MASS BALANCE ANALYSIS OF PERSISTENT PERFLUORINATED CHEMICALS IN AFFF POLLUTED ENVIRONMENT IN JAPAN

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Introduction

Concern about fluorinated organic compounds (FOCs), particularly perfluorinated compounds (PFCs), is growing. Several studies suggest that these compounds to be globally distributed, environmentally persistent, bioaccumulative and potentially harmful[1-4]. The toxicity of these compounds is still being investigated. Despite this environmental dynamics of PFCs is less known.

Environmental dynamics of PFCs is complex due to their unique physico-chemical characteristics and due to their release from multitude of sources with various compositions[5]. With the recent development in analytical techniques, the number of PFCs to be detected in the environmental and biological matrixes is increasing. It is of particular of interest to determine total amount of organic fluorine and to compare this measurements of known PFCs. This mass balance approach to study FOCs will enable understanding of distribution and fate of these compounds.

Perfluorooctane sulfonate (PFOS) and related perfluorinated acids are a component of AFFFs[6]. Previous studies have reported environmental contamination by PFCs due to the release of AFFF[6, 8].

A monthly monitoring survey of environmental levels of PFCs and mass balance analysis were conducted in the Tomakomai and Kashima regions, where during fire-accidents in oil refinery (Tomakomai) and TFA production plant (Kashima) AFFFs were released into the environment.

Materials and Methods

Sample collection and preparation. Surface water samples were collected from the coastal and inland area of Tomakomai, lake Utonai and area of Kashima plant. Snow and runoff samples were also collected from locations in Tomakomai area affected by accidental fire. All water samples were extracted using solid phase extraction method (SPE) similar to that described elsewhere[7]. The modifications in extraction procedure were aimed at separating organic fluorine from inorganic fluorine such as fluoride (F^-). The extraction procedures for individual PFCs, total fluorine (TF), extractable organic fluorine (EOF), and inorganic fluorine (IF) in water are shown in Figure 1.

Instrumental analysis. Instrumental determination of individual PFC was accomplished by an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA, USA) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters) operated in electrospray negative ion mode. Details of this method are reported elsewhere[7]. Analyses of total fluorine and extractable organic fluorine were performed by combustion ion chromatography for fluorine (CIC-F) – a newly developed method for the analysis total fluorine (TF), extractable organic fluorine (EOF). Inorganic fluorine (IF) analyses were performed by ion chromatography. Details of these procedures are reported elsewhere[9].

QA/QC. To determine the precision and accuracy of the extraction and analytical procedures, recovery and blank samples tests were performed. The limit of quantification (LOQ) was determined for each analyte based on the concentration factor and the lowest concentration of the standard injected. Blank tests in all cases showed concentration below LOQ. Results of recovery test and values of LOQ for individual PFCs are summarized in Table 1.

Table 1 Results of recovery test and values of LOQ for individual PFCs

	PFOS	PFHxS	PFBS	PFOSA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
Rec [%]	79.7	75.8	81.6	72.4	82.7	83.7	95.0	100	89.1	89.6
LOQ_sea water [ng/L]	0.03	0.10	0.10	0.03	0.10	0.50	0.50	0.10	0.50	0.10
LOQ_snow [ng/L]	2.50	12.5	12.5	2.5	12.5	50.0	50.0	12.5	50.0	12.5

Results and Discussion

Concentrations of PFCs in snow and sea water samples from Tomakomai area are presented in Table 2.

Relatively high concentrations of individual PFCs were detected in snow samples. It suggests that significant amount of PFCs in AFFF were released into the air and deposited to land through wet deposition process and PFCs released from AFFF into coastal water were at highest concentrations in October[5] but decreased significantly by dilution and exchange of coastal and offshore waters. Moreover the pattern of individual compounds was different for snow and seawater samples (Figure 2). Contribution of known PFCs in total fluorine in sea water samples is less than 0.0005 % while in snow samples it was up to 3% with PFOS as the dominant compound (~2%). Inorganic fluorine is the main part of composition of total fluorine in sea water (~90 %) while in snow samples this ratio is changed and PFCs together with non-extractable organic fluorine become dominant part of total fluorine (Figure 3).

In conclusion, significant part of total organic fluorine still remains unknown in water and snow contaminated by the discharge of AFFF. So mass balance analysis showing the difference between TOF and EOF is an important step to understand transport and fate of fluorinated compounds in environmental matrixes, and to identify those unknown EOF.

Table 2 Concentrations of individual PFCs in snow and seawater samples collected in December 2003 from Tomakomai area [ng/L]

Compound	**Concentration in different samples [ng/L]**			
	seawater		**snow**	
	1	**2**	**1**	**2**
PFOS (C8)	3.05	2.42	425	1500
PFHxS (C6)	1.73	<0.13	<12.5	50.8
PFBS (C4)	<0.13	0.14	102	<12.5
PFOSA	0.28	0.13	68.4	149
PFUnDA (C11)	0.30	102	103	35.3
PFDA (C10)	<0.50	<0.50	<50.0	<50.0
PFNA (C9)	1.04	0.71	103	688
PFOA (C8)	1.89	0.73	13.2	79.7
PFHpA (C7)	0.52	0.60	105	103
PFHxA (C6)	1.93	1.52	106	29.5

