

**Supporting Information for:**  
**Certain Perfluoroalkyl and Polyfluoroalkyl Substances**  
**Associated with Aqueous Film Forming Foam Are Widespread**  
**in Canadian Surface Waters**

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## Materials

The methanol used was LC-MS grade and obtained from EMD Millipore (Billerica, MA, USA) and Fisher Scientific (Waltham, MA, USA). Deionized water was generated using a Purelab flex water purification system (ELGA, Woodridge, IL, USA). 28% NH<sub>4</sub>OH (ACS grade), and ammonium acetate for HPLC were all from Sigma Aldrich (St. Louis, MO, USA). Perfluorohexane sulfonamide (FHxSA) was obtained from SynQuest Laboratories (Alachua, FL, USA). 6:2 fluorotelomer sulfonamide (FTSAm), 6:2 fluorotelomer sulfonamide alkylbetaine (FTAB), and 6:2 fluorotelomer sulfonamide alkyl amine (FTAA) were synthesized in house as described previously.<sup>1</sup>

Native standards of perfluoroalkyl carboxylate (PFCA) mixture (MXA), perfluoroalkane sulfonate (PFSA) mixture (MXA), perfluoropentane sulfonate (PFPeS), and perfluoroheptane sulfonate (PFHpS), 4:2 fluorotelomer sulfonic acid (FTSA), 6:2 FTSA, 8:2 FTSA, N-ethyl perfluorooctane sulfonamido ethanol acetic acid (EtFOSAA), and perfluorooctane sulfonamide (FOSA) were obtained from Wellington Laboratories (Guelph, ON, Canada). Mass labelled standards of labelled PFCA/PFSA mixture (MXA), <sup>13</sup>C<sub>5</sub>-perfluoropentanoate (PFPeA), <sup>13</sup>C<sub>4</sub>-perfluoroheptanoate (PFHpA), <sup>13</sup>C<sub>2</sub>-4:2 FTSA, <sup>13</sup>C<sub>2</sub>-6:2 FTSA, <sup>13</sup>C<sub>2</sub>-8:2 FTSA, D<sub>5</sub>-EtFOSAA, and <sup>13</sup>C<sub>8</sub>-FOSA were also from Wellington Laboratories.

## Extraction of Water

Oasis WAX cartridges (6 cc, 200 mg, 30 µm; Waters, Milford, MA) were conditioned with 2 mL of 0.1% NH<sub>4</sub>OH in methanol, 2 mL of methanol, and 2 mL of deionized water. Surface water samples were then loaded, cartridges were rinsed with 2 mL of 25 mM ammonium acetate in deionized water, and dried by centrifugation and under vacuum. The cartridges were then eluted with 4 mL of methanol for the neutral fraction followed by 4 mL of 0.1% NH<sub>4</sub>OH in methanol for the acid fraction. The extracts were evaporated under a gentle stream of nitrogen to a little less than 1 mL and made up to 1 mL with methanol. Extracts were stored at -20°C.

Use of the Oasis WAX sorbent was suitable for retention of a wide variety of PFASs, including cations and zwitterions, because it is a mixed-mode sorbent with a

hydrophilic-lipophilic balance (HLB) polymeric structure that retains a variety of non-polar and polar chemicals. The suitability of the sorbent for cationic and zwitterionic analytes can be assessed based on the surface water matrix spike and recovery experiment, discussed in the Quality Assurance of Data section.

## **Extraction of Sediment**

In the ALFONSE clean lab, the approximately 0.5g sediment subsamples were extracted three times with 2.5 mL of 0.1% NH<sub>4</sub>OH in methanol by vortex mixing 20 sec, sonicating 30 min, shaking at 300 rpm for 1 hour, and centrifuging at 2354 g for 15 min. The supernatants from each extraction were combined and evaporated to approximately 2 mL under a gentle stream of nitrogen. The extracts were then cleaned up using 1mL/100mg Supelclean ENVI-Carb cartridges (Supelco, Bellefonte, PA). The cartridges were conditioned with 3 × 1 mL of methanol. While collecting the final extract, the extracts were loaded and eluted with 4 × 1 mL of methanol. The cleaned up extracts were then evaporated to less than 1 mL under a gentle stream of nitrogen, made up to 1 mL with methanol, and stored at -20°C.

## **Determination of Organic Carbon Content of Sediments**

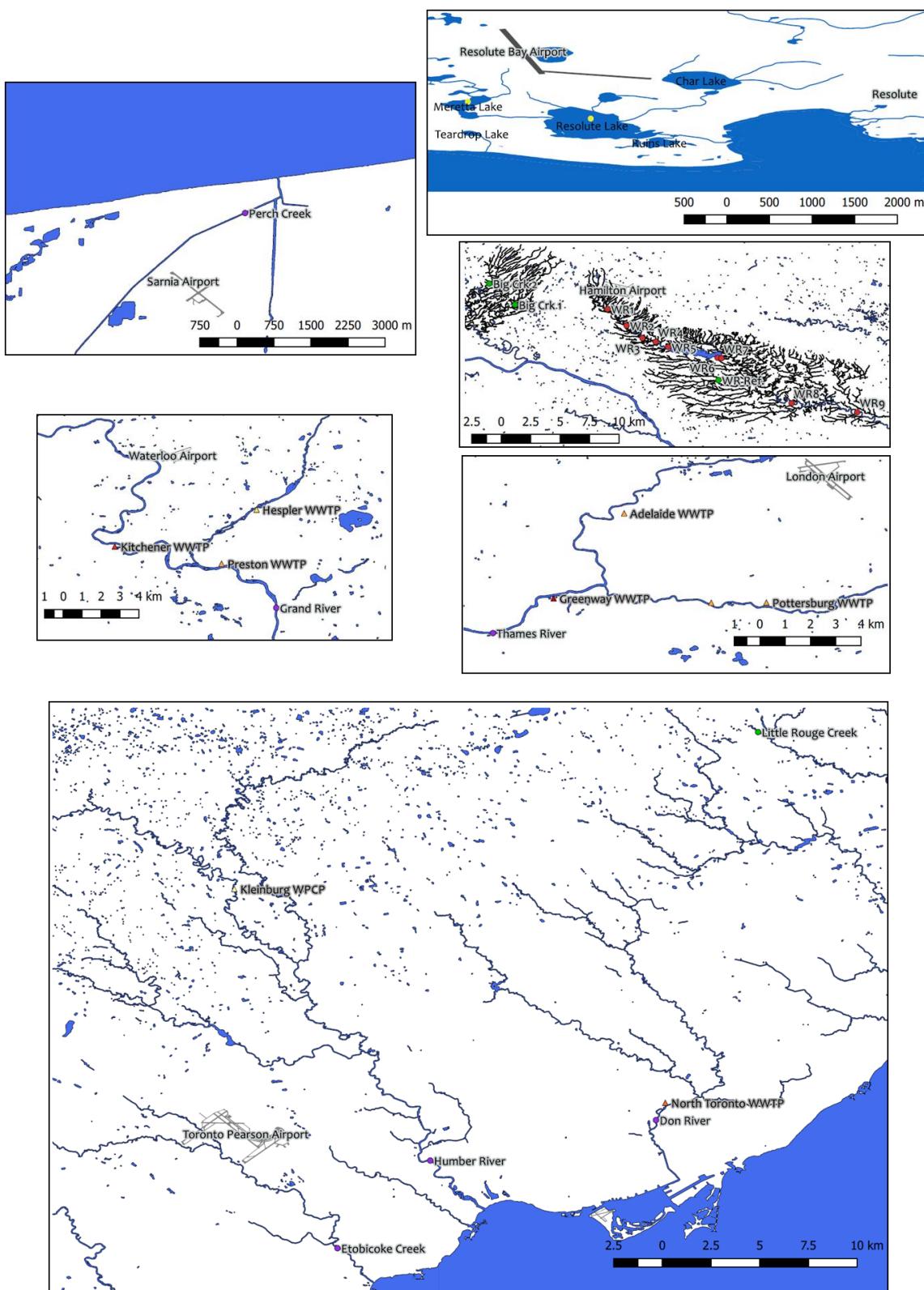
The organic carbon content of the sediments was determined by running samples of each sediment for total carbon and inorganic carbon using a Shimadzu TOC-L Total Organic Carbon Analyzer coupled to a Shimadzu SSM-5000A Solid Sample Module. The system was calibrated with glucose for total carbon and sodium carbonate for inorganic carbon. The organic carbon content of the sediments was determined as total carbon minus inorganic carbon.

