



TOP Assay, Years of Lessons Learned

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Polyfluorinated Compounds



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Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

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- Hundreds to thousands of polyfluorinated compounds may be present in environment
- Approximately 240 of those have been specifically identified in AFFF formulations
- Only 40 to maybe 50 of those have standards that are commercially available

Polyfluorinated Compounds



PFCAs

Perfluorobutanoic acid
Perfluoropentanoic acid
Perfluorohexanoic acid
Perfluorheptanoic acid
Perfluorooctanoic acid
Perfluorononanoic acid
Perfluorodecanoic acid
Perfluoroundecanoic acid
Perfluorododecanoic acid

FTS

4:2 Fluorotelomer sulfonate
6:2 Fluorotelomer sulfonate
8:2 Fluorotelomer sulfonate
10:2 Fluorotelomer sulfonate

PFSAs

Perfluorobutanesulfonate
Perfluorohexanesulfonate
Perfluoroheptanesulfonate
Perfluorooctanesulfonate
Perfluorodecanesulfonate

Sulfonamides

Perfluorooctanesulfonamide
Methylperfluoro-1-octanesulfonamide
Ethylperfluoro-1-octanesulfonamide
N-methylperfluoro-1-octanesulfonamidoacetic acid
N-ethylperfluoro-1-octanesulfonamidoacetic acid
2-(N-methylperfluoro-1-octanesulfamido)-ethanol
2-(N-ethylperfluoro-1-octanesulfamido)-ethanol

FTOH

4:2 Fluorotelomer alcohol
6:2 Fluorotelomer alcohol
8:2 Fluorotelomer alcohol
10:2 Fluorotelomer alcohol

PAP/DiPAP

Perfluorooctyl phosphate
Bis(perfluorooctyl) phosphate

PFPA/PFPiA

Perfluorohexylphosphonic acid
Perfluorooctylphosphonic acid
Bis(perfluorohexyl)phosphonate

Polyfluorinated Compounds



If we wanted to assess the total potential impact of PFAS contamination, how would we approach given the fact that we only have analytical standards available for a small fraction of the potential contaminants present?

Measure total Fluorine content?

- a. PIGE – Proton Induced Gamma Emission Spectroscopy
 - i. Captures fluorine at surface
 - ii. Sensitivity around 2-5 ug/l
- b. AOF/CIC – Absorbable Organic Fluorine/Combustion Ion Chromatography
 - i. Sensitivity around 1 ug/l

Total Oxidizable Precursors - TOP



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Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

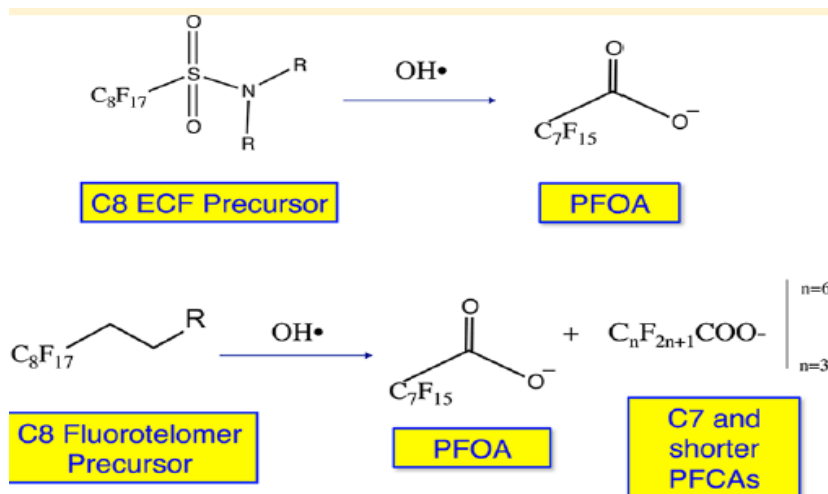
Erika F. Houtz and David L. Sedlak*

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Concept is to analyze a sample for perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) and any identified precursors . Then subject a second aliquot of the sample to relatively harsh oxidative conditions. Analyze the oxidized sample for the same perfluoroalkyl acids and precursors. Expect to see;

- a. Reduction or elimination of the precursors
- b. Increase in concentrations of perfluoroalkyl acids

TOP Assay



Houtz & Sedlak (2012),
ES&T, 9342-9349

- Compounds like fluorotelomer sulfonates, alcohols and sulfonamides considered precursors
- Precursors have some part of organic structure that is susceptible to oxidation, i.e. C-H bond

TOP Assay – Advantage?



