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Species-specific profiles and risk assessment of perfluoroalkyl substances in coral reef fishes from the South China Sea

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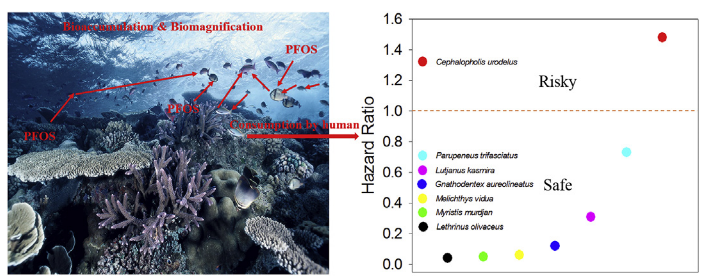
HIGHLIGHTS

- First comprehensive investigation of PFASs in coral reef fishes.
- PFOS was the predominant PFAS found in coral reef fishes from South China Sea.
- PFOS concentrations in coral reef fishes up to 27.05 ng/g wet weight.
- Odd chain PFCA had higher ratios versus the corresponding shorter even-chain PFCA.
- Frequent consumption of *Cephalopholis urodelus* may pose health risk.

GRAPHICAL ABSTRACT



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ABSTRACT

The contamination profiles of sixteen perfluoroalkyl substances (PFAS) were examined in coral reef fish samples collected from the South China Sea (SCS) where no information about this topic was available in the literature. The results revealed that six PFAS were found in coral reef fish samples from the SCS. Perfluorooctane sulfonate (PFOS) was the most predominant PFAS contaminant detected in most of the samples, with the highest concentration value of 27.05 ng/g wet weight (ww) observed in *Cephalopholis urodelus*. Perfluoroundecanoic acid (PFUnDA) and Perfluorotridecanoic acid (PFTrDA) were the second and third dominant PFAS, respectively. Mean PFOS concentrations in muscle of seven coral reef fish varied from 0.29 ng/g ww in *Lethrinus olivaceus* to 10.78 ng/g ww in *Cephalopholis urodelus*. No significant linear relationship was observed between PFOS levels and coral reef fish traits (length, weight) collected in this region. Average daily intake of PFOS for the seven coral reef fishes ranged from 0.79 ng/kg/d for *Lethrinus olivaceus* to 29.53 ng/kg/d for *Cephalopholis urodelus*. The hazard ratio (HR) values for human consumption of PFOS-contaminated coral reef fishes ranged from 0.04 to 1.48, with *Cephalopholis urodelus* having the highest HR value of 1.18 (higher than 1) among the species, indicating frequent consumption of *Cephalopholis urodelus* might pose potential health risk to local population. The present

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work have provided the first hand data of PFAS in coral reef fishes in the SCS and indirectly demonstrated the existence of low level PFAS pollution in the SCS in China.

1. Introduction

Perfluoroalkyl substances (PFAS) are a class of emerging environmental contaminants consisting of both hydrophobic carbon-fluorine chain and a hydrophilic inorganic acid radical. Owing to their high energy of carbon-fluorine covalent bond and amphipathic structure, PFAS are not only resistant to water and oil, but also super persistent in environment (resistant to chemical, thermal and biological degradation) (Hansen et al., 2001; Arsenault et al., 2004). As a result, these chemicals were widely used in cosmetics, water repellents, fire-fighting foams, lubricants, semiconductor, paints and other applications (Key et al., 1997; Kissa, 2001; Prevedouros et al., 2006). Perfluorinated carboxylates (PFCA) and perfluorinated sulfonates (PFSA) are two representative PFAS, which can be produced by the degradation of PFAS-related precursors, such as fluorotelomer alcohols (FTOH) and *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE) (Ellis et al., 2004; Rhoads et al., 2008). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the most typical compounds of PFSA and PFCA, as these two chemicals are dominant PFAS in the environment.

