

# Partitioning Behavior of Per- and Polyfluoroalkyl Compounds between Pore Water and Sediment in Two Sediment Cores from Tokyo Bay, Japan

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The partitioning behavior of per- and polyfluoroalkyl compounds (PFCs) between pore water and sediment in two sediment cores collected from Tokyo Bay, Japan, was investigated. In addition, the fluxes and temporal trends in one dated sediment core were studied. Short-chain perfluoroalkyl carboxylic acids (PFCAs) ( $C \leq 7$ ) were found exclusively in pore water, while long-chain PFCAs ( $C \geq 11$ ) were found only in sediment. The perfluoroalkyl sulfonates (PFSA), *n*-ethylperfluoro-1-octanesulfonamidoacetic acid (*N*-EtFOSAA), and perfluorooctane sulfonamide (PFOSA) seemed to bind more strongly to sediment than PFCAs. The enrichment of PFCs on sediment increased with increasing organic matter and decreasing pH. The perfluorocarbon chain length and functional group were identified as the dominating parameters that had an influence on the partitioning behavior of the PFCs in sediment. The maximum  $\Sigma$ PFC contamination in sediment was observed in 2001–2002 to be a flux of  $197 \text{ pg cm}^{-2} \text{ yr}^{-1}$ . Statistically significant increased concentrations in Tokyo Bay were found for perfluorooctanesulfonate (PFOS) (1956–2008), perfluorononanoic acid (PFNA) (1990–2008), and perfluoroundecanoic acid (PFUnDA) (1990–2008). Concentrations of PFOSA and *N*-EtFOSAA increased between 1985 and 2001, but after 2001, the concentration decreased significantly, which corresponded with the phase out of perfluorooctyl sulfonyl fluoride-based compounds by the 3M Company in 2000.

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## Introduction

In recent years, per- and polyfluoroalkyl compounds (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), have received increasing public attention because of their persistence, bioaccumulative potential (1), and possible adverse effects on living organisms (2, 3). Over the past 50 years, PFCs have been widely used as processing additives during fluoropolymer production and as surfactants in consumer applications, including surface coatings for carpets, furniture, and paper products (4). The production of  $C_8$ -PFC homologous has been restricted in many countries, e.g., the 3M Company, the major producer of perfluorooctyl sulfonyl fluoride (POSF), voluntarily phased out its production in 2000; however, they are still used by other manufacturers (5). Through the production and use of these products, PFCs can be released into the environment, and they have been found ubiquitous in water (6), sediment (7), wildlife (8), and humans (9), with the highest concentrations found in top marine predators (10).

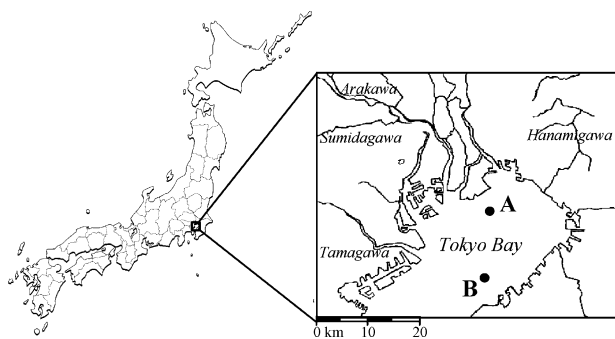
Sediment is an important sink and reservoir of persistent organic pollutants and has a large impact on their distribution, transport, and fate in the aquatic environment. Sediment–water distribution depends on such solution parameters as pH (11, 12) and on the organic carbon fraction ( $f_{oc}$ ) (13). Higgins et al. found that the compound-specific adsorption of PFCs depended on their lipophilic and hydrophilic characteristics, and perfluorooctanesulfonamidoacetic acids (FOSAAs) were found to adsorb more strongly to sediment than PFOS (11). Volatile, neutral precursors can undergo long-range atmospheric transportation (14), whereas ionic PFCs can be transported by ocean currents (6). Sediment possibly acts as a sink for long-chain PFCs (11), but data on the partitioning of PFCs between sediment and pore water are scarce.

In the study reported here, two sediment cores were collected from Tokyo Bay, which is situated near one of the most populous areas in the world, for a determination of the PFCs in pore water and sediment. We investigated the vertical concentration profile and distribution of the PFCs in both. Furthermore, the influence of organic carbon and pH on sediment concentrations was examined. This study provides information on the current and historical contamination status of PFCs in Tokyo Bay and reconstructs the pollution history of these contaminants in the waters. To the best of our knowledge, this is the first field study to examine the partitioning behavior of PFCs between pore water and sediment.

## Experimental Section

**Sampling Campaign.** Two sediment cores were collected from Tokyo Bay using an acrylic tube (120 cm long and 12 cm i.d.) in May 2008 (cores A and B, Figure 1). These cores were sliced at 3 cm intervals for the first 9 cm for core A (6 cm for core B) and then at 2 cm intervals for up to 79 and 70 cm, respectively, using a clean stainless steel slicer and then stored in polypropylene (PP) tubes. Only the inner part of the sediment core was analyzed for PFCs to avoid contaminations from sampling. All of the samples were transported in an ice-cooled box to the lab and stored in a refrigerator at 4 °C. The sampling conditions, including total organic carbon (TOC), total nitrogen (TN), pH, oxygen reaction potential (ORP), moisture and dry density, are shown in Tables S1 and S2 of the Supporting Information.

