Supporting Information

Fate of Per- and Polyfluoroalkyl Ether Acids in the Total Oxidizable Precursor Assay and Implications on Analysis of Impacted Water

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Text S1. Total oxidizable precursor (TOP) assay method validation: To assess comparability to a previous study,[1] TOP assay validation tests were performed with two perfluoroalkyl acid (PFAA) precursors, i.e. 6:2 fluorotelomer sulfonate (6:2 FtS, Figure S4) and perfluorooctanesulfonamide (PFOSA, Figure S5). Results indicated no statistically significant difference (t-test, n=2, $p<0.05$) between the original TOP assay protocol[1] and the one employed here. Therefore, we used the TOP assay protocol without additional modifications to assess the fate of per- and polyfluoroalkyl ether acids (PFEAs) in the TOP assay.

Text S2. TOP assay control experiments: Each TOP assay was performed in duplicate, and measured concentrations of per- and polyfluoroalkyl substances (PFASs) had relative standard deviations of less than 20% across replicates. For negative controls, deionized water was heated with persulfate and NaOH, and no PFAS was formed at measurable levels upon oxidation. Also, heated controls of 6:2 FtS and GenX without the addition of persulfate or NaOH indicated no measurable loss of PFAA precursors or PFEAs upon heating (Figure S6).

Text S3. Solid phase extraction (SPE): Upon addition of isotopically labeled internal standards (Table S1), a vacuum manifold was used to load the entire 125-mL sample onto an Oasis WAX Plus SPE cartridge (225 mg sorbent, 60 µm particle size) that had been pre-rinsed with methanol and deionized water. Upon loading, SPE cartridges were washed with 4 mL of sodium acetate buffer (pH 4.0, 25 mM). For the collection of PFOSA, SPE cartridges were eluted using 4 mL of methanol; for the collection of all other analytes, SPE cartridges were washed with 4 mL of methanol which was then discarded, and eluted using 4 mL of 0.1% NH_4OH in methanol. The eluent was evaporated under nitrogen gas at 40 °C to a volume of approximately 1 mL. Then, 100 µL of concentrated sample was diluted with 300 µL of 0.4 mM ammonium formate in an LC vial for liquid chromatography-high resolution mass spectrometry (LC-HRMS) analysis. Sample preparation by SPE could have led to loss of some transformation products that may have formed in the TOP assay. SPE was used to avoid the injection of large quantities of salt (5 mM of persulfate, 150 mM of NaOH and nitric acid used to neutralize to pH 5-9) from the TOP assay.

Text S4. Mass spectrometry analysis for individual PFEA: LC-HRMS analysis for individual PFEA was performed using an Agilent 1100 series HPLC interfaced with a 6210 series

Accurate-Mass time-of-flight mass spectrometry (TOF MS) system as previously described.[2,3] Chromatographic separation was accomplished using an InfinityLab Poroshell 120 EC-C8 column (2.1 × 50 mm, 2.7 μm; Agilent). The method conditions were as follows: 0.3 mL/min flow rate; column at 30 °C; mobile phases A: ammonium formate buffer (0.4 mM) in water/methanol (95:5 v/v), and mobile phase B: ammonium formate (0.4 mM) in methanol/water (95:5 v/v); gradient: 0−15 min linear from 75:25 A/B to 15:85 A/B; followed by a 4 min post time for equilibration. Compounds were ionized by operating electrospray ionization (ESI) in negative mode. The dual-electrospray source provided purine and hexakis phosphazine as internal reference masses from the secondary spray. The instrument was operated in 4GHz high resolution mode in a mass window of 100-1700 m/z. Raw data were processed using Agilent MassHunter, ProFinder, and Mass Profiler Professional. To probe suspect features, we looked for integrated peak areas that exhibited a 2-fold or greater change between samples following TOP assay treatment and (1) samples before TOP assay treatment and (2) deionized water samples following TOP assay treatment. MS spectra collected for each feature of interest were manually checked to identify fluorinated structures. Emphasis was placed on chemicals demonstrating a negative mass defect, as described elsewhere.[3]

Text S5. Mass spectrometry analysis for Cape Fear River water: Environmental sample analysis was performed using a Thermo Vanquish UPLC interfaced with a Thermo Orbitrap Fusion mass spectrometer. Chromatographic separation was carried out with a Accurcore C18+ column (2.1 mm × 100 mm × 1.5 um particles) at a flow rate of 0.3 mL/min with a binary mobile phase gradient composed of Solvent A (95:5 v/v water:methanol, 0.4mM ammonium formate) and Solvent B (95:5 v/v methanol:water, 0.4 mM ammonium formate). Mobile phase compositions over the gradient were as follow: 0-0.5 min 80:20 A/B, 0.5-2 min linear from 80:20 A/B to 50:50 A/B, 2-3 min 50:50 A/B, 3-3.1 min linear from 50:50 A/B to 40:60 A/B, 3.1-4 min 40:60 A/B, 4-4.1 min linear from 40:60 A/B to 0:100 A/B, and 4.1-6 min 0:100 A/B; with a 3 min post time for equilibration. Detection took place on a coupled Thermo Orbitrap Fusion mass spectrometer operated with a HESI electrospray source in negative mode. High resolution MS1 and MS2 scans were collected in data dependent mode. Scan details can be found in Table S3. Known PFASs were identified by exact precursor mass (+/-5 ppm) and comparison of fragmentation spectra to existing standards. Raw MS data were processed using Thermo

Compound Discoverer 2.1 for sample alignment and feature extraction. Software settings for alignment, peak picking, and chemical formula prediction can be found in Table S3. For suspect features, integrated peak areas for identified chemical features were compared between samples treated before the TOP assay, samples treated after the TOP assay and deionized water treated after the TOP assay. Chemicals of interest were defined as species exhibiting a 2-fold or greater change between samples following TOP assay treatment and (1) samples before TOP assay treatment and (2) deionized water samples following TOP assay treatment. The MS/MS spectra of significantly varying features were manually examined to identify fluorinated structures, but no new fluorinated structures were identified.

