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Observation of a Novel PFOS-Precursor, the Perfluorooctane Sulfonamido Ethanol-Based Phosphate (SAmPAP) Diester, in Marine Sediments

Jonathan P. Benskin,*[,†,‡] Michael G. Ikonomou,[‡] Frank A. P. C. Gobas,[§] Million B. Woudneh,[†] and John R. Cosgrove[†]

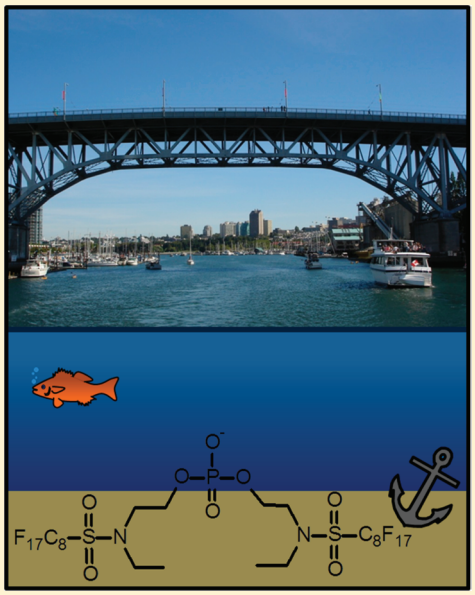
[†]AXYS Analytical Services Ltd., 2045 Mills Road West, Sidney BC, Canada, V8L 5X2

[‡]Institute of Ocean Sciences, Fisheries and Oceans Canada (DFO), 9860 West Saanich Road, Sidney BC, Canada V8L 4B2

[§]School of Resource and Environmental Management, Faculty of Applied Sciences, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Supporting Information

ABSTRACT: The environmental occurrence of perfluorooctane sulfonate (PFOS) can arise from its direct use as well as from transformation of precursors ((*N*-alkyl substituted) perfluorooctane sulfonamides; FOSAMs). Perfluorooctane sulfonamidoethanol-based phosphate (SAmPAP) esters are among numerous potential PFOS-precursors which have not been previously detected in the environment and for which little is known about their stability. Based on their high production volume during the 1970s−2002 and widespread use in food contact paper and packaging, SAmPAP esters may be potentially significant sources of PFOS. Here we report for the first time on the environmental occurrence of SAmPAP diester in marine sediments from an urbanized marine harbor in Vancouver, Canada. SAmPAP diester concentrations in sediment (40−200 pg/g dry weight) were similar to those of PFOS (71−180 pg/g). A significant ($p < 0.05$) correlation was observed between SAmPAP diester and *N*-ethyl perfluorooctane sulfonamido acetate (an anticipated degradation product of SAmPAP diester). ∑PFOS-precursor (FOSAM) concentrations in sediment (120−1100 pg/g) were 1.6−24 times greater than those of PFOS in sediment. Although SAmPAP diester was not detected in water, PFOS was observed at concentrations up to 710 pg/L. Among the per- and polyfluoroalkyl substances monitored in the present work, mean log-transformed sediment/water distribution coefficients ranged from 2.3 to 4.3 and increased with number of CF_2 units and N-alkyl substitution (in the case of FOSAMs). Overall, these results highlight the importance of FOSAMs as potentially significant sources of PFOS, in particular for urban marine environments.



INTRODUCTION

Among the numerous per- and polyfluoroalkyl substances (collectively "PFASs") observed in the global environment, perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) is typically the most common. Due to concerns regarding its persistence in humans[1,2] and the environment,[3,4] as well as the adverse health outcomes linked to this compound,[5] PFOS was voluntarily phased out by its primary manufacturer in 2001/2002, and in 2009 was added to the list of Persistent Organic Pollutants (POPs) regulated by the International Stockholm Convention. However, use exemptions listed under *Annex B* of the Convention have resulted in ongoing manufacture and use of PFOS in developing countries.[6] Although a rapid decline in PFOS concentrations has been observed in some humans and wildlife over the past decade,[1,7,8] samples from other parts of the world indicate a continued increase or no change in levels following the 2002 phase-out.[2,9−12]

The potential sources of PFOS are numerous and not well characterized.[13] In addition to emissions from direct manufacture and use, the environmental occurrence of PFOS can arise from both abiotic[14,15] and biological[16,17] degradation of precursors (i.e., (*N*-alkyl substituted) perfluorooctane sulfonamides; FOSAMs). These substances are structurally and functionally diverse, and only a fraction of them are routinely monitored.[13] In addition to their direct use as commercial products, FOSAMs can arise as unintentional

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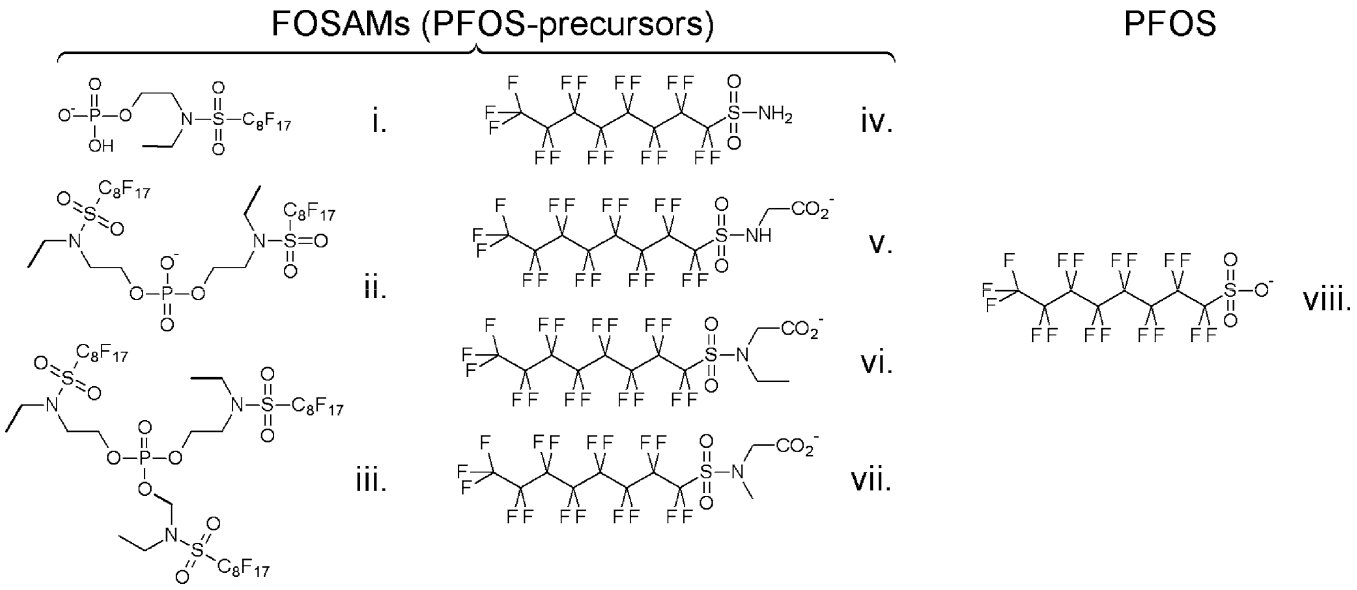

