Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in Marine Sediments

Supporting Information

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Standards and reagents

HPLC-grade methanol (MeOH) and water were obtained from EMD Chemicals (Gibbstown, NJ). HPLC-grade acetonitrile (ACN) and ammonium hydroxide (28%) were obtained from Anachemica Chemicals Inc. (Montreal, QC). Formic Acid (90%) was obtained from J.T. Baker (Phillipsburg, NJ). Ammonium formate (>99%) and Supelclean EnviCarb (120/400 mesh) were obtained from Sigma Aldrich (St. Louis, MO).

Extraction, treatment and analysis of water and sediment samples

PFASs were extracted from 1L of sea water using a previously developed solid-phase extraction (SPE) method,[1] as follows: After spiking samples with mass-labelled internal standards (Table S2, SI), samples were loaded onto Oasis WAX cartridges (150 mg, 6 cc, 30 mm; Waters, Milford MA), which were preconditioned with 5 mL MeOH and 5 mL Millipore water prior to use. Samples were loaded at a rate of 2 drops/second after which cartridges were washed with 5 mL 0.1% formic acid in water and dried under vacuum for 5 min. SPE cartridges were eluted with 14 mL of ACN followed by 5mL of 0.1% ammonium hydroxide in MeOH. Each eluent was used to rinse the empty sample bottle prior to addition to the cartridge. The combined eluants were reduced under nitrogen to 1 mL and a portion was transferred to microvial for analysis by HPLC-MS/MS.

Sediments were dried in a desiccator, homogenized, and then 4g was transferred to a 50mL polypropylene (PP) centrifuge tube and spiked with mass-labelled internal standards (Table S2, SI). Sediment samples were extracted in triplicate using the following method, modified from Powley et al.[2] After adding 10mL of MeOH, the sample was vortexed for 1 min, centrifuged, and then the MeOH was transferred to a clean centrifuge tube. This was repeated

two more times (3 extractions total) and the combined extracts were reduced to 1 mL under nitrogen. Following addition of 50 mg of ENVI-Carb (120/400 mesh; Sigma Aldrich, Oakville ON), the extracts were vortexed, centrifuged, and a portion of the supernatant was transferred to microvial for analysis by HPLC-MS/MS.

PFAS quantification was accomplished by a previously developed high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) method[3] which utilized a Dionex HPLC coupled to a API 5000Q triple quadrupole Mass Spectrometer (Applied Biosystems / Sciex, Concord, ON, Canada). Briefly, extracts (10 μL) were injected onto a Ascentis Express F5 Column (2.7 μm, 90Å, 10 cm × 2.1 mm, Sigma-Aldrich) equipped with an Ascentis Express F5 guard column (2.7 μm, 5.0 mm x 2.1 mm), both of which were maintained at 30 °C. Two Waters Xterra C18 columns (each 5 μm, 4.6 mm x 30mm) connected in series were placed directly upstream of the injector to separate PFASs originating from the LC pump from those injected onto the analytical column. The mobile phase consisted of 0.1% ammonium formate / 0.3 % formic acid in water (solvent A) and 100% MeOH (solvent B) maintained at a flow rate of 250 μL/min. The starting mobile phase composition was 90% A which was held for 1 min, followed by a decrease to 40% A by 3 min, then 12% A by 14min and finally 0% A by 14.5min. The column was held at 0% A for 2 min before being returned to starting conditions. A diverter valve (VICI Valco Canada, Inc., Brockville, ON) was placed downstream of the analytical column to divert flow to waste for the first 8 min of the run, after which time the flow was redirected to the mass spectrometer. 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).

Quantification of SAmPAP diester by standard addition

The SAmPAP diester standard addition experiment was accomplished as follows: four separate portions of east basin-3 sample extract were spiked with 0, 1.2, 2.4, or 6.0 ng of SAmPAP diester (5µL spike into 200µL extract volume; quantities corrected for chemical purity), then analyzed individually. A linear regression was performed using the response of each spiked sample (plotted on the y-axis), versus the amount of SAmPAP diester added (plotted on the x-axis). The quantity of SAmPAP diester in the unspiked extract was then determined by the intersection of the line with the x-axis.

Stability of FOSAMs in marine sediments

Bacteria present in False Creek sediments are known to be biologically active,[4] thus it was important to assess whether biodegradation of FOSAMs could occur during sample storage. Stability tests involving SAmPAP diester incubated with marine sediments indicated negligible losses after 4 weeks at 4°C, demonstrating that degradation of SAmPAP diester during sampling and long-term storage at -20°C was negligible. Minor degradation of perfluorooctane sulfonamidoethanol ($C_8F_{17}SO_2NH(C_2H_5)C_2H_4OH$) was observed under these conditions (estimated half life >100 days), but this is not expected to have affected the profiles significantly during sampling or under long-term storage conditions at -20°C.