Text S6. PFAS quantitation: PFAS concentrations in all samples were calculated from area ratios (i.e. peak area for the native standard divided by the peak area for the isotopically labeled internal standard) and standard curves. To develop a standard curve, calibration standards were prepared from 10 ng/L to 1,500 ng/L, with seven calibration points. Calibration standards were analyzed in duplicate before and after each sample batch. After mass spectrometry analysis, area ratios were plotted against known concentrations of the calibration standards. Standard curves were mathematically described by a concentration weighted (1/x), second-order polynomial fit. The R_2 for legacy PFASs was >0.99 and for PFEA > 0.97. At the selected ionization conditions, variability in PFEA responses exceeded that of PFCA and PFSA responses. Example standard curves are shown in Figure S7. The quantitation limit (QL) was defined as the first point of the standard curve with detectable peak area, which yielded calculated values within ± 30% error. The QL for LC-TOF MS was 50 ng/L for PFO4DA, 100 ng/L for PFO2HxA, PFO3OA and PFO5DoA, and 10 ng/L for all other PFASs. The QL for high-resolution quadrupole Orbitrap mass spectrometry was 100 ng/L for PFO2HxA, and 10 ng/L for all other PFASs.

Text S7. Quality assurance/quality control (QA/QC): QC samples included instrument blanks (no isotopically labeled internal standard added), method blanks, and continuing calibration verification at 100 and 500 ng/L using standards from a second source when possible (acceptable within ± 30% error). Instrument blanks (75:25 water:methanol) were run between samples to verify that there was no carry over. The storage time for samples was less than three weeks at 4°C.

Text S8. Calculation of molar yield: Molar yields of PFASs from thermolyzing PFEAs in the TOP assay shown in Table S2 were calculated from the following equation:

$$\Delta[Product]/[PFEA]_0 = \frac{\overline{b}}{\overline{a}} \pm \frac{\overline{b}}{\overline{a}} \sqrt{(\frac{S_a}{\overline{a}})^2 + (\frac{S_b}{\overline{b}})^2}$$

where $\overline{a}$ and $\overline{b}$ are the average concentrations of PFEAs before and after oxidation in duplicate experiments, respectively; S_a and S_b are the standard deviations of concentrations of PFEAs before and after oxidation in duplicate experiments, respectively.

Table S1. Per- and polyfluoroalkyl substances (PFASs) targeted in this study

Analyte	Formula	CAS# (hyperlinked to US EPA Chemicals Dashboard)	Source [a]	Mass-Labeled Internal Standard
Class 1: Perfluorocarboxylic acids (PFCAs)				
Perfluorobutanoic acid (PFBA)	$C_4HF_7O_2$	375-22-4	1	$^{13}C_4$-PFBA
Perfluoropentanoic acid (PFPeA)	$C_5HF_9O_2$	2706-90-3	1	$^{13}C_4$-PFBA
Perfluorohexanoic acid (PFHxA)	$C_6HF_{11}O_2$	307-24-4	1	$^{13}C_2$-PFHxA
Perfluoroheptanoic acid (PFHpA)	$C_7HF_{13}O_2$	375-85-9	1	$^{13}C_2$-PFHxA
Perfluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	335-67-1	1	$^{13}C_4$-PFOA
Perfluorononanoic acid (PFNA)	$C_9HF_{17}O_2$	375-95-1	1	$^{13}C_5$-PFNA
Perfluorodecanoic acid (PFDA)	$C_{10}HF_{19}O_2$	335-76-2	1	$^{13}C_2$-PFDA
Class 2: Perfluorosulfonic acids (PFSAs)				
Perfluorobutane sulfonic acid (PFBS)	$C_4HF_9SO_3$	375-73-5	1	$^{18}O_2$-PFHxS
Perfluorohexane sulfonic acid (PFHxS)	$C_6HF_{13}SO_3$	355-46-4	1	$^{18}O_2$-PFHxS
Perfluorooctane sulfonic acid (PFOS)	$C_8HF_{17}SO_3$	1763-23-1	1	$^{13}C_4$-PFOS
Class 3: Per- and polyfluoroalkyl ether acids (PFEAs)				
Perfluoroalkyl mono-ether carboxylic acids (mono-ether PFECAs)				
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	674-13-5	2, 3	$^{13}C_4$-PFBA
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	$C_4HF_7O_3$	377-73-1	4	$^{13}C_4$-PFBA
Perfluoro-2-methoxypropanoic acid (PMPA)	$C_4HF_7O_3$	13140-29-9	3	$^{13}C_4$-PFBA
Perfluoro-4-methoxybutanoic acid (PFMOBA)	$C_5HF_9O_3$	863090-89-5	4	$^{13}C_2$-PFHxA
Perfluoro-2-ethoxypropanoic acid (PEPA)	$C_5HF_9O_3$	267239-61-2	3	$^{13}C_2$-PFHxA
Perfluoro-2-propoxypropanoic acid (PFPrOPrA) = Hexafluoropropylene oxide-dimer acid (HFPO-DA) = parent acid of "GenX"	$C_6HF_{11}O_3$	13252-13-6	1	$^{13}C_3$-PFPrOPrA
Perfluoroalkyl multi-ether carboxylic acids (multi-ether PFECAs)				
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	39492-88-1	3	$^{13}C_4$-PFBA
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	39492-89-2	3	$^{13}C_2$-PFHxA
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	$C_6HF_{11}O_6$	39492-90-5	3	$^{13}C_2$-PFHxA
Perfluoro(3,5,7,9,11-pentaoxadodecanoic) acid (PFO5DoA)	$C_7HF_{13}O_7$	39492-91-6	3	$^{13}C_5$-PFNA
Polyfluoroalkyl ether acids				
Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Nafion	$C_7H_2F_{14}SO_5$	749836-20-2	3	$^{13}C_4$-PFOS

by-product 2)