Figure 1. Structures of SAmPAP mono-, di-, and tri-esters (i–iii, respectively), FOSA, FOSAA, EtFOSAA, MeFOSAA (iv–vii, respectively), and PFOS (viii) examined in the present study. Other FOSAMs are possible.

synthetic byproducts during the manufacture of commercial polymers and phosphate surfactants (1–2% of final product).[18] These latter substances contain $C_8F_{17}SO_2N$- units bound to a polymeric backbone or phosphate moiety via ester linkages which, if hydrolyzed, could lead to the formation of PFOS. In fact, pre-2002 production volume estimates[19,20] indicate that FOSAM-based commercial polymers and surfactants may be among the largest potential historical reservoirs of PFOS of all FOSAM or PFOS-containing commercial substances, but to date these substances have never been detected in the environment, and there are limited data available on their stability.[21]

FOSAM-based phosphate surfactants were first introduced in 1974 by the 3M Co. for use in food contact paper and packaging.[22] Formulations typically consisted of 10% mono-, 85% di-, and 5% tri-substituted phosphate esters of *N*-ethyl perfluorooctane sulfonamido ethanol ($(C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2-)_nPO_4$, n = 1–3; collectively termed "SAmPAPs",[23] Figure 1, structures i, ii, iii, respectively).[18] In 1997, sales of FC-807 (a commercial SAmPAP formulation) represented the highest quantity of PFOS-equivalents sold by 3M out of all PFOS-precursor (i.e., FOSAM) or PFOS-containing commercial substances.[20] The 3M Co. ceased production of these materials along with other perfluorooctane sulfonyl fluoride-based products in 2002[24] but since then a resurgence in their production has occurred in Asia.[6,13] Howard and Muir[25] recently included SAmPAP mono- and diesters among their predictions of 610 commercially relevant, persistent, and bioaccumulative organics (Table S1, SI) but to date these substances remain unquantified in any environmental samples. In fact, only two studies (both examining human sera), have attempted to monitor for SAmPAP diesters,[23,26] and only one of these reported detection, albeit below quantification limits. In contrast, polyfluoroalkyl phosphoric diesters (diPAPs; e.g. $C_8F_{17}CH_2CH_2O)_2PO_2^-$), which have replaced SAmPAPs in the food packaging and paper industry, have been detected at elevated concentrations in human sera[23,27] and environmental samples,[27,28] and have been shown to biodegrade to fluorotelomer alcohols and perfluoroalkyl carboxylates (PFCAs) in wastewater treatment plant sludge and in rats.[29−31]

Recent studies of marine sediments from Baltimore Harbor (MD),[32] the San Francisco Bay area,[32] and Tokyo Bay (Japan)[33] have reported potential SAmPAP transformation products (e.g., *N*-ethyl perfluorooctane sulfonamidoacetate; EtFOSAA)[33] at concentrations similar to or exceeding the concentration of PFOS. Due to their extensive historical production and their anticipated partitioning to sediment (sediment/water partition coefficients tend to increase with number of CF_2 units),[34,35] it is reasonable to hypothesize that the occurrence and biodegradation of SAmPAPs in sediment may contribute to the elevated concentration of other FOSAMs and PFOS in urban marine sediments. In this work, we examined water and sediment samples from an urban marine inlet in Vancouver, BC, Canada for the presence of SAmPAP diester and other FOSAMs; as well as perfluoalkyl sulfonates (PFSAs) and PFCAs. Spatial distribution, sediment–water partition coefficients, and potential sources are discussed. To our knowledge this is the first study which has quantified SAmPAP diester in any environmental samples and provides baseline information on the occurrence and disposition of this historical, high-production volume chemical.

EXPERIMENTAL METHODS

Standards and Reagents. A full list of reagents is provided in the SI. Perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluorooctanoate (PFOA), and PFOS were all ≥97% purity and were purchased from Sigma-Aldrich (Milwaukee, WI). Perfluorooctane sulfonamide (FOSA) was purchased from SynQuest Laboratories (Alachua, FL). Perfluorodecanesulfonate (PFDS), perfluorooctane sulfonamido acetate (FOSAA), *N*-methyl perfluorooctane sulfonamidoacetate (MeFOSAA), EtFOSAA, and all isotopically labeled internal standards (see Table S2, SI) were purchased from Wellington Laboratories (Guelph, ON, Canada). A solution of FC-807 commercial product containing SAmPAP

