



Distribution, bioaccumulation and trophic transfer of chlorinated polyfluoroalkyl ether sulfonic acids in the marine food web of Bohai, China

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ARTICLE INFO

Article history:

Received 21 February 2018

Accepted 25 May 2018

Available online 4 June 2018

Keywords:

Fluorinated alternatives

Levels

Seasonal variation

Emission

The Bohai sea of China

ABSTRACT

Chlorinated polyfluoroalkyl ether sulfonic acids (Cl-PFESAs) caused great concerns recently as novel fluorinated alternatives. However, information on their bioconcentration, bioaccumulation and biomagnification in marine ecosystems is limited. In this study, 152 biological samples including invertebrates, fishes, seabirds and mammals collected from Bohai Sea of China were analyzed to investigate the residual level, spatial distribution, bioaccumulation and biomagnification of Cl-PFESAs. 6:2 Cl-PFESA was found in concentrations ranging from <MDL (method detection limit) to 3.84 ng/g ww and it is the dominant congener when compared with concentrations of 8:2 Cl-PFESA. Compared with other bays and regions, levels of 6:2 Cl-PFESA are relatively high in bivalves and fishes from Liaodong Bay. These levels were also found to tend to increase as compared with those in 2010–2014. Logarithm bioaccumulation factors (BAFs) for 6:2 Cl-PFESA ranged from 2.23 to 4.21, implying the bioaccumulation of this compound. The trophic magnification factor (BMF) for 6:2 Cl-PFESA was determined to be 3.37 in the marine food web, indicating biomagnification potential along the marine food chain.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) comprise a large group of chemicals which have been widely used in the manufacturing of stain repellents, surface coatings, firefighting foams and cleaners since the 1950s (Paul et al., 2009; Wang et al., 2014; Shi et al., 2015). Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the most extensively studied PFASs and have been detected in wildlife and humans globally, even in the remote Arctic regions (Giesy et al., 2001; Houde et al., 2006; Kannan et al., 2001; Martin et al., 2004a; Martin et al., 2004b; Olsen et al., 2003; Smithwick et al., 2005; Tomy et al., 2004; Van de Vijver et al., 2005). Due to their persistence, bioaccumulation potential,

and toxic effects, regulatory actions and voluntary phase-out initiatives by the fluorochemical industry for this class of chemicals were established (Lindstrom et al., 2011). In 2009, PFOS was added to Annex B of the Stockholm Convention for Persistent Organic Pollutants (UN, 2009). Therefore a large number of PFAS alternatives were developed. One of the important alternatives is the class of chlorinated polyfluoroalkyl ether sulfonic acids (Cl-PFESAs), with the trade name of F-53B (Shi et al., 2015). The two major components of F-53B are 6:2 Cl-PFESA and 8:2 Cl-PFESA.

Cl-PFESAs have been applied as a mist suppressant to prevent the emissions of the toxic substance, chromium, for decades in Chinese chrome plating industry (Wang et al., 2013). China is the only country with documented usage of PFESAs (Wang et al., 2013). The annual production of F-53B in China was estimated to be 20–30 tons in China (Shi et al., 2015). Due to the phase-out of PFOS, F-53B as its alternative may be expected to obtain a larger market share and potentially expand from being solely used in the metal plating industry to other PFOS-related industries (Wang et al., 2013). Although Cl-PFESAs have been used in the metal plating

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industry for more than 30 years (SGEP, 1976), their occurrence in the environment including wildlife, surface water (Wang et al., 2013; Wang et al., 2016), sewage sludge (Ruan et al., 2015), fishes (Shi et al., 2015), black-spotted frog (Cui et al., 2018) and Greenland marine mammals (Gebbinck et al., 2016), was only recently discovered. A few studies also focused on the bioavailability, bioaccumulations and biomagnifications of Cl-PFESAs. Wen et al. (2016) found dissolved organic matter had effects on PFAS bioconcentration and thus their bioavailability. Shi et al. (2015) indicated that F-53B is highly bioaccumulated in crucian carps. Liu et al. (2017) revealed that 6:2 Cl-PFESA could be magnified along the food chain. However, the bioaccumulation study was only focused on one species in freshwater; and the biomagnification study did not include high trophic level organisms, such as marine mammals. Collectively, available data regarding the pollution, bioaccumulation and biomagnification of Cl-PFESAs is still limited.

Bohai Sea is a large semi-enclosed inner sea with a narrow strait to the Yellow Sea, and the half-exchange time of seawater in one of the bay (Liaodong Bay) can be as long as about 3 years. Our previous study (Chen et al., 2017) indicated that F-53B concentrations in seawater in this area can be as high as 7.85 ng/L. It provides a representative marine ecosystem influenced by the estuary to investigate the pollution, bioaccumulation and biomagnification of Cl-PFESAs. Thus in the current study, the aims were (1) to investigate levels of Cl-PFESAs in marine organisms at different sampling sites and different trophic levels; and (2) to evaluate the bioaccumulation and biomagnification of Cl-PFESAs in the marine ecosystem.

