Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: A mass balance approach to determine individual perfluorinated chemicals in water

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Abstract

Perfluorinated compounds (PFCs) such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) have received worldwide attention because of their environmental persistence and widespread distribution. Because of the lack of robust analytical methods and standards to detect all of the PFCs, and their precursors and metabolic intermediates, a mass balance approach involving the determination of total fluorine (TF), followed by fractionation of samples to separately determine inorganic and organic fluorine, is needed. In this study, we have developed a method to determine low µg/L levels of total fluorine (TF) in seawater samples. Further, seawater samples were fractionated into organic and inorganic fractions by extraction with organic solvents, which were then analyzed for TF, extractable organic fluorine (EOF) and inorganic fluorine (IF; i.e., fluoride). Concentrations of known perfluorinated compounds (PFCs) including PFOS and PFOA were also determined in water samples by liquid chromatography–tandem mass spectrometry (LC–MS/MS) to enable calculation of the fraction of fluorine that is contributed by PFCs to TF. A major proportion of fluorine in seawater was in the form of fluoride (>90% in locations not affected by direct discharges). Nevertheless, within the organofluorine fraction, a major percentage (60–90%) of fluorine still remains unknown in water samples, suggesting the occurrence of other fluorinated acids in addition to known perfluorinated acids. Further studies are needed to identify and quantify the unidentified organofluorines in seawater. Mass balance analysis of total organic fluorine (TOF) and EOF is important, if we are to understand transport and fate of fluorinated compounds in the environment, and if we are to identify the sources of unidentified fluorinated compounds.

1. Introduction

Perfluorinated compounds (PFCs) such as perfluorooctane-sulfonate (PFOS) and perfluorooctanoate (PFOA) have received worldwide attention because of their environmental persistence

and widespread distribution [1]. In addition to PFOS and PFOA, fluorochemicals such as fluorotelomer alcohols (FTOHs) and long-chain perfluorocarboxylates (PFCAs) have been detected in air and water [2–4]; these compounds are becoming important in monitoring surveys and risk evaluation. Because of the lack of robust analytical methods and standards to detect all of the PFCs, as well as their precursors and metabolic intermediates, a mass balance approach, entailing the determination of total fluorine (TF) followed by fractionation of samples to separately determine inorganic and organic fluorine, is needed. The mass balance analysis is expected to provide useful information on the extent of unknown fluorinated chemicals in environ-

mental and biological media. Nevertheless, it is a challenging task, because of the difficulties in trace level determination of TF using conventional ion chromatography (IC) techniques [5–7]. PFCs are present at parts-per-trillion (ppt) or parts-per-quadrillion (ppq) levels in aqueous media [2,8,9]. The current limit of quantitation of TF using conventional combustion ion chromatography (CIC) has been in the sub-parts-per-million (ppm) or high parts-per-billion (ppb) levels [5,6]. The high background levels arising from instrumental and procedural blanks and interference of several anions (e.g., sulfate, chloride) and low molecular weight acids (e.g., acetate, formate) confound accurate determination of TF in water matrices, particularly seawater samples. In this study, we developed a method to determine low ppb (μg/L) levels of TF in seawater. Further, seawater samples were fractionated into organic and inorganic fractions by extraction with organic solvents, which were then analyzed for TF, extractable organic fluorine (EOF), and inorganic fluorine (IF). Concentrations of known PFCs were also analyzed in water samples by liquid chromatography–tandem mass spectrometry (LC–MS/MS), to determine the fraction of fluorine contributed by known PFCs to TF. This comparison enabled the identification of the extent of unknown organofluorines in water samples.