**Sediment Dating.** The sedimentation rate was estimated from the excess  $^{210}\text{Pb}$  (dpm) in each layer and the cumulative



**FIGURE 1.** Map showing sampling locations A ( $35^{\circ}34'60''$  N/ $139^{\circ}55'01''$  E) and B ( $35^{\circ}29'18''$  N/ $139^{\circ}54'24''$  E) in Tokyo Bay, Japan.

weight ( $\text{g cm}^{-2}$ ) in core A. The average sedimentation rates of the dry matter were calculated to be  $0.76 \text{ g cm}^{-2} \text{ yr}^{-1}$  for the 1958–2008 time period, which is approximately  $1.5 \text{ cm yr}^{-1}$  for the core sections.

**Separation of Pore Water and Sediment.** Pore water was extracted from wet sediment within 72 h by centrifugation at 10000 rpm for 10 min at a constant temperature of  $10^{\circ}\text{C}$  (Avanti™ J-25 Centrifuge, Beckman, U.S.A.). The sediment was weighed before and after centrifugation to calculate the efficiency of the pore water extraction and then stored in a PP bottle (for details, see Table S3 of the Supporting Information). The pore water was then filtered through  $0.45 \mu\text{m}$  nylon syringe filters (Iwaki, Fukushima, Japan) into a PP bottle. All of the bottles were stored in a refrigerator at  $4^{\circ}\text{C}$  until analysis.

**Extraction and Analysis.** The standards and reagents used have been previously reported (15), and a full list of the PFCs analyzed is shown in Table S4 of the Supporting Information. The 20 to 96 mL pore water samples were extracted by solid-phase extraction with Oasis WAX cartridges (Waters, 150 mg,  $6 \text{ cm}^3$ ,  $30 \mu\text{m}$ ) as described by Taniyasu et al. (16). Briefly, after preconditioning with 4 mL ammonium hydroxide in methanol, 4 mL methanol, and then 4 mL Millipore water, the cartridges were loaded with 20–96 mL samples at approximately  $1 \text{ drop sec}^{-1}$ . Before loading, the pore water samples were spiked with 1 ng absolute of an internal standard (IS) mix (i.e., [ $^{13}\text{C}_4$ ]-PFBA, [ $^{13}\text{C}_4$ ]-PFOA, [ $^{13}\text{C}_5$ ]-PFNA, [ $^{13}\text{C}_2$ ]-PFDA, [ $^{13}\text{C}_2$ ]-PFUnDA, [ $^{13}\text{C}_2$ ]-PFDoA, [ $^{13}\text{C}_4$ ]-PFOS, and  $100 \mu\text{L}$  of a  $10 \text{ ng mL}^{-1}$  solution; Table S4 of the Supporting Information). 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 methanol and the second with 4 mL 0.1% ammonium hydroxide in methanol. Both fractions were reduced to  $0.5 \text{ mL}$  under a nitrogen stream and analyzed separately.

The half-dry sediment was extracted using the method described by Powley et al. (17) with a few modifications. Briefly, a 5 g sediment sample was weighed into a PP tube, and 2 mL of 100 mM sodium hydroxide in 20% Millipore water and 80% methanol was added and then soaked for 30 min. The extraction was carried out with 20 mL methanol, and 1 ng absolute IS mix was spiked. The sample was then shaken in a wrist-action shaker at 250 rpm for 30 min. After shaking, the tube was centrifuged at 3000 rpm for 15 min, and the supernatant was decanted into another PP tube. The extraction was repeated with 1 mL of 100 mM sodium hydroxide in 20% Millipore water and 80% methanol, soaked for 30 min, and then with 10 mL of methanol, shaken at 250 rpm for 30 min, and centrifuged at 3000 rpm for 15 min. Both extracts were combined and acidulated with  $0.1 \text{ mL}$  of 4 M hydrochloric acid. This extract was centrifuged again at 3000 rpm for 5 min, and an aliquot of one-eighth ( $4.15 \text{ mL}$ ) of the

supernatant was used for the cleanup with Supelclean ENVI-Carb cartridges (100 mg, 1 mL, 100–400 mesh, Supelco, U.S.A.). The conditioning of the cartridges was carried out three times with 1 mL of methanol. Afterward, the sample extract and then three times 1 mL of methanol were added to the cartridge and directly collected in another vial. Finally, the extract was reduced to  $1 \text{ mL}$  under a nitrogen stream.

