Chemosphere 79 (2010) 266–272

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan

Lutz Ahrens [a,*], Sachi Taniyasu [b], Leo W.Y. Yeung [b,c], Nobuyoshi Yamashita [b], Paul K.S. Lam [c], Ralf Ebinghaus [a]

[a] Institute for Coastal Research, GKSS Research Centre Geesthacht, D-21502 Geesthacht, Germany
[b] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
[c] Department of Biology and Chemistry, City University of Hong Kong, HKSAR, China

ARTICLE INFO

Article history:
Received 18 November 2009
Received in revised form 15 January 2010
Accepted 23 January 2010
Available online 23 February 2010

Keywords:
PFCs
Polyfluoroalkyl compounds
Water
Suspended particulate matter
Sediment
Partitioning coefficients

ABSTRACT

This study examined the environmental behaviour and fate of polyfluoroalkyl compounds (PFCs) found in water, suspended particulate matter (SPM) and sediment. The sampling of the sediment was performed at two stations from Tokyo Bay, Japan, in 2008. In addition, a depth profile of seawater was collected at three water layers from both sampling stations. The ∑PFC concentrations ranged from 16.7 to 42.3 ng L^{-1} in the water column, from 6.4 to 15.1 ng g^{-1} dry weight (dw) in the SPM fraction and from 0.29 to 0.36 dw in surface sediment. The distribution of PFCs was found to depend on their physicochemical characteristics. While short-chain perfluoroalkyl carboxylic acids (PFCAs) ($C < 7$) were exclusively detected in the dissolved phase, longer-chain PFCAs ($C \geqslant 7$), perfluoroalkyl sulfonates (PFSAs), ethylperfluorooctane sulfonamidoacetic acid (EtFOSAA), and perfluorooctane sulfonamide (PFOSA) appeared to bind more strongly to particles. Results showed that the sorption of PFCs on SPM increases by 0.52–0.75 log units for each additional CF_2 moiety and that the sorption of PFSAs was 0.71–0.76 log units higher compared to the PFCA analogs. In addition, the sorption of PFCs was influenced by the organic carbon content. These data are essential for modelling the transport and environmental fate of PFCs.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Polyfluoroalkyl compounds (PFCs), such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are persistent against the typical environmental degradation processes and have been found around the globe in water, wildlife and human tissues (Kannan et al., 2004; Yamashita et al., 2005; Houde et al., 2006). The long-chain PFCs are known to be bioaccumulative (Martin et al., 2003a,b) and to have toxic effects in wildlife and humans (Lau et al., 2007; Joensen et al., 2009). Despite their detection in sediment (Higgins and Luthy, 2006) and bodies of water, such as rivers (McLachlan et al., 2007; Ahrens et al., 2009c) and oceans (Yamashita et al., 2005; Yamashita et al., 2008; Ahrens et al., 2009a), data on the concentration levels in suspended particulate matter (SPM) and the partitioning of PFCs between sediment or SPM and dissolved phase are scarce. These data are essential for modelling the transport and environmental fate of PFCs.

In a recent laboratory study, Higgins and Luthy found that the sorption of PFCs increases for each CF_2 moiety by 0.50–0.60 log units of the measured partition coefficients (Higgins and Luthy, 2006). Furthermore, the partition coefficient of the perfluoroalkyl sulfonates (PFSAs) was found to be 0.23 log units higher in comparison to the perfluoroalkyl carboxylic acids (PFCAs) with the same carbon chain length (Higgins and Luthy, 2006). Similarly, a specific distribution of PFCs was observed in two sediment cores from Tokyo Bay, Japan, where the PFSAs, ethylperfluorooctane sulfonamidoacetic acid (EtFOSAA) and perfluorooctane sulfonamide (PFOSA), seemed to bind more strongly to sediment than PFCAs and only short-chain PFCAs ($<C_7$) were found exclusively in pore water (Ahrens et al., 2009d). In addition, previous work on the partitioning behaviour of PFCs has also demonstrated that the sediment–water distribution depends on such solution parameters as pH (Higgins and Luthy, 2006) and organic carbon fraction (f_{OC}) (Liu and Lee, 2005; Ahrens et al., 2009d). However, no partition coefficients exist for the partitioning between SPM and dissolved phase based on natural samples.

This study investigated the partitioning behaviour of PFCs between the particles (sediment and SPM) and the dissolved phase in two vertical profiles of seawater from Tokyo Bay, Japan. The data on PFCs in sediment were taken from a previous study (Ahrens et al., 2009d). We also examined the influence of physicochemical parameters, such as organic carbon, on the sorption of PFCs onto the SPM. Finally, we were able to calculate the particulate associated fraction (φ) in water and the partition coefficient (K_d) and organic carbon normalised partition coefficient (K_{OC}) for the sorption on sediment and SPM.

* Corresponding author. Tel.: +1 416 739 4473; fax: +1 416 739 4179.
E-mail address: lutz.ahrens@ec.gc.ca (L. Ahrens).

