PERFLUORINATED COMPOUNDS IN MOLLUSKS FROM THE BOHAI SEA OF CHINA

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Abstract

Concentrations and distribution of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS) and seven other perfluorocarboxylic acids (C7–C12, C14) were investigated in mollusks collected from nine coastal cities of the Bohai Sea in 2007. PFCs widely exist in mollusks in the Bohai Sea and PFOA was the prominent PFCs with the detected ratios 75.0%. Among the mollusks selected, clams and Scapharca subcrenata (Sca) were found containing much higher levels (≥10 times) of PFOA concentrations than other species, which indicated their potential higher bioaccumulation capacity for PFOA. The PFOS concentrations were much lower than PFOA.

Introduction

Perfluorinated compounds (PFCs) are a group of emerging and ubiquitous organic pollutant in environment. For their unique properties, PFCs are still extensively employed in numerous consumer and industrial applications[1-3]. PFCs have been reported in higher concentrations in city wastewater and downstream than countryside, indicating urban activities as important source of PFCs besides industrial emission[4, 5]. In China, the study about PFCs is just beginning but increasing attention is being paid to the PFCs pollution in recent several years. More and more works in China revealed that PFCs were found in river water[6], sea water[7] and seafood[8, 9] from south China and Dalian[10].

The Bohai Sea, an important regional economic center of the north China, is a semi-enclosed water body with the coastal line of nearly 3 800 km long. Numbers of works on distribution of POPs and heavy metal have been conducted in the region, revealing the adverse disturbance along with the dense urban activities and the rapid economic development during the past several decades[11-14]. However, few works on the PFCs pollution in this area have been available yet. The present study is aiming to comprehensively investigate the pollution levels of PFCs in the Bohai Sea region. Nine PFCs were analyzed in mollusks of 11 species collected from coastal water of the Bohai Sea.

Materials and Methods

Mollusks were collected from 9 coastal cities of the Bohai Sea region in late July to early August 2007: Dalian (DL), Yingkou (YK), Huludao (HLD), Beidaihe (BDH), Tianjin (TJ), Shouguang (SG), Penglai (PL), Yantai (YT), Weihai (WH). Generally the 84 pooled samples were composed of 11 species, which were *Crassostera talienwhanensis* (Cra), *Chlamys farreri* (Chl), *Amussium* (Amu), *Scapharca subcrenata* (Sca), *Meretrix meretrix*

Linnaeus (Mer), *Mactra veneriformis* (Mac V), *Mactra chinesis* (Mac C), *Mya arenaria* (Mya), *Neverita didyma* (Nev), *Rapana venosa* (Rap) and *Mytilus edulis* (Myt).

Samples were pretreated by alkaline digestion and solid phase extraction, which has been described elsewhere except for some modification [8, 15]. Generally, 0.2 g of tissue sample (dry) was extracted by eight milliliter of 10mM NaOH (in methanol). 4 mL of the extraction was diluted with 36 mL water. Then, the dilution was loaded onto a preconditioned Oasis® WAX cartridge (6 cc, 150 mg; Waters Corp. Milford, USA). The final extraction was centrifuged (10 000 rpm) to remove the particles before injection instead of filtration, for trace PFHpA was found in the nylon syringe filter.

The sample analysis for nine PFCs: Perfluoroheptanoic acid (PFHpA), perflurooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTA), perfluoroundecanoic acid (PFUnDA), potassium salts of perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS) was accomplished with a high performance liquid chromatography equipped with an electrospray ionization tandem mass spectrometer (API 3200; Applied Biosystems/MDS SCIEX, US) (HPLC-ESI/MS/MS). Sodium perfluoro-1-(1, 2, 3, 4-$^{13}C_4$)octanesulfonate ($^{13}C_4$-PFOS) was used as the internal standard. PFCs were separated on a Dionex Acclaim 120 C18 column (5 μm, 4.6mm i.d. × 150 mm length; Dionex, Sunnyvale, CA, USA). The limits of detection (LODs) were 0.25 ng g^{-1} for PFHxS, 0.17 ng g^{-1} for PFOS, 0.5 ng g^{-1} for PFHpA, PFOA, PFNA, PFDA and PFUnDA, 0.6 ng g^{-1} for PFDoDA, and 1.0 ng g^{-1} for PFTA, respectively.

