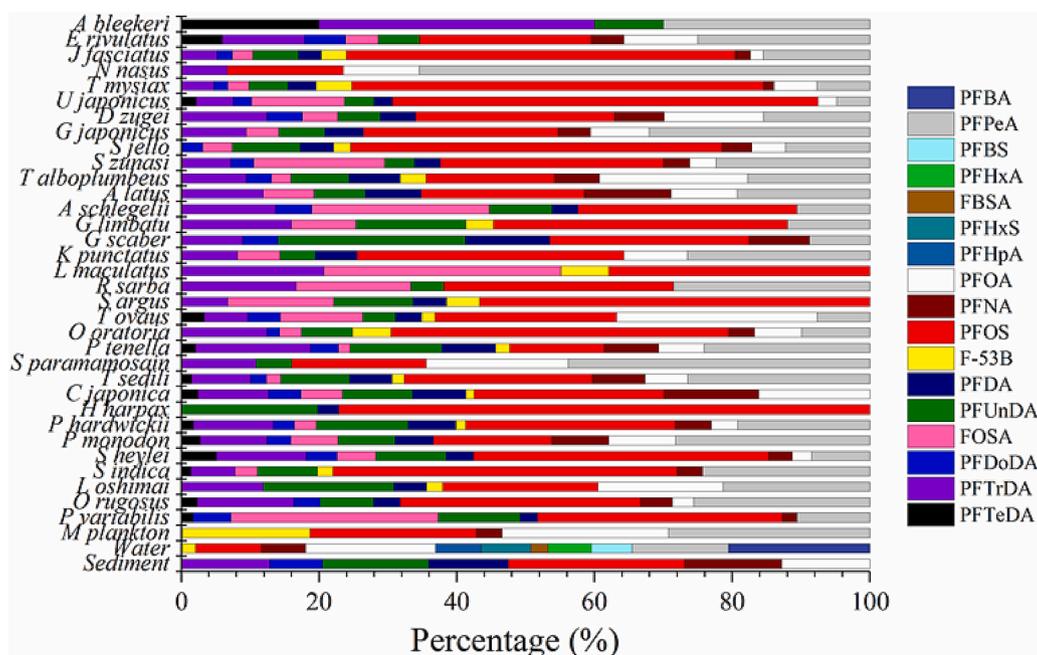


Fig. 2. Patterns of the relative contribution (%) of individual PFASs to the total PFASs in water, sediment and biota samples from the Beibu Gulf (South China).

ng/g ww; Chen et al., 2018). The alternative to PFOS, F-53B, was also detected in the marine organisms with a detection frequency of 44%. The concentrations of F-53B ranged from < LOD to 0.1 ng/g ww, with the mean value of 0.05 ng/g ww that is about an order of magnitude lower than that of PFOS.

Similar to sediments, long-chain PFASs were frequently detected in marine organisms, except for zooplankton (Table 1). This could be explained by the different bioaccumulation capacities among PFASs, as it has been demonstrated that long-chain PFASs have a higher bioaccumulation potential than short-chain PFASs (Fang et al., 2014, 2014b; Chu et al., 2016; Pan et al., 2018a). The seldom detection of long-chain PFASs (especially PFASs with chain length greater than or equal to 10 carbon atoms) in the zooplankton can be explained by its living area. In other words, as zooplankton live in the surface seawater (Casal et al., 2017), this reduces the likelihood to be exposed to long-chain PFASs (carbon atoms ≥ 10 , i.e. PFDA, PFUnDA, PFDoDA and PFTeDA) which mainly accumulate in the sediment. In agreement with our results, many studies reported that long-chain PFASs were more frequently detected with relatively higher concentrations in higher trophic level organisms (Munoz et al., 2017; Gao et al., 2019). Regarding the short-chain PFASs (e.g. PFBA, PFBS), except PFPeA, they were not detected in any of the marine organism samples, even though they were the dominant PFASs detected in the water samples. These results indicate that most short-chain PFASs do not bioaccumulate at significant levels in the marine organisms analyzed here. However, it should be noted that PFPeA (a short-chain PFAS) was the second dominant PFAS detected in marine organisms, constituting 18% of the total PFASs. Likewise, a few studies have observed the dominance of PFPeA in the marine organisms (e.g. gastropod, crab, plankton and seasoned laver) from coastal waters (Hong et al., 2015; Casal et al., 2017; Jeong et al., 2019).

Spearman correlation analysis showed that significantly positive correlations were observed between concentrations of several PFASs ($p < 0.05$) (Table S7). For instance, F-53B was significantly positively correlated with PFOS ($p < 0.01$), suggesting their similar sources and/or environmental behaviors. In fact, F-53B accumulates in the same way as the legacy PFASs by binding to serum albumin (Shi et al., 2015; Liu et al., 2017b; Shi et al., 2018). There were no significant correlations between lipid contents and any PFASs, which indicates that target PFASs

do not tend to accumulate in adipose tissue (Liu et al., 2017b; Munoz et al., 2017; Martín et al., 2019). Additionally, no significant correlations were found between PFASs and length or body weight of marine organism ($p > 0.05$), suggesting that size or length cannot be used as the proxy to predict the PFASs concentration in the biota samples from the Beibu Gulf.