0045-6535/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2010.01.045

2. Materials and methods

2.1. Sampling campaign

Two depth profiles of seawater from Tokyo Bay were collected using a depth-integrating sampler with a 1 L glass bottle and a glass stopper in May 2008 (Fig. 1). The water samples were collected in duplicate at three water layers (surface, middle and bottom water column). At the same stations two sediment cores were collected using an acrylic tube (120 cm long and 12 cm i.d.). These cores were sliced in intervals using a clean stainless steel slicer and then stored in polypropylene (PP) tubes. Only the inner part of the sediment core was analysed for PFCs to avoid contaminations from sampling. The data from the 0–3 cm intervals were used for this study (for details see Ahrens et al., 2009d). The sampling conditions, including temperature, salinity, pH values, conductivity, SPM and organic carbon content in water and sediment were measured (Table 1). After collection, the water samples were transferred directly into polypropylene (PP) bottles and transported in an ice-cooled box to the lab.

2.2. Filtration and extraction

The target analytes include the C_4, C_6, C_8 and C_{10} PFSA and C_4–C_{12}, C_{14}, C_{16} and C_{18} PFCA, 6:2 fluorotelomer sulfonate (6:2 FtS), PFOSA, ethylperfluorooctane sulfonamide (EtFOSA) and EtFOSAA (for details see Taniyasu et al., 2008; Ahrens et al., 2009d). Directly after arrival in the lab, the water samples were filtered using a syringe nylon membrane PP filter (25 mm, 0.45 μm, IWAKI). After cleaning of the nylon membrane PP filter, using 2 × 5 mL methanol and 2 × 5 mL Millipore water, 100 mL of the seawater sample was pushed through the filter using a PP syringe. During this procedure the dissolved phase was collected in a PP bottle. Thereafter, the filter was dried using ambient air and the PFCs on the SPM were eluted with 3 × 5 mL methanol in a PP tube. Finally, the volume was reduced to 0.5 mL under a nitrogen stream.

The filtered water samples (dissolved phase) were extracted by solid phase extraction with Oasis WAX cartridges (Waters, 150 mg, 6 mL, 30 μm) as described elsewhere (Taniyasu et al., 2008). Briefly, after preconditioning with 4 mL of ammonium hydroxide in methanol, 4 mL of methanol, and then 4 mL of Millipore water, the cartridges were loaded with the samples at approximately one drop per second. Before loading, the dissolved phase was spiked with 1 ng absolute of an internal standard (IS) mix (i.e., [$^{13}C_4$]-PFBA, [$^{13}C_4$]-PFOA, [$^{13}C_5$]-PFNA, [$^{13}C_2$]-PFDA, [$^{13}C_2$]-PFUnDA, [$^{13}C_2$]-PFDoA, [$^{13}C_4$]-PFOS, and 100 μL of a 10 ng mL^{-1} solution). The cartridges were then washed with 4 mL of 25 mM ammonium acetate buffer (pH 4) in Millipore water and dried by centrifugation at 3000 rpm for 2 min. The elution was then divided into two fractions. The first fraction was carried out with 4 mL of methanol for the neutral PFCs and the second with 4 mL of 0.1% ammonium hydroxide in methanol for the ionic PFCs. Both fractions were reduced to 0.5 mL under a nitrogen stream and analysed separately.

2.3. Instrument analysis and quality assurance

The concentrations of PFCs in the extracts were determined using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). An HP1100 HPLC-system (Agilent Technologies, Palo Alto, CA) was equipped with a Betasil C_{18} column (2.1 mm i.d. × 50 mm in length, 5 μm; Thermo Hypersil-Keystone, Bellefonte, PA), a XDB-C8 (12.5 mm × 2.1 mm, 5 μm; Agilent Technologies, Foster City, CA) as a guard column and a RSpak JJ-50 2D column (2.0 mm i.d. × 150 mm in length, 5 μm; Shodex, Showa Denko K.K., Kawasaki, Japan). A triple-quadrupole mass spectrometer, supplied by Micromass (Quattro Ultima Pt, Beverly, MA), used an electrospray ionization (ESI) interface in negative ionization mode. The flow rate was set to 300 μL min^{-1} and 10 μL of the sample was injected. Details of the extraction, instrumental conditions and quantification for PFC analysis have been described elsewhere (Taniyasu et al., 2008).

All fluorinated materials that could come into contact with the sample during collection, sample preparation or instrumental analysis were removed to avoid contaminations (for details, see (Yamashita et al., 2004). All procedural blanks, which were extracted in the same manner as the samples, using 100 mL of Millipore water for filtration and extraction, were below the method quantification limits (MQLs). The MQLs were determined at a signal-to-noise ratio (S/N) of 10 and ranged between 0.05 and 0.13 ng L^{-1} for the dissolved phase and between 0.13 and 0.33 ng g^{-1} dry weight (dw) for the SPM fraction. The matrix spike recoveries for all analytes ranged between 81% and 128% for dissolved phase, with a mean standard deviation (SD) of 3.4% (n = 3), and between 86% and 116% for the SPM fraction, with a mean SD of 4.2% (n = 3). The duplicate samples were analysed separately, their relative standard deviations were less than 20%.

Statistical analyses was performed using SPSS for Windows (version 16) and Microsoft Excel at a significance level of α = 0.05. Pearson correlation analysis was used for the correlations between concentrations of individual compounds and to assess significant correlations between PFC concentrations in the SPM fraction and the physicochemical parameters.