1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonate (NVHOS)	$C_4H_2F_8SO_4$	801209-99-4	3	$_{18}O_2$-PFHxS
4,8-dioxa-3H-perfluorononanoic acid = parent acid of "ADONA"	$C_7H_2F_{12}O_4$	919005-14-4	1	$_{13}C_4$-PFOA
2,2,3,3-tetrafluoro-3-((1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl)oxy)propanoic acid (HydroEVE)	$C_8H_2F_{14}O_4$	773804-62-9	3	$_{13}C_4$-PFOA
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS, main component of F-53B)	$C_8HF_{16}SO_4Cl$	756426-58-1	1	$_{13}C_4$-PFOS

a Source: 1 Wellington Laboratories (Guelph, ON, Canada), 2 Fluoryx Labs (Carson City, NV), 3 The Chemours Company (Wilmington, DE), 4 SynQuest Laboratories (Alachua, FL).

Highlighted chemicals indicate structural isomers. See Figure S1.

CAS#s are hyperlinked to the US EPA chemicals dashboard for additional information. Unique searchable DTXSIDs for each chemical are found at the end of each hyperlink. For example PFOAs hyperlink is https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID8031865 with a unique DTXSID of DTXSID8031865.

Table S2. Molar yields of PFASs from per- and polyfluoroalkyl ether acids (PFEAs) in the TOP assay

PFEA	[Persulfate]$_0$	[PFEA]$_0$	Product	[Product]	Δ[Product]/ [PFEA]$_0$ [a]
PFMOAA	5 mM	3.0 nmol/L	PFMOAA	3.0 nmol/L	100% ± 7%
PFMOPrA	5 mM	5.1 nmol/L	PFMOPrA	4.9 nmol/L	96% ± 17%
PMPA	5 mM	2.9 nmol/L	PMPA	3.0 nmol/L	105% ± 9%
PFMOBA	5 mM	3.4 nmol/L	PFMOBA	3.4 nmol/L	100% ± 21%
PEPA	5 mM	2.4 nmol/L	PEPA	2.5 nmol/L	102% ± 16%
PFPrOPrA	5 mM	2.3 nmol/L	PFPrOPrA	2.3 nmol/L	100% ± 14%
PFO2HxA	5 mM	4.0 nmol/L	PFO2HxA	3.6 nmol/L	91% [b]
PFO3OA	5 mM	2.7 nmol/L	PFO3OA	3.0 nmol/L	109% ± 1%
PFO4DA	5 mM	2.5 nmol/L	PFO4DA	2.3 nmol/L	95% ± 6%
PFO5DoA	5 mM	2.4 nmol/L	PFO5DoA	2.2 nmol/L	90% ± 3%
Nafion by-product 2	5-20 mM [c]	0.88 nmol/L	ND [d]		
NVHOS	5-20 mM	2.2 nmol/L	ND		
ADONA	5 mM	3.2 nmol/L	PFMOPrA	3.1 nmol/L	98% ± 19%
HydroEVE	5 mM	2.7 nmol/L	ND		
F-53B	5 mM	0.66 nmol/L	F-53B	0.68 nmol/L	104% ± 13%

[a] Calculation of molar yield is detailed in Text S8.

[b] Standard deviation of molar yield for PFO2HxA was not calculated due to a lack of duplicates.

[c] TOP assays were conducted with 5 mM and 20 mM persulfate, and results indicated precursors were completely converted under both conditions.

[d] No product or intermediate was detected above QL by LC-HRMS in the sample after oxidation.

Table S3. Scan details and software settings for the Thermo Orbitrap Fusion mass spectrometer

Parameter	Setting value
Ion source	
Ion source type	H-ESI
Spray voltage	Static
Positive ion (V)	3500
Negative ion (V)	2200
Sheath gas (Arb)	25
Aux gas (Arb)	6
Sweep gas (Arb)	0
Ion transfer tube temp (°C)	300
Vaporizer temp (°C)	30
MS1 scan	
Detector type	Orbitrap
Resolution	30000
Scan range (m/z)	100-1000
RF lens (%)	60
AGC target	4.0e5
Maximum injection time (ms)	50
Filters	
Expected peak width (FWHM,s)	2
Desired apex window (%)	30
Intensity threshold	2.5e4
Data dependent mode	Cycle time
Time between master scans (s)	0.3
DDA MS2 scan	
Isolation mode	Quadrupole
Isolation window (m/z)	1.6
Activation type	HCD
HCD collision energies (%)	30, 40, 50
Detector type	Orbitrap
Resolution	30000
First mass (m/z)	50
AGC target	5.0e4
Maximum injection time (ms)	54

Table S4. Comparison of analyte lists for the current TOP assay and the expanded TOP assay

Class	Analyte list for the current TOP assay	Proposed analyte list for the expanded TOP assay	
PFCAs	PFBA		
	PFPeA		
	PFHxA		
	PFHpA		
	PFOA		
	PFNA	Same as the current TOP assay	
	PFDA		
	Perfluoroundecanoic acid (PFUnA) [a]		
	Perfluorododecanoic acid (PFDoA) [a]		
	Perfluorotridecanoic acid (PFTrDA) [a]		
	Perfluorotetradecanoic acid (PFTA) [a]		
PFSAs	PFBS		PFBS
	Perfluoropentane sulfonic acid (PFPeS) [a]		PFPeS
	PFHxS		PFHxS
	Perfluoroheptane sulfonic acid (PFHpS) [a]	Same as the current TOP assay	PFHpS
	PFOS		PFOS
	Perfluorononane sulfonic acid (PFNS) [a]		
	Perfluorodecane sulfonic acid (PFDS) [a]		
PFEAs	Not applicable	PFMOAA	
		PFMOPrA	
		PMPA	
		PFMOBA	
		PEPA	
		PFPrOPrA	
		PFO2HxA	
		PFO3OA	
		PFO4DA	
		PFO5DoA	
		F-53B	

[a] Compounds were not targeted in this paper, but were included in EPA method 537.1 or targeted in other paper.