## **LC-MS/MS**

The column was a Waters Acquity UPLC BEH C18 column with 1.7 µm particles (2.1 mm x 75mm) used with a flow rate of 0.5 mL/min and a column temperature of 60°C. The mobile phase consisted of 10 mM ammonium acetate in deionized water (A) and methanol (B) and the gradient started at 90% A: 10% B, changed to 22% A: 78% B over 7 min, changed to 10% A: 90 %B over 0.4 min, returned to 90% A: 10% B in 0.1

min, and held at 90% A: 10% B for 3 min for a total run time of 10.5 min. Injection volumes were 2  $\mu$ L.

In positive mode electrospray ionization (ESI+) the electrospray voltage was 3300 V and in negative ion mode electrospray ionization (ESI-) the electrospray voltage was -2480 V. The nebulizing nitrogen gas was 5.5 Bar, desolvation gas was nitrogen at 650 L/hr, cone nitrogen gas flow rate was 150 L/hr, and the helium collision gas flow rate was 0.12–0.15 mL/min. The Xevo TQ-S was operated in MRM mode with dwell times of at least 0.01 sec per transition. Multiple reaction monitoring (MRM) transitions that were used in this study are given in Table S2.



**Figure S1:** Maps showing sampling sites and upstream airports and wastewater treatment plants.

**Table S1:** Sampling dates and locations

Location	Coordinates	Date(s)
Welland R. 1	43.1508, -79.9446	Oct. 22, 2015
Welland R. 2	43.1333, -79.9246	Oct. 22, 2015
Welland R. 3	43.1206, -79.9083	Oct. 22, 2015
Welland R. 4	43.1168, -79.8947	Oct. 22, 2015
Welland R.5	43.1113,-79.8815	Oct. 22, 2015
Welland R. 6	43.1001,-79.8298	Oct. 22, 2015
Welland R. 7	43.0995,-79.8259	Oct. 22, 2015
Welland R. 8	43.0528,-79.7529	Oct. 22, 2015
Welland R. 9	43.0432, -79.6844	Oct. 22, 2015
Welland R. Ref.	43.0768, -79.8288	Oct. 22, 2015
Big Crk. 1	43.1552,-80.0408	Oct. 22, 2015
Big Crk. 2	43.1775,-80.0678	Oct. 22, 2015
Etobicoke Crk.	43.6071, -79.5645	Aug. 10, 2015; Sept. 29, 2015
Don R.	43.6885, -79.3622	Sept. 29, 2015
Humber R.	43.6628, -79.5055	Sept. 29, 2015
Grand R.	43.3589, -80.3162	Aug. 6, 2015
Thames R.	42.9584, -81.3112	July 7, 2015
Perch Crk.	43.0195, -82.2976	July 8, 2015
Little Rouge Crk.	43.1775, -80.0678	Feb. 6, 2016
Meretta Lk.	74.695, -94.993	Aug. 4, 2014
Resolute Lk.	74.687, -94.942	Aug. 1, 2012; Aug. 6, 2014
Lake of Bays	45.2395, -78.9135	Sept. 27, 2015

**Table S2:** Tandem mass spectrometry transitions for all AFFF-related PFASs monitored

Compound	ESI Mode	Mass Transition	Cone Voltage (V)	Collision Energy (V)
PFPeA	–	263.03>219.04	24	8
M-PFPeA	–	268.10>223.03	24	8
PFHxA	–	313.00>269.00	26	10
M-PFHxA	–	315.00>270.00	26	10
PFHpA	–	363.00>169.00	30	19
M-PFHhpA	–	363.00>319.00 <sup>q</sup>	30	10
PFOA	–	413.00>168.90	30	18
M-PFOA	–	417.00>372.00	30	10
PFBS	–	299.00>80.00 <sup>q</sup>	40	30
PFBS	–	299.00>99.00	40	31
PFPeS	–	349.00>80.00 <sup>q</sup>	42	32
PFPeS	–	349.00>99.00	42	31
PFHxS	–	399.00>80.00 <sup>q</sup>	45	33
PFHxS	–	399.00>99.00	45	31
M-PFHxS	–	403.00>103.00	45	30
PFHpS	–	449.00>80.00 <sup>q</sup>	48	34
PFHpS	–	449.00>98.90	48	34
PFOS	–	499.00>80.00 <sup>q</sup>	60	39
PFOS	–	499.00>99.00	60	38
M-PFOS	–	503.00>80.00	60	39
EtFOSAA	–	584.03>418.99	20	18
M-EtFOSAA	–	589.03>418.99	44	20
4:2 FTSA	–	327.03>81.00	60	30
4:2 FTSA	–	327.03>307.07 <sup>q</sup>	60	20
M-4:2 FTSA	–	329.03>81.00	60	30
6:2 FTSA	–	427.10>81.00	38	32
6:2 FTSA	–	427.10>407.08 <sup>q</sup>	38	22
M-6:2 FTSA	–	428.84>81.00	86	32
8:2 FTSA	–	527.10>81.00	68	34
8:2 FTSA	–	527.10>507.13 <sup>q</sup>	68	26
M-8:2 FTSA	–	529.10>81.00	68	34
FHxSA	–	398.00>78.00	62	26
FOSA	–	498.00>78.00	66	28
M-FOSA	–	506.00>78.00	66	28
6:2 FTSAm*	–	425.65>345.90	28	22
6:2 FTSAm*	–	425.65>365.99 <sup>q</sup>	28	16
4:2 FTAB	+	470.90>340.00	50	30
4:2 FTAB	+	470.90>104.06	50	30
6:2 FTAB*	+	570.90>440.00 <sup>q</sup>	50	30
6:2 FTAB*	+	570.90>104.06	50	30
8:2 FTAB*	+	670.90>539.99	96	32
8:2 FTAB*	+	670.90>104.06	96	32