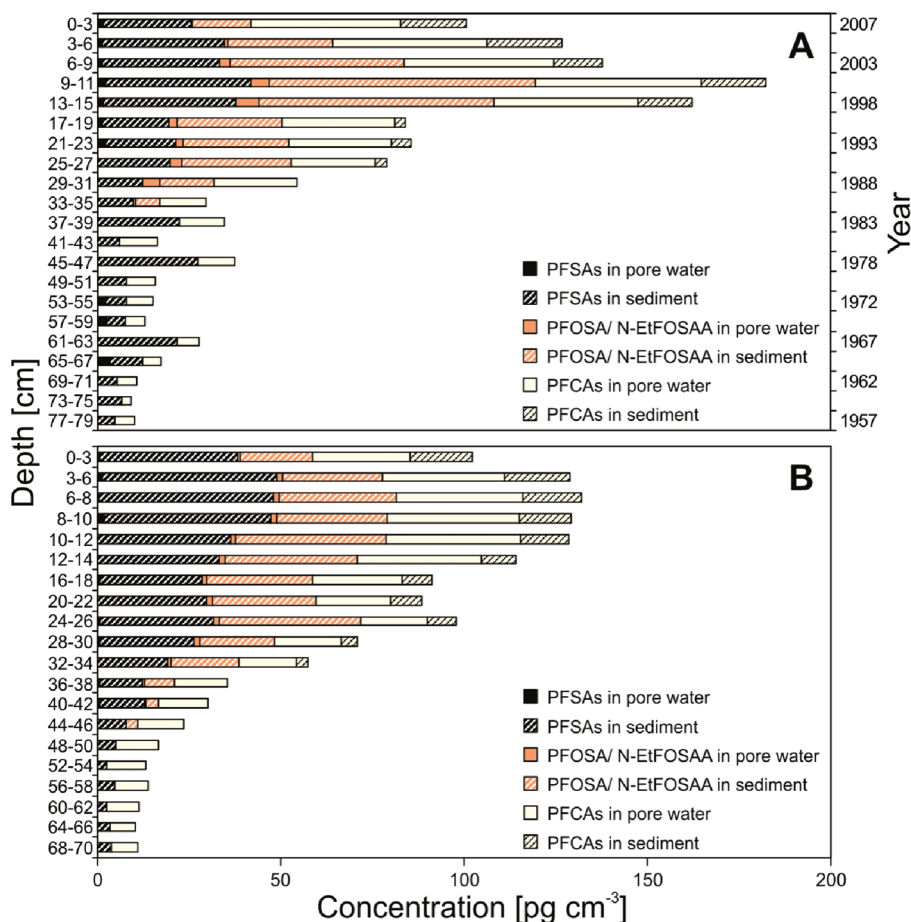
All of the extracts were analyzed for PFCs in their ionic form using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). An HP 1100 HPLC-system (Agilent Technologies, Palo Alto, CA) was equipped with a Betasil C18 column ( $2.1 \text{ mm i.d.} \times 50 \text{ mm}$  in length,  $5 \mu\text{m}$ ; Thermo Hypersil-Keystone, Bellefonte, PA), with XDB-C8 ( $12.5 \text{ mm} \times 2.1 \text{ mm}$ ,  $5 \mu\text{m}$ ; Agilent Technologies, Foster City, CA) as a guard column and a RSpak JJ-50 2D column ( $2.0 \text{ mm i.d.} \times 150 \text{ mm}$  in length,  $5 \mu\text{m}$ ; Shodex, Showa Denko K.K., Kawasaki, Japan). A triple-quadrupole mass spectrometer, supplied by Micromass (Quattro Ultima Pt, Beverly, MA), was used an electrospray ionization (ESI) interface in negative ionization mode. The flow rate was set to  $300 \mu\text{L min}^{-1}$ , and  $10 \mu\text{L}$  of the sample was injected. Details of the extraction, instrumental conditions, and quantification for PFC analysis are shown in the Supporting Information and have been described elsewhere (15).

## Results and Discussion

**Blank Contamination and Method Quantification Limits and Recoveries.** All fluorinated materials that could come into contact with the sample during sampling, sample preparation, or instrumental analysis were removed to avoid contaminations (for details, see ref 18). All procedural blanks, which were extracted in the same manner as the samples, using 100 mL of Millipore water for pore water and 1 mL of methanol for sediment analysis, were below the method quantification limits (MQLs). The MQLs were determined at a signal-to-noise ratio (S/N) of 10 and ranged between 0.1 and  $0.5 \text{ pg cm}^{-3}$  for pore water ( $50 \text{ mL}$  of the pore water sample used) and between 0.37 and  $1.86 \text{ pg cm}^{-3}$  for sediment ( $5 \text{ g}$  of the sediment sample used), depending on the sample size and relative response. The recoveries for water analysis ranged between 81% (*N*-EtFOSAA) and 128% (PFHxA), with a mean standard deviation (SD) of 3.4% ( $n = 3$ ), and for sediment between 78% (*N*-EtFOSAA) and 112% (PFHxA), with a mean SD of 5.3% ( $n = 3$ ) (Table S4 of the Supporting Information). The analysis of the sediment samples without cleanup using the Supelclean ENVI-Carb cartridges resulted in the degradation of the recoveries (Figure S1 of the Supporting Information). This could have been caused by the matrix effects, which led to signal enhancement for PFBS, PFHxS, and PFOS and to signal suppression for all other PFCs.