2. Experimental

2.1. Chemicals and standards

A mixture of perfluorinated compounds containing PFOS, perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), perfluorooctanesulfonamide (PFOSA), perfluorooctadecanoate (PFOcDA), perfluorohexadecanoate (PFHxDA), perfluorotetradecanoate (PFTeDA), perfluorododecanoate (PFDoDA), perfluoroundecanoate (PFUnDA), perfluorodecanoate (PFDA), perfluorononanoate (PFNA), PFOA, perfluoroheptanoate (PFHpA), perfluorohexanoate (PFHxA), perfluoropentanoate (PFPeA), perfluorobutanoate (PFBA), 6:2 FtS (fluorotelomer sulfonate), *N*-EtFOSA (*n*-ethyl perfluorooctanesulfonamide), *N*-EtFOSAA (*n*-ethyl perfluorooctanesulfonamidoacetate), 8:2 FTOH, 10:1 FTOH, 8:2 FTCA (fluorotelomer carboxylate), 8:2 FTUCA (fluorotelomer unsaturated carboxylate) at 50 ng/mL was purchased from various commercial suppliers as described earlier [2]. Methanol, ammonium acetate, and acetic acid were purchased from Wako Pure Chemicals Industries, Ltd. (Tokyo, Japan). Milli-Q water was obtained from Milli-Q Gradient A-10 (Millipore, Billerica, MA).
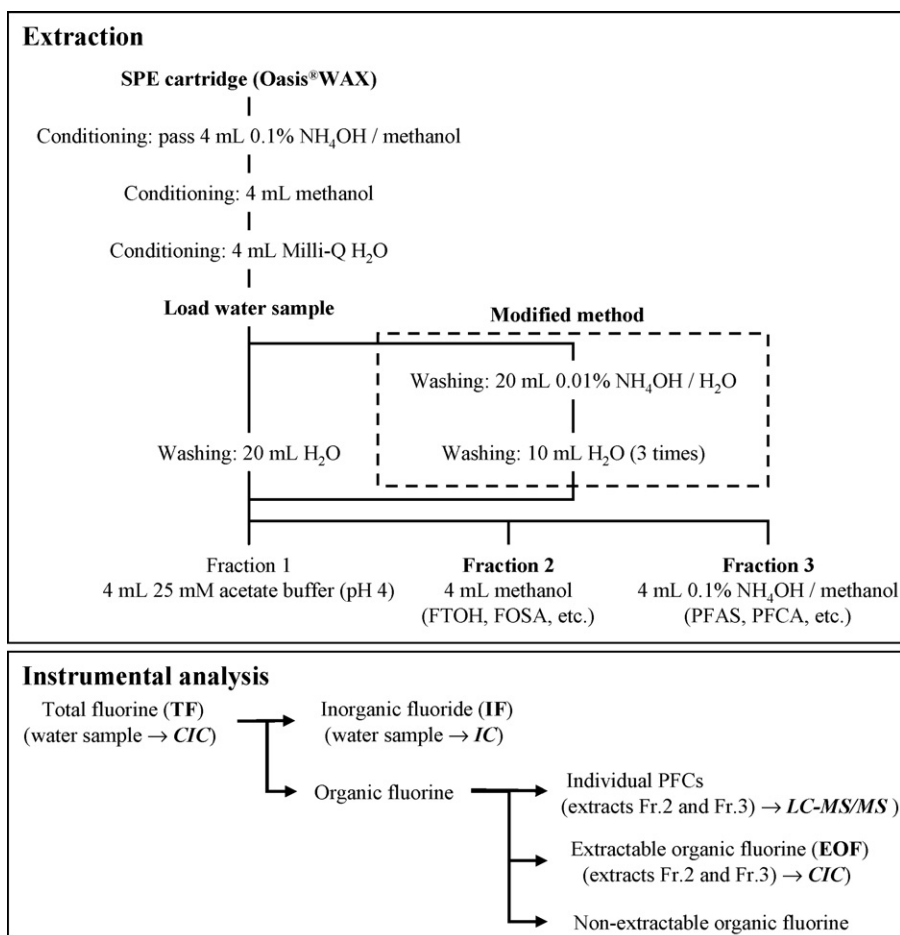

Fig. 1. Schematic outline of the extraction methods for total fluorine (TF), extractable organic fluorine (EOF), and inorganic fluorine (IF) in water using combustion ion chromatography (CIC).

2.2. Water sample collection

Coastal seawater samples were collected at Tomakomai ($n = 2$), Hokkaido, Japan, on 22 December 2003; at this site, aqueous film forming foam (AFFF) containing PFCs had been used in a fire accident on 26–30 September 2003 [10]. Seawater and brackish water samples were also collected at Osyamanbe ($n = 1$) and Hakodate ($n = 1$), Hokkaido, Japan, on 23 April 2004, and water from these sites served as reference samples (no known source of contamination).