Compound	ESI Mode	Mass Transition	Cone Voltage (V)	Collision Energy (V)
5:3 FTB*	+	413.78>58.10 413.78>104.13	36 36	30 28
5:1:2 FTB*	+	431.78>58.10 431.78>372.05	40 40	32 32
7:3 FTB*	+	513.84>58.17 513.84>104.06	82 82	36 32
7:1:2 FTB*	+	531.71>58.10 531.71>472.05	50 50	36 38
9:3 FTB	+	613.84>58.17 613.84>104.06	82 82	36 32
9:1:2 FTB	+	631.71>58.10 631.71>572.05	50 50	36 38
6:2 FTAA*	+	512.90>439.98 <sup>q</sup> 512.90>85.93	40 40	30 34
4:2 FTSAS-SO <sub>2</sub>	-	517.80>206.00 517.80>151.97	50 50	35 40
6:2 FTSAS-SO <sub>2</sub> <sup>a</sup>	-	617.80>206.00 617.80>151.97	50 50	35 40
8:2 FTSAS-SO <sub>2</sub>	-	717.80>206.00 717.80>151.97	50 50	35 40
6:2 FTSHA-SO	+	511.84>166.08 511.84>116.15	50 50	20 24
C6 FASADA*	+	628.97>187.20 628.97>70.06	40 40	36 56
C5 FASADA*	+	579.03>187.14 579.03>70.06	60 60	34 52
C4 FASADA	+	529.03>187.14 529.03>70.06	60 60	34 52
C3 FASADA	+	479.03>187.14 479.03>70.06	60 60	34 52
C6 FASAAA*	+	556.97>129.03 556.97>84.96	52 52	30 34
C5 FASAAA*	+	506.90>129.09 506.90>85.02	60 60	30 30
C4 FASAAA	+	456.90>129.09 456.90>85.02	60 60	30 30
C3 FASAAA	+	406.90>129.09 406.90>85.02	60 60	30 30
C6 FASAB	+	556.97>118.00 556.97>84.96	52 52	32 34
C5 FASAB	+	506.90>118.00 506.90>85.02	60 60	30 30
C4 FASAB	+	456.90>118.00 456.90>85.02	60 60	30 30

Compound	ESI Mode	Mass Transition	Cone Voltage (V)	Collision Energy (V)
C3 FASAB	+	406.90>118.00 406.90>85.02	60 60	30 30
C6 FASAAm*	+	484.84>85.02 484.84>70.06	60 60	30 34
	-	436.71>90.93 436.71>376.98	22 22	15 11
6:2 FTSAS*	-	585.71>135.01 585.71>206.00	90 90	42 35
6:2 FTSAS-SO*	-	601.78>255.98 601.78>151.97	62 62	24 40
	-	450.65>378.96 450.65>338.99	32 32	15 14
	+	548.90>504.00 548.90>475.98	42 42	28 34
	+	606.84>504.02 606.84>104.06	36 36	26 22
	+	522.90>478.06 522.90>392.97	60 60	26 38
	+	580.97>478.07 580.97>392.97	42 42	24 42
	+	537.10>478.08	32	24
	+	552.84>207.10 552.84>148.01	28 28	20 30
6:2 FTSHA*	+	495.78>393.02 495.78>437.03	48 48	36 28
	+	600.84>58.10 600.84>448.02	80 80	32 36

\*Transitions for AFFF components optimized with diluted AFFF or in-house synthesized standards

<sup>q</sup> indicates quantifying transitions for compounds with quantitative standards for calibration

<sup>a</sup> indicates that 6:2 FTSAS-SO<sub>2</sub> transition was guessed based on mass spectrum reported by Harding-Marjanovic *et al.*<sup>2</sup> due to insufficient quantity in AFFF extract

**Table S3:** Recoveries of PFASs from water and sediment matrices ( $\pm$  standard deviation)

Compound	% Recovery from Water	% Recovery from Sediment
PFPeA	96 $\pm$ 4	81 $\pm$ 11
PFHxA	87 $\pm$ 7	84 $\pm$ 4
PFHpA	96 $\pm$ 12	78 $\pm$ 7
PFOA	94 $\pm$ 7	82 $\pm$ 7
PFBS	93 $\pm$ 5	81 $\pm$ 8
PFPeS	92 $\pm$ 6	80 $\pm$ 9
PFHxS	95 $\pm$ 7	83 $\pm$ 11
PFHpS	93 $\pm$ 9	94 $\pm$ 5
PFOS	90 $\pm$ 8	91 $\pm$ 5
4:2 FTSA	86 $\pm$ 5	82 $\pm$ 4
6:2 FTSA	88 $\pm$ 4	89 $\pm$ 10
8:2 FTSA	91 $\pm$ 7	87 $\pm$ 9
EtFOSAA	86 $\pm$ 10	83 $\pm$ 4
FHxSA	76 $\pm$ 6	76 $\pm$ 2
FOSA	77 $\pm$ 7	77 $\pm$ 3
6:2 FTSAm	80 $\pm$ 5	80 $\pm$ 5
6:2 FTAA	71 $\pm$ 12	90 $\pm$ 5
6:2 FTAB	88 $\pm$ 24	31 $\pm$ 2