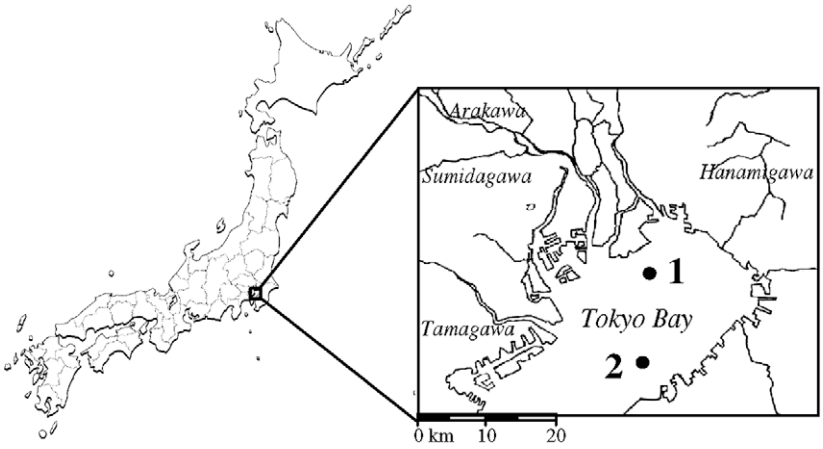

Fig. 1. Map showing the sampling locations 1 (N35°34′60″/ E139°55′01″) and 2 (N35°29′18″/ E139°54′24″) in Tokyo Bay, Japan.

Table 1
Summary of water and sediment sampling information and chemical analyses.[a]

Sampling location	Sample type	Depth (m)	T (°C)	Salinity (‰)	pH	Conductivity (mS cm^{-1})	SPM (mg L^{-1})	DOC (mg L^{-1})	f_{OC} (%)	∑PFCs			
										c_w[b]	c_{SPM1}[c]	c_{SPM2}[d]	c_s[e]
1	Water A[f]	0.5	17.7	30.1	8.3	39.9	3.5	1.8	10.3	38.7	1.60	13.6	–
	Water B[g]	6	17.6	30.2	8.3	39.9	3.2	1.7	10.6	42.1	0.93	15.1	–
	Water C[h]	11	16.9	31.0	8.2	40.2	3.8	1.5	7.9	34.5	0.58	14.0	–
	Sediment[i]	12	–	–	7.4	–	–	–	1.7	–	–	–	0.36
2	Water A	0.5	17.2	30.4	8.2	39.7	4.3	1.9	8.8	42.3	1.19	14.9	–
	Water B	10	15.6	32.8	8.0	41.1	5.0	1.6	6.4	28.6	1.21	7.4	–
	Water C	20	15.3	33.3	8.0	41.4	3.6	1.2	6.7	16.7	1.33	6.4	–
	Sediment	21	–	–	7.1	–	–	–	1.5	–	–	–	0.29

[a] SPM = suspended particulate matter; DOC = dissolved organic carbon in water; f_{OC} = fraction organic carbon.
[b] Concentration in the dissolved phase (ng L^{-1}).
[c] Concentration in the SPM phase (ng L^{-1}).
[d] Concentration in the SPM phase when normalised to content of SPM in unit of ng g^{-1} dw.
[e] Concentration in surface sediment (ng g^{-1} dw).
[f] The upper layer of the water column.
[g] The middle layer of the water column.
[h] The bottom layer of the water column.
[i] Surface sediment (0–3 cm) (for details see Ahrens et al. (2009d)).

3. Results and discussion

3.1. PFC distribution in water, SPM and sediment

PFSA, PFOSA/EtFOSAA, and PFCA concentrations were observed in the dissolved phase and SPM fraction at different water layers in the two depth profiles (see Fig. 2). In the dissolved phase ~97% of the ∑PFCs were distributed, while ~3% of the ∑PFCs were found in the SPM fraction.

The PFCs quantified in the dissolved phase included C_6 and C_8 PFSAs, PFOSA, EtFOSAA, C_4–C_{11} PFCAs. PFOSA and EtFOSAA are potential precursor compounds which can degrade to PFSAs (Tomy et al., 2004; Xu et al., 2004). Perfluorobutanoic acid (PFBA) was the predominated PFC with a contribution of 52 ± 2%, followed by PFOA (17 ± 2%) and perfluorononanoic acid (PFNA, ~11 ± 1%). PFOS had a contribution of only 4 ± 0.2% with a concentration range of 0.9–2.2 ng L^{-1}, which is ~15 times lower than found in water samples from Tokyo Bay collected in a previous study in 2002 (Taniyasu et al., 2003). The decreasing PFOS concentration could be caused by the phase-out of perfluorooctyl sulfonyl fluoride (POSF) by the 3 M Company (of which 4 plants were in Japan), reduction of PFC emissions by optimisation of the production process and/or production shift to shorter-chained PFCs (Paul et al., 2009). The PFC concentrations found in this study were in the same range as that in other coastal areas, such as the German Bight, the Pearl River Delta (China), and the coastal areas of Hong Kong, Korea and Dalian, China (So et al., 2004; Yamashita et al., 2005; Ju et al., 2008; Ahrens et al., 2009b). However, there are few data available about PFCs in coastal waters and most studies have concentrated only on selected compounds like PFOS and PFOA.