2.3. Extraction and purification

The analytical procedure for PFCs in water samples using solid-phase extraction (SPE) is similar to that described earlier [2]. An aliquot of water sample was subjected to fractionation, as illustrated in Fig. 1, for the determination of individual PFCs, EOF, TF, and IF. In brief, Oasis®WAX cartridges were conditioned by passage of 4 mL of 0.1% NH₄OH in methanol, 4 mL of methanol and 4 mL of Milli-Q water, in sequence, prior to loading of the 400 mL of water samples. The cartridges were then eluted with 4 mL of 25 mM sodium acetate buffer (Fraction 1), followed by with 4 mL of methanol (Fraction 2). Fraction 3 was collected by eluting the cartridges with 4 mL of 0.1% NH₄OH in methanol. Fractions 2 and 3 were injected into HPLC–MS/MS and CIC customized for fluorine analysis (hereafter, CIC-F) for the determination of individual PFCs and EOF, respectively. Fraction 1 did not contain fluorine and therefore was not analyzed.

Seawater samples were passed/treated through OnGuard II Ba, OnGuard II Ag, and OnGuard II H cartridges (Dionex Corp., Sunnyvale, CA), to remove interfering anions, and were then analyzed for IF and TF. The IF was determined by injecting the treated water into an IC. For TF determination, an aliquot of the water was placed directly into the CIC-F.

2.4. Instrumental analysis and quantification

PFCs in water samples were identified and concentrations of individual PFCs were determined, by HPLC–MS/MS, as described in detail elsewhere [2]. Concentrations of fluoride ion (F⁻) in water samples were determined by IC, following the analytical conditions given in Table 1. Determination of TF and EOF was performed by CIC-F [11,12]. Fifty to 100 μL of the water samples and extracts from the SPE procedure were set on a silica boat and combusted in a furnace at 900–1000 °C to convert organofluorine and/or inorganic fluorine compounds in the water and extracts into hydrogen fluoride (HF), which was then absorbed into sodium hydroxide solution. The concentration of F⁻ was measured by IC. Details of this procedure are reported elsewhere [12]. This method was developed recently with some modifications to conventional CIC, by a combination of an automated combustion unit (AQF-100 type AIST; Dia Instruments Co., Ltd.) and an IC system (ICS-3000 type AIST; Dionex Corp., Sunnyvale, CA), which enabled trace level determination of fluoride at sub ppb (μg-F/L) levels. We removed possible sources of contamination by fluorochemicals within the

Table 1
Analytical conditions for total fluorine and extractable organic fluorine determination using combustion ion chromatography

Combustion conditions	
Instrument	AQF-100 (type AIST); Dia Instruments Co. Ltd.
Furnace temperature	900–1000 °C
Carrier gas	150 mL/min
	→ Inlet boat (3.5 min hold)
	→ Switch over O₂ (3 min hold)
Water supply[a]	150 mL/min
Gas (Ar)	
O₂ gas	300 mL/min
Set volume	10–100 μL
Ion chromatographic conditions	
Instrument	ICS-3000 (type AIST); Dionex Co. Ltd.
Detector	Conductivity detector
Column	Ionpac AS20 (2 mm i.d.)
Mobile phase	Potassium hydroxide
	2 M (2 min)
	→ 5.4 mM/min (7 min)
	→ 40 mM (4 min)
	→ 2 mM (8 min)
Flow rate	0.25 mL/min
Column oven temperature	35 °C
Injection volume	500–1500 μL

[a] Water (1–2 mL/min) is supplied with argon gas in the furnace for complete hydride generation and to improve the recovery of total fluorine.

instrument, including certain parts of the instrument itself, and replaced them with fluorine-free materials, to enable sub-ppb level of quantitation.

