

DISTRIBUTION OF PERFLUORINATED COMPOUNDS IN SEA WATER AND SEDIMENT IN EAST CHINA SEA

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Abstract

Perfluorinated compounds (PFCs) are fully fluorinated organic compounds, which are distributed all over the world and have been found even in remote regions far from human activities. The objectives of the study were to identify the distribution of PFCs in East China Sea in water and sediment and to estimate the historic PFCs contamination in this area. Surveys were conducted in East China Sea and samples were collected from surface water, deep water and sediment. A solid phase extraction (SPE) coupled with HPLC-ESI-MS/MS were used. PFCs were detected in all samples indicating PFCs are remained intact in the environment for long periods of time. PFCs concentrations in surface water from ES-1 to ES-8 were ranged from 772 – 1,040 pg/L. PFOA (45%) and PFOS (20%) were predominant compounds which were found in East China Sea. In sediment sample at ES-6, PFOS concentration ranged from not detected (ND) – 4,265 pg/g dry wt (Geomean = 281 pg/g). PFOA was in the ranged of ND – 1,164 pg/g dry wt (Geomean = 126 pg/g). PFOS was found higher in the sediment than PFOA. PFOS was detected the highest concentration in 1986, while PFOA was detected in the highest concentration in 2004.

Introduction

Perfluorinated compounds (PFCs) especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are global environmental contaminants. Currently, these chemicals are labeled as new Persistent Organic Compounds (POPs) which are persistent, bio-accumulating, and having potential of causing adverse effects to humans and environment¹. Used to make various products worldwide for some 40 years, PFOS production is now in decline owing largely to a decision made by major US manufacturer (3M) in 2000 to phase out the manufacture and use of PFOS beginning in 2001. PFOA is still being manufactured and used. Released into the water environment through both point-source and non-point-source discharges for many decades, the persistence, presence in the environment and bioaccumulation potential of both these micropollutants are now the cause of global concern.^{2,3,4} PFCs have also been found even in remote regions far from human activities such as the Arctic, the Antarctic, and the open ocean^{5,6,7} due to their persistent and remain intact in the environment for long periods of time. PFCs might enter to the food chain through aquatic animals and cause adverse effect to human. The study on fate and transportation of PFCs in the open sea was needed to understand their behavior in the environment. The survey was conducted in East China Sea. Because of the rapid industrial growth in East Asian countries in recent years, it is high possibility of detecting PFCs in the area. The objectives of the study were to identify the distribution of PFCs in East China Sea in water and sediment and to estimate the historic PFCs contamination in this area.

Material and Method

Sampling Location: The survey was conducted in a part of East China Sea. Sampling started from Okinawa, Japan (2009/7/2) and finished at Kyushu, Japan (2009/7/12) following the Kuroshio ocean current direction (Figure 1). A ship from Japan Coast Guard was used in the sampling. Seven sampling points were selected. Surface water samples were collected in each sampling point (ES-1 to ES-8). Deep water samples were collected at ES-6 for the estimation of PFCs vertical distribution in East China Sea. Core sediment sample (20 cm) was collected in ES-6 to estimate the historic PFCs contamination in the area.

Sample Collection: Surface water was collected by polypropylene (PP) bucket. Niskin water sampler from General Oceanic, Inc., U.S.A. (10L) was used for collecting deep water samples. Sediment core samples were

collected by small size multiple core samplers (the core length of 400 mm, 4 groups) from Rigosha Co., Ltd. All of the samples were transferred to PP containers for storing samples. Sampling equipments were washed by methanol and *ultrapure* water before use. Containers were also rinsed three times with water at sampling site before collection.