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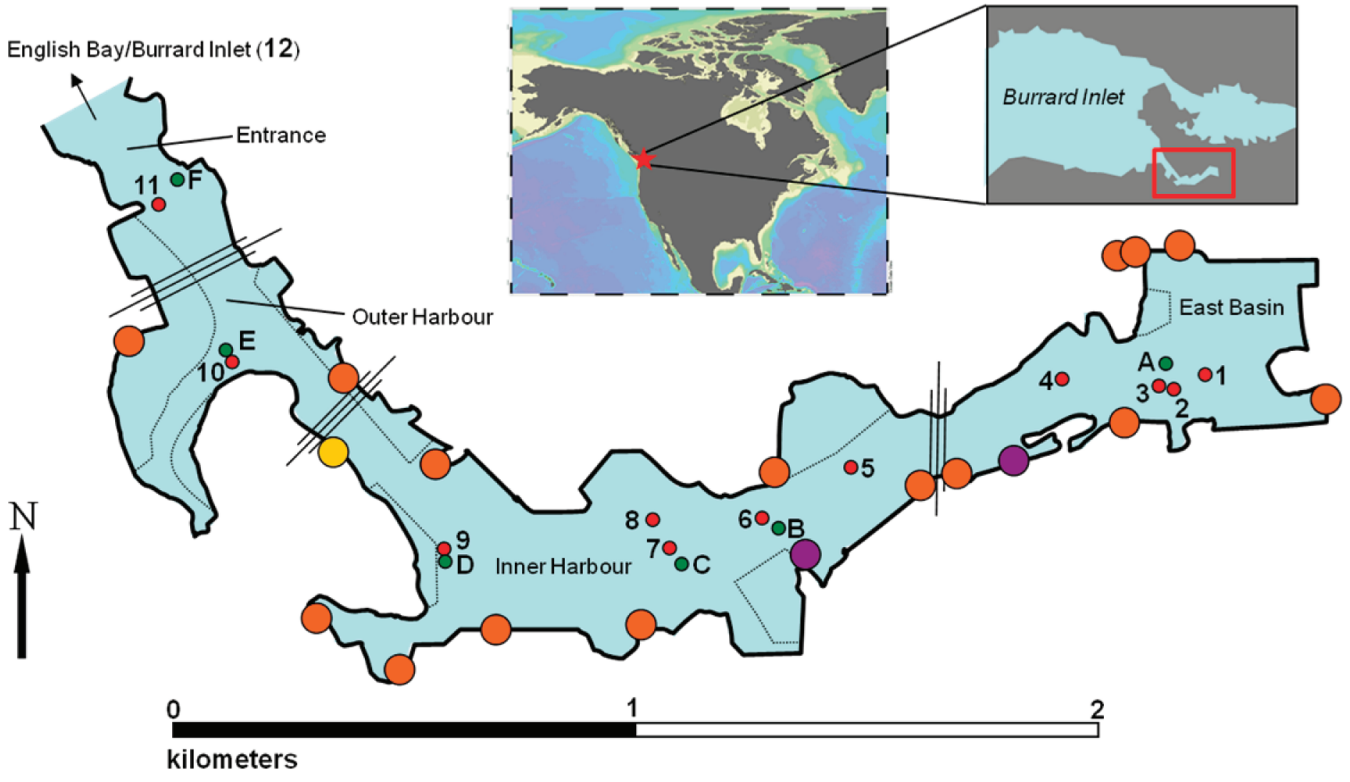

Figure 2. Map of False Creek Harbor (Vancouver, BC, Canada) showing water (letters/green circles) and sediment (numbers/red circles) sampling locations. Orange circles represent stormwater outfalls, yellow circle indicates a permitted effluent outfall, and purple circles denote combined sewer overflows. Dotted lines denote local marinas while parallel lines represent bridges. Tidal flow was east to west during sampling.

diester at a concentration of 30% (w/v) in isopropanol/water was provided by Timothy Begley (U.S. Food and Drug Administration).

Sample Collection. Samples were collected using a 14-ft skiff on August 3, 2011 from False Creek, a relatively small (4.0 × 0.3 km) and shallow (mean depth of 8 m) marine embayment of Burrard Inlet in the city of Vancouver, BC (population ~612,000; ~2.2 million in greater Vancouver). A total of 18 effluent outfalls exist in False Creek, including 1 permitted effluent, 2 sewer overflows, and 15 stormwater outfalls (Figure 2). In addition, the harbor contains 7 marinas, including houseboat mooring, and a mix of industrial, commercial, and residential buildings. Tides were ebbing (east to west flow) throughout the sampling trip (high tide 3.9 m at 08:48 hrs, low tide 1.5 m at 14:58 hrs). The sample area was divided into 7 study regions: east basin, inner harbor-east, inner harbor-central, inner harbor-west, outer harbor, and entrance (Figure 2). Within each region, between 1 and 4 individual sediment samples were collected using a petit ponar and spoon (the latter rinsed with MeOH and HPLC-grade water between each use) and then transferred to high-density polyethylene (HDPE) bottles (top 0.5−1.0 cm layer, later split into triplicate). Subsurface water samples (1 L, n = 3 samples/region; <1 m depth) were collected by hand using HDPE bottles. Additional sediment was collected from reference sites in Burrard Inlet north of downtown Vancouver (49.30° N, 123.09° W) and from underneath a marine salmon farm located off Althorp Point on Hardwicke Island, BC (50.47° N, 125.80° W). All samples were kept on ice during sampling and then frozen at −20 °C for 4 weeks prior to extraction. Stability tests indicated negligible biodegradation of precursors under these conditions (see SI for details).

Extraction, Treatment, and Analysis of Water and Sediment Samples. All seawater samples (1 L) and blanks were spiked with isotopically labeled internal standards (Table S2, SI) and extracted using a previously developed solid-phase extraction (SPE) method,[36] details of which are provided in the SI. Samples were not filtered prior to extraction based on previous reports of chain-length dependent sorption of PFASs to glass fiber or nylon filters (45−60% sorption for PFDS, PFTriDA, and PFTeDA using Nylon and 25−30% sorption for PFUnDA, PFDoDA, PFTrDA, PFTeDA, and PFDS using glass fiber).[37] In-house filter sorption tests have demonstrated that diPAPs are also prone to filter sorption (up to 60%, depending on chain length and filter material). Since the bias introduced by filtration is expected to be far greater than that potentially introduced by quantifying suspended solid PFAS concentrations as part of the aqueous phase, whole water was extracted.

Sediments were dried in a desiccator, homogenized, then 4 g was transferred to a 50-mL polypropylene (PP) centrifuge tube and spiked with isotopically labeled internal standards (Table S2, SI). Sediment samples were extracted in triplicate using a method modified from Powley et al.[38] (see SI for details).

Analysis of extracts was accomplished by a previously developed high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) method[39] which utilized a Dionex HPLC coupled to a API 5000Q triple quadrupole mass spectrometer (Applied Biosystems/Sciex, Concord, ON, Canada). Mass spectral data were collected under negative ion, multiple reaction monitoring (MRM) mode. Ions used for quantification and confirmation are stated in Table S2 (SI). Details of HPLC gradient conditions and optimized instrument parameters can be found in the SI.

