

DISTRIBUTION OF PERFLUORINATED COMPOUNDS IN SURFACE SEAWATERS BETWEEN ASIA AND ANTARCTICA

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Abstract

Perfluorinated compounds (PFCs) are known to be important global contaminants. They are persistent and widely distributed in the environment. A total of fourteen PFCs were quantified in surface seawater samples collected between Asia and Antarctica. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were the two dominant compounds, with mean concentrations ranging from <5 to 72 pg/L and <5 to 442 pg/L, respectively. The greatest concentrations of PFOS and PFOA were measured in water samples from two locations near Shanghai, a major industrial and financial center in China. In contrast, the concentrations of these compounds in water samples from the open ocean were very low. Different ratios of perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) were observed in different locations indicating that the sources of PFCs in these regions are different.

Introduction

Perfluorinated compounds (PFCs) have been manufactured and used for over 50 years.¹ The ability of these compounds to repel both water and oil, together with their chemical and thermal stability, make them of great use in many commercial applications. However, there is increasing concern about these compounds due to their environmental persistence, potential toxicity, and bioaccumulative potential.¹⁻⁴

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the two compounds that are most frequently found in environmental samples across the globe. They often occur in the greatest concentrations of all the PFCs in environmental samples, even in remote regions far from human activities such as the Arctic, the Antarctic, and the open ocean.^{1, 3-5}

Although earlier studies investigated the distribution of PFCs in water samples that were collected from remote regions,^{6, 7} little is known about the presence of PFCs in the Indian Ocean. This study aimed to fill this gap in the knowledge by investigating the concentrations and distribution of PFCs between Asia and Antarctica.

Materials and methods

Surface seawater samples were collected from coastal waters as well as the open ocean between Asia and Antarctica

(Figure 1). Three liters of surface water were collected from each location by using a stainless steel bucket that was pre-cleaned by rinsing with methanol and Milli-Q water. The samples were stored in 1L PP bottles and kept at 4°C during transportation and were then stored at -20°C in the laboratory until analysis. The water samples were extracted using Oasis WAX (6cc) solid phase extraction (SPE) cartridges (Waters Corp., Milford, USA). The details of the extraction procedure are described elsewhere.⁸

The concentrations of PFCs that included PFOS, perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS), perfluorooctane sulfonamide (PFOSA), PFOA, perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA), were determined by HPLC-MS/MS. The separation of the analytes was performed using an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) that was interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) and operated in the electro-spray negative mode. A 10- μ L aliquot of extract was injected into a Keystone Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 μ m, 100Å pore size, endcapped) with 2 mM of ammonium acetate and methanol as the mobile phases. The details of the procedure for LC-MS/MS are reported elsewhere.⁸

Results and discussion

Blank and recovery tests were conducted on each batch of sample extraction, and the concentrations of PFOS, PFHxS, PFBS, PFDoDA, PFDA, PFNA, PFOA, PFHpA, and PFHxA were measured. The PFOSA, PFOcDA, PFHxDA, PFTeDA, and PFUnDA concentrations were all below LOQ. The results of the blank, recovery tests and the PFC concentrations are summarized in Tables 1 and 2.

PFOS and PFOA were the two dominant compounds, with concentrations ranging from <5 to 72 pg/L and <5 to 442 pg/L, respectively. The greatest PFOS concentrations were measured in coastal areas near Shanghai, SH-1 (53 pg/L) and SHB-1 (72 pg/L), where the PFOA concentrations were 278 pg/L and 442 pg/L, respectively. These two locations are very close to Shanghai, which is the largest city in terms of population in China and has many possible sources of PFCs that are associated with industrial and urban areas. These results are either comparable or smaller than those measured in other regions of China (PFOS in the range of 20 to 12000 pg/L and PFOA in the range of 240 to 16000 pg/L⁹; PFOS in the range of 10 to 99000 pg/L and PFOA in the range of 850 to 260000 pg/L⁴). Most of the PFC concentrations in the open ocean were below LOQ. The PFOS and PFOA concentrations in the Indian Ocean ranged from <5 to 8.6 pg/L and 6.4 to 11 pg/L, which are lower than those previously detected in the Atlantic Ocean (PFOS in the range of 8.6 to 73 pg/L and PFOA in the range of 100-439 pg/L)⁶ and the Pacific Ocean (PFOS in the range of 1.1 to 78 pg/L and PFOA in the range of 15-142 pg/L).⁶ These concentrations appear to be background values for remote marine waters not subject to anthropogenic activities.