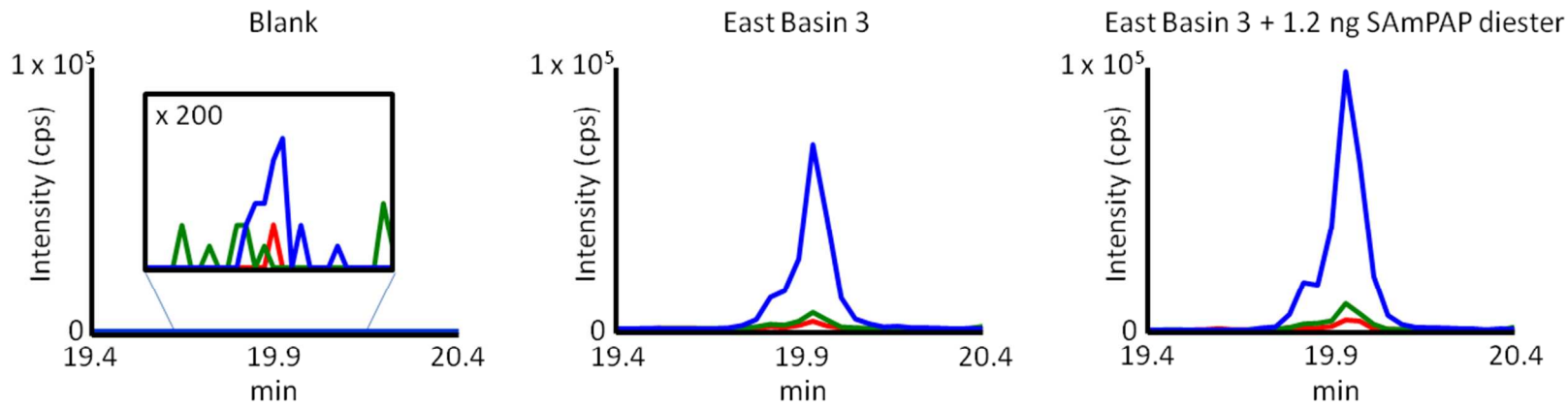

Figure S1. SAmPAP chromatograms in procedural blank, East Basin 2 and East Basin 2 following standard addition. Blue trace represents *m/z* 1203/526, green trace represents *m/z* 1203/169, and red trace represents *m/z* 1203/650. The shoulder of the SAmPAP diester peak likely represents branched isomer impurities arising from the electrochemical fluorination (ECF) manufacturing process which were not fully separable by our LC-method.