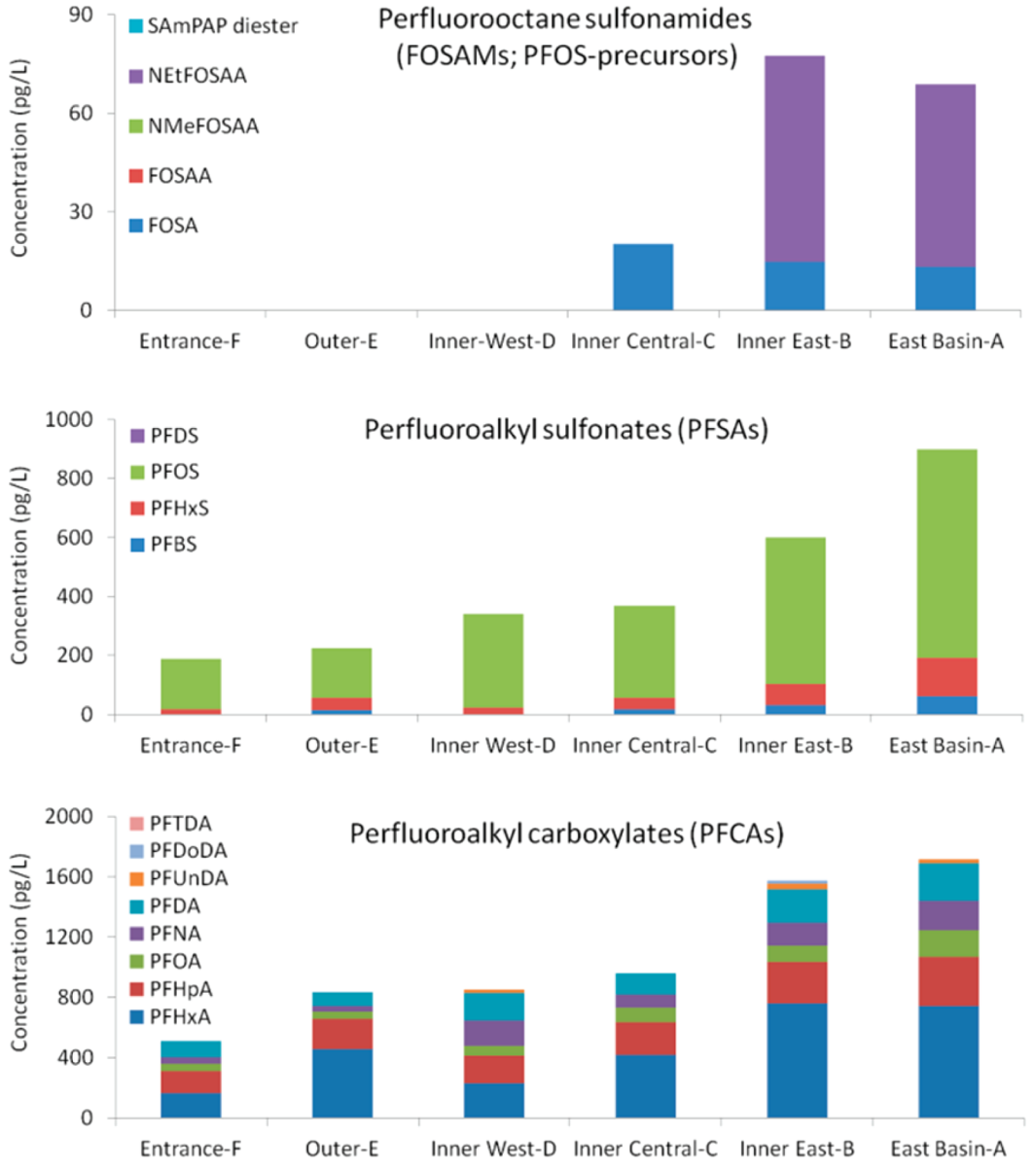

Figure 3. Mean (n = 3) PFAS concentrations in False Creek Seawater. Letters correspond to locations in Figure 2.

PFAS Quantification and QA/QC. All PFASs in water and sediment samples were quantified by isotope dilution using nonextracted, solvent calibration curves. A full list of native PFASs and their corresponding internal standards is provided in Table S2. All concentrations are reported as the mean ± standard error of the mean (SEM; $\sigma/n^{1/2}$).

Standard reference materials (SRMs) for PFASs in water or sediment are not currently available. In the absence of such materials, we evaluated the accuracy of our extraction procedures using spike/recovery experiments by spiking 2 ng of PFASs into 1 L of seawater (n = 3) or 4 g sediment (n = 3) collected from outside False Creek, and extracting these samples along with unspiked samples. Method recoveries from these spiked, extracted samples were assessed relative to a standard prepared in MeOH.

Field blanks consisted of Millipore water (3 × 1 L) which was transported to False Creek and then processed along with samples. Lab blanks (n = 3) were also prepared by spiking internal standards directly onto SPE cartridges (i.e., Millipore water was not used). For sediment, MeOH rinsate from 3 empty HDPE screw-cap bottles (the same type used for sediment collection) underwent the sediment extraction procedure. Additional sediments collected from two reference sites (Burrard Inlet and Althorp Point) were processed in triplicate alongside samples from False Creek.

An authentic SAmPAP diester standard is not commercially available, thus we relied on a sample of FC-807 commercial formulation for optimization of instrument parameters and quantification of samples. This formulation was provided as a solution containing SAmPAP diester at a concentration of 30% w/v. Although reported concentrations of SAmPAP diester in the present work have been corrected for chemical purity, these remain estimates only and require further validation once an authentic standard becomes commercially available.