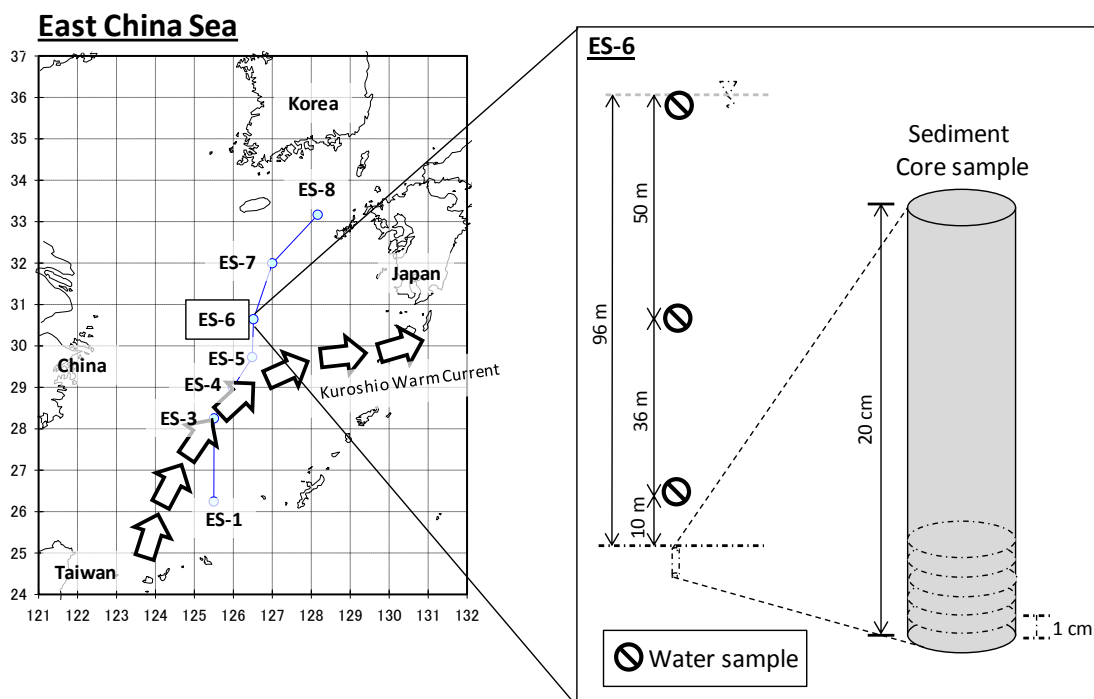


Figure 1 Sampling locations in East China Sea

Sample Preparation: A collected sample (4,000 mL) was passed through a PresepC-Agri (C18) cartridge (Wako, Japan) inline connected to Oasis[®]HLB (Waters, Japan). PFCs surrogate standards (¹³C₄-PFOA, ¹³C₂-PFDA, and ¹³C₄-PFOS) were spiked (250 pg/L) into a sample before cartridges loading to identify their recoveries. The above procedures were completed in the ship and the cartridges were brought back to Kyoto University laboratory for further analysis. In the laboratory, each cartridge was dried, eluted with 2 mL HPLC-grade methanol followed by 2 mL HPLC-grade acetonitrile, evaporated to dryness, and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetonitrile) to a final volume 1 mL. PFCs in filtrates were concentrated by a factor of 4,000 times. Sediment samples were separated in each centimeter. Each centimeter of the core sample from 4 groups (sampler) were mixed together. Sediment were dried and crushed into powder. One gram (dry weight) of the sample was added into 15 mL tube and mixed with 10 mL methanol (HPLC-grade). PFCs surrogate standards were spiked (10 ng/g) into the sample to identify their recoveries. Sample was mixed with vortex and extracted by shaking for 30 min. Then, extracted sample was centrifuged and supernatant was separated. The extraction was done for two times. Supernatant was mixed and passed through ENVI-carb filter (Supelco, U.S.A.) to eliminate matrix. Then, sample was evaporated to dryness, and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetonitrile) to a final volume 1 mL.

Instrumental Analysis and Quantification: Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, Japan). For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). The analytical parameters of each PFC are shown in Table 1.

Calibration and Validation: The calibration curves for quantification, consisting of seven points covering 0.01 to 10 µg/L (2.5 to 2,500 pg/L with concentrated factor), generally provided linearity with determination coefficients

(R^2) more than 0.995 in every compound. Instrumental quantification limit (IQL) was used for quantifying analyte, which was defined by S/N 10:1 (Table 1). During the sample collection and analysis, analytical blanks were performed by using *ultrapure* water. PFCs concentrations were less than the IQL , indicating no contamination during the process. The recovery rates were calculated by spiking PFCs standards into samples. For water samples, standards were spiked before loading to the cartridges, while, the standards were spiked before extraction for sediment analysis. The range of the recovery rates of $^{13}C_4$ -PFOA, $^{13}C_2$ -PFDA, and $^{13}C_4$ -PFOS were 66 – 117% , 51 – 113% and 73 – 157% , respectively.