2. Materials and methods

2.1. Chemicals and reagents

Samples were analyzed for 21 PFASs, including 13 PFCAs, 4 PFASs, 2 precursors and 2 Cl-PFESAs. 6:2 and 8:2 Cl-PFESAs were kindly donated by Dr. Ting Ruan at Research Center for Eco-Environmental Science, Chinese Academy of Sciences, and had a stated purity of $\geq 95\%$ (Ruan et al., 2015). Other native PFASs and all isotopically labeled standards were purchased from Wellington Laboratories (Guelph, ON, Canada). The matched stable isotope standards are listed in Table 1, respectively. HPLC-grade methanol and acetonitrile were supplied by Sigma-Aldrich. Milli-Q water was further treated using Waters Oasis WAX cartridges to remove the potential PFAS residues. All reagents were used as received.

2.2. Study area and sampling

The present study was conducted along the coastline of the Bohai Sea in China. Bohai Sea is a semi-enclosed inland sea of China, covering a total area and coastal line of about 77 000 km², and 2668 km, respectively. As shown in Fig. 1 from our previous study

Table 1
Parameters for instrumental analysis, MDL and extraction process recovery for each measured compound.

	Measured compound		
	PFOS	6:2 Cl-PFESA	8:2 Cl-PFESA
Internal standard	¹³ C ₄ PFOS		
Precursor ion	498.7	531	631
Product ion	98.7	351	451
Fragmentor (V)	200	70	70
Collision (V)	40	24	24
MDL (ng/g)	0.093	0.056	0.062
Recovery (mean \pm SD)	81.5 \pm 6.8	78.9 \pm 8.3	61.2 \pm 9.8

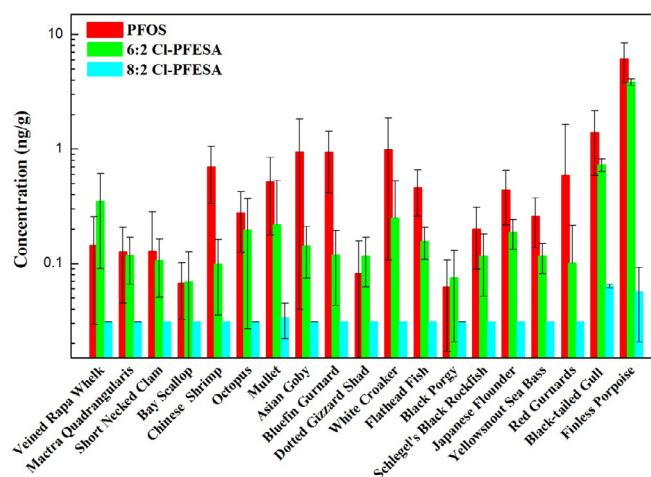


Fig. 1. 6:2 Cl-PFESA, 8:2 Cl-PFESA and PFOS concentrations (mean \pm standard deviation) in various marine organism from Bohai Sea of China.

(Chen et al., 2017), there are three provinces (Liaoning Province, Hebei Province and Shandong Province) and one municipality (the city of Tianjin) around the Bohai Sea, China. The population density is high around the Bohai Sea (a population of about 292 million in this basin in 2014) and numerous industrial activities are also located there. Due to the discharge of riverwater and industrial wastewater and the limited seawater exchange, the pollution of PFASs in Bohai Sea has been frequently investigated, and it is one of the most polluted sea areas in China.

152 aquatic biological samples were collected from Bohai Sea of China. As shown in Table 2, aquatic organisms include six benthic invertebrate species, ten fish species, one seabird, and one marine mammal. Invertebrates and fishes were caught with a bottom trawl. All samples were transported with ice to laboratory after being wrapped in aluminum foil and sealed in zip locked bags. The soft tissues of invertebrate and muscles of other species were dissected via stainless steel scalpel blades and then were stored at -20°C until analysis.

2.3. Sample preparation and instrumental analysis

The methods for extraction and cleanup were similar to methods previously reported (Liu et al., 2017; Shi et al., 2015). In brief, 0.5 g tissue samples were spiked with 5 ng of internal standards, mixed with 10 mL of 10 mM KOH methanol solution and then shaken at 250 rpm for 16 h. The supernatant was transferred and concentrated to 1 mL under nitrogen gas. The concentrated extract was diluted to 50 mL with Milli-Q water, and loaded onto a WAX SPE cartridge (6 cc, 150 mg; Waters Corp. Milford, USA) for cleanup. The cartridges were preconditioned using 4 mL of 0.1% ammonium hydroxide solution, 4 mL of methanol and 4 mL of Milli-Q water by a Sep-Pak concentrator (Waters Corp., Milford, MA). The loaded cartridges were then washed with 4 mL of buffer solution (25 mM acetic acid/ammonium acetate, pH = 4) and 8 mL of Milli-Q water and centrifuged at 5000 rpm for 10 min to remove the residual water. Finally, the target compounds were eluted using 4 mL of methanol and 4 mL of 0.1% ammonium hydroxide methanol solution. The eluate was concentrated to 200 μL under nitrogen gas prior to injection.

An Agilent 1200 high performance liquid chromatography system (Palo Alto, CA) coupled with an Agilent 6410 Triple Quadrupole mass spectrometer (Santa Clara, CA, HPLC-MS/MS) was used to identify PFAS in samples. The mobile phase was 10 mM ammonium

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