The total concentrations of perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) in the seawater samples were compared (Figure 2), and different ratios were observed in different locations suggesting that the sources of PFC contamination may differ across areas. Different levels of hydrologic activity may also have contributed to the differing

contamination patterns. To our knowledge, this is the first report of PFCs in coastal seawater from Antarctica and surface water from the Indian Ocean.

Reference

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Figure 1. Sampling locations of surface seawater samples between Asia and Antarctica.

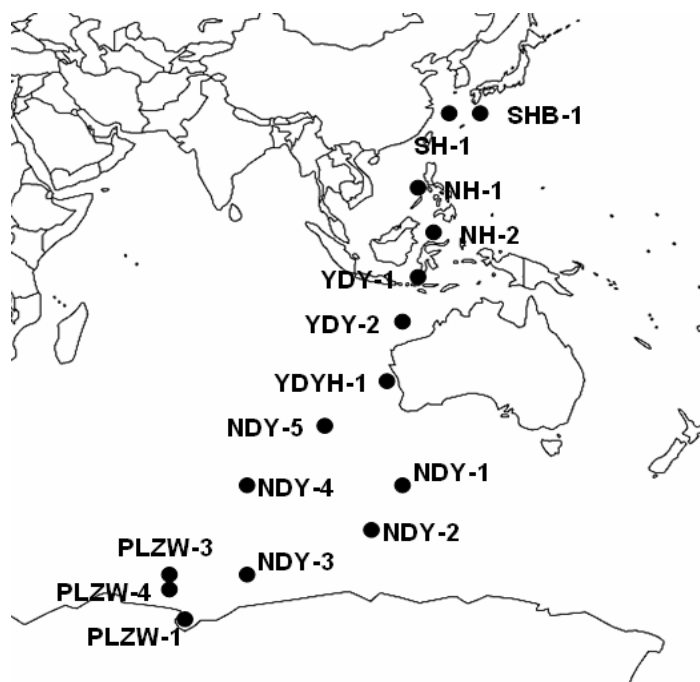


Figure 2. Comparison of total concentrations of PFSA and PFCAs in surface seawater samples from different locations between Asia and Antarctica.