Sodium fluoride (99% purity) from Wako Pure Chemical Industries (Tokyo, Japan) was used as a standard for the quantification. Five-point standard calibration curve was prepared at 0.2, 1, 5, 25, and 100 μg/L and injected at 1.5 mL; calibration curves were prepared routinely, to check for linearity. Quantification was based on the response of the external standard that bracketed the responses found in samples. The analytical conditions of IC are given in Table 1. All solutions were prepared in Milli-Q water (18 MΩ cm); the fluoride concentration in the Milli-Q water was <0.025 μg/L. The total time for the analysis of TF is approximately 20 min per sample. Concentrations of known PFCs, EOF, IF, and TF are reported as corresponding F⁻ (ng or μg-F/L) to enable comparisons. The concentrations were converted to fluoride ion C_F (ng-F/L) according to the equation:

$$C_F = \frac{nM_F}{M_{PFC}} C_{PFC} \tag{1}$$

in which C_{PFC} is concentration of PFC (ng/L), M_{PFC} is molecular weight of corresponding PFC (g/mol), n is the number of fluorines in the compound, and M_F is the molecular weight of fluorine (g-F/mol).

3. Results and discussion

3.1. Removal of chloride and sulfate in water samples

One of the issues with the determination of IF and TF in seawater is the occurrence of large amounts of chloride (Cl⁻)
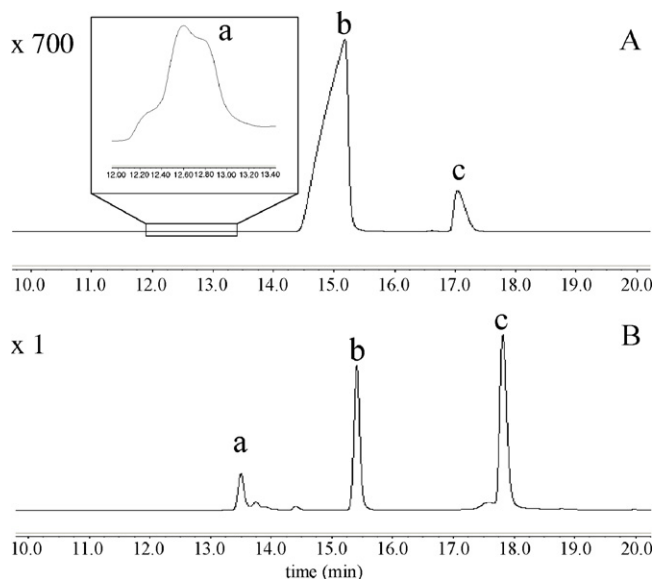
Fig. 2. Chromatograms of fluoride, chloride, and sulfate (A) before and (B) after the treatment of seawater samples by OnGuard II Ba/Ag/H cartridges. Peak 'a' corresponds to fluoride ion; peak 'b' corresponds to chloride ion; peak 'c' corresponds to sulfate ion.
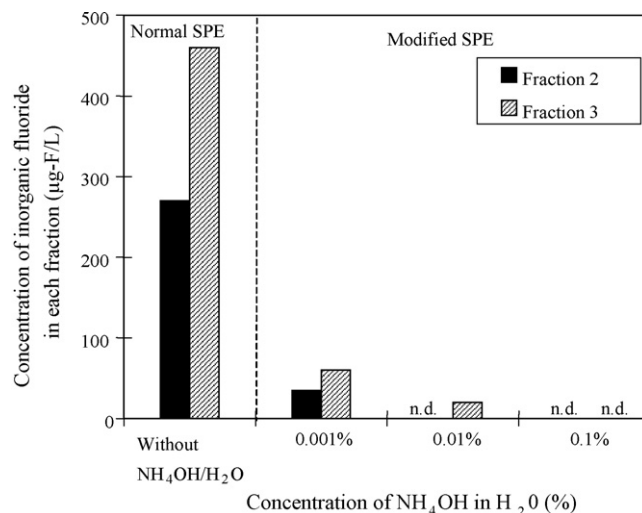

Fig. 3. Mean concentrations of fluoride ion (spiked to Milli-Q water at 1000 ng-F/mL to test fractionation) in each fraction identified in Fig. 1, using a solid phase extraction procedure as described in Taniyasu et al. (Ref. [2]; left) and a modified procedure to separate inorganic fluorine (right) with 10 mL of NH_4OH/H_2O ($n=2$); n.d. refers non-detection at 6 μg-F/L.