Table 1 Analytical parameters of each PFC by HPLC-ESI-MS/MS analysis

Compound	Abbreviation	Molecular Structure	Parent ion (m/z)	Daughter ion (m/z)	CE (eV)	Retention time (min)	IDL ($\mu\text{g/L}$)	IQL ($\mu\text{g/L}$)
Perfluorooctanoic acid	PFOA	$\text{CF}_3(\text{CF}_2)_6\text{COOH}$	413	369	5	7.2	0.02	0.06
Perfluorononanoic acid	PFNA	$\text{CF}_3(\text{CF}_2)_7\text{COOH}$	463	419	5	9.9	0.02	0.04
Perfluorodecanoic acid	PFDA	$\text{CF}_3(\text{CF}_2)_8\text{COOH}$	513	469	5	12.7	0.02	0.08
Perfluoroundecanoic acid	PFUnA	$\text{CF}_3(\text{CF}_2)_9\text{COOH}$	563	519	5	15.4	0.14	0.44
Perfluorododecanoic acid	PFDoA	$\text{CF}_3(\text{CF}_2)_{10}\text{COOH}$	613	569	5	18.0	0.14	0.44
Perfluorooctane sulfonate	PFOS	$\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{Na}$	499	80	55	13.8	0.02	0.08
Perfluoro- n -[1,2,3,4- $^{13}C_4$]octanoic acid	MPFOA	$\text{CF}_3(\text{CF}_2)_3(^{13}\text{CF}_2)_3^{13}\text{COOH}$	417	373	5	7.2	0.02	0.06
Perfluoro- n -[1,2- $^{13}C_2$]decanoic acid	MPFDA	$\text{CF}_3(\text{CF}_2)_7^{13}\text{CF}_2^{13}\text{COOH}$	515	471	5	12.7	0.02	0.06
Sodium perfluoro-1-[1,2,3,4- $^{13}C_4$]-octanesulfonate	MPFOS	$\text{CF}_3(\text{CF}_2)_3(^{13}\text{CF}_2)_4\text{SO}_3\text{Na}$	503	80	55	13.8	0.02	0.08

Note: CE = Collision Energy

IDL = Instrument Detection Limit

IQL = Instrument Quantification Limit

Results and Discussion

Concentration of six PFCs measured in each sampling point is shown in Figure 2. PFCs were detected in all samples indicating PFCs remain intact in the environment for long periods of time. PFCs concentrations in surface water from ES-1 to ES-8 were ranged from 772 – 1,040 $\mu\text{g/L}$. The highest concentration was found at ES-1. ES-1 is located in the direction of ocean current from Taiwan and China, where should be the possible source of PFCs. PFCs concentrations remained at the similar level to ES-8. PFOA (45%) and PFOS (20%) were predominant compounds which were found in East China Sea. Deep water samples were collected in ES-6. PFOS was likely to sink to the bottom of the sea as the concentration increasing by depth, while PFOA was found the higher concentration on the surface and in the middle of the sea.

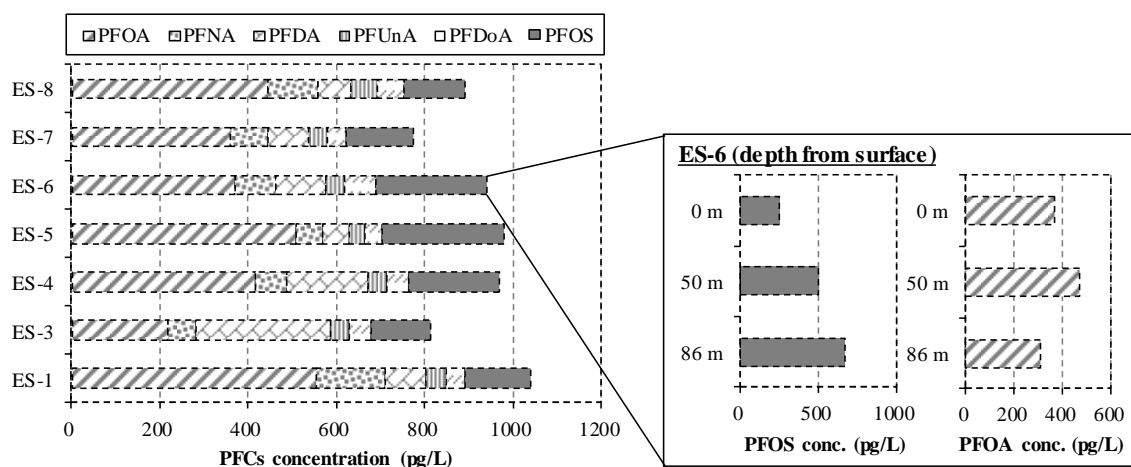


Figure 2 PFCs concentrations in East China Sea (ES-1 to ES-8) and deep water sample from ES-6