Observation of SAmPAP diester in samples was confirmed by (a) matching the retention time of peaks observed in the sample to that of our reference material (FC-807), and (b) observation of multiple product ions (i.e., m/z 1203/526 ($[C_8F_{17}SO_2NC_2H_5]^-$; m/z 1203/650, $[C_8F_{17}SO_2N(C_2H_5)$-$C_2H_2OPO_3H]^-$; and m/z 1203/169; $[C_3F_7]^-$) in ratios

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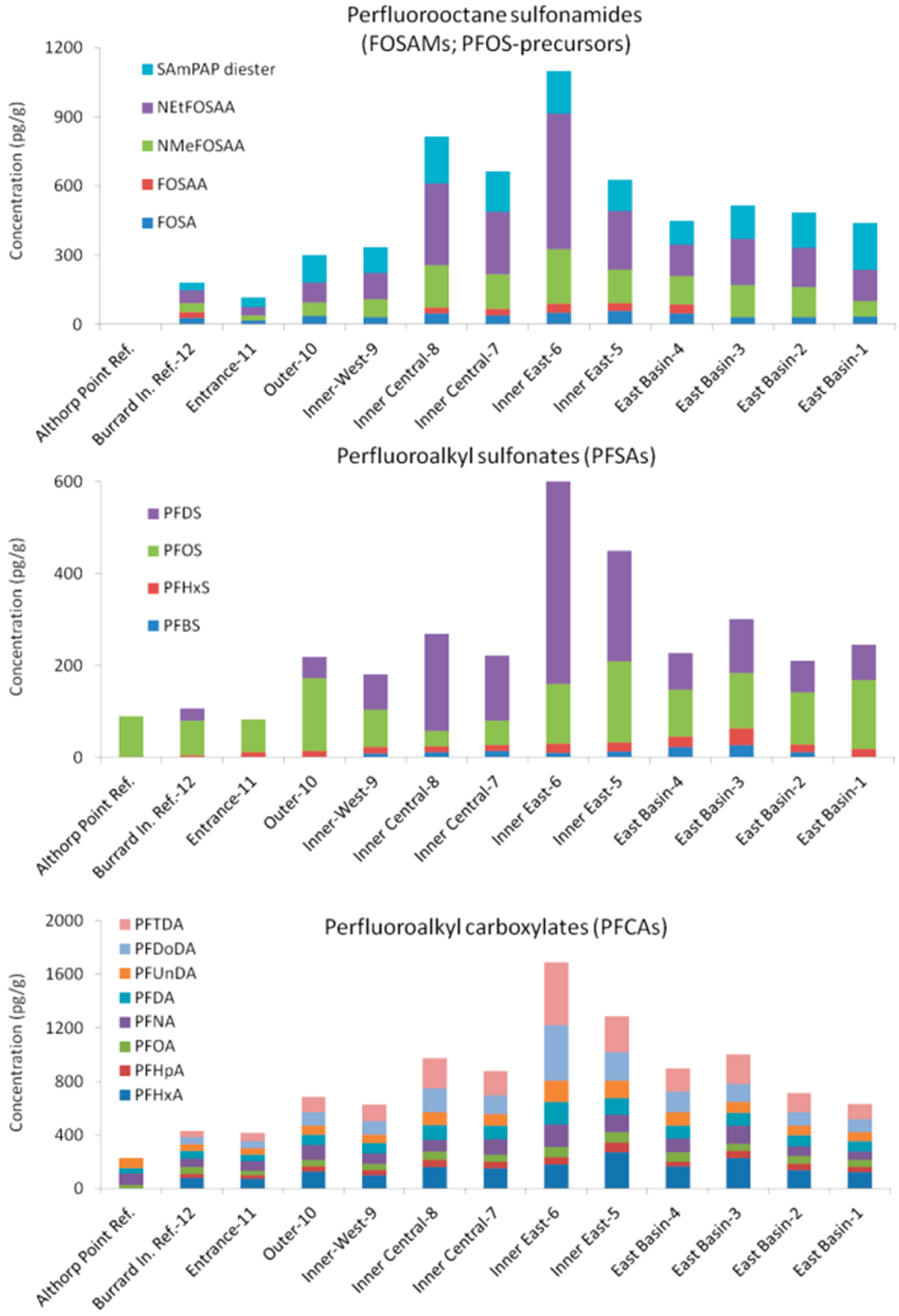

Figure 4. Mean (n = 3) PFAS concentrations in False Creek sediment. Numbers correspond to locations in Figure 2.

consistent with our reference material. The concentration of SAmPAP diester in samples generated using a solvent calibration curve was confirmed by a standard addition experiment using east basin-3 sediment extracts, details of which can be found in the SI.

Calculation of Field-Based Sediment–Water Distribution Coefficients. Field-based sediment–water distribution coefficients (K_D, L/kg) were calculated for each of the six sampling regions of False Creek (i.e., east basin, east inner harbor, central inner harbor, west inner harbor, outer harbor, and entrance; Figure 2) by dividing the concentration in sediment (pg/kg dry weight) by the concentration in water (pg/L). Based on the shallow average depth of False Creek (8 m), we assumed that PFAS concentrations in subsurface samples would be approximately equivalent to concentrations near the bottom. When more than one sediment sample was

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collected within a single region (e.g., east basin contained 4 sediment sampling sites), the mean concentration of all samples from that region was used for calculation of the K_D. Concentrations less than the method detection limit (MDL) were not included in the calculation of the mean unless all samples from that region were <MDL, in which case a concentration of $^1/_2$ MDL was used for obtaining a lower or upper bounds estimate of the K_D. When concentrations in both water and sediment were <MDL, the log K_D could not be calculated. Mean log K_Ds were calculated by averaging the log K_Ds from individual sites (i.e., geometric mean). Error represents ± SEM.

Statistical Analysis. SigmaPlot Version 11.0 (Systat Software, Inc.) was used to test for significant ($p < 0.05$) correlations between concentrations of individual PFASs in sediment. Because these data were approximately normally distributed ($p \geq 0.05$, Shapiro−Wilk test), statistical associations were tested using Pearson Product Moment.