and sulfate (SO_4^{2-}) in the samples [5,13]. Direct IC analysis of water samples offered poor peak shape for the fluoride ion. Furthermore, certain low-molecular-weight organic acids such as formic acid, lactic acid, and acetic acid co-eluted with fluoride ion [12,13]. The respective concentrations of chloride and sulfate ions are generally 20,000 and 2500 times higher than the fluoride concentration in seawater samples [14]. The anions were removed by passing the solution through OnGuard II Ba, OnGuard II Ag, and OnGuard II H cartridges. The OnGuard II Ba and OnGuard II Ag cartridges respectively removed sulfate and chloride, by precipitation. The OnGuard II H, which has a very high selectivity for multivalent cations, removed sodium, silver, barium, and calcium. The ion chromatograms of water samples before and after the passage through the OnGuard cartridges

are shown in Fig. 2. After the treatment, the fluoride peak and peaks for other organic acids were fully resolved, because the concentrations of chloride and sulfate in the samples had been decreased by <200 μg Cl/L and <500 μg SO_4/L, respectively. The removal rates of chloride and sulfate from water samples were greater than 99.5%, and the recovery of fluoride was 96.5%.

3.2. Separation of inorganic and organic fluorine in extracts

Separation efficiency of inorganic and organic fluorine through our fractionation procedure, as outlined in Fig. 1, was examined by spiking known concentrations of sodium fluoride (1000 ng-F/mL) into Milli-Q water, followed by extraction via SPE. Since the fluoride ion was found to adsorb strongly onto
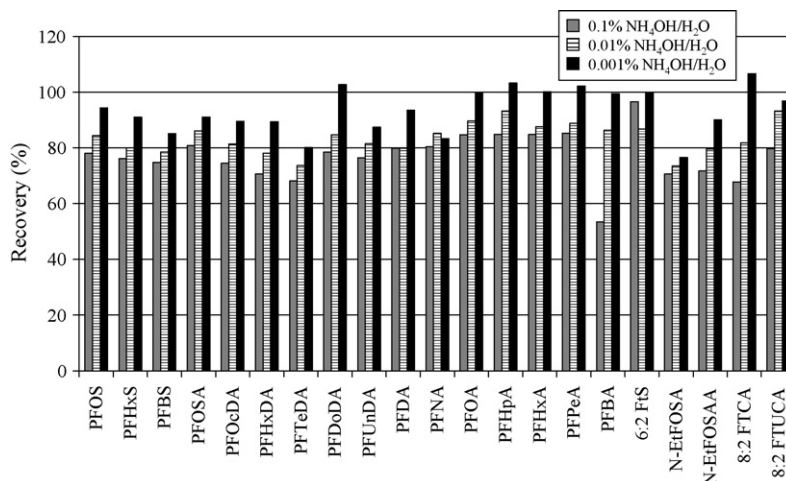

Fig. 4. Mean recoveries of individual perfluorochemicals using 10 mL of various concentrations of NH_4OH/H_2O ($n=2$–4) through the solid phase extraction procedure.
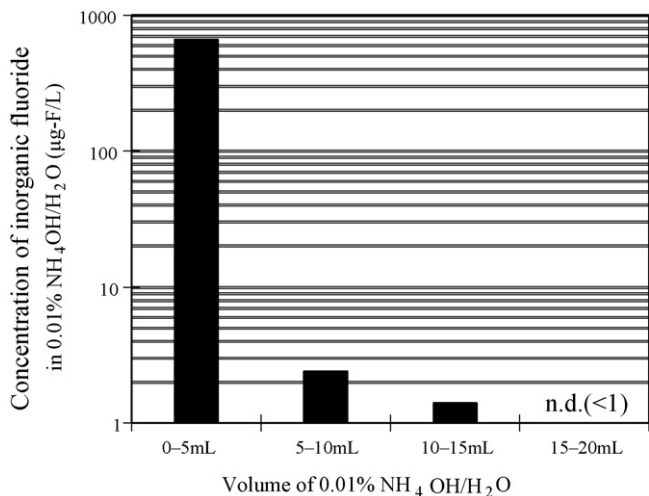
Fig. 5. Mean concentrations of fluoride eluting in various fractions of 0.01% NH$_4$OH in water (initial spike concentration: 1000 ng/mL).

Oasis®WAX cartridges used for SPE of water samples, a modified elution profile was developed. Elution of the Oasis®WAX cartridge (after loading the sample) with 10 mL of different concentrations of NH$_4$OH/H$_2$O enabled desorption of fluoride ion from the cartridge. This method allowed the separation of fluoride ion from organofluorine such as PFCs.