**Vertical Profiles.** The PFC concentrations were corrected for dry density by multiplying the concentrations measured in pore water and sediment by their observed density. The concentration of the remaining pore water in the sediment was subtracted from the sediment concentration. In the following, the concentrations in pore water and sediment (solid phase) are expressed in  $\text{pg cm}^{-3}$  to enable a direct comparison of their concentration levels. Perfluoroalkyl sulfonate (PFSA), PFOSA/*N*-EtFOSAA, and perfluoroalkyl carboxylic acid (PFCA) concentrations were observed in pore water and sediment at different depths in two sediment cores (Figure 2 and Tables S5–S8 of the Supporting Information).

In this study, 11 PFCs were found in pore water with concentration levels of  $<0.1$ – $0.54 \text{ pg cm}^{-3}$  for PFHxS,  $<0.1$ – $3.49 \text{ pg cm}^{-3}$  for PFOS,  $<0.1$ – $0.84 \text{ pg cm}^{-3}$  for TH-PFOS,  $<0.1$ – $6.26 \text{ pg cm}^{-3}$  for *N*-EtFOSAA,  $<0.5$ – $26.1 \text{ pg cm}^{-3}$  for PFBA,  $<0.1$ – $3.15 \text{ pg cm}^{-3}$  for PFPeA,  $1.17$ – $4.74 \text{ pg cm}^{-3}$  for PFHxA,  $<0.1$ – $0.45 \text{ pg cm}^{-3}$  for PFHpA,  $0.44$ – $11.0 \text{ pg cm}^{-3}$  for PFOA,  $<0.5$ – $6.29 \text{ pg cm}^{-3}$  for PFNA, and  $<0.1$ – $0.47 \text{ pg cm}^{-3}$



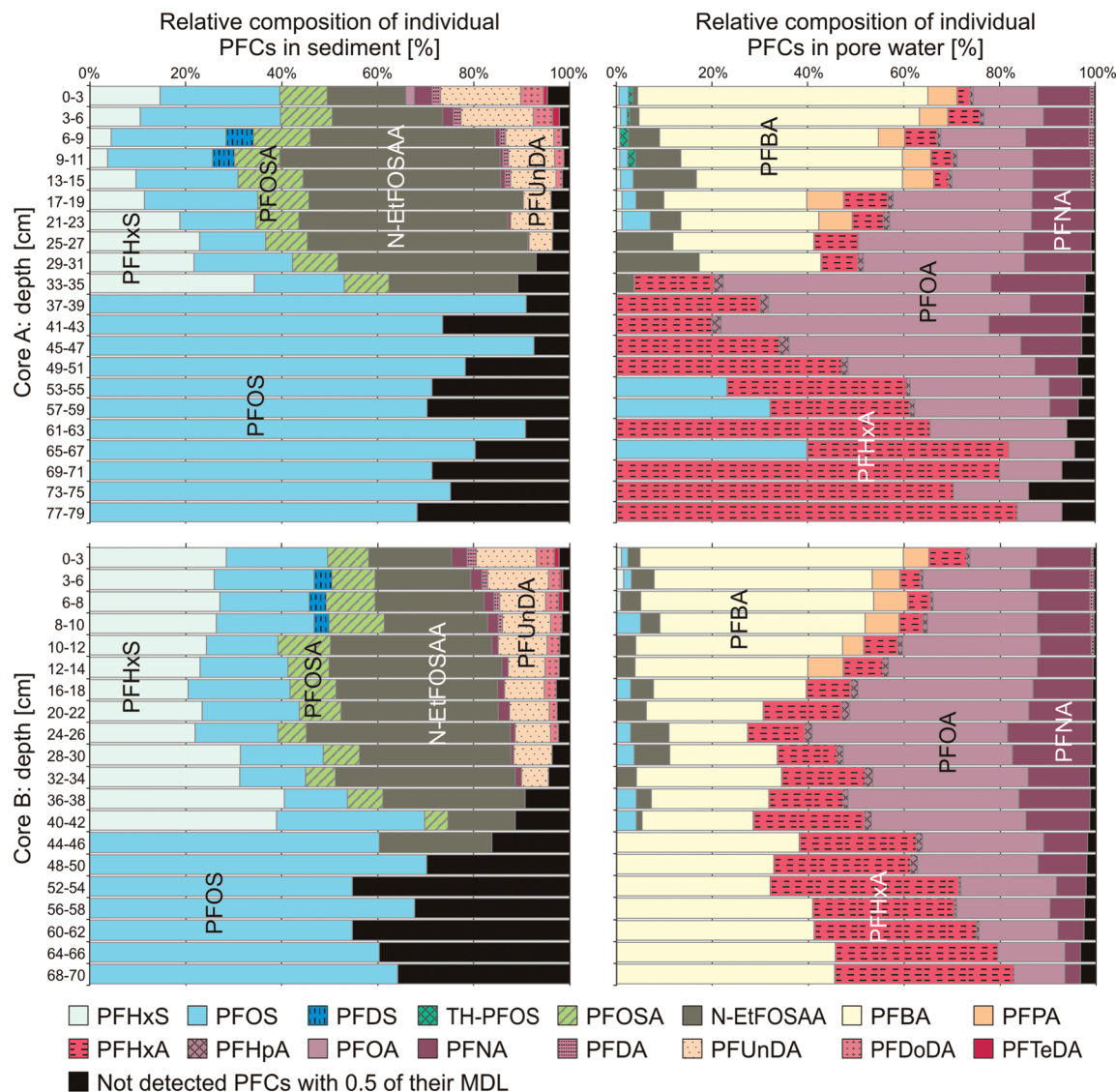
**FIGURE 2.** Vertical profile of PFASs, PFOSA/*N*-EtFOSAA, and PFCAs in pore water and sediment in  $\text{pg cm}^{-3}$  from two sediment cores (A and B) collected from Tokyo Bay, Japan.

