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Spatial distribution and fate of perfluoroalkyl substances in sediments from the Pearl River Estuary, South China

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ABSTRACT

In this study, 54 sediment samples were collected from the Pearl River Estuary (PRE) in Southern China to study the spatial distribution and patterns of PFASs in this region. PFAS concentrations in the sediment samples ranged from nd (below detection limit) to 2.41 ng g^{-1} dw (dry weight) with an average value of 0.79 ng g^{-1} dw. PFAS concentrations were higher at the nearshore sampling sites than in the others. Perfluorobutanesulfonate (PFBS) and perfluorohexanesulfonate (PFHxS) were the two dominant compounds among the target PFASs, which may be due to their production and use as PFOS substitutes in the Pearl River Delta (PRD) areas. Significant linear relationships were found between total PFAS concentrations and total organic carbon (TOC) ($R = 0.30$, $p < 0.05$). The preliminary environmental risk assessment indicated that PFOS and PFOA in the regional sediments posed no significant ecological risk to the benthic organisms at present levels.

1. Introduction

Perfluoroalkyl substances (PFASs), such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are produced for consumer and industrial purposes because of their excellent properties of thermal stability, surfactant functions, hydrophobicity and oleophobicity (Lindstrom et al., 2011; Prevedouros et al., 2006). Because of their persistence in the environment (Lindstrom et al., 2011), global distribution including the Arctic (Benskin et al., 2012), bioaccumulation in organisms (Naile et al., 2013), and potential toxicity (Vieira et al., 2013), PFASs have received growing concern worldwide. Perfluorooctanesulfonic acid (PFOS), its salts and perfluorooctanesulfonyl fluoride (PFOSF) have been listed in Annex B of the Stockholm Convention as new persistent organic pollutants (POPs) in 2009 (UNEP, 2009).

The 3 M Company, the largest producer of PFOS in the world, has halted the production of PFOSF in 2002. However, the production of PFOS-related chemicals in China increased rapidly from 2003 to 2006, and the annual production has continued high until now. Up to 2011, about 1800 t of PFOS-related chemicals for both domestic use and export have been produced in China, and nearly half of the national output was for export in recent years (Xie et al., 2013b). Most of the manufacturing plants are located in the southern and eastern part of China, including Hubei, Fujian, Guangdong provinces and Shanghai (Xie et al., 2013b). Recent studies have reported that PFASs could be detected in various matrices in China such as water, seafood, and human blood (Cai et al., 2012; Wu et al., 2012b; Yang et al., 2011; Yeung et al., 2006).

Aquatic transport is supposed to be one of the important long range transport routes of PFASs (Prevedouros et al., 2006). A previous study showed that PFASs discharged into the aquatic environment could distribute in water, particulate and sediment (Ahrens et al., 2010), Sediment plays an important role in the aquatic system. It is the important sink for PFASs and other pollutants (Prevedouros et al., 2006). The river estuary can reflect pollutants being transported from the river to the sea. The Pearl River is one of the largest rivers in south China. The Pearl River Estuary (PRE) located in South China links the Pearl River and the South China Sea. The rapid economic development of the Pearl River Delta (PRD) has brought a large number of pollutants such as trace metals, mercury, DDT (Dichlorodiphenyltrichloroethane) and HCH (Hexachlorocyclohexane) to the surrounding region (Chen et al., 2012; Shi et al., 2010; Zhang et al., 2002). Moreover, PFASs have already been detected in water, sediment and seafood in the Pearl River and the nearshore region (Loi et al., 2013; Pan et al.,

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2014; So et al., 2007; Wu et al., 2012b; Zhao et al., 2014b). However, study of PFASs in the sediments from the Pearl River Estuary and the adjacent marine environment is still limited.

The objective of this work is to carry out a systematic survey to trace the spatial distribution and patterns of PFASs in sediments in the PRE. The factors such as total organic carbons (TOC) and pH that relate to the accumulation of PFASs in the sediments were also investigated to examine possible sources, anthropogenic impacts, and environmental fate of PFASs in the estuary. Finally, the potential risk of PFOS and PFOA to the aquatic ecosystem was assessed in this region.

