NATIONWIDE MONITORING OF PERFLUORINATED COMPOUNDS (PFCs) IN SEAWATER, SEDIMENT AND BIVALVES FROM KOREAN COASTAL WATERS

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Introduction

Perfluorinated compounds (PFCs) have been widely used in many consumer products and industrial applications for over 60 years[1,2], due to their unique properties such as water and oil repelling. PFCs can be released into the environment through the production and the use of PFCs containing products. PFCs have been found in the various environmental compartments such as water[3], sediment[4], wildlife[5] and humans[6]. PFCs are bioaccumulative and have adverse health effects in wildlife and humans[7]. Once released of PFCs into the environment, they are finally reached to the marine environment. Therefore, the survey on marine environment is important to understand environmental fate of PFCs[8,9]. Most of the PFCs had high water solubility and moderate sorption to solids. As a result, PFCs are widely present in surface seawater in oceans all over the world[8-10]. However, only limited information is available on contamination by PFCs in Korean coastal waters. Only a few studies have reported contamination of PFCs in coastal waters of Korea[11] as well as in marine mammals[5]. In addition, there have no reports on nation-wide survey on PFCs in marine environment of Korea. The objectives of this study were to investigate spatial distribution of PFCs in marine environment and to assess ecological risks based on the bioaccumulation factors and comparison with criteria for PFCs.

Materials and methods

Marine environment samples such as seawater, sediment and bivalves were collected at 50 locations along the Korean coastline between February to March in 2013. The seawater samples were collected with a 1 L polypropylene (PP) bottle. The surface sediments (0-4 cm) were collected using a box-core sampler and were stored with a pre-cleaned aluminum foil. The bivalve samples including mussels (*Mytilus edulis*) and oysters (*Crassostreagigas*) were collected directly in piers, rocks and buoys during low tide. After removing the shells of bivalves, the whole soft tissues were pooled and homogenized with an ultra-disperser. The seawater samples were transported to the laboratory and stored in a freezer at -20°C until extraction. The sediment and bivalves were well-mixed, stored at -20°C and later freeze-dried for extraction. Preparation and instrumental analyses of PFCs in marine environment samples were performed following the methods described elsewhere with some modification[8-10].

Results and discussion

Spatial distribution of PFCs in coastal environments of Korea

The spatial distributions of PFCs in seawater, sediment and bivalves collected from Korean coastal waters are presented in Figure 1. The total concentrations of PFCs (ΣPFC; the sum of 16 PFCs) ranged from <LOQ to 11533 (mean: 1764) pg/L, from 3.32 to 1166 (178) pg/g dw and from 799 to 22038 (4407) pg/g dw in seawater, sediment and bivalves, respectively. The spatial distribution of PFCs in seawater and sediment showed similar patterns. The average concentrations of PFCs in seawater and sediment collected from western coast of Korea (3634 pg/L and 229 pg/g dw) were found higher than those measured in those collected from southern (1539 pg/L and 194 pg/g dw) and eastern (332 pg/L and 107 pg/g dw) coasts of Korea. However, the spatial distribution of PFCs in bivalves showed different patterns compared with those measured in seawater and sediment samples. The average concentrations of PFCs in bivalves collected from eastern coast of Korea (7640 pg/g dw) were found higher than those measured in bivalves from southern (3889 pg/g dw) and western (2117 pg/g dw) coast of Korea.

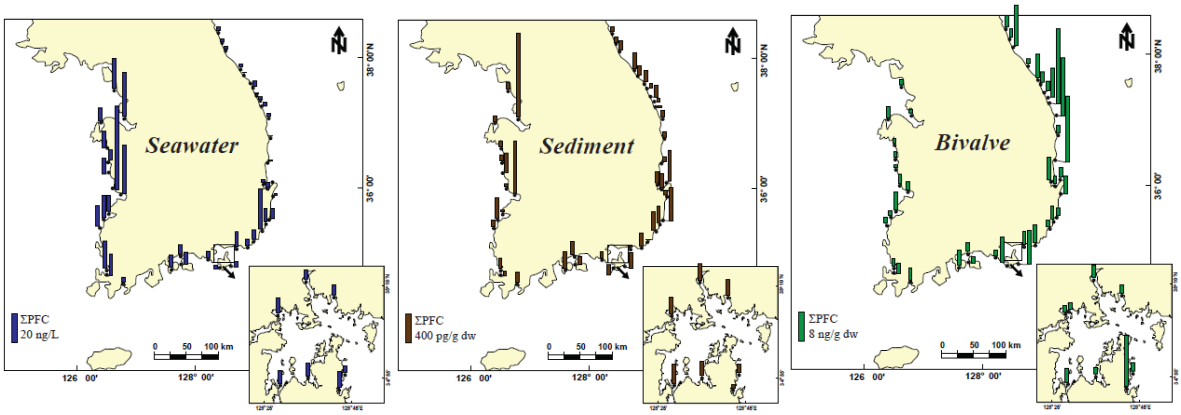

Figure 1. Spatial distribution of PFCs in seawater, sediment and bivalves from Korean coastal waters in 2013.