The effect of concentration of NH$_4$OH, at 0.1%, 0.01%, and 0.001 % on the elution profile of fluoride ion and recoveries of PFCs in various fractions were examined (Fig. 3). The recoveries of individual PFCs, especially short-chain PFCs (C4–C5) were considerably reduced at high concentrations (0.1%) of NH$_4$OH (Fig. 4). The recoveries of individual PFCs were considerably higher when 0.001% of NH$_4$OH/H$_2$O solution was used to elute the sample through the SPE cartridges; however, this concentration was not adequate to completely desorb F$^-$ from the cartridge. While 0.1% NH$_4$OH/H$_2$O desorbed F$^-$ completely (Fig. 3), this concentration reduced the recovery rates of short-chain PFCs. Therefore, an intermediate concentration, 0.01% NH$_4$OH/H$_2$O, was selected to fractionate F$^-$ from organofluorines such as PFCs.

We examined the volume of NH$_4$OH/H$_2$O needed to remove F$^-$ from the cartridge by collecting four 5 mL fractions with 20 mL of 0.01% NH$_4$OH/H$_2$O (Fig. 5). We found that more than 99.995% of the originally spiked fluoride was removed by the elution with 20 mL of 0.01% of NH$_4$OH in water from SPE cartridges.

After the elution profile, volume, and concentration of solvents for SPE had been optimized, 80 μL of 50 ng/mL solution of individual PFCs were spiked into 100 mL of Milli-Q water and passed through the Oasis®WAX cartridge. The same procedure was employed for fluoride, by spiking sodium fluoride at 1000 ng/mL. It was confirmed that the elution profile developed in this study adequately separated inorganic fluorine (i.e., fluoride) from organic fractions (< 6 ng F/mL) with acceptable recoveries (81–109%) for wide range of PFCs including perfluoroalkylsulfonates (PFASs: C4–C8), perfluoroalkylcarboxylates (PFCAs: C4–C18), and some fluorotelomer carboxylates.

Table 2
Concentrations of individual perfluorinated acids (PFCs), extractable organic fluorine (EOF), inorganic fluoride (IF), and total fluorine (TF) in seawater samples from reference and contaminated sites (ng-F/L)[a]

Type	Sample ID	PFASs			PFCAs									Sum PFCs	EOF	IF	TF
		PFOS	PFHxS	PFBS	PFOSA	PFOcDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA				
Recovery (%) (average, n=3)		87	84	89	91	79	80	92	90	83	93	86	89				
LOQ		0.018	0.016	0.016	0.019	0.020	0.100	0.020	0.020	0.020	0.019	0.019	0.089				
Reference site																	
Seawater	CO1	0.119	0.0899	0.0260	<LOQ	<LOQ	<LOQ	0.0310	0.0877	0.148	0.0434	0.0777	0.0908	0.713	80.0	79,6000	81,5000
Brackish water	CO2	0.181	0.0165	0.0610	0.0298	<LOQ	0.130	0.0774	0.633	0.501	0.0649	0.323	0.580	2.60	106	22,7000	28,1000
Contaminated site																	
Seawater	CT1	18.9	3.15	0.0709	3.48	<LOQ	0.397	<LOQ	13.6	2.32	0.545	2.03	1.15	45.6	134	83,9000	97,6000
Seawater	CT2	201	66.3	4.16	6.82	0.0313	1.54	0.199	47.7	6.73	2.06	14.2	5.52	357	991	77,5000	98,0000

