OCCURRENCE AND DISTRIBUTION OF PERFLUOROALKYL SUBSTANCES (PFASs) IN SOUTH CHINA SEA

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Introduction

The fate and input of the perfluoroalkyl substances (PFASs) into the environment has been recognized as an emerging issues in the past recent decades. Owing to their surface active properties, high chemical and thermal stability, PFASs have been extensively used in a wide range of industrial and commercial applications, such as surface treatment, paper packaging, cookware, textiles and performance chemicals.[1-4] PFASs can be released into the environment during their usage, disposal and manufacturing processes,[5] of which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are even persistent and ubiquitously distributed in various environmental matrices.[6-9] Recent attention has also been focused on the fluorinated phosphate surfactants, as they were mainly applied in human food and skin contact products which elevated the potential risk of human exposure[10, 11].

Atmospheric and hydrospheric transport mechanisms of PFASs have been proposed.[12, 13] Evidence suggests the presence of perfluoroalkyl acids (PFAs) and their precursors in both the aquatic and atmospheric environment. Volatile precursor compounds (i.e., perfluorooctane sulfonamides/sulfonamidoethanols (FOSA/SEs), fluorotelomer alcohol (FTOHs), and etc) can undergo long range transportation and then be degraded into perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) under OH radical initiation in the atmospheric environment,[12, 14-15] and microbial processes in the aquatic and wastewater treatment systems[16]. In addition, the ionic nature of PFAs enables them to be highly mobile in aqueous systems and these compounds can be transported from domestic, commercial and industrial discharge into natural waters. PFAs entered the environment through direct release from aqueous film-forming foam (AFFF) products, related industrial/chemical manufacturing facilities, wastewater effluent, surface runoff and agriculturalirrigation.[17] Previous study have even suggested PFAs could be one of the excellent tracers of global circulation of oceanic waters due to their persistency and high water solubility.[14]

With a population of 1.3 billion, China is the world's second-largest economy by nominal gross domestic products (GDP). China initiated large production of perfluorooctanesulfonyl fluoride (POSF)/PFOS in 2003, after those major manufacturers, such as, 3M, phased out their production, and produced more than 200 tons of POSF in 2006 by 15 Chinese enterprises[18]. In recent years, China has become the largest manufacturer of PFAS-containing products in the world due to the fast growing field of textiles, electronics, printing and packaging industries. However, there were insufficient clear management measures/guidelines of these chemicals existed in their rate of production and disposal, leading to their direct/indirect discharge into the atmospheric environment and aquatic systems. Monitoring studies of PFASs in the coastal waters have been focused in the East China Sea,[19] Dalian[20] and Pearl River Delta.[21] However, information on PFAS contamination in the South China Sea is still very limited. In light of this, this study aims (1) to study the occurence and distribution of PFASs in the surface waters of the South China Sea, (2) to identify the sources of PFAS contamination and (3) to perform international comparison of PFASs with other surface water conducted elsewhere.

Materials and methods

Surface water samples were collected at 52 stations from the eastern part of South China Sea during a scientific expedition cruise in July to August, 2012. South China Sea is a marginal sea that is part of the Pacific Ocean, and it is the second most used sea lane in the world. In addition, surface water samples were also collected from

Hong Kong (n=9) in August 2012 and Macau (n=1) in April 2013 (Fig 1), which are the two cities situated at the mouth of the Pearl River Delta.

One to two litres of seawater were collected from each sampling point using a stainless steel bucket. Water samples were stored in polypropylene (PP) containers with narrow mouth and screw tops. Stainless steel bucket was pre-cleaned by rinsing with methanol and then water from specific locations before sample collection to avoid any PFC contamination. All samples were stored at -20°C until analysis. Unfiltered samples were extracted using solid phase extraction Oasis®WAX (6 cc) cartridges (Water Corp., Milford, U.S.A). The analytical procedures were similar to those reported earlier with some modifications.[22,23] Fifteen PFCs, including C_4, C_6, C_8 and C_{10} PFASs, C_4-C_{12}, C_{14} PFCAs and perfluorooctane sulfonamide (PFOSA) were quantified. Separation, identification and quantification of the analytes were performed by using an Agilent 1290 Infinity ultra-performance liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a 5500 QTRAP mass spectrometer (AB Sciex, Foster City, CA, USA). Two Aligent Zorbax Eclipse XBD-C8 guard columns (Agilent, Palo Alto, CA, USA) were utilized to assist the analytical column to separate the instrumental PFC background. To ensure trace level analysis of the sea water samples, strict quality control and quality assurance (QA/QC) measures were performed.