**Table S4:** Limit of detection (LOD) and limit of quantitation (LOQ) for PFASs in water and sediment

PFAS	LOD water (ng/L)	LOQ water (ng/L)	LOD sediment (ng/g)	LOQ sediment (ng/g)
PFPeA	0.75	5	0.15	0.5
PFHxA	0.75	2.5	0.06	0.2
PFHpA	0.4	2	0.02	0.1
PFOA	0.25	0.6	0.06	0.2
PFBS	0.05	0.3	0.04	0.15
PFPeS	0.07	0.2	0.06	0.2
PFHxS	0.4	1.2	0.05	0.2
PFHpS	0.2	0.7	0.04	0.2
PFOS	0.05	0.2	0.05	0.2
4:2 FTSA	0.008	0.025	0.03	0.1
6:2 FTSA	0.008	0.025	0.03	0.1
8:2 FTSA	0.015	0.065	0.03	0.1
EtFOSAA	0.05	0.2	0.02	0.09
FHxSA	0.01	0.04	0.02	0.06
FOSA	0.02	0.1	0.03	0.1
6:2 FTSAm	0.2	0.65	0.06	0.2
4:2 FTAB	0.04	0.15	0.03	0.1
6:2 FTAB	0.03	0.2	0.03	0.1
8:2 FTAB	0.03	0.2	0.03	0.1
5:3 FTB	0.09	0.5	0.02	0.1
5:1:2 FTB	0.2	0.8	0.05	0.2
7:3 FTB	0.05	0.2	0.02	0.1
7:1:2 FTB	0.16	0.45	0.05	0.2
9:3 FTB	0.1	0.3	0.02	0.1
9:1:2 FTB	0.1	0.4	0.05	0.2
6:2 FTAA	0.03	0.1	0.025	0.1
6:2 FTSAS-SO2	0.02	0.1	nd	nd
6:2 FTSHA-SO	0.08	0.25	nd	nd
C6 FASADA	0.01	0.06	nd	nd
C5 FASADA	0.002	0.05	nd	nd
C4 FASADA	0.002	0.05	nd	nd
C3 FASADA	0.01	0.06	nd	nd
C6 FASAAA	0.2	0.8	nd	nd
C5 FASAAA	0.1	0.5	nd	nd
C4 FASAAA	0.3	1	nd	nd
C3 FASAAA	0.15	0.6	nd	nd
C6 FASAB	0.2	0.7	nd	nd
C5 FASAB	0.1	0.5	nd	nd
C5 FASAAm	nd	nd	0.08	0.3

nd: These PFASs were not detected with a S/N above 3 in the matrix, LOD and LOQ not determined.

**Table S5:** Concentrations of PFAAs in water samples in ng/L. ( $\pm$  standard deviation)

Sample	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFPeS	PFHxS	PFHps	PFOS
Welland R. 1	150 $\pm$ 40	100 $\pm$ 20	51 $\pm$ 10	52 $\pm$ 7	12 $\pm$ 1	15 $\pm$ 2	150 $\pm$ 30	4.7 $\pm$ 0.5	150 $\pm$ 40
Welland R. 2	100 $\pm$ 30	65 $\pm$ 6	32 $\pm$ 6	24 $\pm$ 4	11 $\pm$ 1	11 $\pm$ 1	92 $\pm$ 21	3.0 $\pm$ 0.2	110 $\pm$ 20
Welland R. 3	150 $\pm$ 20	88 $\pm$ 11	41 $\pm$ 11	27 $\pm$ 4	12 $\pm$ 1	14 $\pm$ 1	140 $\pm$ 20	3.9 $\pm$ 0.1	150 $\pm$ 20
Welland R. 4	150 $\pm$ 30	94 $\pm$ 22	35 $\pm$ 13	27 $\pm$ 4	13 $\pm$ 1	13 $\pm$ 1	140 $\pm$ 20	3.9 $\pm$ 0.4	140 $\pm$ 20
Welland R. 5	140 $\pm$ 30	86 $\pm$ 15	30 $\pm$ 2	27 $\pm$ 3	12 $\pm$ 2	11 $\pm$ 1	110 $\pm$ 20	2.7 $\pm$ 0.2	80 $\pm$ 12
Welland R. 6	50 $\pm$ 10	34 $\pm$ 3	17 $\pm$ 1	22 $\pm$ 3	4.6 $\pm$ 0.3	4.6 $\pm$ 0.2	43 $\pm$ 7	2.2 $\pm$ 0.1	92 $\pm$ 18
Welland R. 7	60 $\pm$ 10	38 $\pm$ 8	19 $\pm$ 3	22 $\pm$ 3	4.4 $\pm$ 0.5	4.6 $\pm$ 0.4	57 $\pm$ 10	2.5 $\pm$ 0.5	140 $\pm$ 30
Welland R. 8	40 $\pm$ 4	27 $\pm$ 2	13 $\pm$ 4	17 $\pm$ 1	3.8 $\pm$ 0.5	3.2 $\pm$ 0.1	34 $\pm$ 3	1.6 $\pm$ 0.2	58 $\pm$ 5
Welland R. 9	37 $\pm$ 3	26 $\pm$ 3	8.6 $\pm$ 2.9	17 $\pm$ 1	3.8 $\pm$ 0.4	2.5 $\pm$ 0.2	28 $\pm$ 2	1.0 $\pm$ 0.1	65 $\pm$ 6
Welland R. Ref	nd	nd	nd	<0.6	<0.3	nd	nd	nd	2.5 $\pm$ 0.2
Big Creek 1	6.6 $\pm$ 2.2	4.5 $\pm$ 0.5	<2	2.6 $\pm$ 0.1	1.7 $\pm$ 0.2	nd	<1.2	nd	1.7 $\pm$ 0.1
Big Creek 2	<5	<2.5	<2	1.1 $\pm$ 0.1	1.4 $\pm$ 0.1	nd	1.3 $\pm$ 0.2	nd	1.2 $\pm$ 0.1
Etobicoke Crk. Aug	18 $\pm$ 1	16 $\pm$ 1	4.9 $\pm$ 1.5	8.0 $\pm$ 0.7	4.4 $\pm$ 0.1	1.3 $\pm$ 0.2	4.7 $\pm$ 0.3	<0.7	16 $\pm$ 1
Etobicoke Crk. Sep	11 $\pm$ 1	15.7 $\pm$ 0.4	3.4 $\pm$ 0.4	9.0 $\pm$ 0.1	4.1 $\pm$ 0.3	0.40 $\pm$ 0.07	2.2 $\pm$ 0.7	<0.7	11 $\pm$ 1
Don R.	<5	10 $\pm$ 1	3.1 $\pm$ 0.5	6.0 $\pm$ 0.4	2.5 $\pm$ 0.1	nd	<1.2	<0.7	7.3 $\pm$ 1.2
Humber R	<5	6.7 $\pm$ 0.4	<2	3.3 $\pm$ 0.4	3.0 $\pm$ 0.1	<0.2	1.7 $\pm$ 0.3	<0.7	7.2 $\pm$ 0.4
Grand R.	5.8 $\pm$ 0.6	5.4 $\pm$ 0.3	<2	3.7 $\pm$ 0.1	1.7 $\pm$ 0.3	nd	1.2 $\pm$ 0.1	nd	2.8 $\pm$ 0.1
Thames R.	<5	3.9 $\pm$ 0.6	<2	2.7 $\pm$ 0.1	1.4 $\pm$ 0.1	<0.2	1.5 $\pm$ 0.2	nd	5.7 $\pm$ 1.5
Perch Crk	7.3 $\pm$ 1.3	10.4 $\pm$ 0.7	2.7 $\pm$ 0.3	6.4 $\pm$ 0.3	4.0 $\pm$ 0.1	1.6 $\pm$ 0.2	13 $\pm$ 1	0.9 $\pm$ 0.1	22 $\pm$ 2
Little Rouge Crk	<5	<2.5	<2	<0.6	0.31 $\pm$ 0.03	<0.2	nd	nd	<0.2
Meretta Lk 2014	76 $\pm$ 14	38 $\pm$ 6	22 $\pm$ 3	14 $\pm$ 1	1.9 $\pm$ 0.2	1.8 $\pm$ 0.2	30 $\pm$ 4	0.8 $\pm$ 0.1	46 $\pm$ 10
Resolute Lk 2014	25 $\pm$ 1	17 $\pm$ 2	9.3 $\pm$ 1.2	7.7 $\pm$ 0.4	0.8 $\pm$ 0.1	0.73 $\pm$ 0.09	13 $\pm$ 1	<0.7	24 $\pm$ 1
Resolute Lk 2012	47 $\pm$ 11	28 $\pm$ 3	14 $\pm$ 3	9.1 $\pm$ 0.3	1.1 $\pm$ 0.1	1.2 $\pm$ 0.1	21 $\pm$ 1	0.70 $\pm$ 0.1	41 $\pm$ 5
Lake of Bays	nd	nd	nd	0.7 $\pm$ 0.1	nd	nd	nd	nd	0.36 $\pm$ 0.07