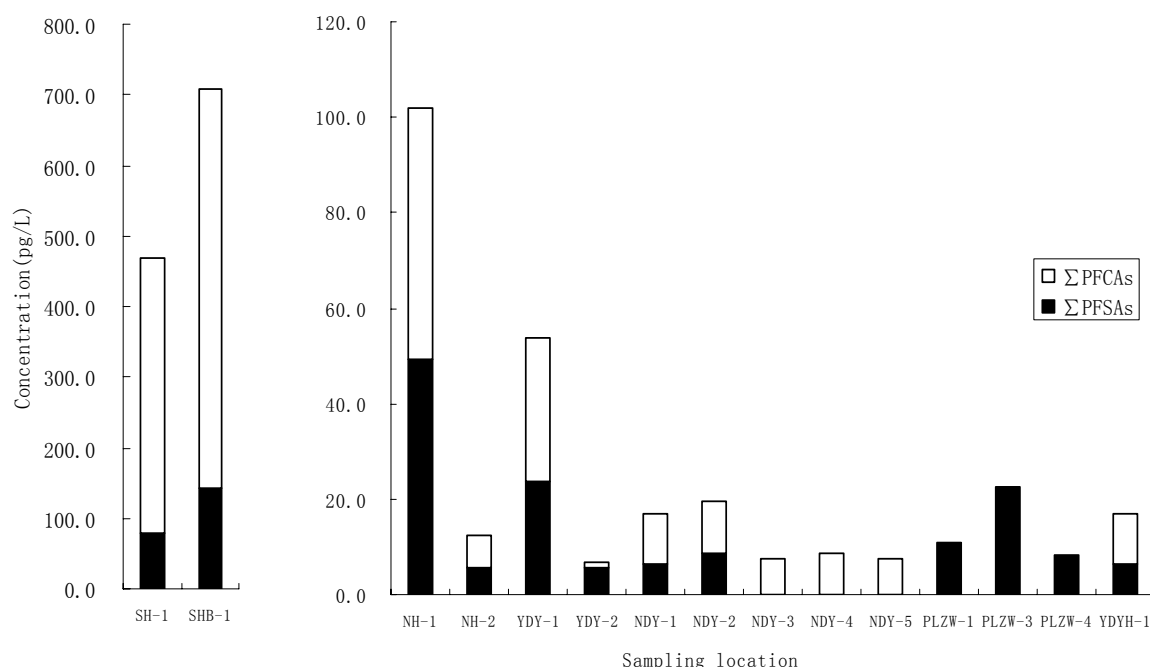


Table 1. Recoveries (%) and blanks (pg/L) for individual PFCs.

	PFOS	PFHS	PFBS	PFD _o DA	PFDA	PFNA	PFOA	PFHpA	PFHxA
Blank (n=3)	<5	<5	<5	<1	<5	<5	<5	<5	<5
Travel blank (n=12)	<5	<5	<5	<1	<5	<5	<5	<5	<5
Recovery (n=3)	108	97	103	113	106	106	114	109	113
S.D.	4	2	3	8	8	11	2	9	4

Table 2. Concentrations (pg/L) of PFCs in surface seawater samples between Asia and Antarctica.

Sample location	Perfluorosulfonates (PFSA)			Perfluorocarboxylates (PFCAs)					
	PFOS	PFHS	PFBS	PFD _o DA	PFDA	PFNA	PFOA	PFHpA	PFHxA
SH-1	52.6 ± 6.4	10.2 ± 0.1	16.8 ± 0.8	3.1 ± 0.8	8.7 ± 0.0	35.5 ± 1.7	278.4 ± 68.8	64.4 ± 14.6	<5
SHB-1	71.7 ± 9.7	<5	70.2 ± 5.6	<1	<5	24.0 ± 3.3	441.6 ± 6.4	40.5 ± 0.7	59.5 ± 17.4
NH-1	39.3 ± 1.7	9.8 ± 0.8	<5	1.2 ± 0.2	5.1 ± 0.0	25.4 ± 0.9	21.3 ± 1.5	<5	<5
NH-2	5.7 ± 0.7	<5	<5	1.7 ± 0.4	<5	5.2 ± 0.2	<5	<5	<5
YDY-1	23.9 ± 8.7	<5	<5	1.2 ± 0.0	5.4 ± 0.4	11.5 ± 1.5	11.9 ± 1.1	<5	<5
YDY-2	5.8 ± 0.8	<5	<5	1.1 ± 0.1	<5	<5	<5	<5	<5
NDY-1	6.5 ± 1.4	<5	<5	<1	<5	<5	10.6 ± 4.1	<5	<5
NDY-2	8.6 ± 0.6	<5	<5	<1	<5	<5	11.0 ± 1.5	<5	<5
NDY-3	<5	<5	<5	1.3 ± 0.3	<5	<5	6.4 ± 1.4	<5	<5
NDY-4	<5	<5	<5	1.1 ± 0.1	<5	<5	7.7 ± 1.6	<5	<5
NDY-5	<5	<5	<5	<1	<5	<5	7.4 ± 0.1	<5	<5
PLZW-1	10.8 ± 1.5	<5	<5	<1	<5	<5	<5	<5	<5
PLZW-3	22.6 ± 2.4	<5	<5	<1	<5	<5	<5	<5	<5
PLZW-4	8.3 ± 3.3	<5	<5	<1	<5	<5	<5	<5	<5
YDYH-1	6.5 ± 1.5	<5	<5	1.4 ± 0.0	<5	<5	8.9 ± 2.4	<5	<5