Global comparison of PFOS and PFOA

The concentrations of PFOS and PFOA in seawater measured in our study are compared with those reported for other countries (Figure 2). The average concentration of PFOS (0.36 ng/L) measured in our study were comparable to those found in seawater from China (0.23 ng/L), Baltic Sea (0.42 ng/L) and Japan (1.52 ng/L). However our results were higher than those reported for open oceans such as Atlantic Ocean (0.06 ng/L) and Eastern Pacific ocean (0.07 ng/L). The average concentration of PFOA (0.56 ng/L) measured in our study were comparable to those found in seawater from China (0.56 ng/L) and Baltic Sea (0.65 ng/L). However our results were higher than those reported for open oceans such as Atlantic Ocean (0.12 ng/L) and Pacific ocean (0.14 ng/L).

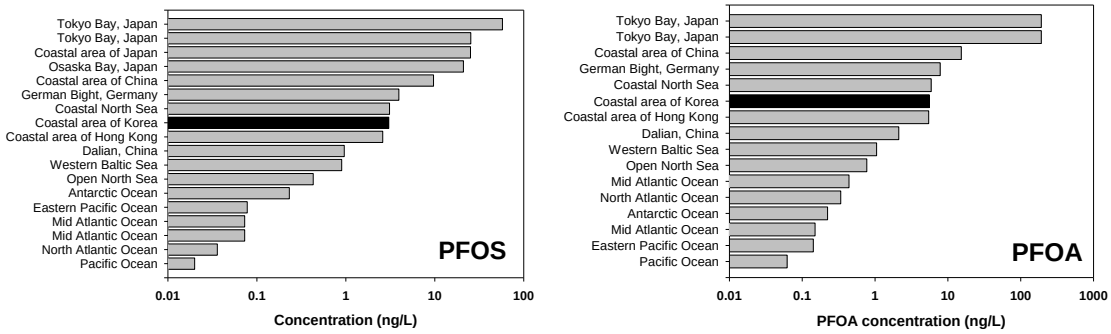

Figure 2. Global comparison of PFOS and PFOA in sewater. Data source: Tokyo Bay, Japan and Mid atlantic Ocean [8,9], Coastal area of Japan [12], Osaka Bay, Japan, Coastal area of China, Coastal area of Hong Kong and North Atlantic Ocean [9], German Bight, Germany [4], Coastal North Sea, Western Baltic Sea and Open North Sea [13], Dalian, China [14], Antarctic Ocean [3], Eastern Pacific Ocean [8].

Composition profiles of PFCs

The relative contributions of PFCs measured in seawater, sediment and bivalves from Korean coastal waters are presented in Figure 3. The major PFCs in seawater, sediment and bivalves were PFOA, PFOS and PFTrDA, which accounted for 36%, 48% and 28% to the ΣPFC concentrations, respectively. The second major contributors to the ΣPFC concentrations were PFUnDA, PFTrDA and PFOS in seawater, sediment and bivalves, which accounted for 15%, 15% and 21% to the ΣPFC concentrations, respectively. Interestingly, PFTrDA was dominant PFC found in sediment and bivalves. This observation is different with previous studies, which only PFOS is usually the dominant PFC in sediment and bivalves. In earlier studies, PFTrDA was not measured in sediment and bivalve samples because of less contribution of PFTrDA to the ΣPFC concentrations. However, long-chain perfluorinated carboxylates (PFCAs) including PFUnDA and PFTrDA were found rapidly increasing

patterns in recent years from core sediment[15]. As a result of global reduction of middle-chain PFCs (PFOS and PFOA), the production and use of long-chain PFCs can be increased as alternatives.