RESULTS AND DISCUSSION

QA/QC. Spike/recovery experiments indicated the extraction procedures produced acceptable results for most compounds, with average recoveries of 108 ± 6% for sediment (Table S3) and 102 ± 7% for water (Table S4). Concentrations in samples were not recovery-corrected. Recoveries were lower for extraction of PFTeDA and PFDS from water (56 ± 16% and 40 ± 7%, respectively) and FOSAA from sediment (42 ± 2%), possibly due to a lack of isotopically labeled internal standards for these PFASs. PFDA displayed high recoveries from water (171 ± 15%), which was surprising considering an exact isotopically labeled internal standard was used to track potential matrix enhancement and procedural losses for this compound, and water blanks only contained low levels of PFDA. Further discussion on the effect of high PFDA recoveries on K_D values is presented in the Field-Based Sediment−Water Distribution Coefficients section. MDLs, calculated based on the concentration in 1 L of water or 4 g of sediment producing a signal-to-noise ratio of 3:1, were 10−50 pg/L in water and 1.8−14 pg/g in sediment (Tables S3 and S4).

Sediment blanks ($n = 3$) contained low but reproducible levels of PFOS (22 ± 2.2pg/g) and FOSA (25 ± 0.4 pg/g) which were subtracted from concentrations in all sediment samples. In water field blanks, PFOS (138 ± 17 pg/L) and PFDA (100 ± 5.7 pg/L) were the dominant PFASs detected; concentrations of remaining PFASs were <80 pg/L (Table S4). The mean concentration of PFASs observed in water field blanks was subtracted from all samples. SAmPAP diester was not observable in any blanks processed by either our water or sediment extraction methods, nor was it observable in the Althorp Point reference sediment.

PFAS Congener Profiles in Marine Water and Sediments. All 17 PFASs monitored (8 PFCAs, 4 PFSAs, and 5 FOSAMs) were detected in water and/or sediment from False Creek, with ∑PFAS concentrations ranging from 0.70 to 2.7 ng/L in water (Figure 3 and Table S5) and 0.61 to 3.4 ng/g in sediment (Figure 4 and Table S6). To our knowledge, this is the first report on the occurrence of PFASs in water and sediment from the Pacific Northwest.

In water samples, PFCAs with chain lengths shorter than PFUnDA (i.e., PFHxA, 170−760 pg/L; PFHpA, 140−320 pg/L; PFOA, 50−180 pg/L; PFNA, 41−190 pg/L; and PFDA, 89−250 pg/L) as well as PFSAs (PFHxS, 18−130 pg/L; PFOS, 170−710 pg/L) were the predominant congeners in water samples. Longer chain-length PFCAs (i.e., PFUnDA, PFDoDA and PFTeDA), PFDS, and all FOSAMs were only occasionally detectable at concentrations of a few tens of pg/L in water. Concentrations reported here are similar to those observed in coastal areas of Asia and Europe. For example, Cai et al. reported 0.13−3.3 ng/L ∑PFASs in coastal water from the East and South China Seas, which they attributed specifically to industrial activities on the Yangtze River.[40] Among individual PFASs measured in that study, PFHxA (<27.2−304 pg/L) and PFHpA (ND−422 pg/L) concentrations were similar to those found in False Creek, while PFOA (37.5−1541 pg/L) and PFBS (23−941 pg/L) were much higher in Chinese waters. In coastal Germany, ∑PFAS concentrations (9.36 −31.2 ng/L) were higher than those in False Creek, with the major congeners, PFBS, PFOS, and PFHxA, present at concentrations of 3.38−17.7, 0.69−3.95, and 0.47−9.56 ng/L, respectively.[41] The authors pointed to wastewater treatment plants or industrial activities on the Weser or Elbe rivers as potential sources of PFASs. PFOA was also a major congener (2.67−7.84 ng/L) in German waters, consistent with observations in coastal China.

The lower concentrations of PFASs (in particular PFOA) in False Creek may be due to less industrialization relative to sites in Germany or Asia (False Creek contains primarily residential housing and marinas, along with minor industrial activities). The 2002 phase-out of PFOA by the major manufacturer and recent emissions reductions strategies may also contribute to low observed PFOA concentrations in False Creek. Further work is needed to idnetify regional point sources, as well as the extent to which highly populated areas (e.g., Vancouver, Seattle, Portland) contribute to PFAS concentrations in the ambient environment of the Pacific Northwest.

In sediment, PFHxA (80−270 pg/g), PFDoDA (50−410 pg/g), PFTeDA (60−470 pg/g), PFDS (<2−470 pg/g), EtFOSAA (40−590 pg/g), MeFOSAA (20−240 pg/g), and SAmPAP diester (40−200 pg/g) were consistently among the major PFASs detected, while concentrations of other individual PFASs were typically <170 pg/g (Table S6, SI). In comparison, individual PFAS concentrations from Burrard Inlet and Althorp Point reference sediments were <81 and <89 pg/g, respectively, among all congeners (Table S3, SI). PFAS profiles in Burrard Inlet reference sediment were similar to those in False Creek, which is not surprising considering both sites are probably subject to PFAS contamination from downtown Vancouver. Water flow at the Burrard Inlet Reference site is less restricted than in False Creek, thus the lower concentrations relative to False Creek may reflect increased dilution from Pacific waters. The observation of PFOS and C8−C11 PFCAs in Althorp Point reference sediment (collected underneath a marine salmon farm) may be a result of atmospheric deposition,[42] or alternatively from the use of fish feed, which is a known source of contaminants in farmed fish.[43] This latter hypothesis is supported by studies of farmed fish from Asia[44,45] as well as Europe and South America,[45] where PFOS and PFUnDA were often the major PFASs detected, consistent with our observations in Althorp reference sediment.[45] PFOS-precursors (FOSA, FOSAA, EtFOSAA, MeFOSAA, and SAmPAP diester) were not detected at the Althorp Point reference site.

