

## PERFLUORINATED CARBOXYLATES AND SULFONATES IN OPEN OCEAN WATERS OF THE PACIFIC AND ATLANTIC OCEANS

Sachi Taniyasu<sup>1</sup>, Nobuyoshi Yamashita<sup>1</sup>, Kurunthachalam Kannan<sup>2</sup>, Yuichi Horii<sup>1</sup>,  
Ewan Sinclair<sup>2</sup>, Gert Petrick<sup>3</sup>, Toshitaka Gamo<sup>4</sup>

<sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba

<sup>2</sup>Wadsworth Center, New York State Department of Health, Albany

<sup>3</sup>Institute for Marine Research, University of Kiel, Kiel

<sup>4</sup>Ocean Research Institute, University of Tokyo, Tokyo

### Introduction

Environmentally stable perfluorinated compounds (PFCs) have appeared as a new class of global pollutants within the last four years. These compounds in general, and perfluorooctane sulfonate (PFOS) in particular, can elicit toxic effects in wildlife and humans (1,2). PFCs have unique physicochemical properties due to the highly persistent C-F bond of the non-polar moiety and exhibit a wide variety of volatility/ water solubility depending on the nature of the substituted polar moiety. Environmental kinetics of PFCs is very complex because of the unique characteristics and their wide applications in various products. It is clear that PFCs pollution is a global problem involving several international organizations such as OECD. We have reported the initial survey of open ocean pollution by PFCs in 2003 (3,4). Our studies have shown that part per quadrillion (ppq) level analysis of PFCs is necessary to obtain reliable information of open ocean pollution. We have developed reliable analytical and sampling method for ultra-trace level analysis of PFCs that is applicable to global survey of open ocean pollution.

Analysis of PFCs in open ocean waters is challenging because of the need for ppq level analysis and no earlier studies have reported such a sensitive method. There were two approaches to enable trace level analysis of PFCs, namely, to decrease the blank and to solve co-elution problem. We have tested low blank solid phase extraction method and improvements in the analytical procedures and instrumentation, the blank/background levels of target perfluorinated acids were reduced significantly. Field blanks containing 800 mL of HPLC-grade water taken in a polypropylene bottle were transported to sampling locations. Two hundred microliter of sodium thiosulfate solution has been added to the field blanks. Although the concentrations of target fluorochemicals in field blanks were similar to those in procedural blanks in most cases, any sample sets that were found to have notable contamination in field blanks were eliminated from further analysis.

## Materials and Methods

Analysis of trace level determination of PFCs (PFOS, perfluorooctanoic acid (PFOA), perfluorononaic acid (PFNA), perfluorooctane sulfonamide (PFOSA), perfluorohexane sulfonate (PFHS), perfluorobutane sulfonate (PFBS)) was performed using a high performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS), comprising an Agilent HP1100 liquid chromatograph interfaced with a Micromass® (Beverly, MA, USA) Quattro Ultima Pt mass spectrometer operated in the electro spray negative ionization mode. A 5 or 10- $\mu$ L aliquot of the sample extract was injected into a guard column (XDB-C8, 2.1 mm i.d. x 12.5 mm, 5 $\mu$ m; Agilent Technologies, Palo Alto, CA) connected sequentially to a Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 $\mu$ m; Termo Hypersil-Keystone, Bellefonte, PA) with 2 mM ammonium acetate/methanol as mobile phase, starting at 10% methanol. At a flow rate of 300 mL/min, the gradient was increased to 30% methanol at 0.1 min, 75% methanol at 7 min, and 100% methanol at 10 min, and was kept there until 12 min before reversion to original conditions, at 20-min. The capillary was held at 1.2 kV. Cone-gas and desolvation-gas flows were kept at 60 and 650 L/h, respectively. Source and desolvation temperatures were kept at 120 and 420°C respectively. MS/MS parameters were optimized so as to transmit the [M-K]<sup>-</sup> or [M-H]<sup>-</sup> ions. Eight calibration curve points bracketing the concentrations in samples were prepared routinely, to check for linearity.