3.3. BAFs and BSAFs of PFASs

Log BAFs for individual PFASs in the marine samples from the Beibu Gulf are summarized in Table S8 and Fig. 3. BAF values varied among species and individual PFASs. The log BAF values of PFASs detected ranged from 2.02 for PFOA in *Octopus rugosus* (a Cephalopod) to 4.21 for PFOS in *Johnius fasciatus* (a fish). The median log BAF values followed

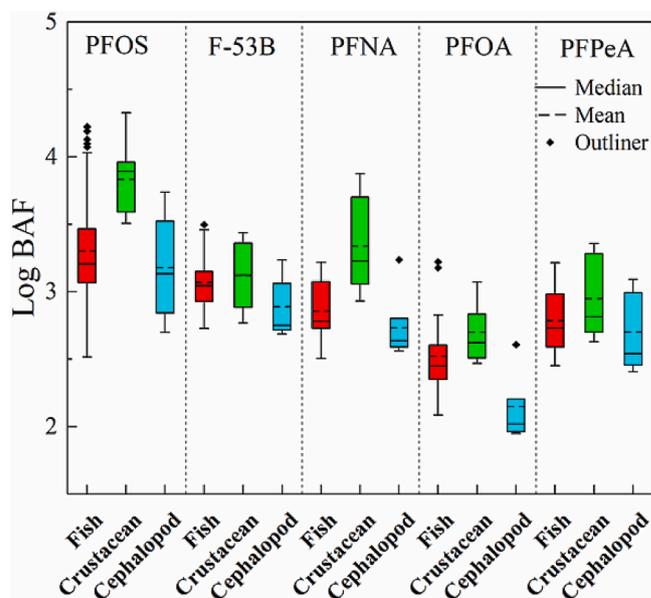


Fig. 3. Box and whisker plots of BAFs for PFOS, F-53B, PFNA, PFOA and PFPeA in different marine biota groups from Beibu Gulf.

the order: PFOS (3.35) > F-53B (3.04) > PFNA (2.94) > PFPeA (2.89) > PFOA (2.54). The greatest log BAF values for PFOS (4.21) and F-53B (3.43) were both found in *Johnius fasciatus* indicating that PFOS and F-53B were bioaccumulative. Additionally, the mean log BAFs for PFOS were somewhat higher than those of F-53B in all taxa (Fig. S3). In contrast, higher BAFs for F-53B relative to PFOS have been reported in freshwater organisms (Liu et al., 2011; Shi et al., 2015; Cui et al., 2018). Such difference might be ascribed to the different physiological parameters and exposure conditions between fresh and marine organisms. The mean log BAF for PFOS (3.43) in marine organisms was higher than that of PFOA (2.55), which is consistent with the previous result that the bioaccumulation of PFSA was stronger than that of PFCA of the same fluorinated carbon chain length (Conder et al., 2008; Pan et al., 2014a).

The calculated log BAFs for the detected PFASs were in the range of 2.04 - 4.21, 2.02 - 3.90, and 2.48 - 3.99 for fishes, cephalopods, and crustaceans, respectively (Table S8). Moreover, the mean and median log BAF values for PFASs ranked in the following order: crustacean > fish > cephalopod (Fig. 3), which might be attributed to the different capacities of accumulation and metabolism between different taxa (Xu et al., 2014; Martín et al., 2019). Concerning for PFOS, its log BAF were significantly higher in the crustacean than in the fish ($p < 0.05$), which suggests that benthic crustaceans tended to accumulate more PFOS.

BSAFs were also determined for benthic organisms (crustaceans and cephalopods) with the values being listed in Table S9. The BSAF value for PFCAs and PFASs in the benthic organisms ranged from 0.07 - 2.21 and 0.14 - 3.06, respectively. The highest mean BSAF value was found for PFOS (1.20), followed by PFTrDA (0.80) and PFUnDA (0.59). Furthermore, the log BSAF values for PFCAs were significantly positively correlated with the length of carbon chain (C8 to C13, $p < 0.05$, Fig. S4). Similarly, bioaccumulation factors of perfluoroalkyl acids increase with increasing perfluoroalkyl chain length (Conder et al., 2008; Loi et al., 2011; Pan et al., 2014a).

3.4. Trophic transfer of PFASs in the subtropical marine food web

The stable carbon ($\delta^{13}\text{C}$) and nitrogen isotope ($\delta^{15}\text{N}$) ratios have been applied to determine the trophic relationships in various food webs in many studies (Loi et al., 2011; Liu et al., 2017b; Chen et al., 2018).

$\delta^{15}\text{N}$ was used to determine the trophic levels of marine organisms with values indicating 2-5‰ enrichment with each increasing TL. $\delta^{13}\text{C}$ was used to identify diet composition and food sources in organisms, with the $\delta^{13}\text{C}$ ratio generally indicating 1‰ enrichment per TL (Hobson and Welch, 1992). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios for all the collected marine species are illustrated in Fig. 4. The $\delta^{15}\text{N}$ values ranged from 9.71‰ for *Lateolabrax maculatus* to 13.28‰ for *Grammoplites scaber*, while the adjusted $\delta^{13}\text{C}$ values ranged from -22.28‰ for zooplankton to -15.52‰ for *Sepiella heylei*. In all the investigated organisms, species with similar $\delta^{13}\text{C}$ values indicated that the organisms have similar food sources. TLs were calculated for all organisms based on $\delta^{15}\text{N}$ value with the values ranging from 1.89 for *Lateolabrax maculatus* to 3.89 for *Thryssa mysiax* (Table S2). The TLs of crustaceans, cephalopods and fishes were in the range of 2.64-3.57, 2.38-3.43 and 1.89-3.89, respectively.

To assess whether different species belong to the same food web, we further calculated relative carbon sources of species using TL and adjusted $\delta^{13}\text{C}$ values (Text S4; McKinney et al., 2012; Liu et al., 2017a). The resulted relative carbon sources ranged from 0.19 for *Charybdis japonica* (a crustacean) to 1.09 for zooplankton, with a mean value of 0.51 (Table S2 and Fig. S5). Additionally, the relative carbon sources were close to this mean value for all the sampled species, except for zooplankton (1.09) and *Grammoplites Scaber* (1.05). These results suggest that all species belong to the same food web, except for zooplankton and *Grammoplites Scaber*. Therefore, they were excluded from the calculation of TMF in the present study.