PFAS congener profiles observed in False Creek sediment were similar to those reported for elsewhere in North America as well as Tokyo Bay (Japan). For example, sediments from Baltimore Harbor and around the San Francisco Bay area

contained PFOA, PFNA PFDA, PFUnDA, PFDoDA, and PFTeDA at concentrations ranging from nondetect to several hundred pg/g, while FOSAA, MeFOSAA, and EtFOSAA were observed at concentrations from nondetect to over one thousand pg/g.[32] In that work, the concentration of EtFOSAA exceeded that of PFOS (1060 versus 846 pg/g, respectively) in sediments from Baltimore Harbor, consistent with the present study. Tokyo Bay sediments contained lower concentrations of individual PFCAs (<1−66 pg/g for PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTeDA) and PFDS (<5−25 pg/g) but similar levels of PFHxS (<1−56 pg/g), PFOS (10−128 pg/g), FOSA (<1−62 pg/g), and EtFOSAA (<1−247 pg/g) compared to False Creek.[33] Similar to Baltimore Harbour and False Creek, sediments collected from Tokyo Bay (dated 1985−2004) displayed higher concentrations of EtFOSAA compared to PFOS. The various profiles observed in sediment may reflect regional differences in manufacturing, use, and emission of PFASs, but also the various factors influencing the partitioning of PFASs from water to sediment (i.e., pH, salinity, organic carbon, etc.).[34,46] Further discussion on the occurrence of FOSAMs and PFOS in sediments is provided in the Occurrence of SAmPAP Diester in False Creek section.

Spatial Distribution of PFASs in False Creek. ∑PFAS concentrations in water were highest in the east basin (2700 ± 13 pg/L), and decreased moving west into the inner (1600 ± 330 pg/L) and outer (1100 ± 31 pg/L) harbors of False Creek (Figure 3, SI Table S5). The lowest ∑PFAS water concentrations were observed at the entrance to False Creek (700 ± 12 pg/L). Most PFASs which were routinely detectable in water shared this general trend, with the exception of PFHxA, PFHpA, PFBS, and PFHxS, which decreased from the east basin to the entrance of False Creek, but also displayed a spike in concentration in the outer harbor (site E). Similarly, PFNA, PFDA, and PFUnDA concentrations decreased seaward out of False Creek but displayed a spike in inner harbor-west (site D).

In contrast to water samples, maximum ∑PFAS concentrations in False Creek sediment were observed in the eastern inner harbor (site 6; 3400 ± 37 pg/g), and decreased to the east and west of this site (1300−2400 pg/g in samples 1−5, and 610−2100 pg/g in samples 7−11; Figure 4, SI Table S6). PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, PFDS, EtFOSAA, MeFOSAA all displayed this trend, while maximum concentrations of other PFASs (PFBS, PFHxS, PFOA, PFOS, FOSAA, and SAmPAP diester) were observed between east basin and inner harbor-central, with lower levels at the entrance of False Creek and the Burrard Inlet reference site (Figure 4). Maximum sediment concentrations of PFHxA, PFHpA, and FOSA were less pronounced and were located further east (site 5, inner harbor-east) than maxima observed for other PFASs.

There are numerous potential sources that could be contributing to the apparent divergent trends in water and sediment ∑PFAS concentrations in False Creek. One possibility is that most PFASs are emitted via the sewer overflow outfall in the eastern inner harbor (near samples 5 and 6; Figure 2), where the more hydrophobic PFASs (e.g., PFDS, PFTeDA, SAmPAP diester, etc.) partition directly to sediment, with decreasing concentrations east and west of this location (as was observed). Shorter chain length PFASs (i.e., comparatively less hydrophobic) such as PFHxA and PFHpA are expected to partition primarily to water, allowing for transport into the east basin, explaining the elevated concentrations of these congeners in water from this region. Such chain-length dependent partitioning between water and sediment have been reported by others.[34] PFASs in east basin water may be further concentrated by lower mixing volume and/or increased residency time of this water, but also from decreased salinity, which tends to reduce K_Ds, keeping PFASs in the water column.[47] As water in False Creek is gradually flushed west toward Burrard Inlet, PFAS concentrations in the water are expected to decrease (as observed) due to dilution but also due to increased partitioning to sediment (from higher water salinity). The latter hypothesis would also explain the spike in concentrations in sediment observed in inner harbor east, relative to east basin and sites further west. Although salinity was not measured on this particular sampling trip, measurements made on a prior sampling trip (April 2011) indicated a considerable salinity gradient exists between the east basin (∼17 practical salinity units (p.s.u.)), and the entrance to False Creek (∼24 p.s.u.). Further discussion on the partitioning behavior of PFASs is discussed in the Field-Based Sediment−Water Distribution Coefficients section.

Occurrence of SAmPAP Diester in False Creek. SAmPAP diester was observed in all sediments (with the exception of Althorp Point reference sediment) at concentrations of 100−200 pg/g (mean 150 pg/g) at sites 1−10 (east basin to outer harbor), 40 pg/g at site 11 (entrance), and 32 pg/g at site 12 (Burrard Inlet reference site). This is slightly lower than the sediment concentration of EtFOSAA (86−590 pg/g for sites 1−10, <55 pg/g for 11 and 12), similar to the concentrations of MeFOSAA (60−240 pg/g in sites 1−10, <40 pg/g for 11 and 12), and PFOS (30−180 pg/g in sites 1−10, <80 pg/g for 11 and 12), and typically above the concentrations of FOSA and FOSAA (<60 pg/g in samples 1−10, <30 pg/g for 11 and 12). The concentration of SAmPAP diester in sediment from east basin-3 determined using isotope dilution (150 ± 13 pg/g) was very similar to the value determined by standard addition (140 ± 12 pg/g), demonstrating an absence of matrix-induced signal enhancement or suppression (Figure S1).

To the best of our knowledge, this is the first report in which SAmPAP diester has been quantified in environmental samples. In fact, only two prior studies have attempted to monitor for SAmPAP diester, and both focused on human sera. The first examined North American samples collected in 2009 and while SAmPAP diester was not detected EtFOSAA concentrations of up to 0.17 ng/mL were reported. The second study utilized single-donor samples from two German cities from 1982 to 2009 (Munster) and 1995−2009 (Halle) and SAmPAP diester was observed intermittently (∼30−80% frequency) between 1982 and 2005, but at concentrations below method quantification limits.[26] In that work, EtFOSAA concentrations of up to ∼4.4 ng/mL were observed. The lack of quantifiable amounts of SAmPAP diester in both these studies (but considerable EtFOSAA concentrations) may be related to the hydrophobicity of SAmPAP diester, which could hinder uptake or possibly even favor partitioning to lipid-rich tissues as opposed to protein-rich tissues (the latter of which is common for most PFASs). These are speculative hypotheses and clearly further work is needed to elucidate the disposition of this substance in humans and wildlife. Nonetheless, it is notable that D'eon et al. measured the 10:2 diPAP (a current use phosphate-based surfactant) at concentrations of up to 0.93 ng/mL in human sera,[27] and this substance is only slightly smaller than SAmPAP diester on a molecular weight basis (1189 versus 1203 g/mol, respectively).