In the SPM fraction C_6 and C_8 PFSAs, PFOSA and C_7–C_{11} PFCAs were detected, but, in contrast to the dissolved phase, EtFOSAA or the short-chain PFCAs (C < 7) were not found. The ∑PFC concentration in the SPM fraction ranged between 6.4 ng g^{-1} dw and 15.1 ng g^{-1} dw. The predominant compounds were PFOS, which had a contribution of 48 ± 2%, followed by PFNA (25 ± 2%) and PFOA (12 ± 1%).

Ten PFCs (i.e., C_6, and C_8 PFSAs, PFOSA, EtFOSAA, and C_8–C_{12} and C_{14} PFCA) were detected in the surface sediment (0–3 cm) (Ahrens et al., 2009d). Although perfluorodecane sulfonate (PFDS), EtFOSAA and the C_8–C_{12} and C_{14} PFCAs were not detected on the SPM, a greater sample amount (i.e., 5 g) was used in the extraction of the sediment, which results in lower detection limits. Similar to the SPM fraction, the dominant compound in sediment was PFOS, with a contribution of ~25%. The other major contributions were EtFOSAA (~19%), followed by perfluorohexane sulfonate (PFHxS) (~17%) and perfluoroundecanoic acid (PFUnDA) (~16%). On the other hand, the concentration levels in the sediment were by a factor of 30–40 lower than for the SPM fraction. However, the samples cannot be compared directly, as the surface sediment concentration represents a time period of 3 years (2006–2008) while the SPM fraction was collected on one specific date. In addition, the higher organic content (OC) in the SPM fraction could lead to higher PFC concentrations due to the bioaccumulation in plankton (<0.45 μm) and adsorption to OC (Higgins and Luthy, 2006; Powley et al., 2008; Ahrens et al., 2009d).

Overall, the distribution of individual PFCs in water, SPM and sediment depends on their physicochemical characteristics. PFSAs, EtFOSAA, and PFOSA seem to bind more strongly to particles than PFCAs, whereas only short-chain PFCAs (C < 7) were found exclusively in the dissolved phase. As a consequence, the short-chain PFCs have a higher potential for aqueous long-range transport and, as the long-chain PFCs, the PFSAs, EtFOSAA and PFOSA, are distributed in the surface sediment, which could act as a sink for PFCs.

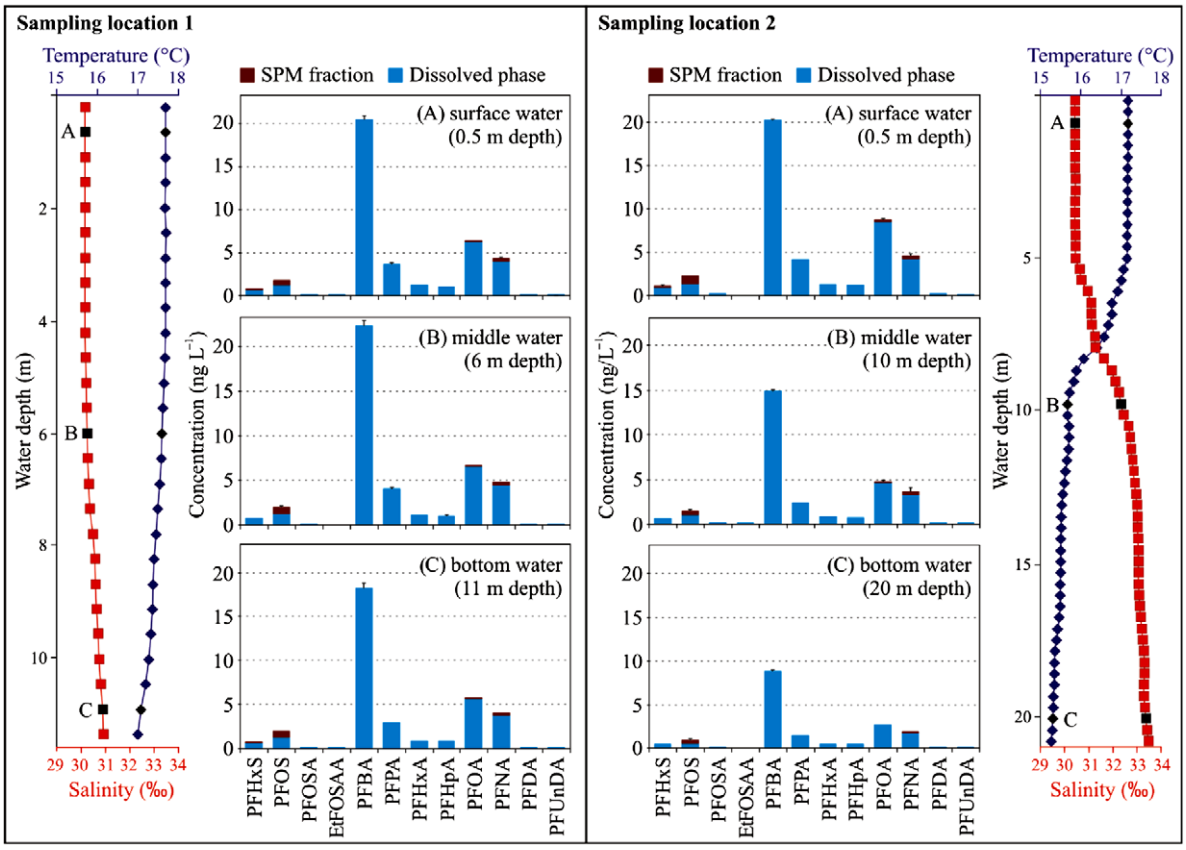

Fig. 2. Vertical profiles of individual PFCs in the dissolved phase and suspended particulate matter (SPM) fraction in ng/L from three water depth levels from Tokyo Bay, Japan. In addition, the vertical profiles of the water temperature in °C (diamond) and salinity in ‰ (square) are shown.