for PFDA. To the best of the authors' knowledge, this is the first report of quantifiable concentrations of PFCs in pore water. The maximum surface water concentrations of PFHxS, PFOS, PFOA, and PFNA observed in Tokyo Bay were approximately 1 order of magnitude higher than those in pore water (6). In contrast to those in pore water, the PFCs in the sediment solid phase showed a different vertical profile. No TH-PFOS or short-chain PFCAs ( $C \leq 7$ ) were detected in the sediment, although PFDS, PFOSA, and long-chain PFCAs ( $C \geq 11$ ) were. These results correspond with the findings that with each  $\text{CF}_2$  moiety the distribution coefficient increase by 0.5–0.6 log units (11) and  $\sim 0.87$  log units (19), respectively. Ten PFCs were quantified in the sediment solid phase with a concentration range of  $<0.37$ – $26.3 \text{ pg cm}^{-3}$  for PFHxS,  $2.63$ – $28.7 \text{ pg cm}^{-3}$  for PFOS,  $<1.86$ – $6.07 \text{ pg cm}^{-3}$  for PFDS,  $<0.37$ – $16.0 \text{ pg cm}^{-3}$  for PFOSA,  $<0.37$ – $60.5 \text{ pg cm}^{-3}$  for *N*-EtFOSAA,  $<0.37$ – $1.07 \text{ pg cm}^{-3}$  for PFOA,  $<0.37$ – $2.51 \text{ pg cm}^{-3}$  for PFNA,  $<0.37$ – $1.61 \text{ pg cm}^{-3}$  for PFDA,  $<0.37$ – $12.6 \text{ pg cm}^{-3}$  for PFUnDA,  $<0.37$ – $3.34 \text{ pg cm}^{-3}$  for PFDoDA, and  $<0.37$ – $1.27 \text{ pg cm}^{-3}$  for PFTeDA. These concentrations were 1–2 orders of magnitude lower than those measured in air-dried sediment samples from the San Francisco Bay area by Higgins et al. (7). The concentrations of PFOA, PFDoDA, PFHxS, PFOS, and PFOSA found in air-dried sediment samples in the Ariake Sea and Tenjin and Katsura River in Japan were also 1–3 orders of magnitude higher (20, 21) than those found in the sediment solid phase in this study. In contrast to these studies, in only one sample PFOA was detected in the sediment solid phase from Tokyo Bay. The higher level of PFCs previously reported in sediments could be explained considering the effect of pore water.

Both cores had a similar vertical profile, with a maximum  $\Sigma\text{PFC}$  concentration at depths of 9–11 and 6–8 cm of  $182 \text{ (sediment core A)}$  and  $132 \text{ pg cm}^{-3}$  (sediment core B), respectively. Close to the surface, these  $\Sigma\text{PFC}$  concentrations were slightly lower, and after reaching their maximum, with increasing sampling depth, they rapidly decreased by a factor of 6–9. In general, PFHxS, PFOS, PFOSA, *N*-EtFOSAA, and, in a lower proportion, PFUnDA accounted for the highest proportion in the sediment, while in the deeper layers only PFOS was found. PFOSA and *N*-EtFOSAA were found only in the upper layers (up to 35 cm in depth in core A to 46 cm in depth in core B), whereas the composition of PFHxS and PFOS increased with increasing depth. Interestingly, the proportion of  $\Sigma\text{PFCs}$  increased in pore water with increasing sampling depth. In pore water, PFBA, PFOA, and PFNA dominated in the upper layers ( $<50 \text{ cm}$ ), but the composition changed in the deeper layers ( $\geq 50 \text{ cm}$ ), in which in addition to PFOA, PFHxA became the predominant compound, whereas PFBA was only predominant in core B (Figure 3).

**Fluxes and Temporal Trends.** Sediment concentration and flux, based on the dry sediment concentration, are shown for individual PFCs in sediment core A in Table 1. The fluxes were calculated using the dry sediment concentration multiplied by the density-corrected yearly sedimentation rate. The highest flux was observed for the  $\Sigma\text{PFCs}$ , with  $197 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in 2001–2002. Before and after these time periods the  $\Sigma\text{PFCs}$  decreased to  $7.1 \text{ (1956–1958)}$  and  $87.7 \text{ pg cm}^{-2} \text{ yr}^{-1}$  (2006–2008). The greatest proportion of the flux was attributable to PFOS and EtFOSAA, whereas PFOS was largely responsible for the increasing flux and EtFOSAA for the reduction of the flux before and after 2001–2002.