2. Materials and methods

2.1. Sample collection

In this study, 54 surface sediment samples (top 0–5 cm) were collected in 2009 (X1–X17) and 2011 (the rest of the samples), and the sampling sites are shown in Fig. 1. The samples were collected using a grab sampler and then stored in polyethylene bags. The collected samples were kept at 4 °C immediately. After being freeze-dried at −50 °C for three days, the samples were ground to small particles with size of less than 200 μm. Then the samples were stored in the refrigerator at −20 °C until analysis.

2.2. Standards and chemicals

Nine PFASs standards (PFBS, PFHxS, PFOS, PFHpA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA) and two internal standards ($^{13}C_4$PFOS and $^{13}C_4$PFOA) were purchased from Wellington Laboratories (Canada). Methanol (HPLC grade) was purchased from J.T.Baker (USA) and ammonium acetate (HPLC grade) from Alfa Aesar (Ward Hill, MA, USA). Water was prepared using a Milli-Q Advantage A10 system (Millipore Corp., USA). The Oasis-HLB cartridge (6 cc, 150 mg) was purchased from Waters (Milford, MA, USA).

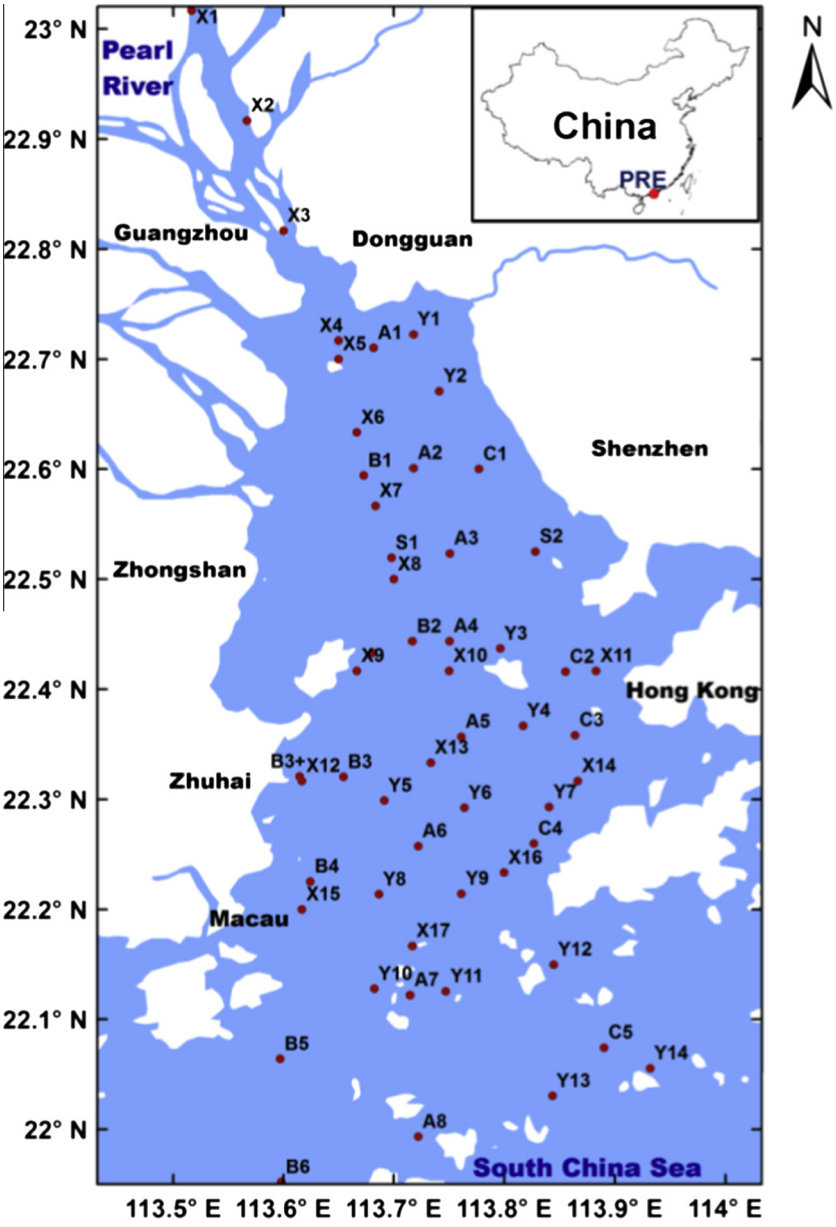

Fig. 1. Study area and sampling sites for sediments.