SAmPAP diester concentrations in sediment were only significantly ($p < 0.05$) correlated with MeFOSAA and EtFOSAA, while FOSA, FOSAA, EtFOSAA, and MeFOSAA concentrations were all significantly correlated with one another. PFOS was not correlated with any FOSAM (including SAmPAP diester) in sediment, possibly indicating that the major source of PFOS in False Creek sediments is from direct use (i.e., not precursor-derived). The observed correlation between SAmPAP diester and alkyl-substituted FOSAAs may point to a common source, or in the case of EtFOSAA, degradation of SAmPAP diester (Figure S2, SI). Although there are few data pertaining to SAmPAP degradation, unpublished work by the 3M Co. indicated that SAmPAP monoester is rapidly dephosphorylated by human and rat hepatocytes to yield *N*-ethyl perfluorooctane sulfonamido ethanol, which can subsequently degrade to form EtFOSAA and PFOS.[48,49] MeFOSAA is not an anticipated degradation product of SAmPAP diester, thus the correlation between these two substances in False Creek sediment is surprising. MeFOSAA is formed from oxidation of *N*-methyl perfluorooctane sulfonamido ethanol (MeFOSE), which arises as a manufacturing byproduct (or potentially a degradation product) of MeFOSE-based acrylate polymers.[13] These polymers have never been detected in the environment and their stability is unknown, but analogous fluorotelomer alcohol-based acrylate polymers have been shown to degrade in soils.[50] Alternatively, MeFOSE-based phosphate esters may arise as residuals during the manufacture of SAmPAP esters, but this requires further investigation.

Field-Based Sediment–Water Distribution Coefficients. Mean log K_D (i.e., geometric mean of the K_D based on $n = 6$ sites ± SEM) calculated in False Creek ranged from 2.3 to >4.2 for PFCAs, 2.3 to >4.4 for PFSAs, and >3.1 for FOSAMs (Table S8, SI). In general, the log K_D of PFASs increased with increasing number of CF_2 units or *N*-alkyl substitution (in the case of FOSAMs), consistent with reports by others[34,35] (Figure S3, SI). Exceptions to this were PFDA (log K_D = 2.7 ± 0.07) and PFHpA (log K_D = 2.3 ± 0.04), which displayed slightly lower log K_D values than expected, relative to other PFCAs. The lower K_D for PFDA may be a function of the high extraction recoveries (171%) in water. After correcting for these high recoveries, an average log K_D of 3.0 ± 0.07 was obtained for PFDA, which is closer to the log K_D values of PFNA (3.0 ± 0.12) and PFUnDA (>3.7 ± 0.08).

Among FOSAMs, log K_D values increased with increasing *N*-alkyl substitution, with the exception of FOSA (>3.6 ± 0.08), which had a higher log K_D than FOSAA (>3.1 ± 0.04). The presence of FOSAA's carboxylate moiety (which exists as a deprotonated anion at environmental pH) likely improves solubility in water, resulting in a decrease in the observed K_D relative to FOSA. The log K_D for SAmPAP-diester was >4.3 ± 0.10, but could be much larger since this value represents a lower bounds estimate determined using 0.5× the MDL in water.

Log K_D values calculated here are consistently higher than those calculated for water and sediment in Ontario (Canada),[51] but similar to values determined in The Netherlands,[35] China,[46] and Japan[33] for some PFASs. For example, mean log K_D values of 2.89 ± 0.53 and 2.87 ± 0.23 were calculated for PFNA and PFDA in The Netherlands, compared to 3.0 ± 0.12 and 2.7 ± 0.07, respectively, in the present work. Likewise, PFOS log K_D values of 2.88–3.67, 2.35, and 2.4 have been reported in China,[46] The Netherlands,[35] and France,[52] respectively, similar to the mean ($n = 6$) log K_D of PFOS determined in the present study (2.5 ± 0.12). Table S7 (SI) provides further comparison of K_D values determined in the present study versus others. It is acknowledged that in cases where 0.5 × MDL is used in place of nondetects, the true K_D may be much higher (in the cases of water nondetects) or lower (in the case of sediment nondetects) than the estimated values. K_D is known to be influenced by organic carbon content, pH, and salinity, which were not examined in the present work, but may help to explain the differences in apparent K_D values between these studies.

Environmental Implications. The extent to which precursors contribute to overall exposure of humans and wildlife to PFOS is currently a source of considerable debate. Both Vestergren et al.[53] and Fromme et al.[54] predicted that most PFOS in humans arises from exposure to PFOS-precursors in high exposure scenarios. Armitage et al.[55] suggested that the rapid decline of PFOS observed in some Arctic marine biota[7,8] following the 2002 phase-out could only be explained by exposure from uptake and biotransformation of atmospherically transported precursors which had partitioned to the water. Müller et al.[56] also alluded to the significance of precursors in calculation of perfluoroalkyl acid (PFAA) biomagnification and trophic magnification factors.

In the present work, the importance of precursors as potentially significant sources of PFOS for benthic organisms was highlighted by ∑PFOS-precursor (FOSAM) concentrations in sediment exceeding PFOS concentrations by a factor of 2–24 (120–1100 pg/g for FOSAMs versus 71–180 pg/g for PFOS; Figure S4, SI). Considering that 96 PFOS-related (primarily FOSAM) substances were originally nominated along with PFOS to the Stockholm Convention,[57] the actual ∑PFOS-precursor concentration in False Creek sediment may, in fact, be much larger. While most of these substances have been phased-out in North America, a total of 66 PFOS-related substances (including SAmPAP diester) are reportedly manufactured today in China.[6] Only a handful of these substances have been measured in the environment and overall, very little is known about their stability.

■ ASSOCIATED CONTENT

Supporting Information

Further details on materials and methods, sampling locations, PFAA water and sediment concentrations, and sediment/water partition coefficients. This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jbenskin@axys.com; phone: +1 (250) 655-5800; fax: +1 (250) 655-5811.

Notes

The authors declare no competing financial interest.

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