Table S5. PFAS concentrations on a mass basis in a water sample collected at William O. Huske Lock and Dam in August 2014 before and after the TOP assay

Class	PFAS	Average concentration before oxidation (ng/L)	Average concentration after oxidation (ng/L)	% Change in concentration after oxidation to before oxidation
PFCAs	PFBA	32	42	+ 31%
	PFPeA	22	36	+ 60%
	PFHxA	12	16	+ 28%
	PFHpA	12	14	+ 16%
	PFOA	11	16	+ 54%
	PFNA	<10	<10	
	PFDA	<10	<10	
	ΣPFCAs	89	120	
PFSAs	PFBS	<10	<10	
	PFHxS	<10	<10	
	PFOS	17	20	+ 20%
	ΣPFSAs	17	20	
PFEAs	PFMOAA	730,000	710,000	- 3.3%
	PFO2HxA	180,000	190,000	+ 1.5%
	PFO3OA	58,000	61,000	+ 4.8%
	PFO4DA	5,100	4,600	- 9.5%
	PFO5DoA	330	290	- 11%
	PMPA	1,300	1,000	- 22%
	PEPA	420	500	+ 17%
	PFPrOPrA	3,100	3,000	- 2.6%
	Nafion by-product 2	670	<10	>-98%
	NVHOS	44	<10	>-77%
	HydroEVE	1,200	<10	>-99%
	ΣPFEAs	990,000	960,000	
Σ(all targeted PFASs)		990,000	960,000	

Table S6. PFAS concentrations on a mass basis in a water sample collected at Lock and Dam #1 in July 2015 before and after the TOP assay

| Class	PFAS	Average concentration before oxidation (ng/L)	Average concentration after oxidation (ng/L)	% Change in concentration after oxidation to before oxidation
PFCAs	PFBA	26	31	+ 21%
	PFPeA	26	35	+ 33%
	PFHxA	27	33	+ 24%
	PFHpA	22	25	+ 13%
	PFOA	19	21	+ 11%
	PFNA	<10	<10	
	PFDA	<10	<10	
	ΣPFCAs	120	150	
PFSAs	PFBS	<10	<10	
	PFHxS	18	27	+ 49%
	PFOS	27	29	+ 8.4%
	ΣPFSAs	45	56	
PFEAs	PFMOAA	110,000	95,000	- 15%
	PFO2HxA	7,800	8,200	+ 5.4%
	PFO3OA	6,300	7,000	+ 11%
	PFO4DA	350	330	- 4.9%
	PFO5DoA	200	153	- 23%
	PMPA	690	740	+ 6.5%
	PEPA	200	280	+ 39%
	PFPrOPrA	780	790	+ 1.1%
	Nafion by-product 2	83	<10	>-87%
	NVHOS	19	<10	>-47%
	HydroEVE	20	<10	>-50%
	ΣPFEAs	130,000	110,000	
Σ(all targeted PFASs)		130,000	110,000	

Table S7. PFAS concentrations on a mass basis in a water sample collected at William O. Huske Lock and Dam in April 2018 before and after the TOP assay. Only PFMOAA was detected above QL in this water sample.

Class	PFAS	Average concentration before oxidation (ng/L)	Average concentration after oxidation (ng/L)	% Change in concentration after oxidation to before oxidation
PFEAs	PFMOAA	92	89	- 3.2%
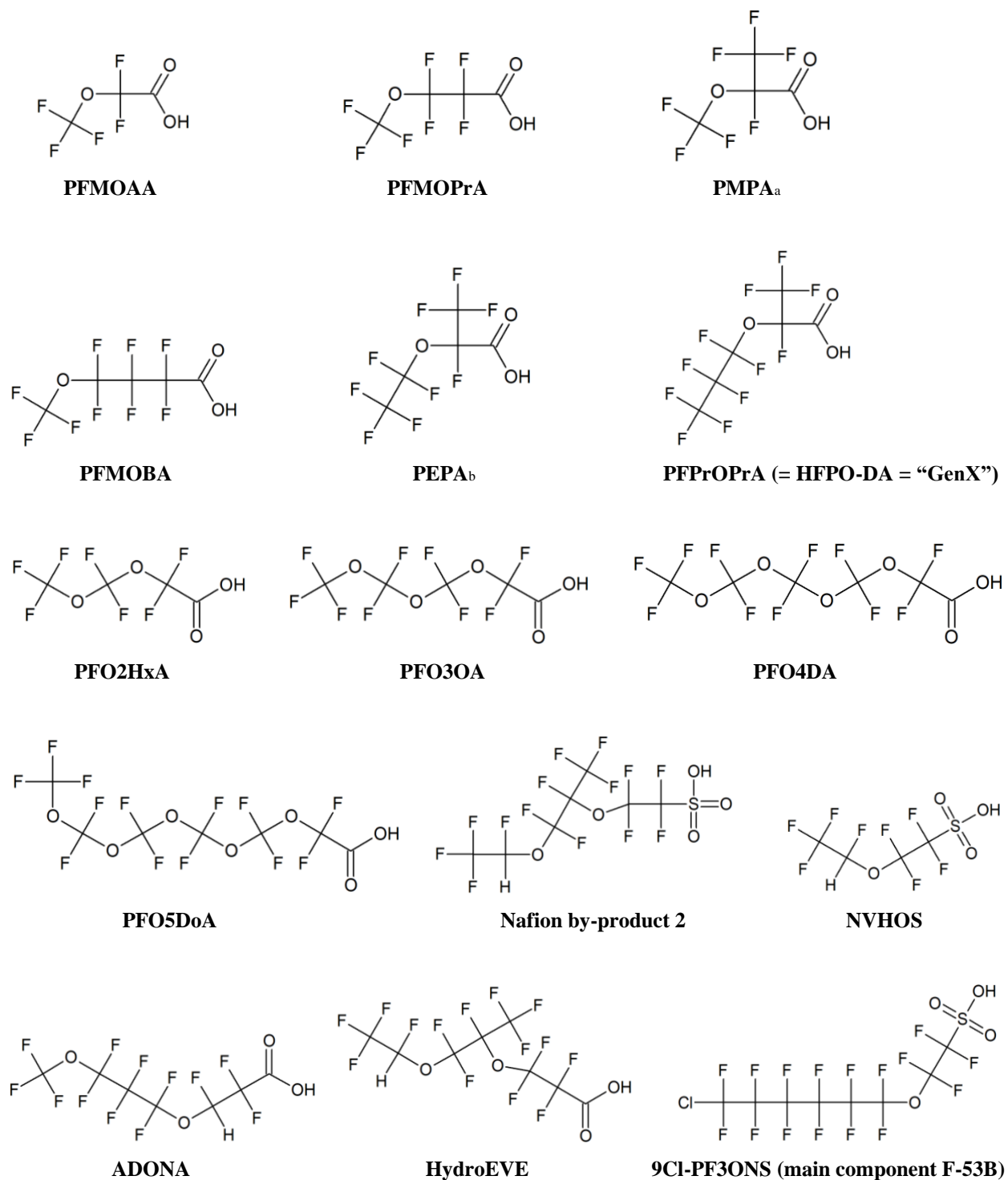
Figure S1. Molecular structures of per- and polyfluoroalkyl ether acids evaluated in this study.