TMF values and the corresponding regression equation of individual PFASs are presented in Table S10. There were significant correlations between TLs and seven PFASs (PFOA, PFNA, PFOS, F-53B, PFUnDA, PFDoDA, and PFTeDA) ($p < 0.05$). Among the PFASs analyzed, PFOS and F-53B showed the highest TMF values (1.76 and 1.69, respectively), indicating biomagnification through the present food web (Fig. 5). Likewise, recent studies also found the trophic biomagnification for PFOS and F-53B in various food webs (Chen et al., 2018; Gao et al., 2019). Interestingly, TMF values for PFOS and F-53B in the present study were lower than those reported in temperate and polar food webs. For instance, TMF values for PFOS and F-53B were respectively 3.94 and 3.37 in the temperate marine food web from the Bohai Sea of China (Chen et al., 2018). Also, a TMF value of 2.92 has been reported for PFOS

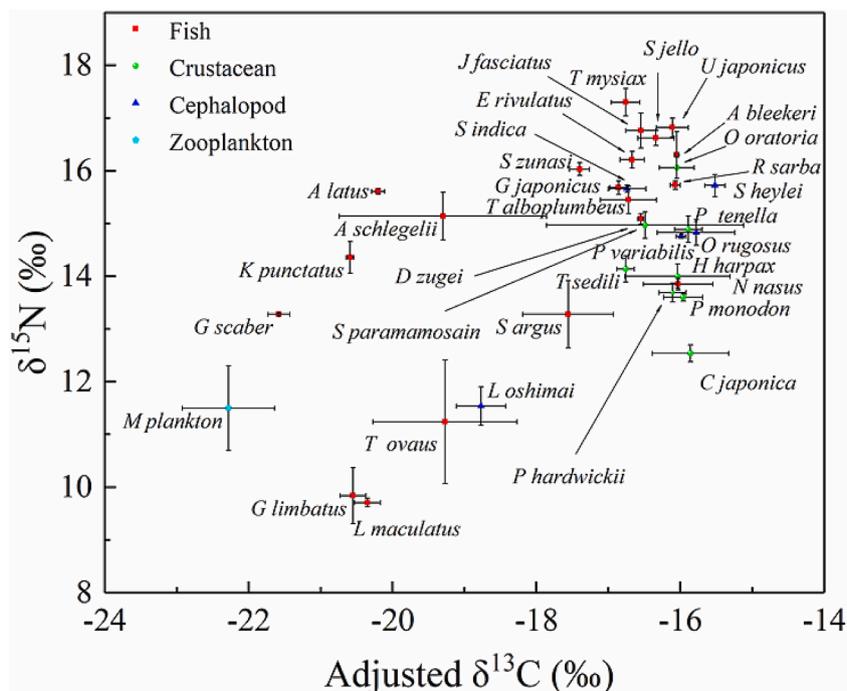


Fig. 4. $\delta^{15}\text{N}$ and adjusted $\delta^{13}\text{C}$ values in marine organisms from the Beibu Gulf.

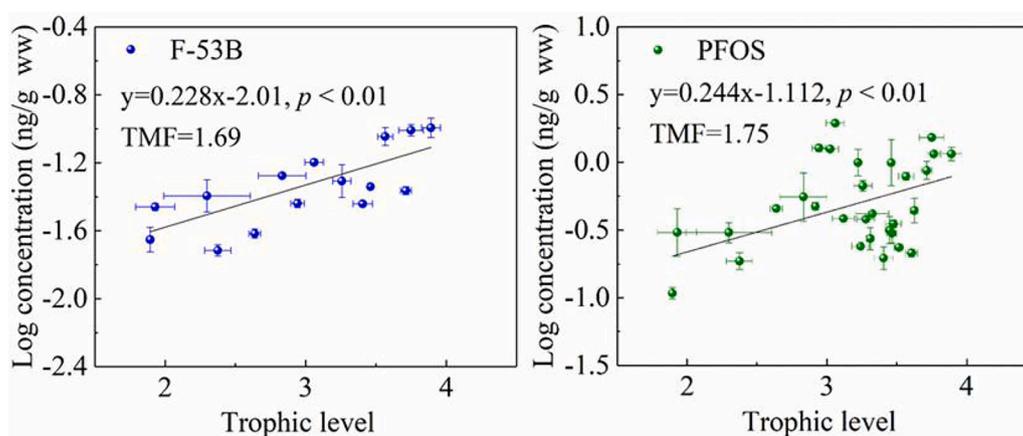


Fig. 5. Relationship between log concentration of F-53B, PFOS and trophic level. Note: green dots and blue dots stand for arithmetic means of trophic level and log concentration of PFOS and F-53B, respectively. Error bar indicates standard deviation.

in the Arctic marine food web from the Fildes Peninsula at King George Island, Antarctica (Gao et al., 2019). Unlike PFOS and F-53B, all the remaining PFASs (PFOA, PFNA, PFDA, PFUnDA, FOSA, PFDoDA, and PFTeDA) showed TMF values lower than 1, suggesting the trophic dilution of these substances through the food web in the Beibu Gulf. Similar results have been reported in previous studies. For example, the TMF values below 1 were reported for both FOSA and PFOA in Lake Ontario (Martin et al., 2004). Moreover, PFTrDA (TMF = 0.66) and PFTeDA (TMF = 0.33) were trophic diluted in the benthic food web from a macrotidal estuary in western Europe (Munoz et al., 2017). However, most previous studies reported opposite results that long-chain PFASs were biomagnified through the food webs (Kelly et al., 2009; Loi et al., 2011; Liu et al., 2017b). For instance, Loi et al. (2011) found that long-chain PFASs such as PFDA, PFUnDA and PFDoDA were biomagnified through the food web in Hong Kong coast.

Generally, the TMF values for most PFASs in the subtropical food webs were lower than those reported in temperate and Arctic food webs (Table 2). This difference can be attributed to several factors, including different environmental parameters (e.g. temperature and salinity), biomass abundance and food web structures between regions. Specifically, higher temperature in subtropical region can promote the metabolism and growth rate of marine organisms, and might alter the physicochemical properties of PFASs and also the physiology of organisms including bioaccumulation and biotransformation. (Verhaert et al., 2017). Salinity can also affect the environmental behaviors of PFASs in aquatic environments, including bioaccumulation, through salting out effects (Jeon et al., 2010). Compared with temperate and polar marine

ecosystems, subtropical marine ecosystems have much higher biomass, which can reduce TMFs by biomass dilution (Borgå et al., 2012). Additionally, variability in TMF between geographical locations may be due to difference in exposure to precursors that can biotransform at different rates along the food chain (Babut et al., 2017). For example, 6:2 FTS was biotransformed to shorter, more water-soluble PFASs in fish by the main mechanism of rapid elimination (Langberg et al., 2019). Overall, our results indicated that TMFs of legacy and alternative PFASs in the marine food web from the Beibu Gulf differed from those reported in Arctic and temperate food webs.