Results and Discussion

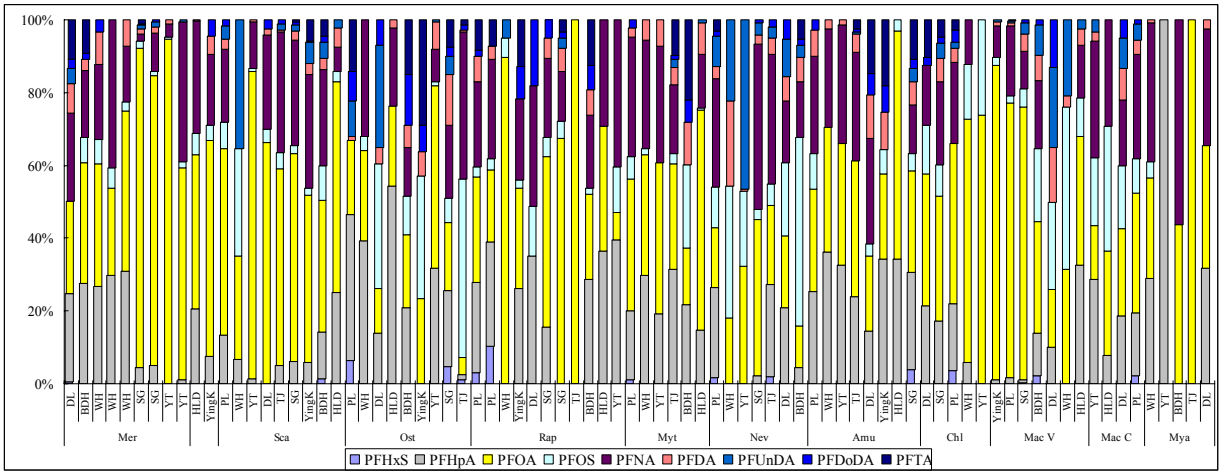

Fig. 1 Composition profiles of perfluorinated compounds in mollusk soft tissue

In the present investigation, the prominent analyte in mollusks is PFOA in the Bohai Sea, as summarized in Fig. 1. Seventy-five percent of these samples were found detectable PFOA and large variations of PFOA levels existed among different species. Generally, concentrations of PFOA in mollusk samples were in order of ark

shell≈ clam > spiral shell > mussel. MacV contained the highest levels of PFOA, which were <0.5~111.0 ng/g (mean 31.3 ng/g, dw), followed by Sca and Mer, in which the PFOA concentrations were <0.5~40.5 ng/g (mean 9.96 ng/g, dw) and <0.5~25.3 ng/g (mean 6.97 ng/g, dw), respectively. The lowest PFOA concentration was found in Mya. The relatively higher concentrations in some mollusks may reflect their potential higher bioaccumulation capacity for PFOA. Among the sampling sites, SG should be paid more attention than other sites for the highest concentration of individual analyte were mostly found in this area in each species. The second and third highest levels of PFOA were observed in YT and YK. The higher levels of PFOA suggested the more often emissions or use of products containing PFCs and related compounds in these sampling sites.

In present study, the concentrations of PFOS and PFHpA were much lower than that of PFOA. The ratio of PFOA/PFOS was found as great as 46 in *Meretrix meretrix Linnaeus*. The highest level of PFOS was also found in *Mactra veneriformis*, which was 1.24 ng g^{-1} (dw). The correlations among concentrations in mollusk were evaluated by SPSS statistical analysis of the Pearson Correlation two-tailed test ($p<0.01$). The concentration of PFOA and PFOS in MacV (2007) and Rap (2007) were significantly correlated (0.947 and 0.944), which may indicate a common source or similar transforming mechanism of these compounds in these organisms.

It is assumed that PFCs can bioaccumulate along the food web. But as a kind of raptatorial shell, Nev was found very low levels of PFOA, with concentration rang <0.5~5.12 ng/g. A study performed on the accumulation of butyltins in mollusks from the Bohai Sea coast [16] showed that the maximum values were found in Mya, yet PFOA and PFOS levels were very low in Mya (Table 1). This finding suggested that the metabolism of butyltins and PFCs could be quite different, which resulted in the distinct distribution of PFCs in mollusks with that of butyltins in the same area [12]. A negative correlation between the $\sum$PFCs concentrations and the trophic levels (TL) were found for the mollusks although the linear correlation was not significant ($p> 0.05$). Similar result has also reported in a recent work in which PCBs and PBDEs were found not biomagnified but negative correlated with the TL of mollusks [12].

Marine foods including oysters, mussels are often involved in studies as potential bioindicator/biomonitor related to aquatic contamination[11, 12, 17]. The studies about PFCs concentrations in mollusks, however, are very few. The profiles of PFCs in mollusk from the Bohai Sea were found completely different from previous study in coastal cities of south China[9] and eastern Arctic[18], but had a similarity with that in the Ariake Sea of Japan[16]. The detailed reason why PFOA is the predominant contaminant remained unclear, but these findings at least revealed the different pollution sources of PFCs in these areas.

Acknowledgments

This work was jointly supported by the High-Technology Research and Development Program of China (2007AA06Z405), Major Research Program of Chinese Academy of Sciences (No. KZCX2-YW-420-1), the National Natural Science Foundation of China (No. 20621703, 20837003) and National Basic Research Program of China (2009CB421605)

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