[a] PFHxA, PFTeA, PFDoA, 8:2FTCA, 8:2FTUCA, N-EtFOSAA, and N-EtFOSA was analyzed in water samples, but the concentrations were below the LOD.
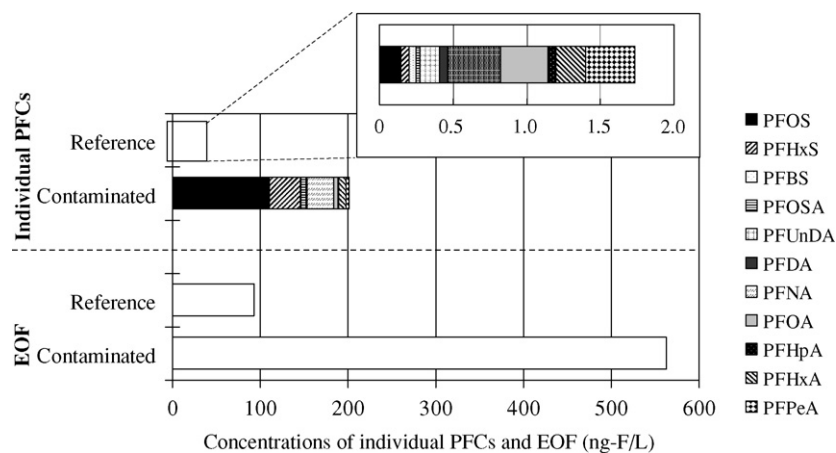
Fig. 6. Mean concentrations of known perfluorochemicals and extractable organic fluorine in coastal seawater samples from Tomakomai (contaminated site) and from two other areas of Hokkaido (reference sites) ($n = 2$).

3.3. Mass balance analysis of water samples

The SPE method developed in this study, for fractionating inorganic and organic forms of fluorine, was applied for mass balance analysis of fluorine in several coastal seawater samples from Tomakomai, Japan, where aqueous film forming foam (AFFF) containing certain PFCs had been used following an accident. This use resulted in a significant contamination of the nearby coastal waters [10]. While water samples from Tomakomai served as a contaminated matrix for the mass balance study, seawater samples from two sites on the west coast of Hokkaido served as reference samples. Concentrations of individual PFCs detected in water samples from the west coast of Hokkaido and from Tomakomai are presented in Table 2.

Concentrations of known PFCs in water samples from the reference site are close to the limit of quantitation (<2 ng/L), while the samples from Tomakomai had concentrations ranging from 45.6 to 357 ng/L for the sum of PFCs (Fig. 6). Moreover, the pattern of individual PFCs differed between Tomakomai (contaminated) and Osyamanbe (reference) locations (Fig. 7). PFOS

and PFNA were the predominant PFCs at the contaminated site whereas PFOA was prevalent at the reference site. Concentrations of EOF measured in fractions 2 and 3 using CIC were, on average, 93 ng/L for the water samples from reference site and 562 ng/L for those from contaminated site. This suggests the occurrence of significant levels of unknown organic fluorine compounds in all of the water samples. PFOS, PFHxS, and PFNA were the dominant PFCs among the known EOF compounds detected in samples from Tomakomai (19.6, 6.2 and 5.4 %, respectively) (Fig. 7). Several other fluorinated acids are expected to contribute to the unknown organofluorines in seawater samples. Studies have reported the occurrence of mono-, di- and trifluoroacetic acid in seawater samples [13,15]. Concentrations of trifluoroacetic acid in waters from the North Pacific Ocean are reported to fall in the range from 1 to 230 ng/L [15]. Fluoroacetic acids are expected to contribute to a considerable portion of TF in seawater samples. Further studies are needed to analyze mono- through trifluoroacetates in seawater.

The contribution of individual perfluoroalkylacids to TF in seawater from the reference site was ∼0.0003%, while in con-
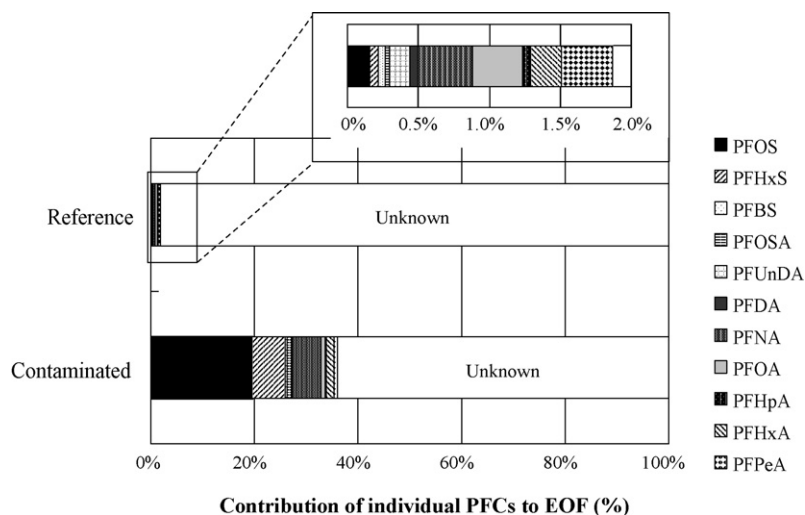