3.5. Human health risk assessment

Dietary intake is considered as the main pathway of exposure to PFASs for humans, especially for aquatic products (Haug et al., 2010; Fair et al., 2019; Meng et al., 2019). Because PFOS and PFOA are prevailing PFASs and the RfDs for these two chemicals are available, here we assessed the human health risks of PFOS and PFOA associated with consumption of seafood from the Beibu Gulf. The mean concentrations in each seafood group (i.e. fish, shrimps, crabs, and cephalopods) were used for assessment in the present study (Table S11). The mean-based EDI for PFOS and PFOA through consumption of seafood for different groups of people are provided in Table S12. EDIs for PFOS and PFOA were in the range of 0.69-1.30 ng/kg/d, 0.13-0.20 ng/kg/d respectively.

Hazard ratios (HRs) for PFOS and PFOA were estimated based on the EDI values and the corresponding RfDs (Table S12). The HR values of PFOS (0.035-0.065) and PFOA (0.007-0.010) in all groups were much

Table 2

Trophic magnification factors (TMFs) of PFASs in different regions around the world.

Region	PFOA	PFNA	PFOS	F-53B	PFDA	PFUnDA	FOSA	PFDoDA	PFTeDA	Max TL in food web	Reference
Arctic	- ^a	-	2.92	-	-	-	-	-	-	3.43	Gao et al., 2019
	3.28	7.03	17.40	-	8.29	7.99	5.09	4.79	-	5.50	Kelly et al., 2009
	-	2.10	2.90	-	3.70	3.10	-	2.40	-	4.60	Xu et al., 2014
	-	-	3.94	3.37	-	-	-	-	-	4.30	Chen et al., 2018
	-	1.85-2.11	3.83-3.88	3.43-4.32	2.21-2.89	1.46-1.52	-	2.28-4.07	3.54-4.40	3.40	Liu et al., 2017b
Temperate	0.58-0.37	1.00	1.86-5.88	-	1.00-3.67	1.00-4.71	0.51	1.00	1.00-2.45	- ^b	Martin et al., 2004
	6.00	0.88-3.10	0.94-3.90	-	1.70	1.80	-	1.30	0.66	-	Munoz et al., 2017
	0.39-0.57	0.61-0.90	1.90-8.30	-	2.60-10.9	2.40-4.20	1.3-5.90	1.80-2.70	1.80-14.90	4.90	Simmonet-Laprade et al., 2019
	1.00	1.00	1.30	-	1.50	1.74	-	1.38	-	5.50	Loi et al., 2011
Subtropical	0.35	0.28	1.76	1.6	0.92	0.72	0.75	0.58	1.06	3.89	Present study

^a The compound was not analyzed.

^b The TL is not available.

lower than unity, which indicates that these two PFASs would not impose any direct health risk associated with the consumption of target marine organisms across the Beibu Gulf. Although the health risks of PFOS and PFOA were quite low, the potential health risks might still exist due to long-term exposure to these and other chemicals.

4. Conclusions

This study investigated for the first time the occurrence, bioaccumulation and trophic transfer of legacy and alternative PFAS in subtropical marine food webs from the Beibu Gulf, South China. Short-chain PFASs (e.g. PFBA) were widely distributed and more abundant in the water phase, while long-chain PFASs (e.g. PFOS) were the predominant PFAS in the sediments and marine organisms. F-53B was detected in Beibu Gulf coastal areas, which further suggests its transport/migration from land to sea. Due to the similar properties between F-53B and PFOS, it is likely that F-53B has the potential to become a globally distributed environmental pollutant. Though PFOS and F-53B were biomagnified through the investigated food web, TMFs of PFASs in this subtropical area were generally lower than those in temperate and Arctic regions.

CRedit authorship contribution statement

Chang-Gui Pan: Conceptualization, Writing - review & editing. **Shao-Ke Xiao:** Investigation, Writing - review & editing. **Ke-Fu Yu:** Validation, Funding acquisition. **Qi Wu:** Investigation. **Ying-Hui Wang:** Conceptualization, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The author would like to thank the financial support by the National Natural Science Foundation of China (41673105), Guangxi Innovation-driven Development Projects (GuikeAA18242031, GuikeAA17204074, AD17129063), and Natural Science Foundation of Guangxi (2018GXNSFAA050144). We would also like to thank anonymous reviewers who have provided many insightful comments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jhazmat.2020.123618>.