nd = not detected above detection limit

**Table S6:** Concentrations of FTSAAs, EtFOSAA, FHxSA, FOSA, and 6:2 FTSAm in water samples in ng/L. ( $\pm$  standard deviation)

Sample	4:2 FTSA	6:2 FTSA	8:2 FTSA	EtFOSAA	FHxSA	FOSA	6:2 FTSAm
Welland R. 1	0.04 $\pm$ 0.01 <sup>a</sup>	2.5 $\pm$ 0.8	<0.065	nd	19 $\pm$ 2	0.17 $\pm$ 0.06	0.84 $\pm$ 0.37
Welland R. 2	nd	0.06 $\pm$ 0.01 <sup>a</sup>	nd	nd	2.5 $\pm$ 0.3	<0.1	nd
Welland R. 3	nd	0.05 $\pm$ 0.01 <sup>a</sup>	nd	nd	2.5 $\pm$ 0.2	<0.1	nd
Welland R. 4	nd	0.04 $\pm$ 0.01 <sup>a</sup>	nd	nd	2.4 $\pm$ 0.1	nd	nd
Welland R. 5	nd	0.07 $\pm$ 0.02 <sup>a</sup>	nd	<0.2	4.2 $\pm$ 0.2	<0.1	nd
Welland R. 6	nd	0.11 $\pm$ 0.03	nd	<0.2	3.6 $\pm$ 0.4	0.33 $\pm$ 0.07	nd
Welland R. 7	nd	0.05 $\pm$ 0.01 <sup>a</sup>	nd	0.26 $\pm$ 0.07	3.1 $\pm$ 0.2	<0.1	nd
Welland R. 8	nd	0.04 $\pm$ 0.01 <sup>a</sup>	nd	0.48 $\pm$ 0.02	1.2 $\pm$ 0.1	0.39 $\pm$ 0.01	nd
Welland R. 9	nd	0.03 $\pm$ 0.01 <sup>a</sup>	nd	0.41 $\pm$ 0.04	1.0 $\pm$ 0.1	0.45 $\pm$ 0.05	nd
Welland R. Ref	nd	<0.025	nd	<0.2	nd	nd	nd
Big Creek 1	nd	<0.025	nd	<0.2	<0.04	<0.1	nd
Big Creek 2	nd	<0.025	nd	nd	nd	nd	nd
Etobicoke Crk. Aug	nd	0.18 $\pm$ 0.03	<0.065	nd	0.53 $\pm$ 0.01	0.37 $\pm$ 0.03	<0.65
Etobicoke Crk. Sept	nd	0.18 $\pm$ 0.03	0.07 $\pm$ 0.01 <sup>a</sup>	<0.2	0.35 $\pm$ 0.03	0.91 $\pm$ 0.11	<0.65
Don R.	nd	0.13 $\pm$ 0.01	0.13 $\pm$ 0.02	0.84 $\pm$ 0.03	0.12 $\pm$ 0.01	1.6 $\pm$ 0.1	0.68 $\pm$ 0.14
Humber R	nd	0.09 $\pm$ 0.01 <sup>a</sup>	<0.065	0.20 $\pm$ 0.01	0.32 $\pm$ 0.01	0.72 $\pm$ 0.05	nd
Grand R.	nd	0.09 $\pm$ 0.01 <sup>a</sup>	nd	<0.2	0.04 $\pm$ 0.01 <sup>a</sup>	<0.1	nd
Thames R.	nd	0.05 $\pm$ 0.01 <sup>a</sup>	nd	<0.2	0.39 $\pm$ 0.05	0.49 $\pm$ 0.01	nd
Perch Crk	nd	0.07 $\pm$ 0.01 <sup>a</sup>	nd	<0.2	0.94 $\pm$ 0.04	0.36 $\pm$ 0.05	nd
Little Rouge Crk	nd	<0.025	nd	nd	nd	nd	nd
Meretta Lake 2014	0.09 $\pm$ 0.01 <sup>a</sup>	0.42 $\pm$ 0.01	nd	nd	2.1 $\pm$ 0.1	nd	nd
Resolute Lake 2014	nd	0.05 $\pm$ 0.01 <sup>a</sup>	nd	nd	1.2 $\pm$ 0.1	nd	nd
Resolute Lake 2012	nd	0.12 $\pm$ 0.03	nd	nd	3.6 $\pm$ 0.1	nd	nd
Lake of Bays	nd	nd	nd	<0.2	nd	nd	nd

nd = not detected above detection limit; <sup>a</sup> indicates concentrations below the lowest calibration level