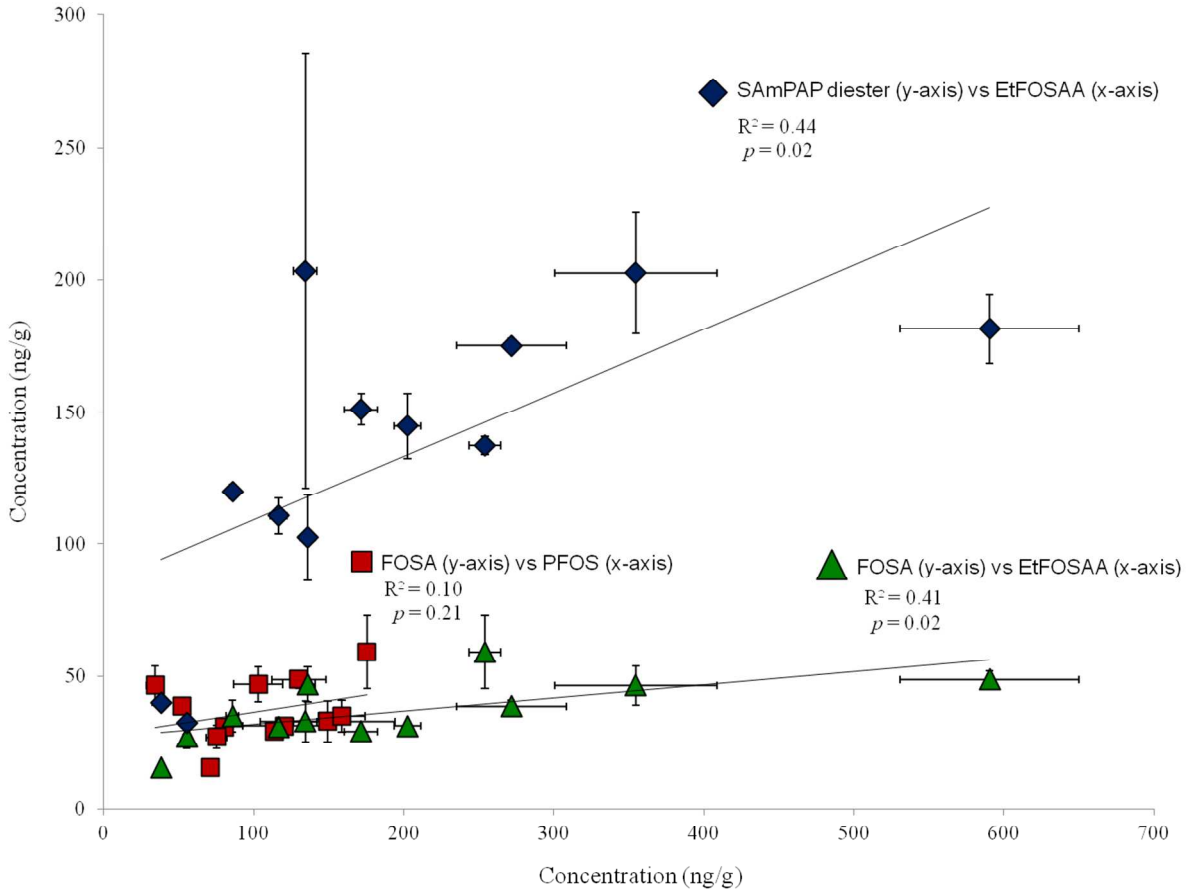

Figure S2. Correlations between concentrations of individual PFASs (PFOS, FOSA, EtFOSAA, SAmPAP diester) in False Creek sediments.