**FIGURE 3.** Relative composition of PFOSA and *N*-EtFOSAA and individual PFSA and PFCAs in pore water and sediment from two sediment cores (A and B) collected from Tokyo Bay, Japan. Note: The PFC concentrations, which were not detected, are shown as the sum of the half values of the method detection limit (MDL).

The calculated flux in sediment core A was used for a rough estimation of the total flux of PFCs in Tokyo Bay sediments from 1956 to 2008, assuming that the sediment surface amount was 1000 km<sup>2</sup>. On the basis of this assumption, the total flux for the 52 year period was estimated to be 28.5 kg total for  $\Sigma$ PFCs in Tokyo Bay sediments: 13.6 kg total for PFSA, 11.6 kg total for PFOSA/*N*-EtFOSAA, and 3.2 kg total for PFCAs. Direct sources of exposure from manufacture and use were estimated as the major source for POSF (22) and PFCAs (5) in the environment. Public wastewater from around 35 million people and industrial wastewater (e.g., from textiles or paper fabrics, etc.) are be considered for the contamination of the Tokyo Bay with PFCs (4). It is also possible that aqueous film-forming foams (AFFFs) reach Tokyo Bay after their use at, for example, airports (23). But a large uncertainty exists about the contribution of the indirect sources (PFC precursors and/or impurities) on the total PFC contamination in the Tokyo Bay (22).

Temporal trends were examined using ANOVA tests (SPSS 16.0 for Windows, 2007) to determine statistically significant differences (significance level  $\alpha = 0.05$ ) of the concentration level and composition pattern between 1956 and 2008 for each analyte. Data were natural-logarithm

transformed prior to statistical analysis to meet assumptions of normality and homogeneity of variances. No significant trend was observed for PFHxS, PFDA, and PFDODA ( $p > 0.073$ ) (Figure S2 of the Supporting Information), whereas concentrations of PFOS ( $p < 0.0001$ ), PFNA ( $p < 0.0001$ ), and PFUnDA ( $p < 0.001$ ) increased from 1956 to 2008, 1990 to 2008, and 1990 to 2008, respectively (Figure 4). Doubling times were calculated with  $t_{1/2} = \ln(2)/m$ , where  $m$  represents the slope of the natural logarithm transformed sediment concentration versus time. The doubling times for PFOS, PFNA, and PFUnDA were 16.1, 4.0, and 5.1 years, respectively. Similar doubling times have been found for PFNA and PFUnDA in polar bears (3.6–5.6 and 4.1–6.1 years, respectively) (24). Conversely, the PFOS doubling times reported here were longer than those reported for guillemot eggs from the Baltic Sea (7–10 years) (25), arctic ringed seals (3.0–7.1 years) (26), and polar bears (9.8–13.1 years) (24). In this study, however, the increasing trend of PFOS slowed between 2001 and 2008 and possibly reached a steady state level currently. The concentrations of *N*-EtFOSAA and PFOSA increased from 1985 to 2001 with doubling times of 4.5 and 6.3 years ( $p < 0.05$ ), respectively, but after 2001, the concentration decreased

**TABLE 1. Concentrations (pg g<sup>-1</sup> dry weight) and Estimated Fluxes (pg cm<sup>-2</sup> yr<sup>-1</sup>) of Individual PFCs in Sediment Core A from Tokyo Bay, Japan<sup>a</sup>**