Fig. 7. Contribution of known PFCs to extractable organic fluorine.

taminated water it was ∼0.02%. This suggested that the known PFCs contributed very little to TF in seawater. In both the reference and the contaminated locations, fluoride ion (93 and 82.5% for the reference site and the contaminated site, respectively) accounted for a major proportion of TF. This suggests the dominance of inorganic forms of fluorine among TF in seawater. Concentrations of fluoride in seawater are reported to be in the hundreds of μg/L up to a few mg/L. Concentrations of fluoride in waters of Tokyo Bay, Japan, were between 0.15 and 1.1 mg/L [16].

In conclusion, fluoride accounts for a major portion of total fluorine in seawater. Nevertheless, within the organofluorine fraction, a major portion still remains unidentified in water samples, suggesting the occurrence of unknown fluorinated acids in addition to known perfluorinated acids such as PFOA, PFNA, and PFOS. Several short-chain fluorinated acids such as monofluoroacetic acid and difluoroacetic acid may contribute to total fluorine burdens in seawater. Although fluoride is a dominant species in seawater, the composition and profiles of fluorinated compounds in freshwater may be different. Mass balance analysis showing the differences in the magnitude of total organic fluorine (TOF) and extractable organic fluorine (EOF) is important to understand the transport and fate of fluorinated compounds in the environment, and to identify the sources of unknown EOF.

Acknowledgments

References

[1] J.P. Giesy, K. Kannan, Environ. Sci. Technol. 35 (2001) 1339.
[2] S. Taniyasu, K. Kannan, M.K. So, A. Gulkowska, E. Sinclair, T. Okazawa, N. Yamashita, J. Chromatogr. A 1093 (2005) 89.
[3] N.L. Stock, F.K. Lau, D.A. Ellis, J.W. Martin, D.C.G. Muir, S.A. Mabury, Environ. Sci. Technol. 38 (2004) 991.
[4] M. Loewen, T. Halldorson, F.Y. Wang, G. Tomy, Environ. Sci. Technol. 39 (2005) 2944.
[5] R. Bose, R. Saari-Nordhaus, A. Sonaike, D.S. Sethi, J. Chromatogr. A 1039 (2004) 45.
[6] S. Thangavel, K. Dash, S.M. Dhavile, S.C. Chaurasia, T. Mukherjee, J. Chromatogr. A 1074 (2005) 229.
[7] Z. Lu, Y. Liu, V. Barreto, C. Pohl, N. Avdalovic, R. Joyce, B. Newton, J. Chromatogr. A 956 (2002) 129.
[8] N. Yamashita, K. Kannan, S. Taniyasu, Y. Horii, T. Okazawa, G. Pertick, T. Gamo, Environ. Sci. Technol. 38 (2004) 5522.
[9] E. Sinclair, D.T. Mayack, K. Roblee, N. Yamashita, K. Kannan, Arch. Environ. Contam. Toxicol. 50 (2006) 398.
[10] N. Yamashita, M.K. So, S. Taniyasu, K. Kannan, A. Gulkowska, P.K.S. Lam, Organohalog. Compd. 72 (2005) 749.
[11] Y. Miyake, M. Kato, K. Urano, J. JPN Soc. Waste Manage. Experts 16 (2005) 245.
[12] Y. Miyake, M.K. So, P. Rostkowski, S. Taniyasu, P.K.S. Lam, K. Kannan, N. Yamashita, Organohalog. Compd. 68 (2006).
[13] F. Wang, G.W. Dicinoski, Y. Zhu, P.R. Haddad, J. Chromatogr. A 1032 (2004) 31.
[14] J.P. Riley, G. Skirrow, Chemical Oceanography, vol. 2, Academic Press, New York, 1965.
[15] B.F. Scott, R. MacDonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer, D.C.G. Muir, Environ. Sci. Technol. 39 (2005) 6555.
[16] Y. Kitime, V. Furukawa, Oceanogr. Soc. Jpn. 28 (1972) 121.