The highest concentrations of target compounds in procedural blanks, which were passed through the entire analytical procedure involving the SPE cartridges, were 0.8 pg of PFOS, 0.4 pg of PFHS, 0.6 pg of PFBS, 5.2 pg of PFOA, 1.8 pg of PFNA, 1 pg of PFOSA, and 1.1 pg of THPFOS in 1L of water sample. The LOQ of target chemicals was evaluated for each sample based on the maximum blank concentration, the concentration factors, the sample volume and a signal-to-noise ratio of 3. Detailed analytical procedure has been reported elsewhere (5).

We applied this method to all seawater samples collected from several international joint cruises. We have conducted six open ocean cruises from 2002 to 2004 as follows; the central to eastern Pacific Ocean (nineteen locations), South China Sea and Sulu Seas (five), north and middle Atlantic Ocean (twelve), Labrador Sea (twenty) and coastal seawater (fifty) from Asian countries (Japan, China, Hong Kong, Korea).

## Results and Discussion

Table 1 shows the concentration of PFOS, PFHS, PFNA, and PFOA in open ocean water samples from the Pacific and Atlantic Oceans and several coastal seawaters from Asian countries.

PFOS and PFOA were found in 80% of the surface seawater and some regions showed characteristic composition of PFCs. There were some similarities between PFCs composition in coastal and open ocean waters in some regions. It appeared that the hydrologic information such as tidal and/or water current was necessary to explain the discharge of PFCs from coastal water to open ocean.

Relatively high concentrations of PFOS, PFHS, and PFOA were detected in Tokyo Bay waters. PFOA is the predominant fluorochemical, ranging in concentration from 1,800 – 192,000 pg/L, followed by PFOS (338 - 57,700 pg /L). Concentration of PFHS was an order of magnitude lower than the concentration of PFOS. High concentrations of PFCs in Tokyo Bay waters suggest sources associated with urban and industrial areas in Tokyo. The higher concentration of PFOA than of PFOS in water samples is an interesting observation. In wildlife samples collected from several locations, PFOS was the predominant compound, rather than PFOA (2). This discrepancy suggests that the bioaccumulation potential of PFOA is relatively lower than that of PFOS. Concentrations of PFOS, PFHS, PFOA, and PFOSA in offshore waters of the Pacific Ocean were

approximately three orders of magnitude lower than those in Tokyo Bay. Concentrations of all of the target fluorochemicals in offshore waters were in the pg/L range. Similar to what was observed for coastal waters, PFOA was the predominant fluorochemical found in the offshore waters of Japan. Variability in the concentrations of PFOA or PFOS in offshore waters was rather lower than for coastal waters, suggesting a generalized source such as atmospheric or hydrospheric transport. PFOSA was also found in these samples, at concentrations comparable to those of PFHS.

Open-ocean water samples collected in the mid-Atlantic Ocean showed the presence of all target PFCs at pg/L levels. Concentrations of PFOA and PFOS were comparable to those in offshore waters collected in the South China and Sulu Seas. The concentrations of PFOA and PFOS in the central to eastern Pacific Ocean waters were from 15 to 62 and 1.1 to 20 pg/L, respectively. These concentrations were an order of magnitude lower than concentrations in offshore waters, and four orders of magnitude lower than concentrations in Tokyo Bay water. These values appear to be the background values for remote marine waters far from local sources. Figure 4 illustrates the spatial trend of PFOS, PFHS, and PFOA from coastal Japan to the central Pacific Ocean. Concentrations of PFCs decreased dramatically by 2-4 orders of magnitude from coastal area to the offshore area. It appears that PFOA pollution is more ubiquitous than PFOS in oceanic waters. This may be similar to trifluoroacetic acid (TFA) pollution in coeans. Scott et al. reported widespread distribution of TFA in open ocean waters (6). Our result suggests that several perfluorinated acids are following similar environmental dynamics as TFA.