**Table S7:** Concentrations of FTABs and approximate concentrations of FTBs in water in ng/L. ( $\pm$  standard deviation)

Averages	4:2 FTAB	6:2 FTAB	8:2 FTAB	5:3 FTB	5:1:2 FTB	7:3 FTB	7:1:2 FTB	9:3 FTB	9:1:2 FTB
Welland R. 1	0.18 $\pm$ 0.06	33 $\pm$ 4	nd	13 $\pm$ 7	42 $\pm$ 36	9.2 $\pm$ 4.7	16 $\pm$ 14	nd	nd
Welland R. 2	nd	<0.2	nd	5.7 $\pm$ 2.9	20 $\pm$ 17	nd	<0.45	nd	nd
Welland R. 3	nd	0.23 $\pm$ 0.01	nd	9.9 $\pm$ 5.4	30 $\pm$ 28	3.2 $\pm$ 2.7	5.7 $\pm$ 5.5	nd	nd
Welland R. 4	nd	<0.2	nd	5.4 $\pm$ 3.0	20 $\pm$ 18	<0.2	0.5 $\pm$ 0.4	nd	nd
Welland R. 5	nd	<0.2	nd	14 $\pm$ 7	39 $\pm$ 34	nd	nd	nd	nd
Welland R. 6	nd	<0.2	nd	6.6 $\pm$ 3.6	19 $\pm$ 16	nd	nd	nd	nd
Welland R. 7	nd	<0.2	nd	6.5 $\pm$ 3.2	18 $\pm$ 16	<0.2	<0.45	nd	nd
Welland R. 8	nd	<0.2	nd	1.7 $\pm$ 0.9	6.5 $\pm$ 6.0	nd	nd	nd	nd
Welland R. 9	nd	<0.2	nd	2.7 $\pm$ 1.4	8.1 $\pm$ 7.0	nd	nd	nd	nd
Welland R.	nd	nd	nd	nd	nd	nd	nd	nd	nd
Big Creek 1	nd	<0.2	nd	nd	nd	nd	nd	nd	nd
Big Creek 2	nd	<0.2	nd	nd	nd	nd	nd	nd	nd
Etobicoke Crk	nd	22 $\pm$ 1	1.5 $\pm$ 0.4	1.9 $\pm$ 1.0	6.1 $\pm$ 5.6	2.8 $\pm$ 1.5	7.4 $\pm$ 7.0	0.41 $\pm$ 0.28	0.42 $\pm$ 0.41
Etobicoke Crk	nd	13 $\pm$ 1	1.2 $\pm$ 0.3	1.3 $\pm$ 0.7	3.7 $\pm$ 3.4	1.8 $\pm$ 1.1	4.8 $\pm$ 4.6	0.31 $\pm$ 0.25	<0.4
Don R.	nd	16 $\pm$ 1	4.6 $\pm$ 1.2	nd	nd	nd	nd	nd	nd
Humber R	nd	4.5 $\pm$ 0.1	1.0 $\pm$ 0.3	nd	nd	nd	nd	nd	nd
Grand R.	nd	0.81 $\pm$ 0.02	nd	nd	nd	nd	nd	nd	nd
Thames R.	nd	<0.2	nd	nd	nd	nd	nd	nd	nd
Perch Crk	nd	0.30 $\pm$ 0.02	nd	nd	nd	nd	nd	nd	nd
Little Rouge	nd	<0.2	nd	nd	nd	nd	nd	nd	nd
Meretta Lk.	nd	<0.2	nd	0.51 $\pm$ 0.28	1.4 $\pm$ 1.3	nd	nd	nd	nd
Resolute Lk.	nd	nd	nd	<0.5	<0.8	nd	nd	nd	nd
Resolute Lk.	nd	nd	nd	<0.5	<0.8	nd	nd	nd	nd
Lake of Bays	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd = not detected above detection limit; Large standard deviations for FTB concentrations are due to use of average of calibrations using both transitions to reflect uncertainty in the calibration sensitivity for the FTBs.

**Table S8:** Concentrations of 6:2 FTAA and approx. concentrations of 6:2 FTSAS-SO<sub>2</sub>, 6:2 FTSHA-SO, and FASADAs in water in ng/L. (± standard deviation)

Averages	6:2 FTAA	6:2 FTSAS-SO <sub>2</sub>	6:2 FTSHA-SO	C6 FASADA	C5 FASADA	C4 FASADA	C3 FASADA
Welland R. 1	nd	nd	nd	0.36 ± 0.14	0.05 ± 0.03 <sup>a</sup>	<0.05	<0.06
Welland R. 2	nd	nd	nd	0.10 ± 0.05	<0.05	nd	nd
Welland R. 3	nd	nd	nd	0.10 ± 0.05	<0.05	nd	nd
Welland R. 4	nd	nd	nd	0.06 ± 0.03 <sup>a</sup>	<0.05	nd	nd
Welland R. 5	nd	nd	nd	<0.06	nd	nd	nd
Welland R. 6	nd	nd	nd	<0.06	nd	nd	nd
Welland R. 7	nd	nd	nd	<0.06	nd	nd	nd
Welland R. 8	nd	nd	nd	nd	nd	nd	nd
Welland R. 9	nd	nd	nd	<0.06	nd	nd	nd
Welland R. Ref	nd	nd	nd	nd	nd	nd	nd
Big Crk. 1	nd	nd	nd	nd	nd	nd	nd
Big Crk. 2	nd	nd	nd	nd	nd	nd	nd
Etobicoke Crk. Aug	0.16 ± 0.03	0.83 ± 0.53	<0.25	nd	nd	nd	nd
Etobicoke Crk. Sept	<0.1	0.24 ± 0.15	0.29 ± 0.10	nd	nd	nd	nd
Don R.	0.11 ± 0.01	<0.1	<0.25	nd	nd	nd	nd
Humber R.	nd	<0.1	<0.25	nd	nd	nd	nd
Grand R.	nd	<0.1	<0.25	nd	nd	nd	nd
Thames R.	nd	<0.1	<0.25	nd	nd	nd	nd
Perch Crk.	nd	nd	nd	nd	nd	nd	nd
Little Rouge Crk.	nd	nd	nd	nd	nd	nd	nd
Meretta Lk. 2014	nd	nd	nd	nd	nd	nd	nd
Resolute Lk. 2014	nd	nd	nd	nd	nd	nd	nd
Resolute Lk. 2012	nd	nd	nd	<0.06	nd	nd	nd
Lake of Bays	nd	nd	nd	nd	nd	nd	nd

nd = not detected above detection limit; Large standard deviations for 6:2 FTSAS-SO<sub>2</sub>, 6:2 FTSHA-SO, and PFASADAs

concentrations are due to use of average of calibrations using both transitions to reflect uncertainty in the calibration sensitivity;