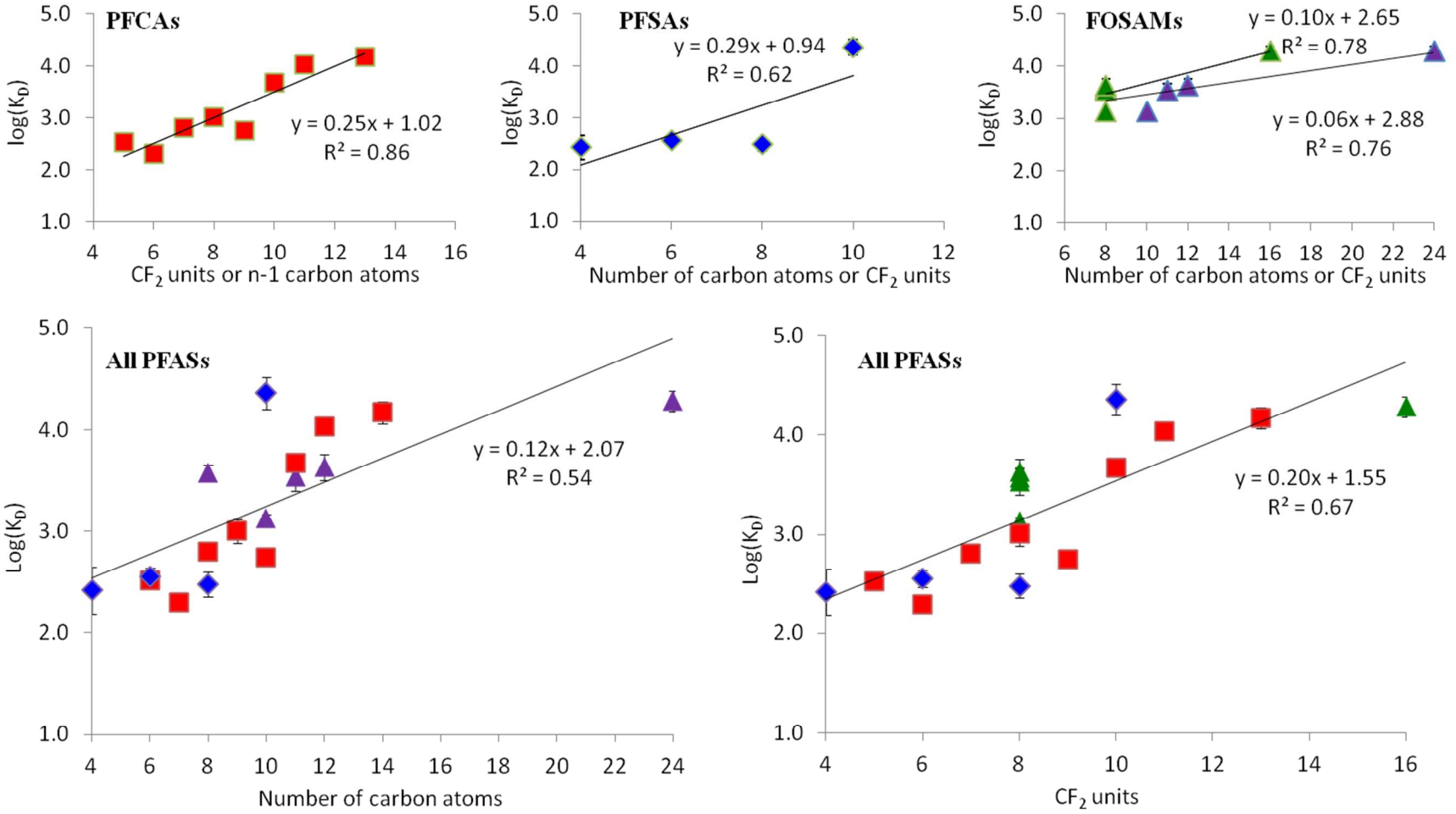

Figure S3. Log(K_D) values versus number of carbon atoms or CF2 units for perfluoroalkyl carboxylates (PFCAs; red squares), perfluoroalkyl sulfonates (PFSAs; blue diamonds), and perfluorooctane sulfonamides (green triangles denote Log(K_D) versus number of CF_2 units, purple triangles denote Log(K_D) versus number of carbon atoms). Error bars represent standard error of the mean.