References

- Babut, M., Labadie, P., Simonnet-Laprade, C., Munoz, G., Roger, M.C., Ferrari, B.J.D., Budzinski, H., Sivade, E., 2017. Per- and poly-fluoroalkyl compounds in freshwater fish from the Rhône River: Influence of fish size, diet, prey contamination and biotransformation. *Science of the Total Environment* 605–606, 38–47. <https://doi.org/10.1016/j.scitotenv.2017.06.111>.
- Borgå, K., Kidd, K.A., Muir, D.C.G., Berglund, O., Conder, J.M., Gobas, F.A.P.C., Kucklick, J., Malm, O., Powell, D.E., 2012. Trophic magnification factors: Considerations of ecology, ecosystems, and study design. *Integrated Environmental Assessment and Management* 8, 64–84. <https://doi.org/10.1002/ieam.244>.
- Casal, P., González-Gaya, B., Zhang, Y., Reardon, A.J.F., Martin, J.W., Jiménez, B., Dachs, J., 2017. Accumulation of perfluoroalkylated substances in oceanic plankton. *Environmental Science and Technology* 51, 2766–2775. <https://doi.org/10.1021/acs.est.6b05821>.
- Chen, H., Han, J., Cheng, J., Sun, R., Wang, X., Han, G., Yang, W., He, X., 2018. Distribution, bioaccumulation and trophic transfer of chlorinated polyfluoroalkyl ether sulfonic acids in the marine food web of Bohai, China. *Environmental Pollution* 241, 504–510. <https://doi.org/10.1016/j.envpol.2018.05.087>.
- Chen, H., Han, J., Zhang, C., Cheng, J., Sun, R., Wang, X., Han, G., Yang, W., He, X., 2017. Occurrence and seasonal variations of per- and polyfluoroalkyl substances (PFASs) including fluorinated alternatives in rivers, drain outlets and the receiving Bohai Sea of China. *Environmental Pollution* 231, 1223–1231. <https://doi.org/10.1016/j.envpol.2017.08.068>.
- Chu, S., Letcher, R.J., McGoldrick, D.J., Backus, S.M., 2016. A New Fluorinated Surfactant Contaminant in Biota: Perfluorobutane sulfonamide in several fish species. *Environmental Science and Technology* 50, 669–675. <https://doi.org/10.1021/acs.est.5b05058>.
- Conder, J.M., Hoke, R.A., Wolf, W.D., Russell, M.H., Buck, R.C., 2008. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environmental Science and Technology* 42, 995–1003. <https://doi.org/10.1021/es070895g>.
- Cui, Q., Pan, Y., Zhang, H., Sheng, N., Wang, J., Guo, Y., Dai, J., 2018. Occurrence and Tissue Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids and Legacy Per/Polyfluoroalkyl Substances in Black-Spotted Frog (*Pelophylax nigromaculatus*). *Environmental Science and Technology* 52, 982–990. <https://doi.org/10.1021/acs.est.7b03662>.
- Ding, Y., Wu, Z., Zhang, R., Yu, K., Wang, Y., Zou, Q., Zeng, W., Han, M., 2019. Organochlorines in fish from the coastal coral reefs of Weizhou Island, south China sea: Levels, sources, and bioaccumulation. *Chemosphere* 232, 1–8. <https://doi.org/10.1016/j.chemosphere.2019.05.199>.
- European Regulation EC/1907/ 2006 of the European parliament and of the council.
- Fair, P.A., Wolf, B., White, N.D., Arnott, S.A., Kannan, K., Karthikraj, R., Vena, J.E., 2019. Perfluoroalkyl substances (PFASs) in edible fish species from Charleston Harbor and tributaries, South Carolina, United States: Exposure and risk assessment. *Environmental Research* 171, 266–277. <https://doi.org/10.1016/j.envres.2019.01.021>.
- Fang, S., Chen, X., Zhao, S., Zhang, Y., Jiang, W., Yang, L., Zhu, L., 2014. Trophic magnification and isomer fractionation of perfluoroalkyl substances in the food web of Taihu Lake, China. *Environmental Science and Technology* 48, 2173–2182. <https://doi.org/10.1021/es405018b>.
- Franklin, J., 2016. How reliable are field-derived biomagnification factors and trophic magnification factors as indicators of bioaccumulation potential? Conclusions from a case study on per- and polyfluoroalkyl substances. *Integrated Environmental Assessment and Management* 12, 6–20. <https://doi.org/10.1002/ieam.1642>.
- Gao, K., Miao, X., Fu, Jie, Chen, Y., Li, H., Pan, W., Fu, Jianjie, Zhang, Q., Zhang, A., Jiang, G., 2019. Occurrence and trophic transfer of per- and polyfluoroalkyl substances in an Antarctic ecosystem. *Environmental Pollution* 257, 113383. <https://doi.org/10.1016/j.envpol.2019.113383>.
- Gebbinck, W.A., Bossi, R., Rigét, F.F., Rosing-Asvid, A., Sonne, C., Dietz, R., 2016. Observation of emerging per- and polyfluoroalkyl substances (PFASs) in Greenland marine mammals. *Chemosphere* 144, 2384–2391. <https://doi.org/10.1016/j.chemosphere.2015.10.116>.
- Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science and Technology* 35, 1339–1342. <https://doi.org/10.1021/es001834k>.
- Gomis, M.I., Wang, Z., Scheringer, M., Cousins, I.T., 2015. A modeling assessment of the physicochemical properties and environmental fate of emerging and novel per- and polyfluoroalkyl substances. *Science of the Total Environment* 505, 981–991. <https://doi.org/10.1016/j.scitotenv.2014.10.062>.
- Guo, J., Wu, F., Shen, R., Zeng, E.Y., 2010. Ecotoxicology and Environmental Safety Dietary intake and potential health risk of DDTs and PBDEs via seafood consumption in South China. *Ecotoxicology and Environmental Safety* 73, 1812–1819. <https://doi.org/10.1016/j.ecoenv.2010.08.009>.
- Haug, L.S., Thomsen, C., Brantsæter, A.L., Kvale, H.E., Haugen, M., Becher, G., Alexander, J., Meltzer, H.M., Knutsen, H.K., 2010. Diet and particularly seafood are major sources of perfluorinated compounds in humans. *Environment International* 36, 772–778. <https://doi.org/10.1016/j.envint.2010.05.016>.
- Hlouskova, V., Hradkova, P., Poustka, J., Brambilla, G., De Filipis, S.P., D'Hollander, W., Bervoets, L., Herzke, D., Huber, S., de Voogt, P., Pulkrabova, J., 2013. Occurrence of perfluoroalkyl substances (PFASs) in various food items of animal origin collected in four European countries. *Food Additives and Contaminants* 30, 1918–1932. <https://doi.org/10.1080/19440049.2013.837585>.
- Hobson, K.A., Welch, H.E., 1992. Determination of trophic relationships within a high Arctic marine food web using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis. *Marine Ecology Progress Series* 84, 9–18. <https://doi.org/10.3354/meps084009>.
- Hong, S., Khim, J.S., Wang, T., Naile, J.E., Park, J., Kwon, B.O., Song, S.J., Ryu, J., Codling, G., Jones, P.D., Lu, Y., Giesy, J.P., 2015. Bioaccumulation characteristics of perfluoroalkyl acids (PFAAs) in coastal organisms from the west coast of South Korea. *Chemosphere* 129, 157–163. <https://doi.org/10.1016/j.chemosphere.2014.06.023>.
- Houde, M., Bujas, T.A.D., Small, J., Wells, R.S., Fair, P.A., Bossart, G.D., Solomon, K.R., Muir, D.C.G., 2006. Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (*Tursiops truncatus*) food web. *Environmental Science and Technology* 40, 4138–4144. <https://doi.org/10.1021/es060233b>.
- Jeon, J., Kannan, K., Lim, H.K., Moon, H.B., Ra, J.S., Kim, S.D., 2010. Bioaccumulation of perfluorochemicals in Pacific oyster under different salinity gradients. *Environmental Science and Technology* 44, 2695–2701. <https://doi.org/10.1021/es100151r>.
- Jeong, Y.J., Bang, S., Kim, Jihyun, Chun, S.H., Choi, S., Kim, Jinhye, Chung, M.S., Kang, G.J., Kang, Y.W., Kim, Junghoan, Kho, Y., Joo, Y., Lee, K.W., 2019. Comparing levels of perfluorinated compounds in processed marine products. *Food and Chemical Toxicology* 126, 199–210. <https://doi.org/10.1016/j.fct.2019.01.028>.
- Kaboré, H.A., Vo Duy, S., Munoz, G., Méité, L., Desrosiers, M., Liu, J., Sory, T.K., Sauvé, S., 2018. Worldwide drinking water occurrence and levels of newly-identified perfluoroalkyl and polyfluoroalkyl substances. *Science of the Total Environment* 616–617, 1089–1100. <https://doi.org/10.1016/j.scitotenv.2017.10.210>.