<sup>a</sup> indicates concentrations below the lowest calibration level

**Table S9:** Approximate concentrations of perfluoroalkane sulfonamide alkylamine acids (FASAAAs) and perfluoroalkane sulfonamide alkylbetaines (FASABs) in water in ng/L. ( $\pm$  standard deviation)

Sample	C6 FASAAA	C5 FASAAA	C4 FASAAA	C3 FASAAA	C6 FASAB	C5 FASAB
Welland R. 1	0.88 $\pm$ 0.22	<0.5	<1	<0.6	1.42 $\pm$ 0.66	<0.5
Welland R. 2	nd	nd	nd	nd	<0.7	nd
Welland R. 3	nd	nd	nd	nd	<0.7	nd
Welland R. 4	nd	nd	nd	nd	<0.7	nd
Welland R. 5	nd	nd	nd	nd	nd	nd
Welland R. 6	nd	nd	nd	nd	nd	nd
Welland R. 7	nd	nd	nd	nd	nd	nd
Welland R. 8	nd	nd	nd	nd	nd	nd
Welland R. 9	nd	nd	nd	nd	nd	nd
Welland R. Ref.	nd	nd	nd	nd	nd	nd
Big Crk. 1	nd	nd	nd	nd	nd	nd
Big Crk. 2	nd	nd	nd	nd	nd	nd
Etobicoke Crk. Aug.	nd	nd	nd	nd	nd	nd
Etobicoke Crk. Sept.	nd	nd	nd	nd	nd	nd
Don R.	nd	nd	nd	nd	nd	nd
Humber R.	nd	nd	nd	nd	nd	nd
Grand R.	nd	nd	nd	nd	nd	nd
Thames R.	nd	nd	nd	nd	nd	nd
Perch Crk.	nd	nd	nd	nd	nd	nd
Little Rouge Crk.	nd	nd	nd	nd	nd	nd
Meretta Lk. 2014	nd	nd	<1	nd	<0.7	nd
Resolute Lk. 2014	nd	nd	<1	nd	<0.7	nd
Resolute Lk. 2012	nd	nd	nd	nd	0.74 $\pm$ 0.33	nd
Lake of Bays	nd	nd	nd	nd	nd	nd

nd = not detected above detection limit

**Table S10:** Summary of Non-Parametric Mann-Whitney U Test Statistics for PFASs in AFFF-impacted ( $n = 14$ ), Urban ( $n = 5$ ), and Rural ( $n = 5$ ) Water

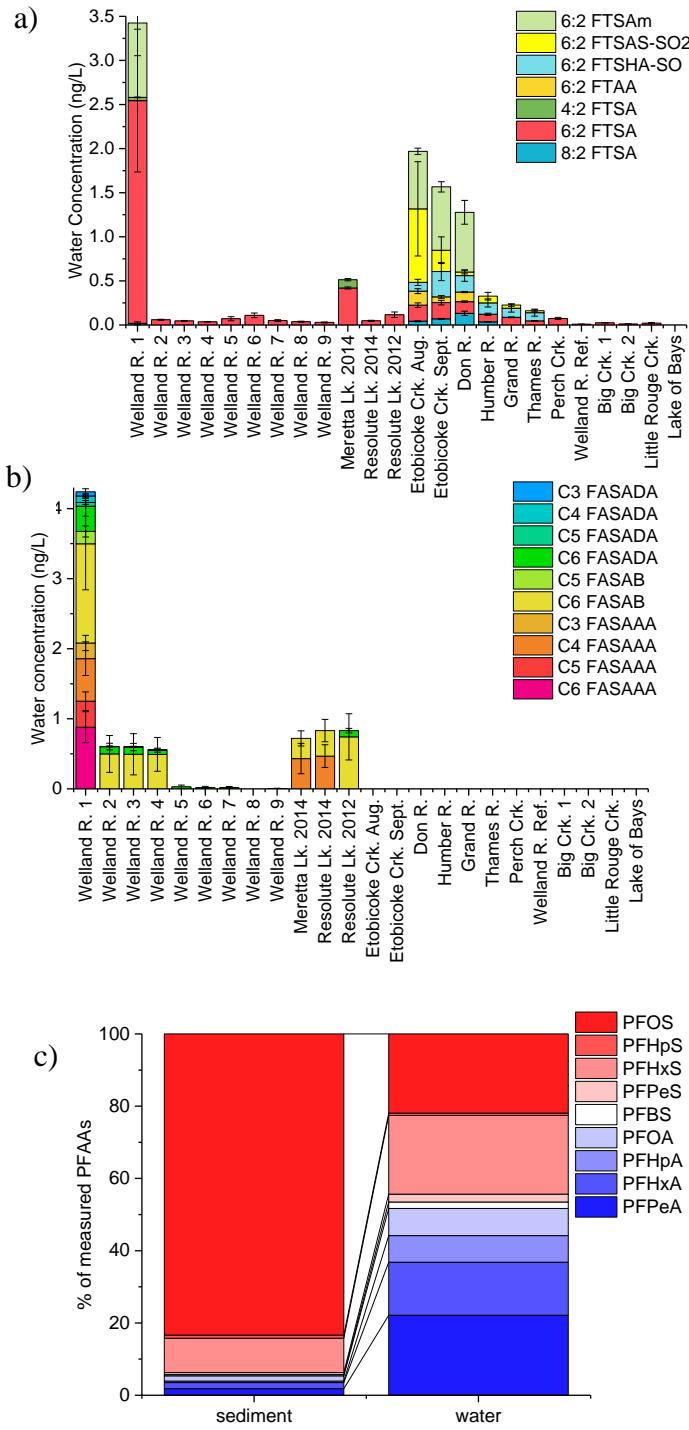
PFAS	AFFF-impacted vs. Urban			AFFF-impacted vs. Rural			Urban vs. Rural		
	Medians (ng/L)	U	p	Medians (ng/L)	U	p	Medians (ng/L)	U	p
PFPeA	53, 5.0	70	0.0014	53, 0.83	70	0.0014	5.0, 0.83	19	0.21
PFHxA	36, 6.7	70	0.0014	36, 0.9	70	0.0014	6.7, 0.9	24	0.021
PFHpA	18, 2.7	70	0.0014	18, 0.4	70	0.0014	2.7, 0.4	23	0.036
PFOA	19, 3.7	70	0.0014	19, 0.7	70	0.0014	3.7, 0.7	25	0.012
PFBS	4.4, 2.5	55	0.07	4.4, 0.3	66	0.0048	2.5, 0.3	23	0.037
PFPeS	3.9, 0.1	66	0.0047	--	--	--	--	--	--
PFHxS	38, 1.5	67	0.0035	38, 0.2	70	0.0014	1.5, 0.2	23	0.034
PFHpS	1.9, 0.3	63	0.011	--	--	--	--	--	--
PFOS	73, 7.2	68	0.0026	73, 1.2	70	0.0014	7.2, 1.2	25	0.012
FHxSA	2.4, 0.32	67	0.0035	--	--	--	--	--	--
6:2 FTSA	0.07, 0.09	32	0.82	0.07, 0.01	70	0.0014	0.09, 0.01	25	0.012
6:2 FTAB	0.05, 0.81	17	0.11	--	--	--	--	--	--