3.2. Vertical profiles of PFCs in the water column

The vertical profiles of individual PFCs in the water column, including the temperature and salinity are shown in Fig. 2. While the surface water concentrations at both sampling locations were similar, they had different vertical concentration profiles. At sampling location 1, the ∑PFC concentration was relatively constant from the surface water (0.5 m depth) to the bottom water level (11 m depth) in the dissolved phase (38.5 ± 3.8 ng L^{-1}, $n = 6$) and SPM fraction (14.2 ± 0.8 ng g^{-1} dw, $n = 6$). Conversely, the ∑PFC concentration at sampling location 2 decreased from top down in the water column by a factor of ~2.5, from 42.3 ng L^{-1} to 16.7 ng L^{-1} in the dissolved phase and from 15.0 ng g^{-1} dw to 6.4 ng g^{-1} dw in the SPM fraction. This disparity can be explained by the influence of seawater at sampling location 2. The water layers at sampling location 1 were well mixed, with a relative constant water temperature (17.7–16.9 °C) and salinity (30.1–31.0‰) profile, whereas at sampling location 2 from top down the water temperature decreased (from 17.2 to 15.3 °C) and the salinity increased (from 30.4‰ to 33.3‰). These changes of the temperature and salinity are forced by the inflow of ocean seawater (Fujiwara and Yamada, 2002). Hence, the decreasing PFC concentration of the middle and bottom water layers at sampling location 2 can be explained by the inflow of lower contaminated seawater.

3.3. Correlation of PFCs in the SPM fraction with the physicochemical parameters

The sorption of PFCs on particles depends on their physicochemical parameters (Higgins and Luthy, 2006). In previous laboratory and field studies, organic carbon was identified as the dominant parameter which influenced the sorption of PFCs on sediment (Ahrens et al., 2009d; Higgins and Luthy, 2006). In this study, a positive correlation was found between organic carbon and PFC concentration in the SPM fraction ($p < 0.0001$, see Fig. 3). This showed that, similar to the sorption on sediment, the organic carbon had a significant influence on the sorption of PFCs onto SPM. The influence of pH could not be investigated because of the similar pH in all water samples (pH = 8.0–8.3). Other factors, which were not investigated in this study, such as the concentrations of calcium cations, may also influence the sorption capacity of SPM for PFCs (Higgins and Luthy, 2006).

3.4. Partitioning coefficient of PFCs between SPM and dissolved phase

While the PFCs were dominantly distributed in the dissolved phase, individual PFCs showed a different partitioning profile. The particulate related fraction (φ) and partitioning coefficients are shown in Table 2.

The particulate related PFC fraction (φ) represents the fraction in the SPM in relation to the dissolved phase.

$$\varphi = c_{SPM}/c_w \times 100 \quad (1)$$

where c_{SPM} is the adsorbed PFC on the SPM fraction and c_w is the mass concentration of PFC in the dissolved phase. The highest particulate associated fraction (φ) was observed for PFUnDA with 62%, while the fraction decreased exponentially with decreasing perfluoroalkyl chain length to 0.8% for perfluoroheptanoic acid (PFHpA) (Table 2). The particulate associated fraction (φ) was also relatively high for PFOS (~32%) and PFOSA (~21%).

The relationship for PFOS and ∑PFCA concentrations between the SPM fraction and dissolved phase is shown in Fig. 4. A significant

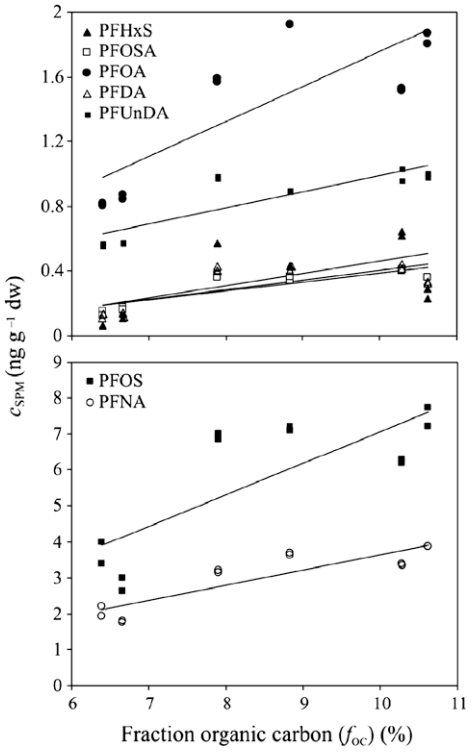

Fig. 3. Dependence of PFC concentrations in the suspended particulate matter (SPM) fraction (c_{SPM}) on fraction organic carbon (f_{OC}).