The other aim of our survey is to understand three-dimensional distribution of PFCs in marine environment. Although the marine environment is three-dimensional, very few studies have investigated persistent organic pollutants (POPs) including PFCs in deep seawaters. We have collected more than thirty deep seawater samples from the above mentioned locations and detected some PFCs. Presence of PFCs in deep-sea water shows the need for comprehensive survey of not only surface water but also vertical profile of PFCs in water column as well as open ocean air. Deep-sea water samples, collected at depths of >1000 m in the Pacific Ocean and the Sulu Sea contained trace levels of PFOS and PFOA. The deep seas play a major role in the dynamics of several POPs and therefore their role in the global fate of PFCs must be examined.

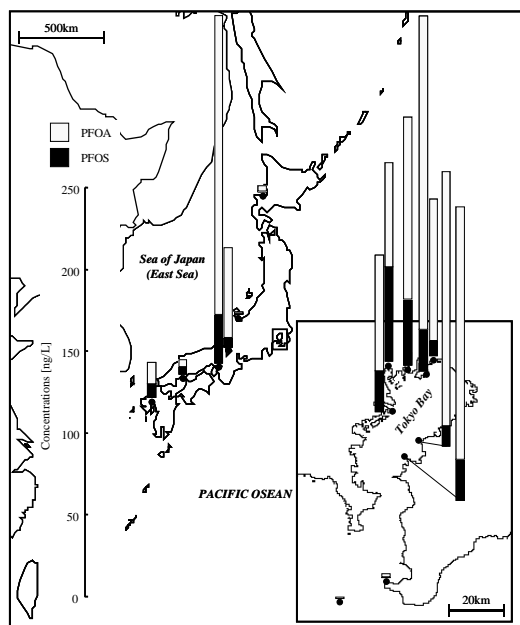
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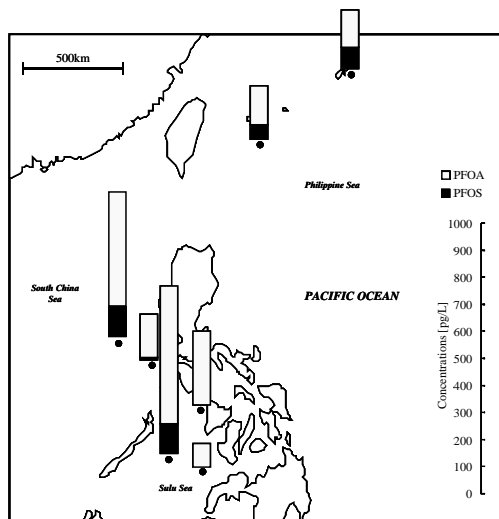
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**Table 1 Concentrations (pg/L) of PFOS, PFHS, PFNA, and PFOA in coastal and open ocean water samples from the Pacific and Atlantic Oceans**