Literature revealed that the global distribution of PFAS resulted from oceanic and atmospheric transport as well as degradation of volatile precursors of PFAS (Ellis et al., 2004; Prevedouros et al., 2006). As a result, PFAS are found ubiquitously in water (Pan et al., 2014b, 2016), sediment (Pan et al., 2015), biota (Pan et al., 2014a; Sedlak et al., 2017) and humans throughout the world (Zhang et al., 2013; Mamsen et al., 2017). Owing to the high water solubility and low vapor pressure of PFAS, the aquatic ecosystem has been regarded as a major sink for these compounds. Previous study estimated that more than eighty percent of the global perfluorooctanoate (PFOA) existed in the world's oceans (Armitage et al., 2006). Similar to other persistent organic pollutants (POPs), long chain PFAS preferentially bioaccumulate and biomagnify in higher trophic level predators (Loi et al., 2011). Meanwhile, PFAS exerted various adverse effects on different organisms (Lau et al., 2007; Tang et al., 2017; Shi et al., 2017). Owing to the global contamination, persistence, bioaccumulation and adverse effects of PFOS, production of POSF-based substances was ceased production in 2009 by former largest producer of 3 M company and these compounds were listed to Annex B in the Stockholm Convention restricting its production and use worldwide (UNEP, 2009).

The South China Sea (SCS), as a marginal sea surrounded by some developing Southeast Asia countries, is the second most used shipping lane in the world (Kwok et al., 2015). Coral reefs are diverse underwater ecosystems in oceans and provide necessary living habitat for innumerable marine species, including fish species. The SCS has widely distributed amounts of coral reefs both in coastal and offshore regions. In fact, a recent survey demonstrated that the SCS hosted more than 570 known coral species (Huang et al., 2015). However, coral reef ecosystems are threatened by global climate change, ocean acidification, dredging, tourism, water pollution and other issues (Ramos and Garcia, 2007; Spalding and Brown, 2015). Due to anthropogenic activities, 88% of Southeast Asian coral reefs are at risk and coral reefs in the SCS underwent a dramatic decline over the past five decades (Burke et al., 2006; Yu, 2012). Recent studies have demonstrated that organic contaminants such as sunscreen (UV filters) could affect development in coral larvae and induce coral bleaching (Danovaro et al., 2008; Downs et al., 2014, 2016). Therefore, it is imperative to protect the coral reef ecosystems and marine ecosystem by controlling discharge of pollutants.

Characterized as a tropical marine monsoon climate with abundant rainfall and high temperature (Morton and Blackmore, 2001), the SCS is surrounded by productive fishing grounds. However, the environment of the SCS is being aggravated by the rapid industrialization and urbanization in recent years. Therefore, various emerging contaminants (including PFAS) could enter the SCS through surface runoff and atmospheric transport (Kwok et al., 2015), and could be further accumulated in marine organisms and biomagnified in higher trophic level fishes. Meanwhile, PFAS in this region could be transported to the global ocean environment as SCS connects Pacific Ocean and the Indian Ocean. Therefore, it is essential to monitor the PFAS in the SCS to get better insight into their global distribution and bioaccumulation.

Most studies to date have mainly focused on PFAS on rivers and coastal regions. However, no investigation focusing on the determination of PFAS in coral reef fishes has been conducted in China, and even in the world. To characterize exposure to PFAS in the SCS coral reef ecosystem, concentrations of PFAS were analyzed in muscle of 82 coral reef fish samples (7 species) from this region. The main objective of this study was to 1) investigate the contamination profiles of sixteen PFAS (11 PFCA and 5 PFSA) in different coral reef fish species from the SCS; and 2) estimate potential health risks for local people consumption of PFAS-contaminated coral reef fish in this region. To our knowledge, this is the first report of the occurrence of PFAS in coral reef fishes in the world.

2. Materials and methods

2.1. Chemical and reagents

Sixteen perfluoroalkyl substances (PFAS) were selected as target compounds in this work, with full name, abbreviations and formula shown in supplementary material Table S1. All standards were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada) with purities higher than 98%. LC-MS grade Ammonium acetic (>99%) and HPLC grade methanol were purchased from Sigma-aldrich (St.Louis, USA) and Merck Corporation (Darmstadt, Germany), respectively. Ammonium hydroxide (10%) and acetic acid were bought from Fluka (Germany). Oasis WAX cartridges (150 mg, 6 mL) were obtained from Waters Corporation (Milford, MA, USA) for sample purification. Ultrapure water was supplied by a Milli-Q system from Millipore (Watford, UK). Analytes and internal standards of PFAS were dissolved in HPLC grade methanol and preserved in polypropylene (PP) bottles at −18 °C. Composite working solutions at the desired concentrations were made by dilution of the stock solutions.

2.2. Sample collection and sample pretreatment

Eighty-two fish samples were collected by fishing in coral reef regions in the SCS in 2015. The sampling coral reef regions were mainly located in Xisha islands, approximately 340 km away from