correlation was found for the PFOS and individual PFCA concentration in the SPM fraction and dissolved phase ($p < 0.001$). But no significant correlation was observed for PFHxS and PFOSA, while the other PFCs were exclusively detected in the dissolved phase. The interaction of this distribution of sorption and desorption can be described by the partition coefficient (K_d) for individual PFCs (Schwarzenbach et al., 2003).

$$K_d = c_{SPM}/c_w \quad (2)$$

The previous section shows that the sorption on SPM depends primarily on the organic carbon fraction (f_{OC}). Hence the organic carbon normalised partition coefficient (log K_{OC}) provides a better indication of the partitioning.

$$K_{OC} = K_d \times 100/f_{OC} \quad (3)$$

The perfluoroalkyl chain length had a high influence on the sorption of PFCs on SPM. The log K_{OC} for the PFSAs increased from 3.7 cm^3 g^{-1} for PFHxS to 4.8 cm^3 g^{-1} for PFOS and for the PFCAs from 2.9 cm^3 g^{-1} for PFHpA to 5.1 cm^3 g^{-1} for PFUnDA. Hence, with each additional CF_2 moiety the log K_{OC} increased by 0.52–0.75 log units for the PFCAs. This was also observed in a previous study for the sorption of PFCs on sediment (Higgins and Luthy, 2006). Furthermore the functional group (i.e., sulfonate, sulfonamide, and carboxylic acid) also had a crucial influence on the sorption on SPM. The log K_{OC} for PFSAs was 0.71–0.76 log units higher than the PFCAs with the same carbon chain length, whereas the log K_{OC} of PFOSA (i.e., 4.5 cm^3 g^{-1}) was 0.25 log units lower than for PFOS but 0.51 log units higher than for PFNA. These results are in agreement with a previous laboratory study of the sorption of PFCs on sediment, where the partition coefficient of PFSAs was 0.23 log units higher than for PFCAs (Higgins and Luthy, 2006). In general, PFSAs, PFOSA and longer-chain PFCAs have a stronger potential to interact with SPM, which could be lead to sedimentation and accumulation in the sediment.

3.5. Partitioning coefficients of PFCs between sediment and dissolved phase

The partitioning coefficients of PFCs between sediment and dissolved phase were calculated using the data on sediment from a previous study (Ahrens et al., 2009d) and the concentration in the dissolved phase from the overlaying water column (surface, middle and bottom water) from the same sampling location. The partition coefficient (K'_d) and organic carbon normalised partition coefficient (log K'_{OC}) for the sorption to sediment was calculated, as shown in the previous section, using the PFC concentration in sediment (c_s) instead of the c_{SPM}. The partitioning coefficients for sediment (i.e., K'_d and log K'_{OC}) are shown in Table 2.

The sediment log K'_{OC} values for PFOS, PFOA, PFNA and perfluorodecanoic acid (PFDA) were more than 1 order of magnitude lower than the SPM log K_{OC} values, while the partition coefficients for the other PFCs were similar. The differences in the partition coefficients can be explained by the following factors. First, the concentrations in the surface sediment and the SPM fraction represent two different time periods of contamination (see discussion above). Furthermore, the structure of the particles from the sediment and SPM could be different which would influence the adsorption capacity of the particles for PFCs. Finally, it is possible that the concentrations measured in the SPM and the dissolved phase were in disequilibrium due to the influx of fresh river water which could increase the PFC concentration in the SPM fraction and lead to a higher log K_{OC}. Hence, the high surface runoff could lead to higher log K_{OC} values being reported during wet periods than during the dry season (Maruya et al., 1996).

In a previous laboratory study, the log K_{OC} values recorded for the sorption on sediment were in the same range for PFOA, PFNA

Table 2
Particulate associated fraction on the suspended particulate matter (SPM) (φ), partition coefficients between SPM and dissolved phase (log K_d), and sediment and overlaying dissolved phase (log K'_d), and organic carbon normalised partition coefficient between SPM and dissolved phase (log K_{OC}), and sediment and overlaying dissolved phase (log K'_{OC}) for individual PFCs ($n = 6$).[a]

	SPM-derived			Sediment-derived	
	φ (%)	Log K_d (cm^3 g^{-1})	Log K_{OC} (cm^3 g^{-1})	Log K'_d (cm^3 g^{-1})	Log K'_{OC} (cm^3 g^{-1})
PFHxS	4.2 ± 2.5	2.6 ± 0.4	3.7 ± 0.3	1.8 ± 0.1	3.6 ± 0.1
PFOS	32 ± 2.2	3.7 ± 0.1	4.8 ± 0.1	2.1 ± 0.1	3.8 ± 0.1
PFOSA	21 ± 4.9	3.4 ± 0.2	4.5 ± 0.1	2.5 ± 0.2	4.3 ± 0.2
EtFOSAA	n.a.	n.a.	n.a.	3.0 ± 0.1	4.8 ± 0.1
PFHpA	0.8 ± 0.01	1.9 ± 0.002	2.9 ± 0.002	n.a.	n.a.
PFOA	2.4 ± 0.3	2.4 ± 0.1	3.5 ± 0.1	0.04 ± 0.03	1.9 ± 0.1
PFNA	7.5 ± 0.8	2.9 ± 0.1	4.0 ± 0.1	0.6 ± 0.1	2.4 ± 0.1
PFDA	23 ± 5.7	3.5 ± 0.2	4.6 ± 0.1	1.8 ± 0.1	3.6 ± 0.1
PFUnDA	62 ± 6.2	4.2 ± 0.2	5.1 ± 0.1	3.0 ± 0.1	4.8 ± 0.2