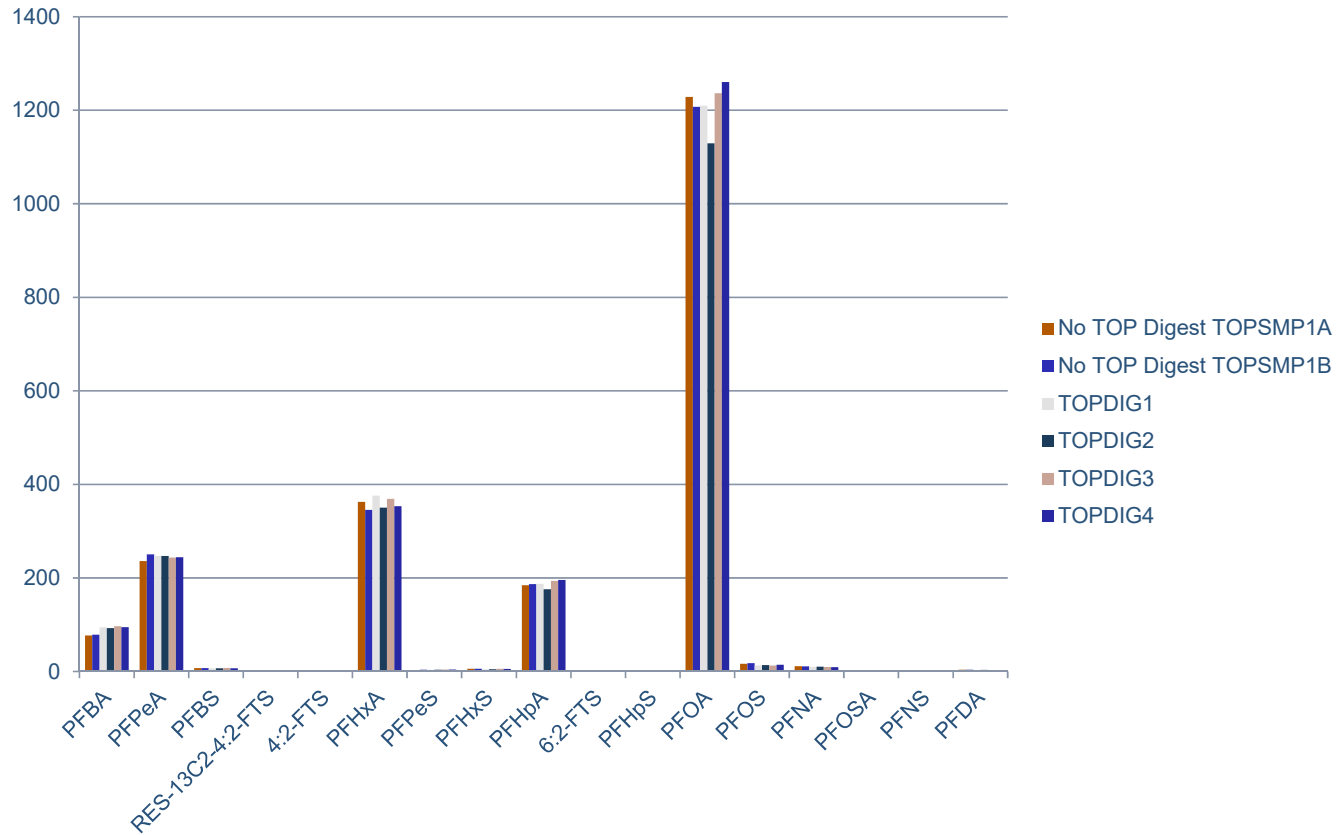
- Oxidation process for TOP Assay addresses those compounds that can be converted to PFCAs.
- Would appear to be little or no influence from other organofluorine compounds.
- Able to take advantage of LC/MS/MS analysis technique that uses isotope dilution.
- Sensitivity better than observed with PIGE and AOF/CIC. Limits in the low ng/l range.

