



## Neutral polyfluoroalkyl substances in the atmosphere over the northern South China Sea<sup>☆</sup>



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### ABSTRACT

Neutral Polyfluoroalkyl substances (PFASs) in the atmosphere were measured during a cruise campaign over the northern South China Sea (SCS) from September to October 2013. Four groups of PFASs, i.e., fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), fluorooctane sulfonamides (FOSAs) and fluorooctane sulfonamidoethanols (FASEs), were detected in gas samples. FTOHs was the predominant PFAS group, accounting for 95.2–99.3% of total PFASs ( $\Sigma$ PFASs), while the other PFASs accounted for a small fraction of  $\Sigma$ PFASs. The concentrations of  $\Sigma$ PFASs ranged from 18.0 to 109.9  $\text{pg m}^{-3}$  with an average of 54.5  $\text{pg m}^{-3}$ . The concentrations are comparable to those reported in other marine atmosphere. Higher concentrations of  $\Sigma$ PFASs were observed in the continental-influenced samples than those in other samples, pointing to the substantial contribution of anthropogenic sources. Long-range transport is suggested to be a major pathway for introducing gaseous PFASs into the atmosphere over the northern SCS. In order to further understand the fate of gaseous PFASs during transport, the atmospheric decay of neutral PFASs under the influence of reaction with OH radicals and atmospheric physical processes were estimated. Concentrations of 8:2 FTOH, 6:2 FTOH and MeFBSE from selected source region to the atmosphere over the SCS after long-range transport were predicted and compared with the observed concentrations. It suggests that the reaction with OH radicals may play an important role in the atmospheric decay of PFAS during long-range transport, especially for shorted-lived species. Moreover, the influence of atmospheric physical processes on the decay of PFAS should be further considered.

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## 1. Introduction

Polyfluoroalkyl substances (PFASs) is a group of man-made organic compounds, involving a wide range of chemicals with different fluorocarbon chains ( $\text{CF}_3[\text{CF}_2]_n$ ) (Buck et al., 2011). Due to

the unique chemical stability and surface-active properties, PFASs have been widely used in inks, varnishes, waxes, fire-fighting foams, coating formulations, repellents for textiles, leather and paper products (Paul et al., 2009). These substances may be directly released into the environment during production, usage and disposal (Giesy and Kannan, 2002; Lindstrom et al., 2011; Paul et al., 2009). PFASs have raised more concerns for their persistence and bioaccumulation, as well as potential toxicity on the human and wildlife in environment (Giesy and Kannan, 2002; Houde et al., 2011; Prevedouros et al., 2006). Perfluorooctanoate (PFOA) and Perfluorooctane sulfonate (PFOS), two of the most widely known PFASs, have been detected in water (Ahrens, 2011; Zhang et al.,

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2013; Zhao et al., 2012, 2014), air (Jahnke et al., 2007; Li et al., 2011; Liu et al., 2015; Shoeib et al., 2005), soil (Meng et al., 2013; Wang et al., 2013), wildlife (Houde et al., 2005; Lam et al., 2014; Schiavone et al., 2009) and human blood (Bao et al., 2011; Kubwabo et al., 2013; Shoeib et al., 2011).

Neutral PFASs in the atmosphere play an important role in the global cycle and distribution of PFASs. It was reported that the degradation of neutral precursors (e.g., fluorotelomer alcohols (FTOHs), fluoroctane sulfonamides (FOSAs) and fluoroctane sulfonamidoethanols (FASEs)) could contribute to the burden of PFOA and PFOS in the atmosphere (D'eon et al., 2006; Ellis et al., 2004; Martin et al., 2006). These precursors are usually volatile or semi-volatile. Therefore, they are capable of escaping into the atmosphere during their manufacture and usage. They have been observed not only in urban areas (Ahrens et al., 2012; Dreyer and Ebinghaus, 2009; Li et al., 2011), but also in remote areas (Cai et al., 2012a; Del Vento et al., 2012; Shoeib et al., 2010; Wang et al., 2015; Xie et al., 2013, 2015). In smog chamber studies, the atmospheric lifetimes were estimated to be approximately 20 days for FTOHs and 20–50 days for FASAs due to their slow reaction with OH radicals (Ellis et al., 2003; Martin et al., 2006). The reaction with OH radicals is suggested as the most important degradation mechanism rather than other processes such as photolysis, wet and dry depositions, reactions with NO<sub>3</sub> radicals, Cl atom and O<sub>3</sub> etc. (Ellis et al., 2003). The neutral PFASs can react with OH radicals in the atmosphere during long-range transport, which has been suggested to be the major source of PFOA and PFOS in remote areas (D'eon et al., 2006; Ellis et al., 2004; Martin et al., 2006).