- Kelly, B.C., Ikonoumou, M.G., Blair, J.D., Surridge, B., Hoover, D., Grace, R., Gobas, F.A.P.C., 2009. Perfluoroalkyl contaminants in an arctic marine food web: Trophic magnification and wildlife exposure. *Environmental Science and Technology* 43, 4037–4043. <https://doi.org/10.1021/es9003894>.
- Kibambe, M.G., Momba, M.N.B., Daso, A.P., Coetzee, M.A.A., 2020. Evaluation of the efficiency of selected wastewater treatment processes in removing selected perfluoroalkyl substances (PFASs). *Journal of Environmental Management* 255, 109945 <https://doi.org/10.1016/j.jenvman.2019.109945>.
- Kwok, K.Y., Wang, X.H., Ya, M., Li, Y., Zhang, X.H., Yamashita, N., Lam, J.C.W., Lam, P.K.S., 2015. Occurrence and distribution of conventional and new classes of per- and polyfluoroalkyl substances (PFASs) in the South China Sea. *Journal of Hazardous Materials* 285, 389–397. <https://doi.org/10.1016/j.jhazmat.2014.10.065>.
- Langberg, H.A., Breedveld, G.D., Gronning, H.M., Kvinnas, M., Jenssen, B.M., Hale, S.E., 2019. Bioaccumulation of fluorotelomer sulfonates and perfluoroalkyl acids in marine organisms living in Aqueous Film-Forming Foam impacted waters. *Environmental Science and Technology* 53, 10951–10960. <https://doi.org/10.1021/acs.est.9b00927>.
- Lao, Q., Su, Q., Liu, G., Shen, Y., Chen, F., Lei, X., 2019. Spatial distribution of and historical changes in heavy metals in the surface seawater and sediments of the Beibu Gulf, China. *Marine Pollution Bulletin* 146, 427–434. <https://doi.org/10.1016/j.marpolbul.2019.06.080>.
- Lee, Y.M., Lee, J.Y., Kim, M.K., Yang, H., Lee, J.E., Son, Y., Kho, Y., Choi, K., Zoh, K.D., 2020. Concentration and distribution of per- and polyfluoroalkyl substances (PFAS) in the Asan Lake area of South Korea. *Journal of Hazardous Materials* 381, 120909 <https://doi.org/10.1016/j.jhazmat.2019.120909>.
- Liu, C., Gin, K.Y.H., Chang, V.W.C., Goh, B.P.L., Reinhard, M., 2011. Novel perspectives on the bioaccumulation of PFCs - The concentration dependency. *Environmental Science and Technology* 45, 9758–9764. <https://doi.org/10.1021/es202078n>.
- Liu, S., Zhao, H., Lehmler, H.J., Cai, X., Chen, J., 2017a. Antibiotic pollution in marine food webs in Laizhou Bay, North China: Trophodynamics and human exposure implication. *Environmental Science and Technology* 51, 2392–2400. <https://doi.org/10.1021/acs.est.6b04556>.
- Liu, W., He, W., Wu, J., Qin, N., He, Q., Xu, F., 2018. Residues, bioaccumulations and biomagnification of perfluoroalkyl acids (PFAAs) in aquatic animals from Lake Chaohu, China. *Environmental Pollution* 240, 607–614. <https://doi.org/10.1016/j.envpol.2018.05.001>.
- Liu, Y., Ruan, T., Lin, Y., Liu, A., Yu, M., Liu, R., Meng, M., Wang, Y., Liu, J., Jiang, G., 2017b. Chlorinated polyfluoroalkyl ether sulfonic acids in marine organisms from Bohai Sea, China: Occurrence, temporal variations, and trophic transfer behavior. *Environmental Science and Technology* 51, 4407–4414. <https://doi.org/10.1021/acs.est.6b06593>.
- Loi, E.I.H., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S., Kannan, K., Yamashita, N., 2011. Trophic magnification of poly- and perfluorinated compounds in a subtropical food web. *Environmental Science and Technology* 45, 5506–5513. <https://doi.org/10.1021/es200432n>.
- Ma, X., Zhang, H., Wang, Z., Yao, Z., Chen, Jingwen, Chen, Jiping, 2014. Bioaccumulation and trophic transfer of short chain chlorinated paraffins in a marine food web from Liaodong Bay, North China. *Environmental Science and Technology* 48, 5964–5971. <https://doi.org/10.1021/es500940p>.
- Martin, Jonathan W., Whittle, D Michael, Muir, Derek C G, Mabury, S.A., 2004. Perfluoroalkyl contaminants in a food web from Lake Ontario. *Environmental Science and Technology* 38, 5379–5385. <https://doi.org/10.1021/es049331s>.
- Martín, J., Hidalgo, F., García-Corcoles, M.T., Ibáñez-Yuste, A.J., Alonso, E., Vilchez, J.L., Zafra-Gómez, A., 2019. Bioaccumulation of perfluoroalkyl substances in marine echinoderms: Results of laboratory-scale experiments with *Holothuria tubulosa* Gmelin, 1791. *Chemosphere* 215, 261–271. <https://doi.org/10.1016/j.chemosphere.2018.10.037>.
- McKinney, M.A., McMeans, B.C., Tomy, G.T., Rosenberg, B., Ferguson, S.H., Morris, A., Muir, D.C.G., Fisk, A.T., 2012. Trophic transfer of contaminants in a changing arctic marine food web: Cumberland sound, Nunavut, Canada. *Environmental Science and Technology* 46, 9914–9922. <https://doi.org/10.1021/es302761p>.
- Meng, J., Liu, S., Zhou, Y., Wang, T., 2019. Are perfluoroalkyl substances in water and fish from drinking water source the major pathways towards human health risk? *Ecotoxicology and Environmental Safety* 181, 194–201. <https://doi.org/10.1016/j.ecoenv.2019.06.010>.
- Munoz, G., Budzinski, H., Babut, M., Drouineau, H., Lauzent, M., Menach, K. Le, Lobry, J., Selleslagh, J., Simonnet-Laprade, C., Labadie, P., 2017. Evidence for the trophic transfer of perfluoroalkylated substances in a temperate macrotidal estuary. *Environmental Science and Technology* 51, 8450–8459. <https://doi.org/10.1021/acs.est.7b02399>.
- Munoz, G., Liu, J., Vo Duy, S., Sauvé, S., 2019. Analysis of F-53B, Gen-X, ADONA, and emerging fluoroalkylether substances in environmental and biomonitoring samples: A review. *Trends in Environmental Analytical Chemistry* 23, e00066 <https://doi.org/10.1016/j.teac.2019.e00066>.
- Nøst, T.H., Vestergren, R., Berg, V., Nieboer, E., Odland, J.Ø., Sandanger, T.M., 2014. Repeated measurements of per- and polyfluoroalkyl substances (PFASs) from 1979 to 2007 in males from Northern Norway: Assessing time trends, compound correlations and relations to age/birth cohort. *Environment International* 67, 43–53. <https://doi.org/10.1016/j.envint.2014.02.011>.
- Pan, C.G., Liu, Y.S., Ying, G.G., 2016. Perfluoroalkyl substances (PFASs) in wastewater treatment plants and drinking water treatment plants: Removal efficiency and exposure risk. *Water Research* 106, 562–570. <https://doi.org/10.1016/j.watres.2016.10.045>.
- Pan, C.G., Ying, G.G., Liu, Y.S., Zhang, Q.Q., Chen, Z.F., Peng, F.J., Huang, G.Y., 2014b. Contamination profiles of perfluoroalkyl substances in five typical rivers of the Pearl River Delta region, South China. *Chemosphere* 114, 16–25. <https://doi.org/10.1016/j.chemosphere.2014.04.005>.