a In Sun et al. (2016),4 this compound was presented as PFMOPrA. However, it is likely that environmental samples contain the branched isomer, PMPA, shown here and in Strynar et al. (2015).2

b In Sun et al. (2016),[4] this compound was presented as PFMOBA. However, it is likely that environmental samples contain the branched isomer, PEPA, shown here and in Strynar et al. (2015).[2]
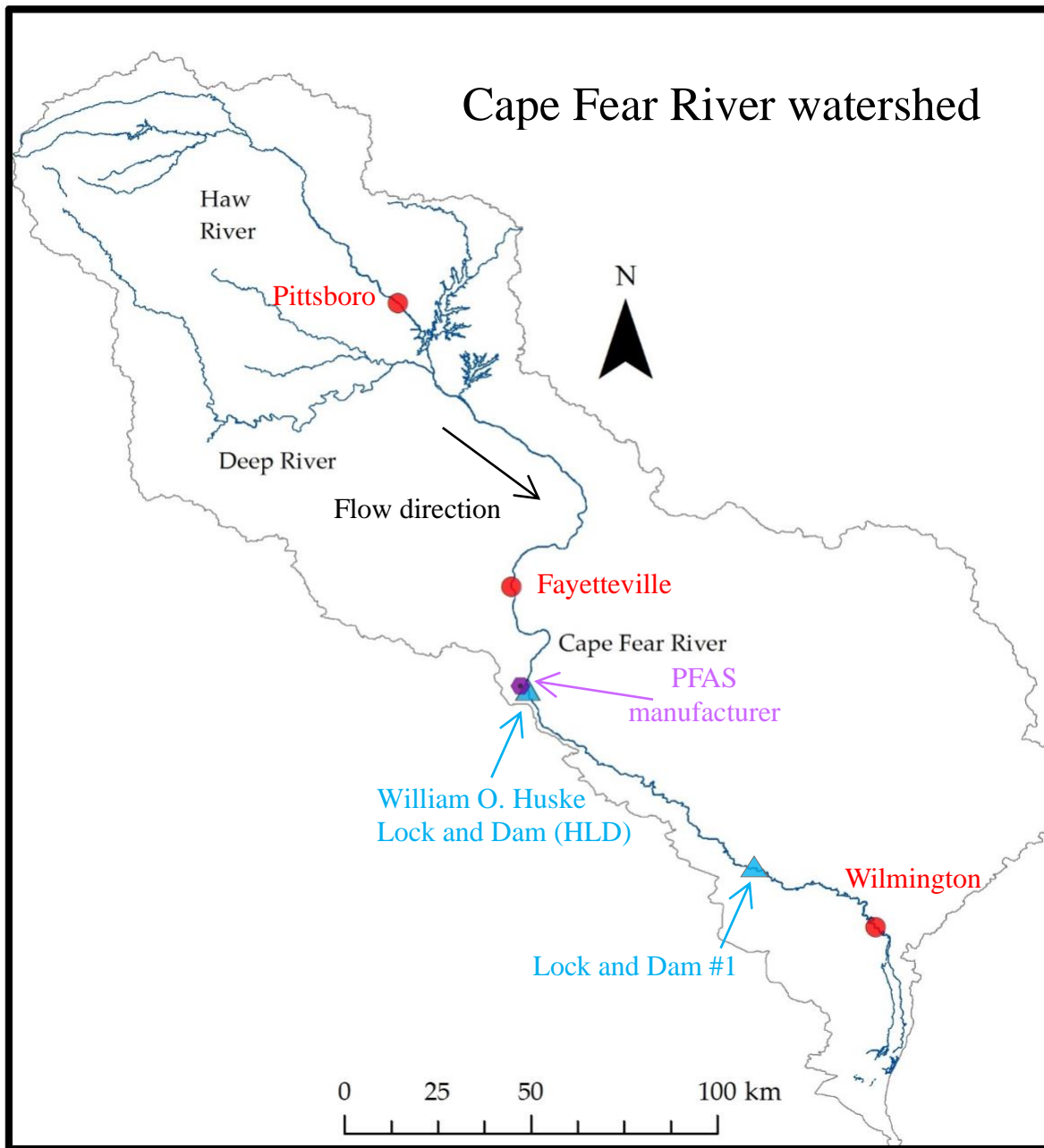
Figure S2. Surface water sampling sites in Cape Fear River watershed of North Carolina.
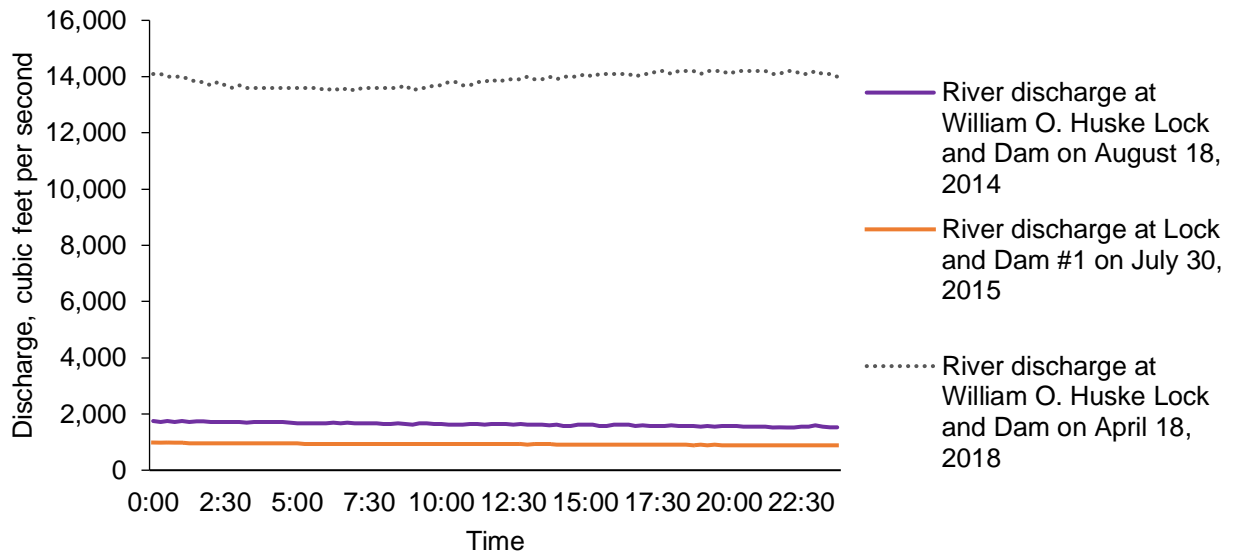
Figure S3. Discharge of Cape Fear River at the selected sampling locations and dates.