The South China Sea (SCS) is a marginal sea surrounded by the fast-developing regions with immense production of industrial products containing PFASs. As mentioned, the release of neutral PFASs could happen during production and usage. Under prevailing winds, air mass carrying neutral PFASs from the surrounding areas could be transported into the atmosphere of the SCS. Although the PFASs in surface water in the SCS has been reported in the previous studies (Cai et al., 2012b; Kwok et al., 2015; Yamashita et al., 2004), few research has been conducted to study the occurrence, sources and fates of atmospheric neutral PFASs over the SCS. Meanwhile, the loss mechanisms of gaseous PFASs have been suggested but only been investigated in laboratory studies. To our best knowledge, there is no study has been conducted to examine the decay of PFASs in the ambient atmosphere of the SCS till now.

In this study, we present the observation of neutral PFASs in gas phase during a cruise campaign in the northern SCS from September to October 2013. The objectives of this work were: (1) to determine the concentrations and composition of neutral PFASs in the atmosphere over the northern SCS; (2) to investigate the sources of neutral PFASs in the oceanic area; (3) to understand how neutral PFASs decay during long-range transport and the possible constraints. The results would help to improve the current understanding of the occurrence, sources, fates and the future perspectives of the neutral PFASs in coastal and oceanic areas.

## 2. Experimental

### 2.1. Sampling information

Ten sets of air samples including gas and particulate matter (PM) samples were collected on the research vessel Experiment III during the northern SCS campaign from September to October 2013 (See Fig. 1) (Lai et al., 2015; Zhao et al., 2016). An integrated high volume air sampler was placed in the upper deck to collect gas and PM samples simultaneously. The sampling unit contains an inlet equipped with a glass fiber filter (GFF, pore size 0.7 μm) to collect PM sample and a self-made column filled with XAD-2 resin was

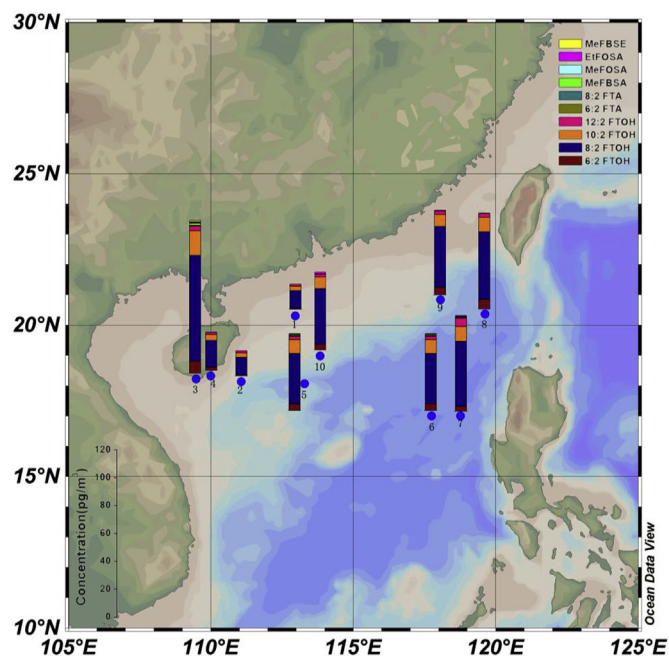


Fig. 1. Variations of neutral PFASs along the cruise in the atmosphere over the northern South China Sea.

followed to trap gaseous substances. The sampling volume of each air sample set ranged from ~120 to ~450 m<sup>3</sup>. After collection, the samples were covered with prebaked aluminum foil bags and stored at -20 °C until analysis. Detailed information of the air samples including date, latitude and longitude, sampling volume, air temperature, relative humidity and wind speed is listed in Table S1.

### 2.2. Sample analysis

The samples were spiked with 2.5 ng of mass labeled internal standards prior to extraction. GFFs and columns were extracted using a MX extractor for 16 h using dichloromethane. Extracts were evaporated to 1–2 mL using hexane as a keeper and then passed through a column packed with 3 g Na<sub>2</sub>SO<sub>4</sub> to remove residual water. The extracts were further concentrated down to 150 μL and spiked with 10 μL of 100 pg μL<sup>-1</sup> FTOH 9:1 as injection standard.

The method of sample analysis has been described elsewhere (Xie et al., 2013). Briefly, the analysis was performed using gas chromatography/mass spectrometry (GC/MS) in selective ion monitoring (SIM) mode using positive chemical ionization (PCI). The response factors were derived from the calibration curves (6-points) made for response ratio between targets compounds (0–0.25 ng μL<sup>-1</sup>) and corresponding surrogate (0.05 ng μL<sup>-1</sup>). The details of the analytes of FTOHs (6:2, 8:2, 10:2 and 12:2 FTOH), FASA (MeFBSA, MeFOSA and EtFOSA) and FASE (MeFBSE) are summarized in Table S2.

### 2.3. Quality assurance/quality control (QA/QC)

Before sample collection, all resin columns were pre-cleaned with organic solvents (methanol, acetone and hexane/acetone in turn for 96 h) and GFFs were baked at 550 °C for 12 h prior to their usage. The columns were covered with aluminum foil during sampling and stored in the aluminum foil bags after sampling to avoid the exposure to ultraviolet and visible light, which can cause the degradation of the target compounds. Contamination of ship

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