Figure 3 shows PFOS and PFOA concentration in sediment at each centimeter from 0 to 20 cm. Core sediment sample was collected in ES-6 to estimate the historic PFCs contamination in the area. The sedimentation rate was calculated by "Pb-210 dating method". PFOS concentration ranged from not detected (ND) – 4,265 pg/g dry wt (Geomean = 281 pg/g). PFOA was in the ranged of ND – 1,164 pg/g dry wt (Geomean = 126 pg/g). PFOS was found higher in the sediment than PFOA. PFOS was likely to attach to the sediment and sludge more than PFOA as reported in the literature⁸. PFOS was detected the highest concentration in 1986, while PFOA was detected in the highest concentration in 2004.

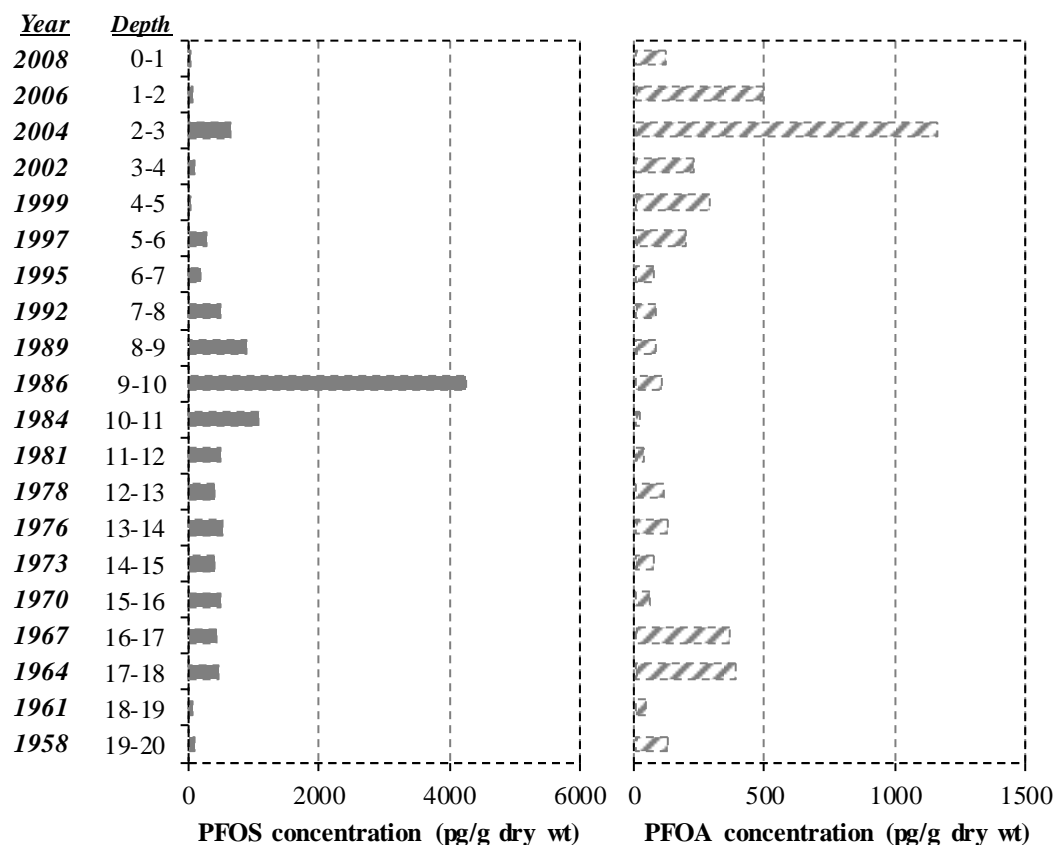


Figure 3 PFOS and PFOA concentrations in core sediment sample from ES-6

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