Average river discharges are summarized as below.

Date	Location	Average river discharge (ft3/s)
August 18, 2014	William O. Huske Lock and Dam	1,600
July 30, 2015	Lock and Dam #1	930
April 18, 2018	William O. Huske Lock and Dam	14,000

Source: https://www.usgs.gov/ (accessed April 13, 2019).
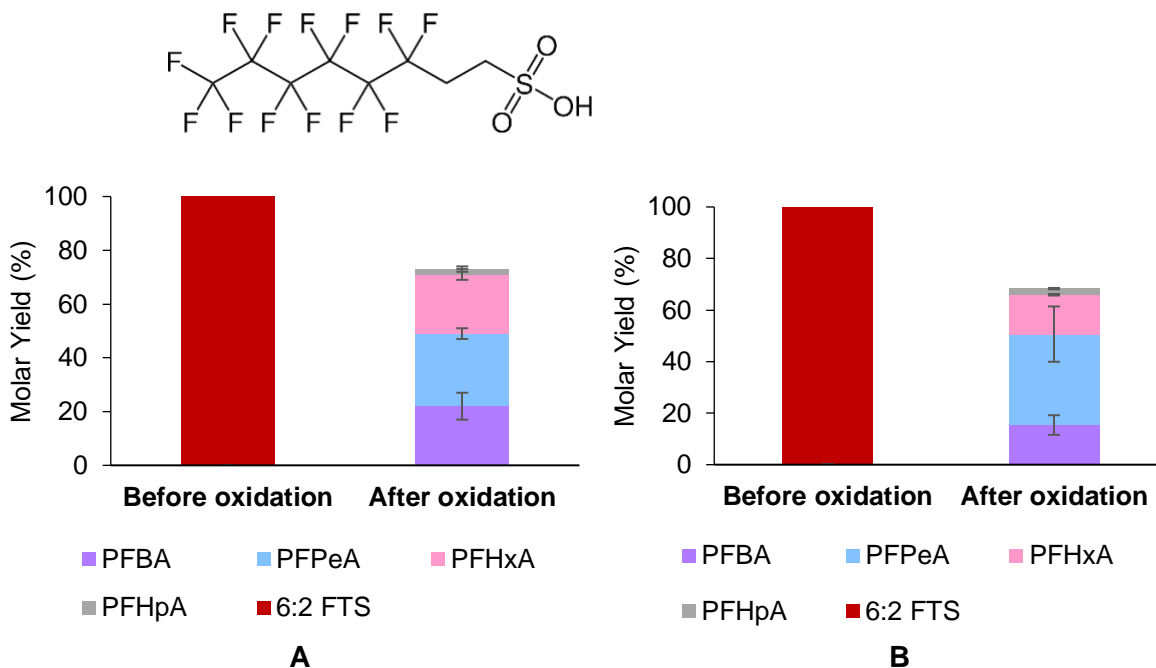
Figure S4. Molar yield of PFCAs from 6:2 fluorotelomer sulfonate (6:2 FtS) thermolyzed in the presence of persulfate in Houtz et al. (2012)[1] (A) and in this study (B).