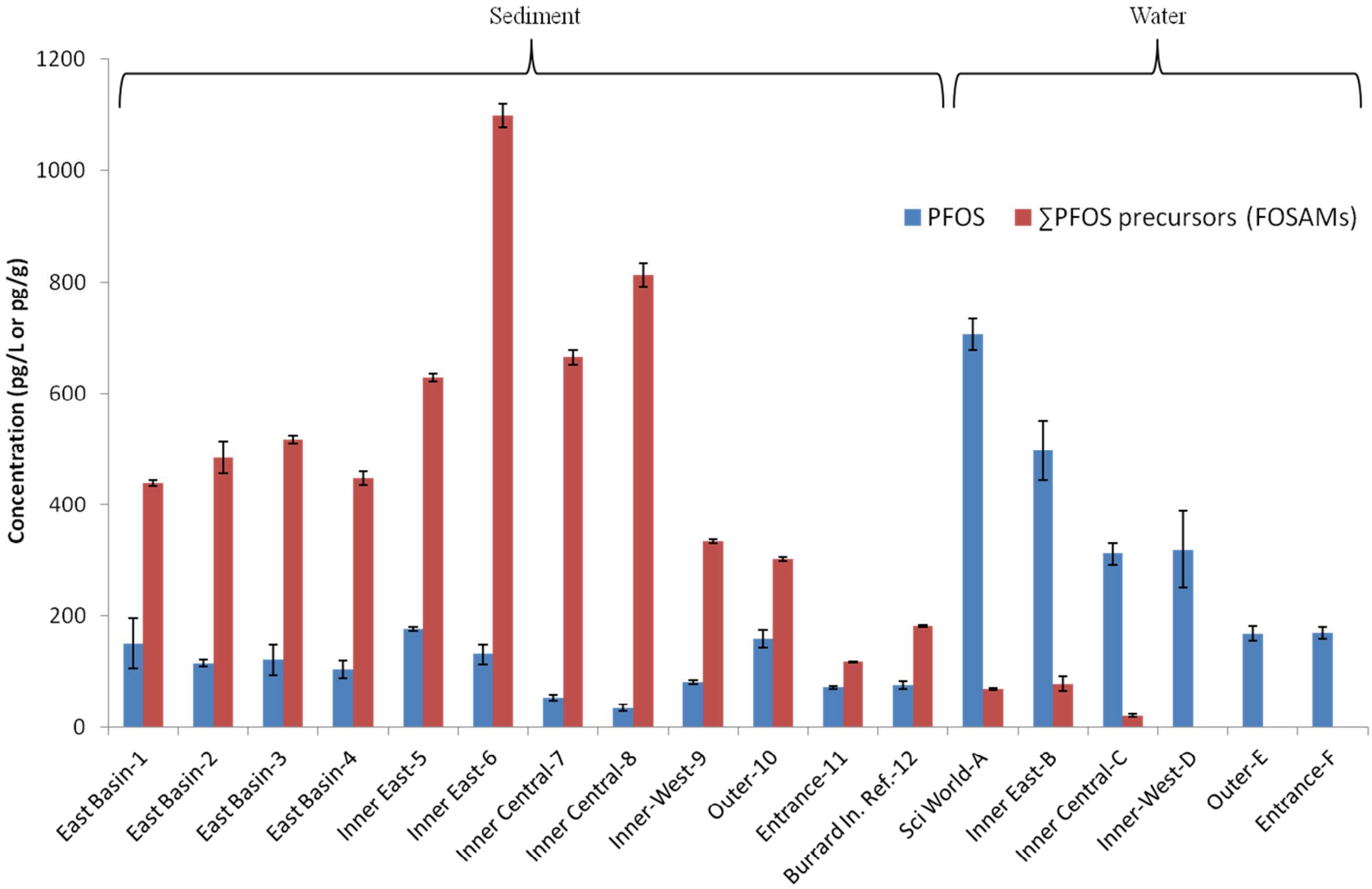

Figure S4. Figure showing ∑PreFOS+PreFOS precursor (i.e. sum of FOSA, FOSAA, EtFOSAA, NMeFOSAA, SAmPAP diester) versus PFOS concentrations.

Table S1. Physico-Chemical properties of SAm-PAP mono- and di-esters predicted by Howard and Muir[5]

	CAS #	P_{vap} (mmHg)	Atmospheric oxidation $t_{1/2}$	Log K_{aw}	Log K_{ow}	Log K_{oa}	BCF	LC_{50} (mg/L)
SAmPAP diester	002965-52-8	1.78×10^{-10}	0.16	-3.84	16.16	20.00	3	Mysid shrimp 96hr $LC_{50}=5.14\times10^{-16}$
SAmPAP monoester	067969-69-1	2.06×10^{-8}	0.25	-18.31	5.61	23.92	6	Mysid shrimp 96hr $LC_{50}=5\times10^{-3}$

Table S2. Per- and polyfluorinated compounds examined in the present study, chemical formulae, precursor, product and confirmation ions, and number of isomers observed.

Class	Perfluorinated compound (acronym)	Chemical Formula	Precursor Ion (*m/z*)	Quantiative Product Ion (*m/z*)	Qualitative Product Ion (*m/z*)	Surrogate
Perfluoroalkyl sulfonates	Perfluorobutane sulfonate (PFBS)	$C_4F_9SO_3^-$	299	80	99	^{13}C-PFOS
	Perfluorohexane sulfonate (PFHxS)	$C_6F_{13}SO_3^-$	399	80	99	^{13}C-PFOS
	Perfluorooctane sulfonate (PFOS)	$C_8F_{17}SO_3^-$	499	80	99, 130, 419	^{13}C-PFOS
	Perfluorodecane sulfonate (PFDS)	$C_{10}F_{21}SO_3^-$	599	80	99	^{13}C-PFOS
Perfluoroalkyl carboxylates	Perfluorohexanoate (PFHxA)	$C_5F_{11}CO_2^-$	313	269	119	^{13}C-PFHxA
	Perfluoroheptanoate (PFHpA)	$C_6F_{13}CO_2^-$	363	169	319	^{13}C-PFOA
	Perfluorooctanoate (PFOA)	$C_7F_{15}CO_2^-$	413	369	169, 219, 119	^{13}C-PFOA
	Perfluorononanoate (PFNA)	$C_8F_{17}CO_2^-$	463	419	219	^{13}C-PFNA
	Perfluorodecanoate (PFDA)	$C_9F_{19}CO_2^-$	513	469	219	^{13}C-PFDA
	Perfluoroundecanoate (PFUnDA)	$C_{10}F_{21}CO_2^-$	563	519	219	^{13}C-PFDA
	Perfluorododecanoate (PFDoDA)	$C_{11}F_{23}CO_2^-$	613	569	169	^{13}C-PFDA
	Perfluorotetradecanoate (PFTeDA)	$C_{13}F_{27}CO_2^-$	713	669	169	^{13}C-PFDA
Perfluoroalkyl sulfonamides	Perfluorooctane sulfonamide (FOSA)	$C_8F_{17}SO_2NH_2$	498	78		^{13}C-FOSA
	Perfluorooctane sulfonamideo acetate (FOSAA)	$C_8F_{17}SO_2NH(CH_2CO_2H)$	556	498	419	d_5-EtFOSAA
	N-methyl perfluorooctane sulfonamido acetate (MeFOSAA)	$C_8F_{17}SO_2N(CH_3)CH_2CO_2^-$	570	419	512	d_5-EtFOSAA
	N-ethyl perfluorooctane sulfonamido acetate (EtFOSAA)	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CO_2^-$	584	419	526	d_5-EtFOSAA
	Bis (N-ethyl perfluorooctane sulfonamido ethanol) phosphate (SAm-PAP diester)	$(C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2O)_2\,PO_2^-$	1203	526	650, 169	^{13}C-8:2 diPAP
Isotope-labelled internal standards	$^{13}C_4$-perfluorooctanesulfonate (^{13}C-PFOS)	$C_8F_{17}[1,2,3,4\text{-}^{13}C_4]SO_3^-$	503	80	99	
	$^{13}C_2$-perfluorohexanoate (^{13}C-PFHxA)	$C_5F_{11}[1,2\text{-}^{13}C_2]CO_2^-$	315	270		
	$^{13}C_4$-perfluorooctanoate (^{13}C-PFOA)	$C_7F_{15}[1,2,3,4\text{-}^{13}C_4]CO_2^-$	417	372		
	$^{13}C_5$-perfluorononanoate (^{13}C-PFNA)	$C_8F_{17}[1,2,3,4,5\text{-}^{13}C_5]CO_2^-$	468	423		
	$^{13}C_2$-perfluorodecanoate (^{13}C-PFDA)	$C_9F_{19}[1,2\text{-}^{13}C_2]CO_2^-$	515	470		
	$^{13}C_8$-perfluorooctane sulfonamide (^{13}C-FOSA)	$C_8F_{17}[1,2,3,4,5,6,7,8\text{-}^{13}C_8]SO_2NH_2$	506	78		
	d5-N-ethyl perfluorooctane sulfonamido acetate (d_5-EtFOSAA)	$C_8F_{17}SO_2N(CD_2CD_3)CH_2CO_2^-$	589	419	531	
	$^{13}C_4$-Bis(1H,1H,2H,2H perfluorooctyl phosphate (^{13}C-8:2 diPAP)	$(C_8F_{17}{}^{13}C_2\,H_4O)_2PO_2^-$	993	79		

