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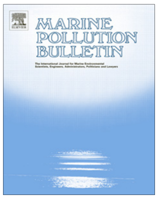

Partitioning behavior of perfluorinated compounds between sediment and biota in the Pearl River Delta of South China

Y.G. Zhao, H.T. Wan, M.H. Wong, Chris K.C. Wong *

State Key Laboratory in Marine Pollution, Croucher Institute for Environmental Sciences, Department of Biology, Hong Kong Baptist University, Hong Kong, China

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ABSTRACT

Surface sediment and biota were collected from 12 sampling sites – seven along the Pearl River Delta and five along the Hong Kong coastline. Perfluorinated compound (PFC) concentrations were detected using a high-performance-liquid-chromatogram–tandem-mass-spectrometry system. Analytical results indicated that the total PFC concentrations were in the range of 0.15–3.11 ng/g dry weight in sediments, while the total PFC concentrations in oyster and mussel samples were between 0.46–1.96 and 0.66–3.43 ng/g wet weight, respectively. The major types of PFCs detected in the sediment samples were perfluorooctanesulfonic acid (PFOS) and perfluorobutanoic acid (PFBA), with concentrations ranging from low limits of quantification to 0.86 ± 0.12 ng/g dry weight and 1.50 ± 0.26 ng/g dry weight, respectively. In bivalve samples, PFOS was the dominant contaminant with concentrations ranging from 0.25 ± 0.09 to 0.83 ± 0.12 ng/g wet weight in oysters and 0.41 ± 0.14 to 1.47 ± 0.25 ng/g wet weight in mussels. An increase in PFC concentration was found to be correlated with increased human population density in the study areas.

1. Introduction

Perfluorinated compounds (PFCs) comprise a large group of synthetic fluorinated hydrocarbons that have been used for over half a century in both industrial and commercial products (Kissa, 2001). These compounds have unique chemo-physical properties such as excellent thermal and chemical stability and confer both water and oil repellency, which is important for their wide range of applications (i.e., surface protecting products, lubricants, coating formulations, and fire-fighting foams) (Paul et al., 2009). However, these properties also make PFCs hard to degrade, leading to their ubiquitous persistence in the environment (Giesy and Kannan, 2001). PFCs are mostly detectable in aquatic systems, and are thought to originate from sewage effluents (Becker et al., 2008; Sinclair and Kannan, 2006), especially industrial wastewater discharge. In aquatic systems, PFCs are retained in bottom sediments via sorption, and are then transferred through aquatic food chains (Higgins and Luthy, 2006; Higgins et al., 2007). Wildlife and human health could be affected by the high concentrations of PFC in the environment and various food sources. Further, the chemicals have been identified as global pollutants, and their distributions in various matrixes have received attention.

The Pearl River Delta (PRD), located in the southern part of China, is one of the world's major manufacturing centers and is highly polluted. As of 2010, approximately 120 million people are living in this region (Vidal, 2010). Upstream of the Pearl River (PR), there are over 70,000 factories (Asianews, 2008) where large-scale manufacturing activities involving electronic, electrical, and telecommunication equipment and machinery account for over one-third of the gross industrial output of the PRD (So et al., 2004). The use and disposal of PFCs in these industries are expected to cause pollution in neighboring river systems (So et al., 2004). Because of the toxicity of PFCs and their presence in the water supply, the subsequent effect on the coastal population is of concern. In 2004, So et al. (2004) reported PFC pollution in the coastal waters of the South China Sea and Hong Kong, where perfluorooctanesulfonic acid (PFOS; 0.02–12 ng/L) and perfluorooctanoic acid (PFOA; 0.24–16 ng/L) were found to be the two dominant contaminants. In a subsequent study, PFC concentrations in the PR and Yangtze River (YR) were measured (So et al., 2007). Compared to that in the previous study, in the 2007 study, PFOS was detected at much higher concentrations (0.90–99 ng/L) in the PRD and an estuary of the PR. The levels of PFCs in the PRD were higher than that in the YR (central China) (<0.01–14 ng/L) (So et al., 2007), suggesting that PFC pollution greatly increased along with rapid expansion of the industrial manufacturing sector in the PRD region.

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* Corresponding author. Address: SCT1017, Cha Cha-ming Science Tower, Ho Sin Hang Campus, Hong Kong Baptist University, Hong Kong, China. Tel.: +852 3411 7053; fax: +852 3411 5995.

E-mail address: ckcwong@hkbu.edu.hk (C.K.C. Wong).

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Many studies have shown PFC contamination in water and seafood; however, available data on sediments of the PRD are inadequate (Prevedouros et al., 2006). The accumulation of PFCs in bottom sediments of coastal regions is known to adversely influence the surrounding aquatic ecosystems (Nakata et al., 2006). Sediment is considered to be the final sink and reservoir for most pollutants (Nakata et al., 2006). A previous study showed that PFCs can bio-accumulate in higher trophic level organisms because it moves through the aquatic food chain (Kannan et al., 2005). Therefore, PFC pollution in sediments in the PRD region is concerning. In this study, marine sediments from 12 locations along the PRD and Hong Kong coastline were collected to determine the status of PFC pollution. To evaluate the transfer of PFCs from the sediment to biota, two filter feeders (oysters and mussels) were collected at the same locations and biota–sediment accumulation factor (BSAF) was measured.