Structure of 6:2 FtS is shown above figure panels. The precursor was oxidized as discussed, and analyzed for the concentrations of PFCAs. Average and standard deviation of duplicate experiments are shown. The results in this study indicated molar yields of $15 \pm 4\%$ for PFBA, $35 \pm 11\%$ for PFPeA, $15 \pm 0.3\%$ for PFHxA, and $2 \pm 0.3\%$ for PFHpA upon oxidation of 6:2 FtS. In the previous study, 6:2 FtS converted to $22 \pm 5\%$ of PFBA, $27 \pm 2\%$ of PFPeA, $22 \pm 2\%$ of PFHxA and $2 \pm 1\%$ of PFHpA in the TOP assay.[1]
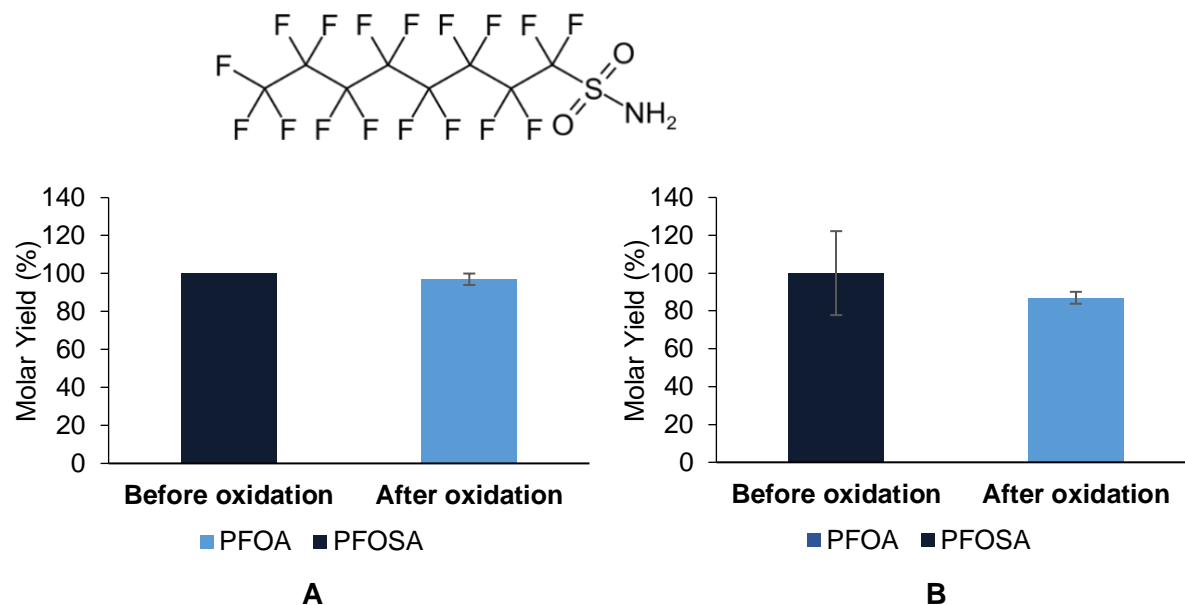
Figure S5. Molar yield of PFOA from perfluorooctanesulfonamide (PFOSA) thermolyzed in the presence of persulfate in Houtz et al. (2012)[1] (A) and in this study (B).