[a] n.a. = not available; $\varphi = c_{SPM}/c_w$ x 100; $K_d = c_{SPM}/c_w$; $K_{OC} = K_d \times 100/f_{OC}$; $K'_d = c_s/c_w$; $K'_{OC} = K'_d \times 100/f_{OC}$; c_{SPM} = PFC concentration on SPM; c_s = PFC concentration in sediment; c_w = PFC concentration in the dissolved phase; f_{OC} = organic carbon fraction.

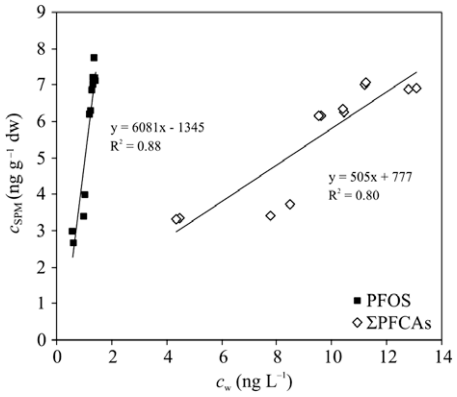

Fig. 4. Relationships of PFOS and ∑PFCA concentrations between suspended particulate matter (SPM) fraction (c_{SPM}) and dissolved phase (c_w).

and PFDA, but were more than one log unit lower for PFOS and PFUnDA. However, partitioning coefficients observed in the natural environment cannot be compared directly with those predicted by linear correlation relationships under laboratory conditions. Generally greater log K_{OC} values have also been observed for estrogens (Lei et al., 2009) and nonylphenol (Düring et al., 2002). For example, particulate structure, heterogeneity of the organic carbon, concentrations of sorbate, ratio between solid and liquid phase and the presence of organisms were completely different to those in the laboratory experiment.

The analysis of the distribution of PFCs in sediment and water provides useful information into processes that control the transport and fate of PFCs. The presence of long-chain PFCAs ($C \geqslant 8$), PFSAs, PFOSA, and N-EtFOSAA in sediment suggests that they are bioavailable to benthic organisms (Higgins et al., 2007) and could adversely affect benthic organisms (Stevenson et al., 2006).

4. Conclusion

This paper presents the first comprehensive survey of four classes on PFC in water, SPM and sediments. It also provides important data on their partitioning behaviour. The PFCs were mostly distributed in the dissolved phase (~97%), with only 3% on the SPM fraction. Furthermore, while the compositions of PFCs on SPM and in sediments were similar, the concentrations of PFCs on SPM were by a factor of 30–40 higher than those in sediments. However, the distribution of PFCs depends on their physicochemical characteristics.

Short-chain PFCAs ($C < 7$) were exclusively detected in the dissolved phase, long-chain PFCAs (C_7–C_{11}), PFHxS, PFOS and PFOSA were detected in the dissolved and in the SPM fraction and long-chain PFCAs ($C > 11$) and PFDS were exclusively detected in sediment. This corresponds with the log K_{OC} values for the PFCAs, which increased by 0.52–0.75 log units with each additional CF_2 moiety, and the log K_{OC} values for the PFSAs, which were 0.71–0.76 log units higher than the PFCAs with the same carbon chain length. PFCs with a high partitioning coefficient could interact with SPM at the particle/water interface leading to their removal from the water column and accumulation in sediment. This behaviour has an impact on their toxicity, bioavailability, and general fate in the marine environment. However, particle/water interactions are very complex and are largely controlled by the interaction with the organic carbon. Overall, the partition coefficient values of PFCs could help improve our understanding of the processes that control the behaviour and fate of PFCs in the marine environment. However, further work on their physical state needs to be done under field conditions.

Acknowledgements

The authors acknowledged the German Federal Environmental Foundation and International Bureau from the Federal Ministry of Education and Research (project JPN 08/A02) for supporting the project. We thank Dr. Wang Yuan, Ms. Mak Y.L., Ms. Lai F.Y, and Mr. Jin L. from the City University of Hong Kong, Dr. Li P. from AIST, and Tokyo Kyuei Co. for the help of sampling in Tokyo Bay.