2. Materials and methods

2.1. Samples, chemicals, and instrumentation

2.1.1. Sample collection

Sediment and biota samples were collected in July 2008 from five cities (at 12 sampling sites) along the PR estuary and South China Sea in 2010 (Fig. 1). Sediment samples ($n = 3$) were collected using a dredge, which was pre-cleaned using tap water, Milli-Q water and methanol (HPLC grade, Tedia). Oyster samples ($n = 3$) were collected from nine sampling sites (Nan Sha, Xia Shan, Zhu Hai, Sha Jin, Airport, Bao An, Da Peng, Lau Fau Shan, and Sai Kung), while mussels ($n = 3$) because of the sample availability were collected only from four sampling sites (Xia Shan, Tsim Sha Tsui [TST], Ma Wan, and Aberdeen).

2.1.2. Sample preparation and extraction

Sediment and biota samples were collected and stored in polypropylene (PP) boxes. After bringing the samples to the laboratory, they were refrigerated at 4 °C before preparation. The sediment samples were air-dried, mixed, and homogenized in a porcelain mortar by using a pestle, sieved through a 0.9-mm mesh, and stored in a dry box at room temperature for the subsequent extraction procedure. Shells were removed from the bivalve samples, and the soft tissues were mixed using a homogenizer (Polytron®, Capitol Scientific, Inc.), wrapped in aluminum foil, and stored at −20 °C until extraction.

Fig. 1. Map showing the sediment and biota sampling sites.

The extraction of sediment samples was conducted according to the procedure described by Wang et al. (2008). Five grams of the sediment and 1 ml Milli-Q water were added in a 50-mL PP centrifuge tube. The homogenate was then mixed with 1 ng of the internal standard, 1 mL of 0.5 M tetrabutylammonium (TBA) hydroxide solution, and 2 mL of 0.25 M sodium carbonate buffer. Next, 5 mL of methyl *tert*-butyl ether (MTBE) was added, and the mixture was shaken for 20 min at 250 rpm by using a reciprocating shaker (HS 501 digital shaker, Janke & Kunkel IKA-Labortechnik). Organic and aqueous layers were separated by centrifugation at 3000 rpm for 15 min. Four milliliters of the organic phase was collected and transferred into a new 15-mL PP tube. The extraction procedure was repeated twice. All three organic extracts were blow-dried using high purity grade nitrogen gas ($N_2 \geqslant 99.995\%$, Hong Kong Oxygen) and re-dissolved in 1 mL of 40% acetonitrile/10 mM of ammonium acetate in Milli-Q water (4:6, v/v). The total organic carbon (TOC) content was determined by igniting the sediment sample at 450 °C for 8 h (Labadie and Chevreuil, 2011).

Biota sample extraction was performed by placing 1 g of homogenized oyster/mussel into a 15-mL PP centrifuge tube, and then performing the ion pairing extraction method as described above, followed by extraction by using an SPE-Oasis HLB cartridge (Waters) for cleanup (So et al., 2004). After the extraction, all three organic extracts were mixed using 2 mL of methanol and then concentrated to 1 mL under N_2. One milliliter of the final solution was used for SPE cleanup. All the biota samples were cleaned using an Oasis HLB cartridge. After cleanup, the eluate was blow-dried using N_2 gas and re-dissolved in 1 mL of 40% acetonitrile/10 mM of ammonium acetate in Milli-Q water (4:6, v/v).

2.1.3. Chemicals for instrumental analysis

MTBE, methanol, and acetonitrile were purchased from Tedia Company Inc. TBA hydroxide solution, sodium carbonate, and sodium hydrogen carbonate was purchased from Sigma–Aldrich. Standard mixture solutions of PFCs—perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), sodium perfluorohexanesulfonate (PFHxS), and sodium perfluorooctanesulfonate (PFOS)—and their mixture mass-labeled solution (used as internal standards)—perfluoro-(1,2,3,4-$^{13}C_4$)-butanoic acid (MPFBA), perfluoro-(1,2-$^{13}C_2$)-hexanoic acid (MPFHxA), perfluoro-(1,2,3,4-$^{13}C_4$)-octanoic acid (MPFOA), perfluoro-(1,2,3,4,5-$^{13}C_5$)-nonanoic acid (MPFNA), perfluoro-(1,2-$^{13}C_2$)-decanoic acid (MPFDA), perfluoro-(1,2-$^{13}C_2$)-undecanoic acid (MPFUdA), perfluoro-(1,2-$^{13}C_2$)-dodecanoic acid (MPFDoA), sodium perfluoro-1-(1,2,3,4-$^{13}C_3$)-hexanesulfonate (MPFHxS), and sodium perfluoro-1-(1,2,3,4-$^{13}C_4$)-octanesulfonate (MPFOS)—were purchased from Wellington Laboratories. The purity of the analytical standard was greater than 98%.

2.1.4. Instrumental analysis

PFC concentrations were measured using an Agilent 1200 Series high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS, Agilent Technologies, City and country), according to our previous study (Zhao et al., 2011).

2.2. Quality assurance and quality control

To minimize background signals, all accessible polytetrafluoroethylene (PTFE) and fluoropolymer tubes/parts were replaced with polyether ether ketone (PEEK) materials to achieve low detection limits in HPLC-MS/MS (Yamashita et al., 2004). All centrifuge tubes (IWAKI, Japan), pipette tips (MBP, United States), auto-sampler

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