depth (cm)	time interval represented	PFHxS		PFOS		PFDS		PFOSA		N-EtFOSAA		PFOA		PFNA		PFDA		PFUnDA		PFDODA		PFTeDA	
		conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux	conc.	flux
0–3	2006–2008	56	13	96	23	<5	<0.2	38	9.0	63	15	6.8	1.6	14	3.4	6.4	1.6	64	15	18	4.2	3.7	0.9
3–6	2004–2006	46	13	128	37	<5	<0.3	48	14	101	29	<1	<0.3	9.3	2.7	7.5	2.2	66	19	18	5.1	6.6	1.9
6–9	2002–2004	18	6.4	97	34	23	8.2	48	17	156	55	<1	<0.4	4.6	1.6	4.9	1.7	40	14	6.7	2.4	<1	<0.4
9–11	2001–2002	20	7.5	117	43	25	9.2	51	19	247	92	<1	<0.4	3.4	1.3	6.6	2.4	51	19	11	4.0	<1	<0.4
13–15	1998–1999	43	17	95	37	<5	<0.4	62	24	185	73	<1	<0.4	3.7	1.4	5.4	2.1	42	17	5.9	2.3	<1	<0.4
17–19	1995–1997	18	8.9	39	19	<5	<0.5	17	8.4	73	35	<1	<0.5	<1	<0.5	<1	<0.5	9.6	4.6	<1	<0.5	<1	<0.5
21–23	1993–1994	29	16	24	13	<5	<0.5	14	7.4	66	36	<1	<0.5	1.1	0.6	<1	<0.5	13	7.2	<1	<0.5	<1	<0.5
25–27	1990–1991	42	19	25	11	<5	<0.5	16	7.3	84	38	<1	<0.5	0.7	0.3	<1	<0.5	8.9	4.1	<1	<0.5	<1	<0.5
29–31	1987–1989	20	9.6	18	9.0	<5	<0.5	8.6	4.2	37	18	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5
33–35	1985–1986	18	9.7	9.9	5.3	<5	<0.5	5.0	2.6	14	7.6	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5
37–39	1982–1983	<1	<0.6	60	34	<5	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6
41–43	1979–1981	<1	<0.6	15	9.2	<5	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6
45–47	1978–1979	<1	<0.6	70	42	<5	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6	<1	<0.6
49–51	1974–1975	<1	<0.7	18	12	<5	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7
53–55	1971–1973	<1	<0.7	13	8.2	<5	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7
57–59	1969–1970	<1	<0.7	12	7.8	<5	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7
61–63	1966–1967	<1	<0.8	43	33	<5	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8
65–67	1964–1965	<1	<0.8	18	13	<5	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8
69–71	1962–1963	<1	<0.8	11	8.2	<5	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8
73–75	1959–1960	<1	<0.8	13	10	<5	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8	<1	<0.8
77–79	1956–1958	<1	<0.7	10	7.1	<5	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7	<1	<0.7

<sup>a</sup> Flux estimates are based on the dry sediment concentration and sedimentation rate at each core section; <x below the respective method quantification limit (MQL).

significantly with half-lives of 2.8 and 13.5 years ( $p < 0.05$ ), respectively (Figure 4 and Figure S2 of the Supporting Information, respectively). This may reflect increased production and emissions since the 1950s in the Tokyo Bay area and the phase out of POSF-based compounds by 3M in 2000, of which at least four companies in Japan were affected (22). Nearly the same temporal trend was observed for PFOSA in melon-headed whales (*Peponocephala electra*) stranded along the Japanese coast, with increasing concentration between 1982 and 2001/2002, followed by a decreasing concentration until 2006 (27).

It should be noted that benthic organisms can change the contamination profiles of sediment cores because of bioturbation or bioaccumulation (28). It is also possible that *N*-EtFOSAA and PFOSA can further biodegrade to PFOS, which would increase the flux of this compound (29). No groundwater flow existed at both sampling stations to a ~80 cm depth; however, horizontal pore water migration for short-chain PFCAs ( $C \leq 8$ ) is possible. In addition, pore water may have caused the migration of PFCs that had collected in deeper layers. Thus, the sediment concentrations of PFOS and *N*-EtFOSAA in the deeper layers (>30 cm) may be artificially inflated by their subsequent deposition. This could explain why a flux of PFOS is seen until 1956. However, no evidence of downward migration in pore water was observed for PFHxS, PFDS, PFOSA, or long-chain PFCAs ( $C \geq 8$ ). This suggests that any migration depends on the partitioning behavior of these compounds between pore water and sediment.

**Influence of Organic Carbon and pH on Sediment Concentrations.** Physical and geochemical characteristics of the vertical sediment profile were variable. While the TOC decreased from 0.7% to 1.7%, the pH increased from 7.3 to 7.7 with the depth. The influence of organic carbon and pH on the sorption of PFCs has been investigated (11, 13). In this study, a positive correlation was found between organic matter and concentrations of PFOS, PFOSA, and PFUnDA ( $p < 0.0001$ , Figure 5) and, with lower significance, *N*-EtFOSAA, PFNA, and PFDODA ( $p < 0.01$ ; Figure S4 of the Supporting Information). This shows that organic matter may have an influence on the vertical distribution of PFCs in the studied sediment cores. Previous studies observed a significant

correlation between the partition coefficients and organic content for PFOS, *N*-EtFOSAA, PFDA (11), and also for 8:2 fluorotelomer alcohol (13).

The concentrations of PFOS, PFNA, and PFDODA increased with decreasing pH ( $p < 0.05$ ; Figure S5 of the Supporting Information). This corresponds with the results of Higgins et al., showing increasing sorption of PFCs with decreasing pH of approximately 0.37 log units per unit pH (11). Other factors, which were not investigated in this study such as the concentration of calcium cations, could have also an influence on the sorption capacity of sediment for PFCs (11).