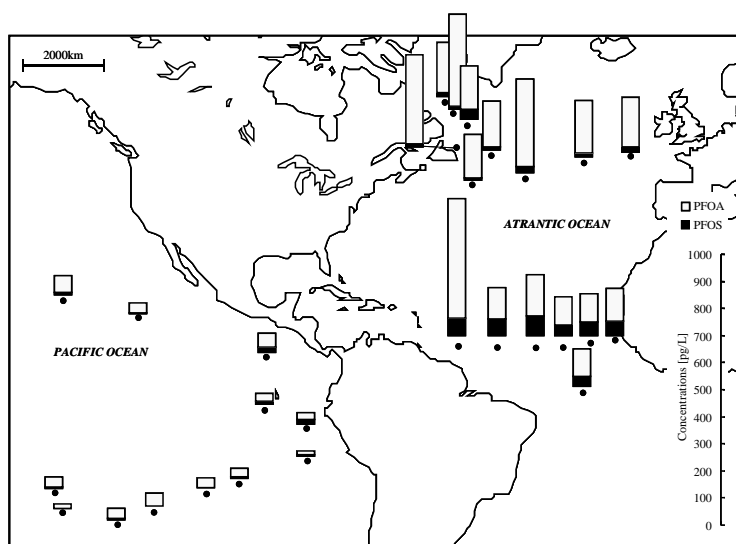
Location	N	PFOS	PFHS	PFNA	PFOA
Tokyo Bay	8	338 - 57,700	17 - 5,600	163 - 71,000	1,800 - 192,000
Offshore of Japan	4	40 - 75	3.0 - 6.1	n.a.	137 - 1,060
Coastal area of Hong Kong	12	70 - 2,600	<5 - 311	22 - 207	673 - 5,450
Coastal area of China	14	23 - 9,680	<5 - 1,360	2.0 - 692	243 - 15,300
Coastal area of Korea	10	39 - 2,530	<5 - 1,390	15 - 518	239 - 11,350
Sulu Sea (surface water)	3	<17 - 109	<0.2	n.a.	88 - 510
Sulu Sea (deep water; 1000-3000m)	2	<17 - 24	<0.2	n.a.	76 - 117
South China Sea	2	8 - 113	<0.2	n.a.	160 - 420
Western Pacific Ocean	2	54 - 78	2.2 - 2.8	n.a.	136 - 142
Central to Eastern Pacific Ocean (surface water)	12	1.1 - 20	0.1 - 1.6	1.0 - 16	15 - 62
Central to Eastern Pacific Ocean (deep water; 4000-4400m)	2	3.2 - 3.4	0.4 - 0.6	n.a.	45 - 56
North Atlantic Ocean	9	8.6 - 36	4.1 - 6.1	15 - 36	160 - 338
Mid Atlantic Ocean	7	37 - 73	2.6 - 12	n.a.	100 - 439



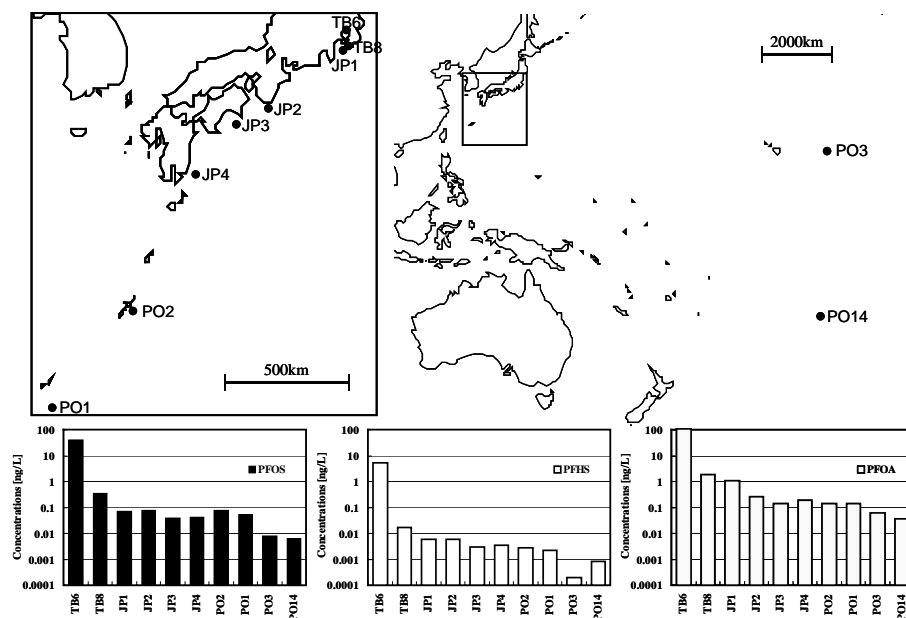
**Fig. 1** Concentration of PFOS and PFOA in surface seawater from Tokyo Bay and coastal Japan.



**Fig. 2** Concentrations of PFOS and PFOA in surface seawater from the South China Sea, Sulu Sea.



**Fig. 3** Concentrations of PFOS and PFOA in surface seawater from the Atlantic Ocean and Eastern Pacific Ocean.



**Fig. 4 Spatial trend of PFOS and PFOA in surface seawater from coastal area of Japan to the central Pacific Ocean.**

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