Concentrations of the target compounds in all procedural blanks were below their corresponding limits of quantification (LOQ) (i.e <0.01-0.05 ng/L). The procedural recoveries (n=4) of individual PFCs ranged from 74% to 97%, while matrix-spike recoveries (n=3; Hong Kong seawater) ranged from 60% to 105%. Surrogate standards $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_4$-PFOA, $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA and $^{13}C_2$-PFDoDA were spiked into each sample to determine the recoveries of the target analytes. PFAS concentrations were not corrected for the recoveries of surrogates. The sample extracts with lower recovery values were removed from the analysis and a new set of samples was analyzed again after resolving any uncertainties due to analytical error. Spearman Rank Order test was employed for the correlation analysis using the statistical software SigmaStat 3.5.
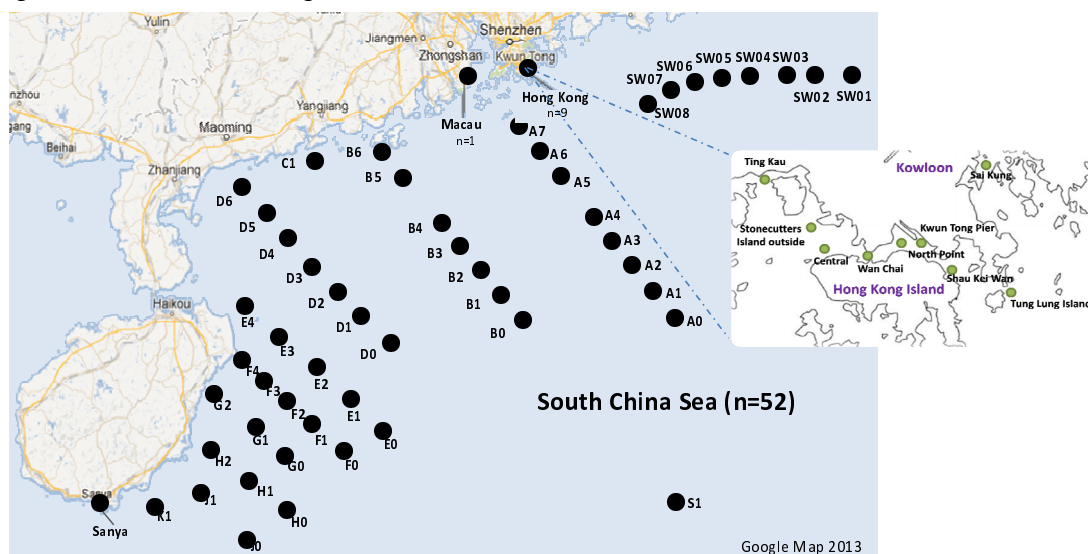

Fig 1. Sampling locations of the surface seawater in South China Sea.

Results and discussion
Preliminary results of PFAS concentration in coastal and oceanic waters of South China Sea
Total PFAS concentrations and composition profiles of the surface sea waters of South China Sea are shown in Fig 2. Among the 33 samples analyzed, 13 PFASs including C_4, C_6, C_8 PFASs, C_4-C_{12} PFCAs and PFOSA were identified. The total PFAS concentrations ranged from 356 to 4926 pg/L, with different dominant compounds detected including PFOS (~28%), PFOA (~21%), PFBA (~13%) and PFBS (~10%). Surprisingly, high levels of PFOS, which was included in Annex B of the Stockholm Convention on persistent organic pollutants in 2009,

were found in the surface water of South China Sea, suggesting the continuous production, usage, and/or leaking from the existing PFAS-containing products in the South China region. Replacement of C8-based compounds by C4-based compounds[24] may increase the concentrations of PFBA and PFBS in the environment.