Table S3. MDLs, % recoveries, blank and reference site concentration for sediment. Concentrations above the MDL in reagent blanks were subtracted from reference sediments.

Analyte	Sediment MDL (pg/g), 4g	Sediment Reagent Blank pg/g ±SEM (*n*=3)	Althorp Reference sediment pg/g ±SEM (*n*=3)	Burrard Inlet Reference sediment pg/g ±SEM (*n*=3)	% Recovery, 4g sediment ± SEM (*n*=3)
PFHxA	14	<14	<14	81±13	99 ± 5
PFHpA	10	<10	<10	27±3.6	110 ± 10
PFOA	6.4	<6.4	29 ± 7	56±8.0	99 ± 8
PFNA	10	<10	86 ± 12	62±7.4	135 ± 11
PFDA	10	<10	38 ± 5	57±2.2	135 ± 7
PFUnDA	4.8	<4.8	75 ± 12	50±1.0	150 ± 12
PFDoDA	4.7	<4.7	<4.7	52±1.0	146 ± 9
PFTeDA	4.8	<4.8	<4.8	47±0.6	119 ± 8
PFBS	1.8	<1.8	<1.8	<1.8	113 ± 5
PFHxS	2.2	<2.2	<2.2	4.5±6.8	104 ± 4
PFOS	2.1	22 ± 2.2	89 ± 10[1]	75±6.9[1]	96 ± 3
PFDS	2.8	<2.0	<2.0	26±1.9	90 ± 4
FOSA	2.2	25 ± 0.4	<2.0[1]	27±4.3[1]	80 ± 4
FOSAA	13	<13	<13	26±0.5	42 ± 2
MeFOSAA	10	<10	<10	40±2.8	95 ± 4
EtFOSAA	10	<10	<10	55±2.6	99 ± 5
SAmPAP diester	5.0	<5.0	<5.0	32±2.4	134 ± 4

[1]Blank subtracted.

Table S4. MDLs, % recoveries and blank concentrations in water.

Analyte	Water MDL (pg/L), 1L	Lab Blank pg/L ± SEM (*n*=3)	Field Blank pg/L ± SEM (*n*=3)	% Recovery, 1L seawater ± SEM (*n*=3)
PFHxA	30	<30	64 ± 6.4	114 ± 7
PFHpA	30	11 ± 3.9	11 ± 3.1	115 ± 5
PFOA	10	56 ± 1.5	59 ± 2.1	105 ± 5
PFNA	40	<40	<40	143 ± 8
PFDA	30	63 ± 11	100 ± 5.7	171 ± 15
PFUnDA	20	47 ± 2.5	80 ± 1.4	90 ± 3
PFDoDA	20	<20	<20	71 ± 10
PFTeDA	20	<20	<20	56 ± 16
PFBS	10	<10	<10	114 ± 9
PFHxS	10	12 ± 1.0	25 ± 4.3	105 ± 6
PFOS	20	90 ± 11	138 ± 17	100 ± 4
PFDS	10	<10	<10	40 ± 7
FOSA	10	20 ± 0.3	42 ± 1.1	99 ± 4
FOSAA	50	<50	<50	112 ± 5
MeFOSAA	50	<50	<50	90 ± 2
EtFOSAA	50	<50	<50	93 ± 2
SAmPAP diester	12	<12	<12	115 ± 7

Table S5. Mean (*n*=3 replicates/ location ± standard deviation about the mean), blank-corrected water concentrations (pg/L) in False Creek Harbour.