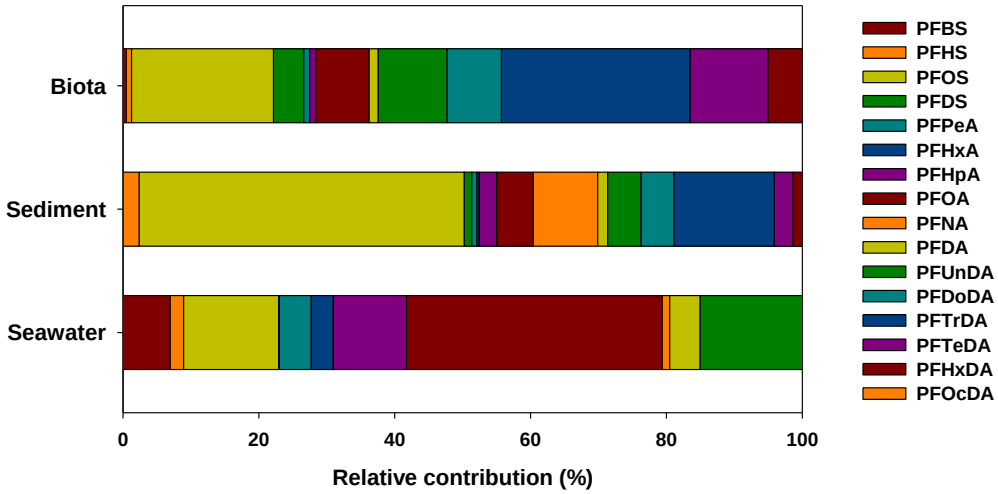

Figure 3. Average normalized relative contribution of individual PFCs in seawater, sediment and bivalves from Korean coastal waters in 2013.

Partition of PFCs between environmental samples

The partition coefficients of PFCs between sediment and surface water were estimated using the concentration of PFCs in the sediment and in the overlaying water at the same location. The partition coefficients (K_d) was calculated by dividing the concentration of PFCs in sediment by those in water. The highest K_d (L/g) value was found in PFOS (mean: 0.41), followed by PFHS (0.06) and PFUnDA (0.04). Based on these values, PFOS adsorbed strongly to sediment in Korean marine environment. These partition patterns are similar with those reported from previous study[7]. The bioconcentration factors (BCF) were calculated for PFCs by dividing the concentration of PFCs in bivalves by those in seawater at the same site. PFOS had the highest BCF (mean: 5580) among PFCs analyzed with a maximum value (104000) in Tongyeong, Korea. This value was lower than value from reported in the west coast of Korea[11]. The next BCF was in the order of PFUnDA (2180), followed by PFDS (860), PFOA (670), PFDA (600) and PFHS (340).

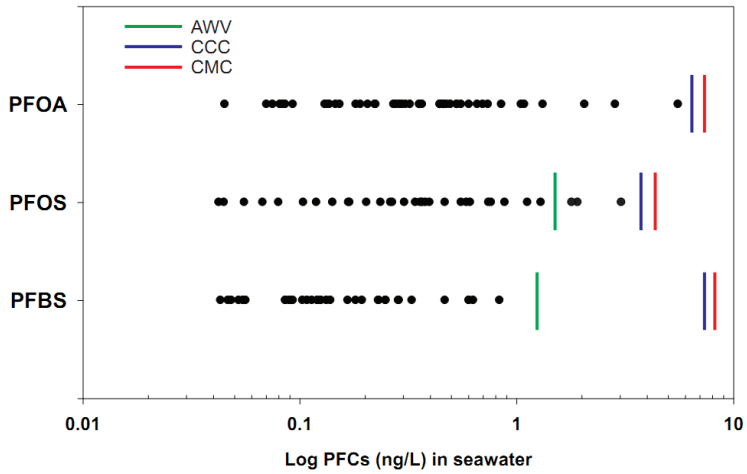

Figure 4. Comparison of selected PFCs (PFBS, PFOS and PFOA) in seawaters from Korean coastal waters with suggested water quality criteria values for the protection aquatic organisms and wildlife, AWV: avian wildlife value, CCC: criteria continuous concentration, CMC: criteria maximum concentration.

To evaluate the ecological risk for selected PFCs, the concentrations of PFBS, PFOA and PFOA determined in seawater were compared to the water quality criteria values[7] (Figure 4). Concentrations of PFOA and PFBS measured in the present study did not approach the water quality criteria such as criteria maximum concentration (CMC; 21 μg/L for PFOS, 25 mg/L for PFOA and 121 mg/L for PFBS), criteria continuous concentration (CCC; 5.1 μg/L for PFOS, 2.9 mg/L for PFOA and 24 mg/L for PFBS) and avian wildlife value (AWV; 17 ng/L for PFBS and 47 ng/L for PFOS). However, some sewater samples containing PFOS (n=3) may have potentially adverse health effects to some wildlife at the top of the food chain by AWV.

Acknowledgments
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