Light grey shading indicates groups not significantly different at  $p < 0.05$  level. Dark grey shading indicated comparisons not made due to non-detects.

**Table S11:** Concentrations of PFASs in sediment samples in ng/g ( $\pm$  standard deviation)

<b>PFAS</b>	<b>Welland R. 1 (3.0% OC)</b>	<b>Welland R. 2 (1.9% OC)</b>	<b>Welland R. 5 (2.8% OC)</b>	<b>Welland R. 6 (1.0% OC)</b>	<b>Big Crk. 1 (3.8% OC)</b>
<b>PFPeA</b>	<0.5	nd	<0.5	nd	nd
<b>PFHxA</b>	0.20 $\pm$ 0.02	nd	<0.2	<0.2	nd
<b>PFHpA</b>	<0.1	nd	nd	nd	nd
<b>PFOA</b>	<0.2	<0.2	<0.2	<0.2	nd
<b>PFBS</b>	<0.15	nd	nd	nd	nd
<b>PFPeS</b>	<0.2	nd	nd	nd	nd
<b>PFHxS</b>	1.1 $\pm$ 0.2	0.21 $\pm$ 0.03	0.81 $\pm$ 0.07	0.24 $\pm$ 0.06	nd
<b>PFHpS</b>	<0.2	<0.2	nd	<0.2	nd
<b>PFOS</b>	10 $\pm$ 1	8.3 $\pm$ 1.1	10 $\pm$ 1	4.2 $\pm$ 0.2	0.82 $\pm$ 0.11
<b>6:2 FTSA</b>	<0.1	nd	nd	nd	<0.1
<b>EtFOSAA</b>	nd	nd	0.094 $\pm$ 0.014	<0.09	nd
<b>FHxSA</b>	0.19 $\pm$ 0.02	<0.06	0.089 $\pm$ 0.011	<0.06	nd
<b>FOSA</b>	nd	nd	<0.1	nd	nd
<b>6:2 FTSAm</b>	<0.2	nd	nd	nd	nd
<b>6:2 FTAB</b>	0.44 $\pm$ 0.05	nd	nd	nd	0.11 $\pm$ 0.04
<b>5:3 FTB</b>	<0.1	nd	<0.1	nd	nd
<b>5:1:2 FTB</b>	<0.2	nd	<0.2	nd	nd
<b>7:3 FTB</b>	0.27 $\pm$ 0.16	<0.1	nd	nd	nd
<b>7:1:2 FTB</b>	1.0 $\pm$ 0.9	<0.2	<0.2	nd	nd
<b>9:3 FTB</b>	<0.1	nd	nd	nd	nd
<b>9:1:2 FTB</b>	<0.2	nd	nd	nd	nd
<b>6:2 FTAA</b>	nd	nd	nd	nd	<0.1
<b>C6 FASAAm</b>	<0.3	nd	nd	nd	nd

nd = not detected above detection limit; OC= organic carbon; Large standard deviations for FTBs and FHxSAAm concentrations are due to use of average of calibrations using both transitions to reflect uncertainty in the calibration sensitivity.



**Figure S2:** a) Concentrations of fluorotelomer substances other than FTABs and FTBs in surface waters in ng/L with error bars showing standard deviations. b) Concentrations of fluorotelomer sulfonamido AFFF components in surface waters in ng/L with error bars showing standard deviations. c) Distribution of PFCAs and PFSAs between sediment and water at Welland River 1 sampling site.

**Table S12:** Sediment water distribution coefficient ( $\log K_d$ ) and organic carbon water distribution coefficient ( $\log K_{oc}$ ) determined from field sediments and waters from the Welland River and Big Creek

PFAS	$\log K_d$ ( $\pm$ standard deviation; $n$ in brackets)	$\log K_{oc}$ ( $\pm$ standard deviation; $n$ in brackets)
PFHxA	0.31 (1)	1.83 (1)
PFHxS	$0.71 \pm 0.25$ (4)	$2.40 \pm 0.27$ (4)
PFOS	$2.03 \pm 0.40$ (5)	$3.67 \pm 0.28$ (5)
FHxSA	$1.17 \pm 0.22$ (2)	$2.71 \pm 0.25$ (2)
EtFOSAA	2.77 (1)	4.33 (1)
6:2 FTAB	1.1 (1)	2.7 (1)
7:3 FTB (qualitative)	1.5 (1)	3.0 (1)
7:1:2 FTB (qualitative)	1.8 (1)	3.3 (1)

See Table S11 for the %OC in the sediment samples and to see which sediments each PFAS was detected in.

## References

- (1) D'Agostino, L. A.; Mabury, S. A. Aerobic biodegradation of 2 fluorotelomer sulfonamide-based aqueous film-forming foam components produces perfluoroalkyl carboxylates. *Environ. Toxicol. Chem.* **2017**, *36* (8), 2012–2021.
- (2) Harding-Marjanovic, K. C.; Houtz, E. F.; Yi, S.; Field, J. A.; Sedlak, D. L.; Alvarez-Cohen, L. Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environ. Sci. Technol.* **2015**, *49* (13), 7666–7674.