		Sampling Location					
	MDL	**Entrance-F**	**Outer Harbour-E**	**Inner Harbour West-D**	**Inner Harbour Central-C**	**Inner Harbour East-B**	**East Basin-A**
PFHxA	30	170±28	460±116	230±43	420±89	760±86	750±25
PFHpA	30	140±3.0	200±24	180±20	220±5	270±21	320±15
PFOA	10	50±0.01	50±0.01	68±48	99±37	110±27	180±23
PFNA	40	43±19	41±7.4	170±14	87±6	150±10	190±19
PFDA	30	110±7.0	89±6.6	190±33	140±30	220±7.6	250±24
PFUnDA	20	<20	<20	22±4.5	<20	33±5.3	29±1
PFDoDA	20	<20	<20	<20	<20	22±4.0	<20
PFTeDA	20	<20	<20	<20	<20	<20	<20
PFBS	10	<10	16±2.4	<10	17±7.2	32±3.4	60±2.7
PFHxS	10	18±6.7	40±9.0	21±8.1	38±17	71±2.2	130±7.3
PFOS	20	170±11	170±13	320±68	310±20	500±53	710±29
PFDS	10	<10	<10	<10	<10	<10	<10
FOSA	10	<10	<10	<10	20±5.5	15±1.8	13±4.4
FOSAA	50	<50	<50	<10	<10	<10	<10
MeFOSAA	50	<50	<50	<50	<50	<50	<50
EtFOSAA	50	<50	<50	<50	<50	63±39	55±4.2
SAmPAP diester	12	<12	<12	<12	<12	<12	<12

Table S6. Mean (*n*=3 replicates/ location ± standard deviation about the mean), blank-corrected sediment concentrations (pg/g dry weight) in False Creek Harbour.

	MDL	Entrance-11	Outer Harbour-10	Inner Harbour West-9	Inner Harbour Central-8	Inner Harbour Central-7	Inner Harbour East-6	Inner Harbour East-5	East Basin-4	East Basin-3	East Basin-2	East Basin-1
PFHxA	14	76±4.2	128±9.2	97±2.7	160±5.4	150±20	180±11	270±8.6	170±25	230±22	130±5.2	140±4.6
PFHpA	10	24±3.8	40±5.2	42±5.1	52±11	48±3.1	52±5.2	72±4.3	36±2.8	53±7.2	39±3.2	48±1.4
PFOA	6.4	34±2.6	49±3.3	47±3.6	62±2.7	57±2.7	78±4.1	78±14	72±28	53±2.3	51±3.6	59±2.7
PFNA	10	71±12	110±7.0	78±8.3	86±6.7	110±36	170±34	130±22	99±18	140±18	62±3.9	73±8.1
PFDA	10	49±3.5	77±3.9	74±4.6	120±7.6	100±0.5	170±20	130±6.9	98±12	92±13	78±11	78±11
PFUnDA	4.8	46±1.6	69±0.5	63±4.6	95±0.8	87±3.0	160±4.1	130±8.6	98±13	82±10	65±3.3	72±2.5
PFDoDA	4.7	55±1.4	100±0.6	100±1.7	180±10	140±2.0	410±31	210±33	150±12	140±13	97±9.6	100±3.9
PFTeDA	4.8	60±2.5	120±2.5	130±1.9	226±11	180±2.6	470±14	270±39	170±14	220±21	120±14	140±4.5
PFBS	1.8	<1.8	<1.8	9.0± 0.01	11±12	14±13	10±1.2	12±2.6	23±4.0	26±3.0	<1.8	11±1.4
PFHxS	2.2	11±23	13±15	13±6.9	13±37	13±11	18±0.6	20±30	21±8.0	37±13	19±41	16±8.8
PFOS	2.1	71±2.5	160±15	81±3.1	34±5.9	52±4.7	130±18	180±3.4	100±16	120±28	150±45	110±5.8
PFDS	2.8	<2	47±4.6	77±14	210±17	140±6.1	470±28	240±63	79±15	120±16	77±41	69±18
FOSA	2.2	15±0.8	35±5.9	31±1.6	46±7.3	39±2.4	49±3.3	59±14	47±6.5	31±1.2	33±7.7	29±0.8
FOSAA	13	<13	<13	<13	27±1.4	29±0.9	39±3.7	32±1.1	39±13	<13	<13	<13
MeFOSAA	10	23±1.2	60±7.1	76±7.2	180±8.6	150±8.4	240±6.1	150±9.2	120±27	140±12	69±2.6	130±9.6
EtFOSAA	10	38±2.1	86±4.3	120±5.7	360±54	270±36	590±59	250±10	140±5.1	200±8.8	130±7.7	170±11
SAmPAP diester	5.0	40±2.3	120±2.8	110±6.7	200±23	180±2.7	180±13	140±3.4	100±16	150±12	200±82	150±5.9

