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Perfluorinated compounds in the Pearl River and Yangtze River of China

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Abstract

A total of 14 perfluorinated compounds (PFCs) were quantified in river water samples collected from tributaries of the Pearl River (Guangzhou Province, south China) and the Yangtze River (central China). Among the PFCs analyzed, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were the two compounds with the highest concentrations. PFOS concentrations ranged from 0.90 to 99 ng/l and <0.01–14 ng/l in samples from the Pearl River and Yangtze River, respectively; whereas those for PFOA ranged from 0.85 to 13 ng/l and 2.0–260 ng/l. Lower concentrations were measured for perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctanesulfoamide (PFOSA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononaoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUnDA). Concentrations of several perfluorocarboxylic acids, including perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were lower than the limits of quantification in all the samples analyzed. The highest concentrations of most PFCs were observed in water samples from the Yangtze River near Shanghai, the major industrial and financial centre in China. In addition, sampling locations in the lower reaches of the Yangtze River with a reduced flow rate might serve as a final sink for contaminants from the upstream river runoffs. Generally, PFOS was the dominant PFC found in samples from the Pearl River, while PFOA was the predominant PFC in water from the Yangtze River. Specifically, a considerable amount of PFBS (22.9–26.1% of total PFC analyzed) was measured in water collected near Nanjing, which indicates the presence of potential sources of PFBS in this part of China. Completely different PFC composition profiles were observed for samples from the Pearl River and the Yangtze River. This indicates the presence of dissimilar sources in these two regions.

Keywords: Perfluorochemicals; PFOS; PFOA; The Pearl River; The Yangtze River

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1. Introduction

Perfluorinated compounds (PFCs) are a group of emerging chemicals of concern in the 21st century. The abilities to repel both water and oil, together with their chemical and thermal stabilities, have made PFCs very useful in many commercial applications (Kissa, 2001). The widespread application, environmental persistence and bioaccumulative potential of PFCs result in the global occurrence of these substances in air (Martin et al., 2002; Stock et al., 2004); water (Saito et al., 2003; Schultz et al., 2004; So et al., 2004; Yamashita et al., 2004); sediment and sludge (Higgins et al., 2005); as well as various wildlife species inhabiting not only locations in close proximity to pollution sources, but also in remote areas (Houde et al., 2006, and references therein). Among the PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), regarded as the terminal degradation end-products, are the two chemicals that have frequently been detected in environmental samples, and very often occur at the highest concentrations.

Potential sources of PFCs in the aquatic environment include the application of PFC-based products such as aqueous film forming foams or the direct release to the environment during manufacturing processes (Poulsen et al., 2005; Prevedouros et al., 2006). PFCs can also be formed from indirect conversion of their precursor compounds. For example, conversion of *N*-ethyl perfluorooctane sulfonaminoethanol (*N*-EtFOSE) and *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA) to PFOS has been observed in liver microsomes of rats (Xu et al., 2004) and rainbow trout (Tomy et al., 2004), respectively. Fluorotelomer alcohols were also suggested to be the precursor compounds of various perfluorocarboxylic acids (PFCAs) (Dinglasan et al., 2004; Ellis et al., 2004). The intentional and unintentional discharges, and the subsequent transformations, may have resulted in the occurrence of various PFCs in groundwater (Schultz et al., 2004); coastal surface water (Saito et al., 2003); drinking water (Harada et al., 2003); as well as open ocean waters (Yamashita et al., 2005). The occurrence of PFCs in open ocean waters indicates that understanding the pollution sources and the water movement patterns would be important to explain the transports of PFCs from coastal regions to the open ocean.

The extent of PFC pollution in the aquatic environment has previously been monitored in the United States (Hansen et al., 2002; Boulanger et al., 2004; Schultz et al., 2004), Canada (Moody et al., 2002) and Japan (Saito et al., 2003; Taniyasu et al., 2003; Yamashita et al., 2004). A recent study reported that ranges of concentrations of PFOS in coastal seawaters of Hong Kong and the Pearl River Delta (PRD) were 0.09–3.1 and 0.02–12 ng/l, respectively, while those for PFOA were 0.73–5.5 and 0.24–16 ng/l, respectively (So et al., 2004).

The rapid industrial development in China in the past decade has transformed China into one of the world's largest economies. Specifically, a large number of private manufacturing operations in the PRD and the Yangtze River Delta (YRD) have transformed these regions into two of the "world's factories". The Yangtze River, one of the largest rivers in the world, extends from Qinghai-Tibet Plateau out to the East China Sea. The water quality of the Yangtze River has been adversely affected by intense industrial and urban activities (Shen et al., 2006). The manufacturing processes associated with industries, such as electronic or electric products, plastic goods and textiles, are expected to be potential sources of PFCs. As part of a continuous study, concentrations of PFCs were monitored in six tributaries of the Pearl River in Guangdong Province, south China, entering the PRD, in an attempt to locate possible pollution sources within the delta, and study their contribution to PFC contamination in the open ocean of the South China Sea. In addition, PFCs were measured in water samples from four sections along the Yangtze River, including Chongqing, Yichang, Nanjing and Shanghai, where the river eventually discharges into the East China Sea. This study was conducted to provide information on the baseline concentrations of PFCs in several major Chinese rivers. In addition, chemical composition profiles of PFCs measured in this study can also be used as fingerprints for source identification of PFCs in the open ocean environment.

2. Materials and methods

2.1. Chemicals and standards

The potassium salt of PFOS was purchased from Tokyo Chemical Industries (Portland, OR). Potassium salts of perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), and perfluorooctanesulfonamide (PFOSA) were provided by the 3M Company. Perfluorononanoic acid (PFNA) was purchased from Avocado Research Chemicals Ltd. (Lancashire, UK). PFOA was from Strem Chemicals Industries (Newburyport, MA). Perfluorohexanoic acid (PFHxA) was purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan). Perfluoroheptanoic acid (PFHpA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorododecanoic acid (PFDoDA) were purchased from Fluorochem Ltd. (Derbyshire, UK). Perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were from SynQuest Lab Inc. (Alachua, FL). Purities of all the analytical standards were $\geqslant 95\%$. Oasis® weak anion exchange (WAX; 6 cc, 150 mg, 30 μm) solid phase extraction (SPE) cartridges were purchased from Waters (Milford, MA). Milli-Q water was used throughout the whole experiment. Methanol (residual pesticide and PCB analytical grade), ammonium acetate (97%), ammonium solution (25%) and acetic acid (99.9%) were from Wako Pure Chemical Industries (Tokyo, Japan).