Structure of PFOSA is shown above figure panels. The precursor was oxidized as discussed, and analyzed for the concentrations of PFCAs. Average and standard deviation of duplicate experiments are shown. The results in this study indicated molar yields of 87 ± 20 % for PFOA upon oxidation of PFOSA. In the previous study, PFOSA converted to $97 \pm 3\%$ of PFOA in the TOP assay.[1]
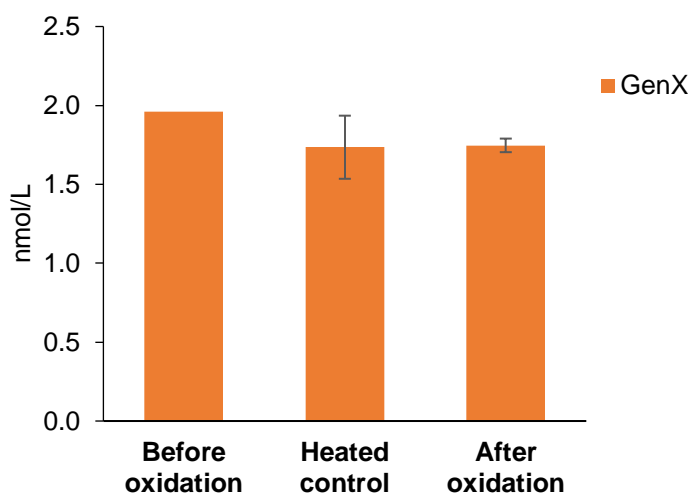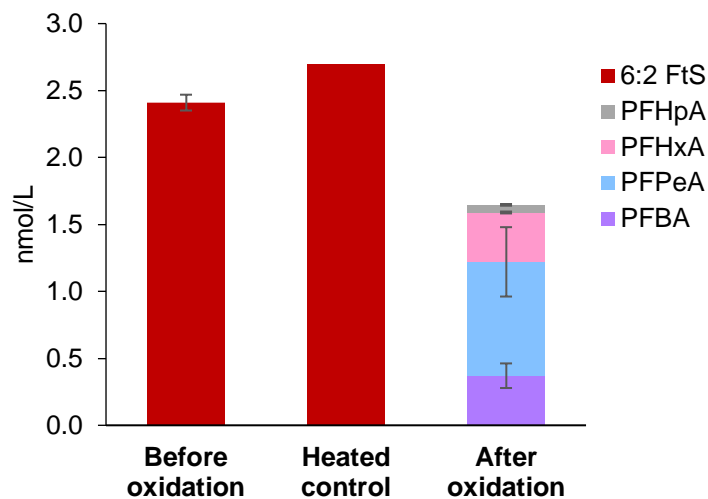
Figure S6. Molar concentrations of PFASs in deionized water before oxidation, heated control (thermolyzed without persulfate or NaOH addition) and after oxidation (heated with 5 mM persulfate and 150 mM NaOH) in the TOP assay. Averages and standard deviations of duplicate experiments are shown.
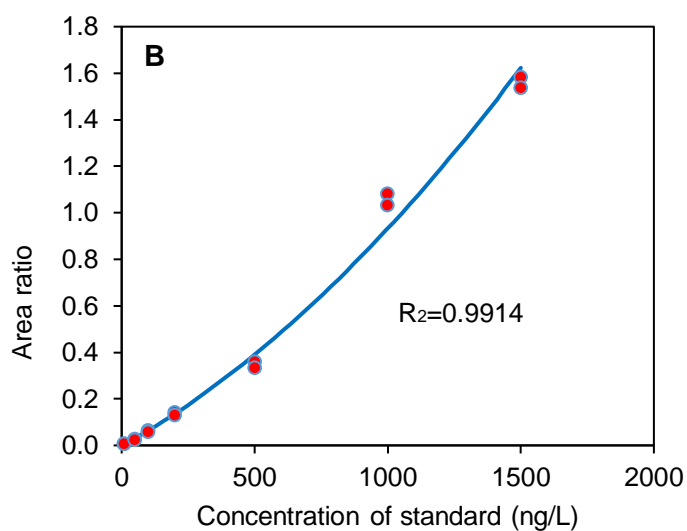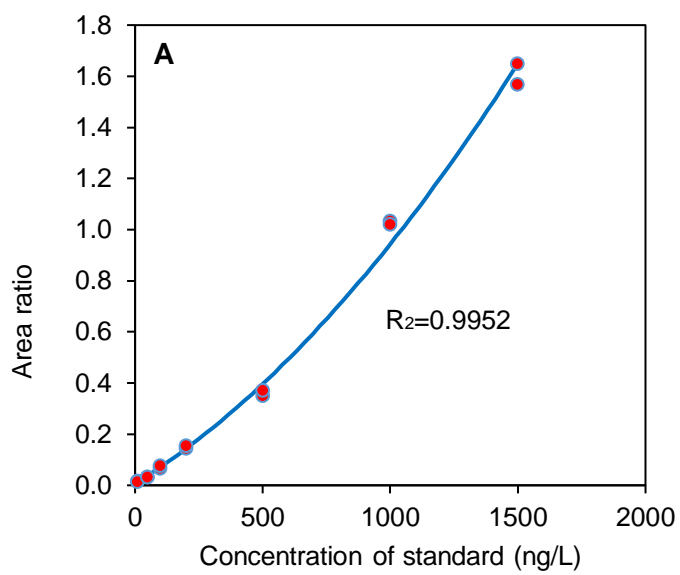
Figure S7. Representative calibration curves for PFBA (A) and ADONA (B). Red dots represent area ratios (i.e. measured peak area for the native standard divided by measured peak area for the isotopically labeled internal standard), and blue line is the concentration-weighted (1/x) second-order polynomial fit.
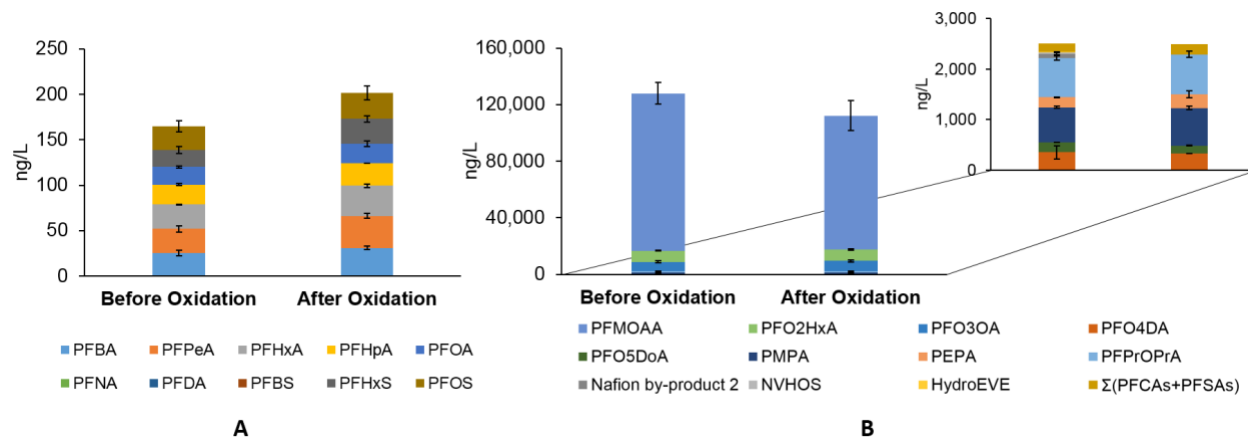
Figure S8. Application of the TOP assay with traditionally analyzed PFCAs and PFSAs (ng/L) (A) and with expanded PFEA analyte list (B) to a water sample collected at Lock and Dam #1 in July 2015. The callout in Figure S8(B) highlights the concentrations of PFASs other than PFMOAA, PFO2HxA and PFO3OA. Averages and standard deviations of duplicate experiments are shown. Dissolved organic carbon (DOC) = 6.6 mg/L.
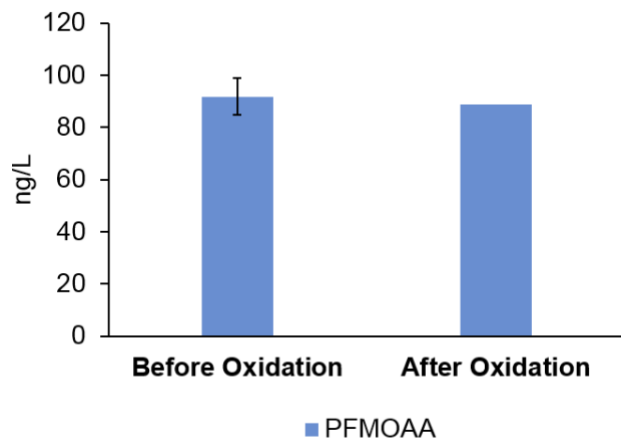
Figure S9. Application of the TOP assay with expanded PFEA analyte list to a water sample collected at William O. Huske Lock and Dam in April 2018. Only PFMOAA was detected above the QL in this water sample. Average and standard deviation of duplicate experiments are shown. DOC = 13.8 mg/L.

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