For coastal waters, similar concentrations of total PFASs (i.e. $C_{4, 6, 8}$ PFAS, C_{4-12} PFCA and PFOSA) and composition profiles were observed among all coastal stations with the exception of A7 (4926 pg/L) which was found to be five to six times higher in concentrations compared to other coastal stations. Sampling station A7 was closer to the Pearl River Delta (PRD), which is receiving serious PFAS contamination from a highly urbanized and industrialized area (i.e. Guangzhou).[9, 21] Manufacturing of plastic products and electronic equipment would potentially involve the use of various PFASs and result in the releases of these compounds into the South China Sea through discharges from wastewater treatment plants (WWTPs) or rivers. Comparable PFAS concentrations were also detected from surface water collected from the Victoria Harbour, Hong Kong (arithmetic mean: 4650 pg/L), suggesting that both locations may be exposed to similar contamination sources of PFASs. A previous study has also examined the concentrations of $C_{4, 6, 8}$ PFSA, PFOA and PFNA at the same location of sampling station A7 in July, 2003[21]. After nine years, two times higher in PFOS concentration and occurrence of PFBS were detected in the surface water, while a slight decrease was observed in PFOA concentration (Fig 3). This result suggests that the production and use of PFSAs have not been decreasing in the PRD region. Furthermore, the ocean currents during the sampling period moved along the PRD to southwest,[25] hence, carrying the PFASs to the western part of PRD and causing elevated concentrations of total PFASs in sampling stations of B6, C1, D6 and E4. In addition to the influence of the ocean currents, terrestrial discharges of PFASs may also contribute to the elevated concentration in these stations. Along the transect A, five to eight times decreases in total concentrations of PFASs were observed in sampling stations from A6 to A0 as compared with that of A7, further indicating that PFAS contamination may be strongly affected by the ocean current[13] instead of dispersing to the offshore area.

In addition, similar total PFAS concentrations were measured in all offshore waters. Relatively lower PFAS concentrations were detected in the offshore region of the South China Sea. Similar composition profiles between the coastal and offshore waters were observed except sampling station A0 which consisted of more than 40% of PFNA detected.
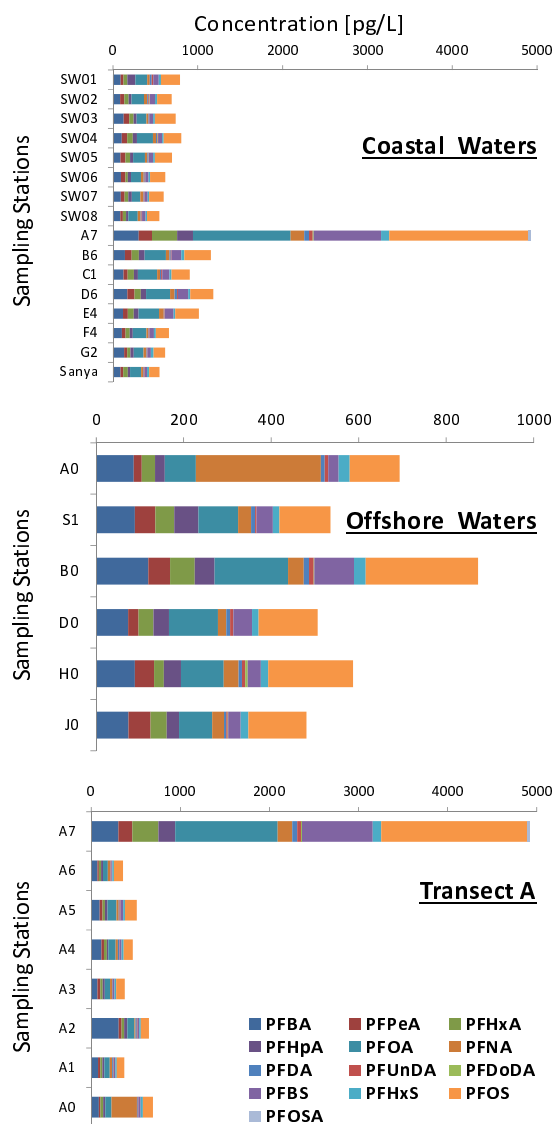

Fig 2. Concentrations and composition profiles of PFAS in coastal and oceanic waters of South China Sea

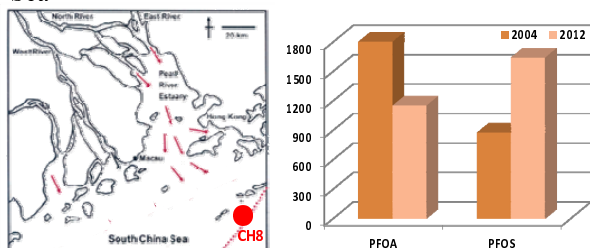Fig 3. Concentrations of PFOS and PFOA at sampling station A7 (Outside PRD) in 2004 and 2012

Source Determination

Correlation analyses of PFAS concentrations were performed for surface sea water samples in order to examine the sources of contamination. The presence of common contamination sources in surface water samples was reflected by significant positive associations (p<0.01) among most of the PFASs. These contamination sources may be associated with the discharges from the continents and atmospheric depositions. Correlations were also observed between PFOA and PFNA (r=0.576, p<0.01) and PFDA and PFUnDA (r=0.591, p<0.01), indicating the degradation of volatile fluorotelomer precursors (i.e., 8:2 FTOH and 10:2 FTOH) through the long range atmospheric transport.

Acknowledgements

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