**Partition Coefficients.** The partitioning behavior of PFCs depends on their physicochemical characteristics as well as on sediment-specific parameters (11). *N*-EtFOSAA showed a good correlation between their concentrations in pore water and sediment ( $r^2 = 0.58$ ,  $p < 0.0001$ ; Figure S3 of the Supporting Information). No relationship was observed for the other PFCs or they were exclusively detected in pore water or sediment. Therefore, the partition coefficient was only calculated for *N*-EtFOSAA. The organic carbon normalized adsorption coefficient ( $K_{OC}$ ) was calculated with the organic carbon fraction ( $f_{OC}$ ) as described in the following.

$$K_{OC} = (c_s / c_{aq}) \times 100 / f_{OC} \quad (1)$$

where  $c_s$  is the adsorbed PFC on sediment in pg g<sup>-1</sup>,  $c_{aq}$  is the mass concentration of PFC in the aqueous phase pg cm<sup>-3</sup>, and  $f_{OC}$  is the organic carbon fraction in percentage (30). The log  $K_{OC}$  of *N*-EtFOSAA is with  $2.99 \pm 0.21$  cm<sup>3</sup> g<sup>-1</sup> in the same range as determined experimental by Higgins et al. (log  $K_{OC}$   $3.23 \pm 0.18$  L/kg<sub>OC</sub>,  $n = 5$  (11)). Further investigations on the adsorption and solution processes of PFCs are necessary.

**Environmental Significance.** Our study showed the partition behavior of PFCs between pore water and sediment in two sediment cores. Pore water concentrations of PFCs were determined for the first time. PFSAs, *N*-EtFOSAA, and PFOSA seemed to bind more strongly to sediment than PFCAs, whereas only short-chain PFCAs ( $C \leq 7$ ) could be found exclusively in pore water. These results corroborate the laboratory findings of Higgins et al. (11), and thus show that the perfluorocarbon chain length and functional group

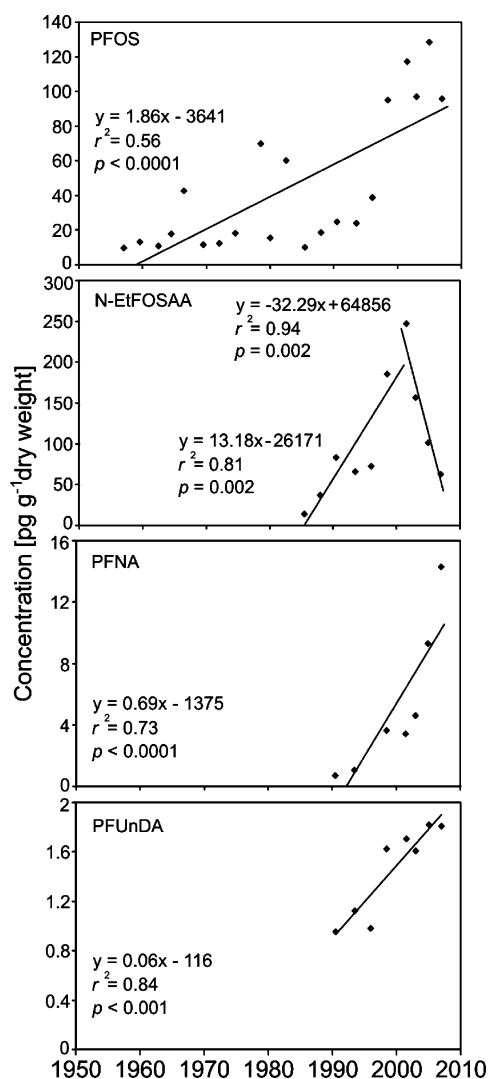


FIGURE 4. Temporal trends of PFOS, N-EtFOSAA, PFNA, and PFUnDA in sediment core A from Tokyo Bay, Japan.

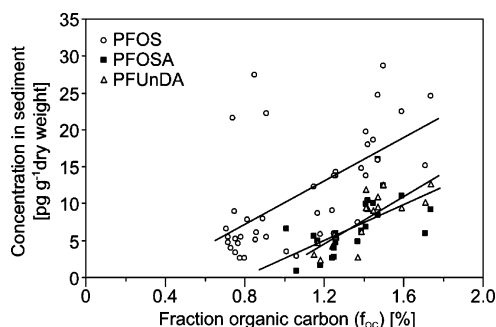


FIGURE 5. Dependence of PFOS, PFOSA, and PFUnDA concentrations in sediment on sediment fraction organic carbon ( $f_{oc}$ ).

influence partitioning behavior of PFCs in the real environment. In addition, an increasing sorption was found with increasing organic matter and decreasing pH, which correspond with experimental data (11, 19). However, other factors like geochemical parameters (e.g., metal cations, etc.) (11) or benthic organisms (e.g., degradation, bioturbated mixing, etc.) could have an influence on the partitioning behavior of PFCs in sediment. The presence of long-chain PFCAs ( $C \geq 8$ ), PFSA, PFOSA, and N-EtFOSAA in sediment suggests that they are bioavailable to benthic organisms (28) and that aquatic sediment possibly acts as a sink for these

compounds. Future work could link the pore water and sediment concentrations of PFCs to bioconcentration factors, uptake routes, and possible adverse effects. The temporal trend data presented here provide a basis for future trend studies of PFCs in sediment cores.

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## Supporting Information Available

Additional information about the sampling campaign, chemicals, analysis, method recovery rates, overview of PFC concentrations, temporal trends, and dependence of PFC concentration in sediment on fraction organic carbon and pH value. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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