Table S7. Field-based sediment/water log distribution coefficients (log (K_D); L/kg) calculated for individual False Creek Sampling Locations (letters and numbers in parenthesis correspond to water and sediment sampling locations, respectively in Figure 2). In cases where all samples from a given site were <MDL, a concentration of 0.5 × MDL was used for estimation of K_Ds.

	Log K_D (L/kg)											
Study	**Present Work**							**Awad et al.[6]**	**Pan and You[7]**	**Ahrens et al.[8]**	**Kwadijk[9]**	**Labadie[10]**
Location	East Basin (A, 1-4)	Inner Harbour-East (B, 5, 6)	Inner Harbour-Central (C, 7, 8)	Inner Harbour-West (D, 9)	Outer Harbour (E, 10)	Entrance (F, 11)	Mean ± SEM	Ontario, Canada	Yangtze River Estuary, China	Tokyo Bay, Japan	The Netherlands	Orge River, France
PFHxA	2.3	2.5	2.6	2.6	2.4	2.7	2.5±0.05					0.8±0.0
PFHpA	2.1	2.4	2.4	2.4	2.3	2.2	2.3±0.04					0.8±0.1
PFOA	2.5	2.8	2.8	2.8	3.0	2.8	2.8±0.06	0.65±0.07		0.5-1.25	1.83±0.40	
PFNA	2.7	3.0	3.1	2.7	3.4	3.2	3.0±0.12	1.43±0.06			2.89±0.53	1.5±0.1
PFDA	2.5	2.8	2.9	2.6	2.9	2.6	2.7±0.07	1.75±0.06			2.87±0.23	2.4±0.2
PFUnDA	3.4	3.6	>4.0	3.5	>3.8	>3.7	>3.7±0.08	1.85				3.4±0.1
PFDoDA	>4.1[1]	4.1	>4.2	>4.0	>4.0	>3.7	>4.0±0.07					4.3±0.2
PFTeDA	>4.2	>4.6	>4.3	>4.1	>4.1	>3.8	>4.2±0.11					
PFBS	2.5	2.5	2.8	n.d.	<1.8[2]	n.d.	<2.4±0.23				1.42±0.50	
PFHxS	2.2	2.4	2.5	2.8	2.5	2.8	2.6±0.09	0.54±0.20				0.9±0.0
PFOS	2.2	2.5	2.1	2.4	3.0	2.6	2.5±0.12	1.22±0.08	2.88-3.67	0.5-2	2.35±0.35	2.4±0.2
PFDS	>4.2	>4.9	>4.5	>4.2	>4.0	n.d.	>4.4±0.15					
FOSA	3.4	3.6	3.3	3.8	3.8	3.5	>3.6±0.08	1.65±0.10		0.5-2.5		
FOSAA	3.2	3.2	3.0	n.d.	n.d.	n.d.	>3.1±0.04					
MeFOSAA	>3.7	>3.9	>3.8	>3.5	>3.4	>3.0	>3.5±0.14					
EtFOSAA	3.5	3.8	>4.1	>3.7	>3.5	>3.2	>3.6±0.13					
SAmPAP diester	>4.4	>4.4	>4.5	>4.3	>4.3	>3.8	>4.3±0.10					

[1.] Concentration in water was below MDL for all samples from this site, therefore a water concentration of 0.5 × MDL was used for calculation of the K_D. The value shown therefore represents a lower bounds estimate of the true Log K_D.

[2.] Concentration in sediment was below MDL, therefore a sediment concentration of 0.5 × MDL was used for calculation of the K_D. The value shown therefore represents an upper bounds estimate of the true Log K_D.

n.d.- Indicates that the concentration in both water and sediment were below the method detection limit and thus log K_D could not be estimated.

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