References

Ahrens, L., Barber, J.L., Xie, Z., Ebinghaus, R., 2009a. Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. Environ. Sci. Technol. 43, 3122–3127.
Ahrens, L., Felizeter, S., Ebinghaus, R., 2009b. Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. Chemosphere 76, 179–184.
Ahrens, L., Felizeter, S., Sturm, R., Xie, Z., Ebinghaus, R., 2009c. Polyfluorinated compounds in effluents of waste water treatment plants and surface water along the River Elbe, Germany. Marine Poll. Bull. 58, 1326–1333.
Ahrens, L., Yamashita, N., Yeung, L.W.Y., Taniyasu, S., Horii, Y., Lam, P.K.S., Ebinghaus, R., 2009d. Partitioning behaviour of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay. Jpn. Environ. Sci. Technol. 43, 6969–6975.
Düring, R.-A., Krahe, S., Gäth, S., 2002. Sorption behavior of nonylphenol in terrestrial soils. Environ. Sci. Technol. 36, 4052–4057.
Fujiwara, T., Yamada, Y., 2002. Inflow of oceanic water into Tokyo Bay and generation of a subsurface hypoxic water mass. J. Geophys. Res. C Oceans 107, 13.1–13.10.
Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediment. Environ. Sci. Technol. 40, 7251–7256.
Higgins, C.P., McLeod, P.B., MacManus-Spencer, L.A., Luthy, R.G., 2007. Bioaccumulation of perfluorochemicals in sediments by the aquatic oligochaete Lumbriculus variegatus. Environ. Sci. Technol. 41, 4600–4606.
Houde, M., Martin, J.W., Lethcher, R.J., Solomon, K.R., Muir, D.C.G., 2006. Biological monitoring of polyfluoroalkyl substances: a review. Environ. Sci. Technol. 40, 3463–3473.
Joensen, U.N., Bossi, R., Leffers, H., Jensen, A.A., Skakkebæk, N.E., Jørgensen, N., 2009. Do perfluoroalkyl compounds impair human semen quality? Environ. Health Perspect. 117, 923–927.
Ju, X., Jin, Y., Sasaki, K., Saito, N., 2008. Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian coastal waters in China. Environ. Sci. Technol. 42, 3538–3542.
Kannan, K., Corsolini, S., Falandysz, J., Fillmann, G., Kumar, K.S., Loganathan, B.G., Ali Mohd, M., Olivero, J., Van Wouwe, N., Ho Yang, J., Aldous, K.M., 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ. Sci. Technol. 38, 4489–4495.
Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., 2007. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol. Sci. 99, 366–394.
Lei, B., Huang, S., Zhou, Y., Wang, D., Wang, Z., 2009. Levels of six estrogens in water and sediment from three rivers in Tianjin area, China. Chemosphere 76, 36–42.
Liu, J., Lee, L.S., 2005. Solubility and sorption by soils of 8:2 fluorotelomer alcohol in water and cosolvent systems. Environ. Sci. Technol. 39, 7535–7540.
Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003a. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). Environ. Toxicol. Chem. 22, 196–204.
Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003b. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). Environ. Toxicol. Chem. 22, 189–195.
Maruya, K.A., Risebrough, R.W., Horne, A.J., 1996. Partitioning of polynuclear aromatic hydrocarbons between sediments from San Francisco Bay and their porewaters. Environ. Sci. Technol. 30, 2942–2947.
McLachlan, M.S., Holmstrom, K.E., Reth, M., Berger, U., 2007. Riverine discharge of perfluorinated carboxylates from the European continent. Environ. Sci. Technol. 41, 7260–7265.
Powley, C.R., George, S.W., Russell, M.H., Hoke, R.A., Buck, R.C., 2008. Polyfluorinated chemicals in a spatially and temporally integrated food web in the Western Arctic. Chemosphere 70, 664–672.
Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. Environmental Organic Chemistry. Wiley-Interscience, Hoboken, NJ.
So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H., Lam, P.K.S., 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. Environ. Sci. Technol. 38, 4056–4063.
Stevenson, C.N., MacManus-Spencer, L.A., Luckenbach, T., Luthy, R.G., Epel, D., 2006. New perspectives on perfluorochemical ecotoxicology: inhibition and induction of an efflux transporter in the marine mussel, Mytilus californianus. Environ. Sci. Technol. 40, 5580–5585.
Taniyasu, S., Kannan, K., Horii, Y., Hanari, N., Yamashita, N., 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. Environ. Sci. Technol. 37, 2634–2639.
Taniyasu, S., Kannan, K., Yeung, L.W.Y., Kwok, K.Y., Lam, P.K.S., Yamashita, N., 2008. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry:

Comparison to patterns of long-chain perfluorinated acids (C5–C18). Anal. Chim. Acta 619, 221–230.

Tomy, G.T., Tittlemier, S.A., Palace, V.P., Budakowski, W.R., Braekevelt, E., Brinkworth, L., Friesen, K., 2004. Biotransformation of n-ethyl perfluorooctanesulfonamide by rainbow trout (*Oncorhynchus mykiss*) liver microsomes. Environ. Sci. Technol. 38, 758–762.

Xu, L., Krenitsky, D.M., Seacat, A.M., Butenhoff, J.L., Anders, M.W., 2004. Biotransformation of n-ethyl-n-(2-hydroxyethyl) perfluorooctanesulfonamide by rat liver microsomes, cytosol, and slices and by expressed rat and human cytochromes P450. Chem. Res. Toxicol. 17, 767–775.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Okazawa, T., Petrick, G., Gamo, T., 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. Environ. Sci. Technol. 38, 5522–5528.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans. Marine Poll. Bull. 51, 658–668.

Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P.K.S., Kannan, K., 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70, 1247–1255.