- Pan, C.G., Yu, K.F., Wang, Y.H., Zhang, R.J., Huang, X.Y., Wei, C.S., Wang, W.Q., Zeng, W. Bin, Qin, Z.J., 2018a. Species-specific profiles and risk assessment of perfluoroalkyl substances in coral reef fishes from the South China Sea. *Chemosphere* 191, 450–457. <https://doi.org/10.1016/j.chemosphere.2017.10.071>.
- Pan, C.G., Yu, K.F., Wang, Y.H., Zhang, W., Zhang, J., Guo, J., 2019. Perfluoroalkyl substances in the riverine and coastal water of the Beibu Gulf, South China: Spatiotemporal distribution and source identification. *Science of the Total Environment* 660, 297–305. <https://doi.org/10.1016/j.scitotenv.2019.01.019>.
- Pan, C.G., Zhao, J.L., Liu, Y.S., Zhang, Q.Q., Chen, Z.F., Lai, H.J., Peng, F.J., Liu, S.S., Ying, G.G., 2014a. Bioaccumulation and risk assessment of per- and polyfluoroalkyl substances in wild freshwater fish from rivers in the Pearl River Delta region, South China. *Ecotoxicology and Environmental Safety* 107, 192–199. <https://doi.org/10.1016/j.ecoenv.2014.05.031>.
- Pan, Y., Zhang, H., Cui, Q., Sheng, N., Yeung, L.W.Y., Sun, Y., Guo, Y., Dai, J., 2018b. Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water. *Environmental Science and Technology* 52, 7621–7629. <https://doi.org/10.1021/acs.est.8b00829>.
- Penland, T.N., Cope, W.G., Kwak, T.J., Strynar, M.J., Grieshaber, C.A., Heise, R.J., Sessions, F.W., 2020. Trophodynamics of Per- and Polyfluoroalkyl Substances in the Food Web of a Large Atlantic Slope River. *Environmental Science and Technology* 54, 6800–6811. <https://doi.org/10.1021/acs.est.9b05007>.
- Princz, J., Jatar, M., Lemieux, H., Scroggins, R., 2018. Perfluoroalkyl sulfonate in surface soils: Effects on reproduction in the collembolan, *Folsomia candida*, and the oribatid mite, *Oppia nitens*. *Chemosphere* 208, 757–763. <https://doi.org/10.1016/j.chemosphere.2018.06.020>.
- Prosser, R.S., Mahon, K., Sibley, P.K., Poirier, D., Watson-Leung, T., 2016. Bioaccumulation of perfluorinated carboxylates and sulfonates and polychlorinated biphenyls in laboratory-cultured *Hexagenia* spp., *Lumbriculus variegatus* and *Pimephales promelas* from field-collected sediments. *Science of the Total Environment* 543, 715–726. <https://doi.org/10.1016/j.scitotenv.2015.11.062>.
- Shi, Y., Vestergren, R., Nost, T.H., Zhou, Z., Cai, Y., 2018. Probing the differential tissue distribution and bioaccumulation behavior of Per- and Polyfluoroalkyl substances of varying chain-lengths, isomeric structures and functional groups in crucian carp. *Environmental Science and Technology* 52, 4592–4600. <https://doi.org/10.1021/acs.est.7b06128>.
- Shi, Y., Vestergren, R., Zhou, Z., Song, X., Xu, L., Liang, Y., Cai, Y., 2015. Tissue distribution and whole body burden of the chlorinated polyfluoroalkyl ether sulfonic acid F-53B in crucian carp (*Carassius carassius*): Evidence for a highly bioaccumulative contaminant of emerging concern. *Environmental Science and Technology* 49, 14156–14165. <https://doi.org/10.1021/acs.est.5b00429>.
- Simonnet-Laprade, C., Budzinski, H., Babut, M., Le Menach, K., Munoz, G., Lauzent, M., Ferrari, B.J.D., Labadie, P., 2019. Investigation of the spatial variability of poly- and perfluoroalkyl substance trophic magnification in selected riverine ecosystems. *Science of the Total Environment* 686, 393–401. <https://doi.org/10.1016/j.scitotenv.2019.05.461>.
- Stevenson, C.N., MacManus-Spencer, L.A., Luckenbach, T., Luthy, R.G., Epel, D., 2006. New perspective on perfluorochemical ecotoxicology: Inhibition and induction of an efflux transporter in the marine mussel. *Environmental Science and Technology* 40, 5580–5585. <https://doi.org/10.1021/es0602593>.
- Sun, M., Arevalo, E., Strynar, M., Lindstrom, A., Richardson, M., Kearns, B., Pickett, A., Smith, C., Knappe, D.R.U., 2016. Legacy and Emerging Perfluoroalkyl substances are important drinking water contaminants in the Cape Fear River Watershed of North Carolina. *Environmental Science and Technology Letters* 3, 415–419. <https://doi.org/10.1021/acs.estlett.6b00398>.
- US EPA (United States Environmental Protection Agency), 2016a. Health effects support document for perfluoroalkyl sulfonate (PFOS). https://www.epa.gov/sites/production/files/201605/documents/pfos_hesd_final_508.pdf.
- US EPA (United States Environmental Protection Agency), 2016b. Drinking water health advisory for perfluoroalkyl sulfonate (PFOS), pp. 1–103. https://www.epa.gov/sites/production/files/201605/documents/pfoa_health_advisory_final_plain.pdf.
- Verhaert, V., Newmark, N., D'Hollander, W., Covaci, A., Vlok, W., Wepener, V., Ado-Bediako, A., Jooste, A., Teuchies, J., Blust, R., Bervoets, L., 2017. Persistent organic pollutants in the Olifants River Basin, South Africa: Bioaccumulation and trophic transfer through a subtropical aquatic food web. *Science of the Total Environment* 586, 792–806. <https://doi.org/10.1016/j.scitotenv.2017.02.057>.
- Wang, S., Huang, J., Yang, Y., Hui, Y., Ge, Y., Larssen, T., Yu, G., Deng, S., Wang, B., Harman, C., 2013. First report of a Chinese PFOS alternative overlooked for 30 years: Its toxicity, persistence, and presence in the environment. *Environmental Science and Technology* 47, 10163–10170. <https://doi.org/10.1021/es401525n>.
- Wang, S., Ma, L., Chen, C., Li, Y., Wu, Y., Liu, Y., Dou, Z., Yamazaki, E., Yamashita, N., Lin, B. Le, Wang, X., 2020. Occurrence and partitioning behavior of per- and polyfluoroalkyl substances (PFASs) in water and sediment from the Jiulong Estuary-Xiamen Bay, China. *Chemosphere* 238, 124578. <https://doi.org/10.1016/j.chemosphere.2019.124578>.
- Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. *Environment International* 70, 62–75. <https://doi.org/10.1016/j.envint.2014.04.013>.
- Wang, Z., Dewitt, J.C., Higgins, C.P., Cousins, I.T., 2017. A never-ending story of per- and polyfluoroalkyl substances (PFASs)? *Environmental Science and Technology* 51, 2508–2518. <https://doi.org/10.1021/acs.est.6b04806>.
- Wilkinson, J.L., Hooda, P.S., Swinden, J., Barker, J., Barton, S., 2018. Spatial (bio) accumulation of pharmaceuticals, illicit drugs, plasticisers, perfluorinated