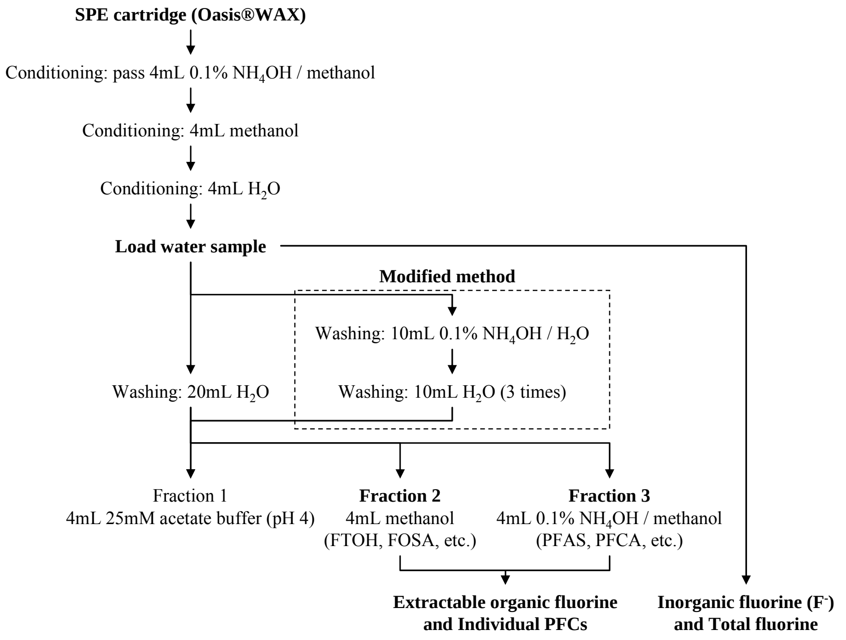

Figure 1 Extraction procedures used in this study

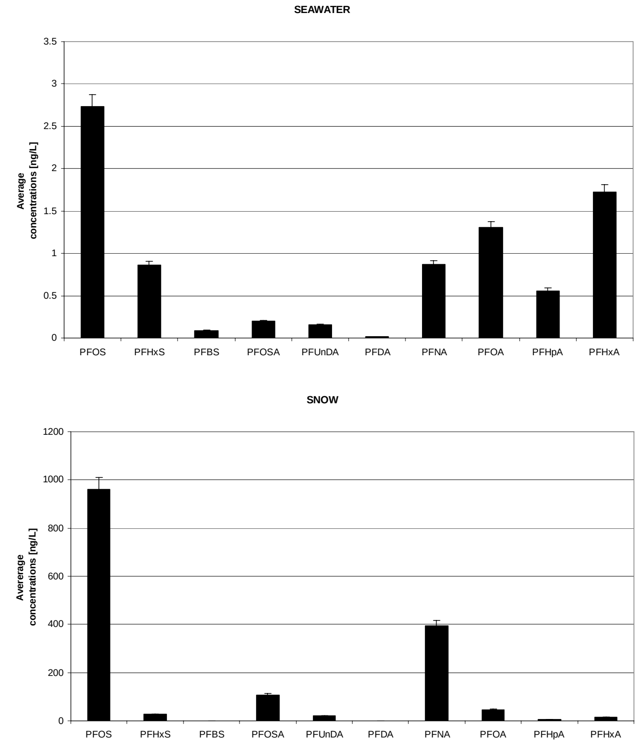

Figure 2 Pattern of individual PFCs in seawater and snow samples from Tomakomai

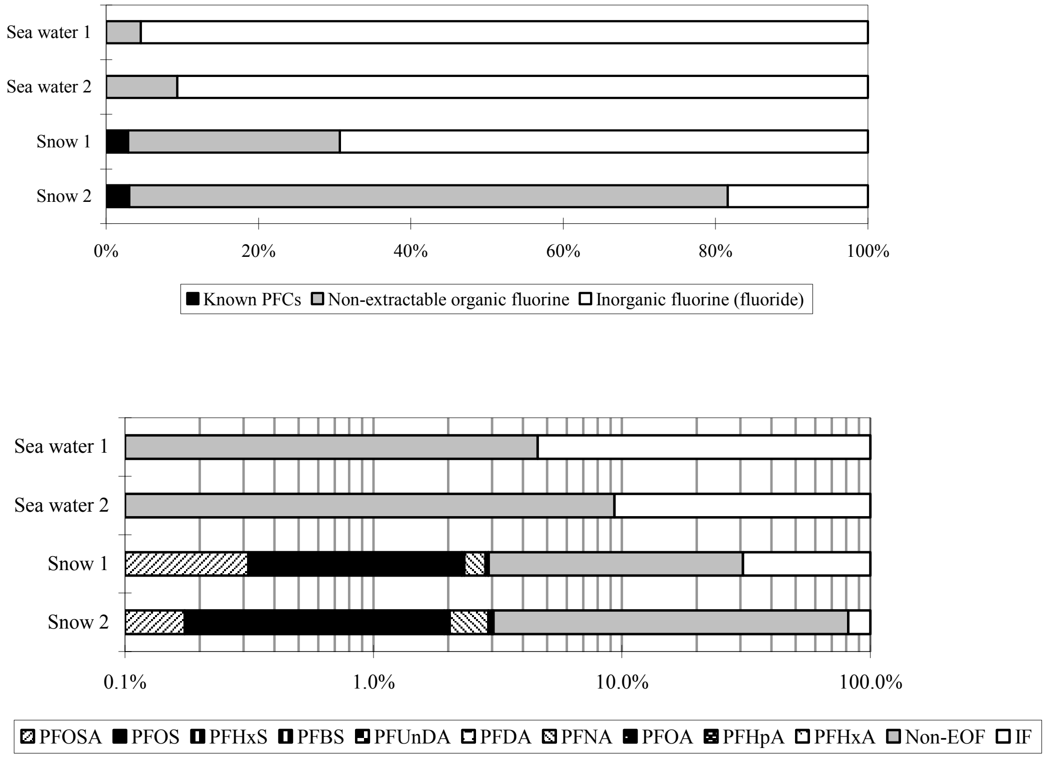

Figure 3 Contribution of known PFCs in total fluorine

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