- compounds and metabolites in river sediment, aquatic plants and benthic organisms. *Environmental Pollution* 234, 864–875. <https://doi.org/10.1016/j.envpol.2017.11.090>.
- Xu, J., Guo, C.S., Zhang, Y., Meng, W., 2014. Bioaccumulation and trophic transfer of perfluorinated compounds in a eutrophic freshwater food web. *Environmental Pollution*. 184, 254–261. <https://doi.org/10.1016/j.envpol.2013.09.011>.
- Yang, X., Li, Y., Ma, G., Hu, X., Wang, J., Cui, C., Wang, Z., Yu, W., Yang, Z., Zhai, F., 2005. Study on weight and height of the Chinese people and the differences between 1992 and 2002. *Chinese Journal of Epidemiology*. 26, 489–493 (In Chinese).
- Zhang, R., Yu, K., Li, A., Zeng, W., Lin, T., Wang, Y., 2020. Occurrence, phase distribution, and bioaccumulation of organophosphate esters (OPEs) in mariculture farms of the Beibu Gulf, China: A health risk assessment through seafood consumption. *Environmental Pollution* 263, 114426. <https://doi.org/10.1016/j.envpol.2020.114426>.
- Zhou, Z., Shi, Y., Vestergren, R., Wang, T., Liang, Y., Cai, Y., 2014. Highly elevated serum concentrations of perfluoroalkyl substances in fishery employees from Tangxun Lake, China. *Environmental Science and Technology*. 48, 3864–3874. <https://doi.org/10.1021/es4057467>.