TOP Assay – Oxidation

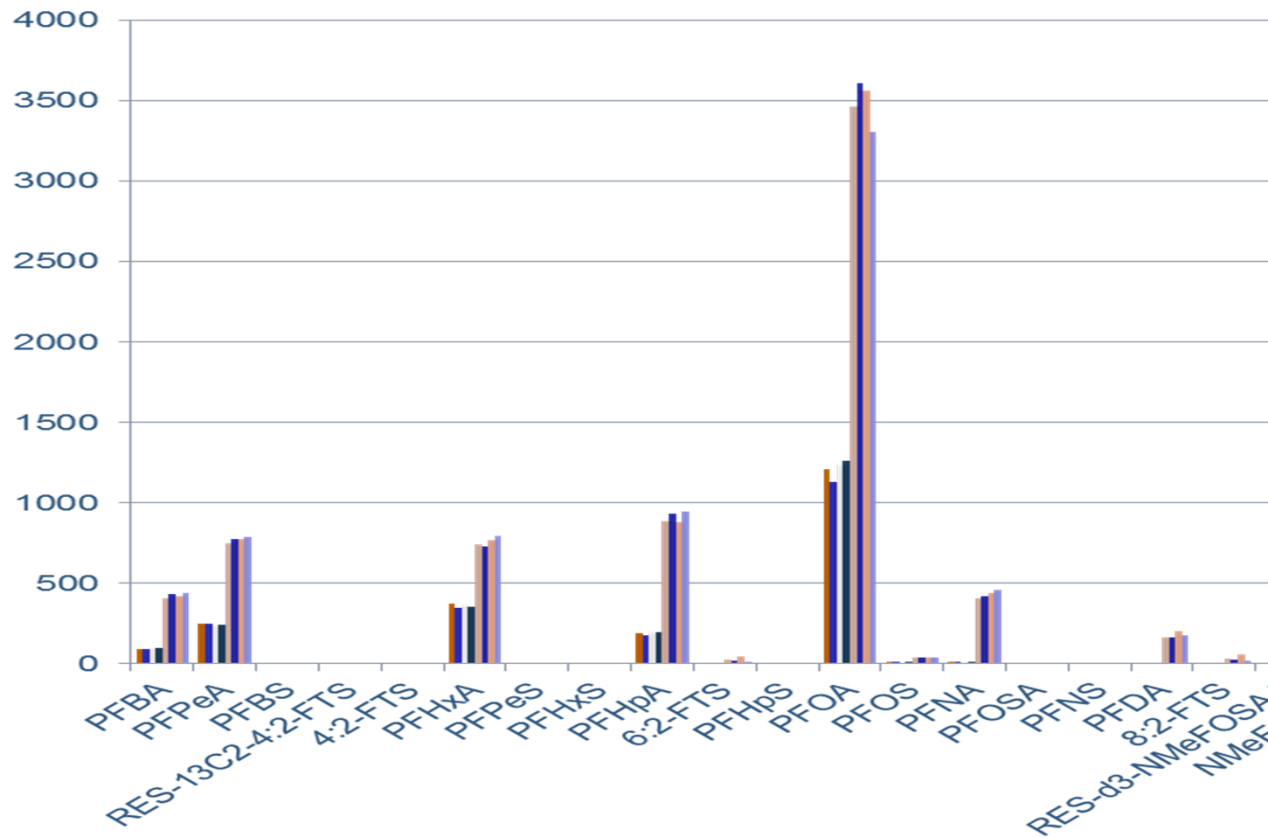


- After analysis of sample(s) by normal LC/MS/MS isotope dilution procedure, take second aliquot
- Spike sample with TOP oxidation appropriate QC
- Add potassium persulfate and NaOH solutions to aliquot of sample until potassium persulfate at 60mM and NaOH at 125 mM. Resulting pH should be approximately 13.
- 85C bath for 6 hours
- Quench with HCl, adjust pH to approximately neutral

Results – TOP Assay



Results – Spiked w/Precursors

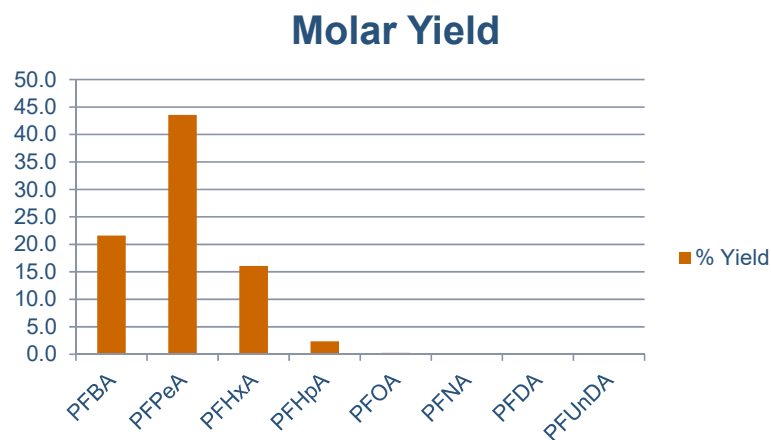


TOP Assay – 6:2 FTS



Results of oxidation of 6:2 Fluorotelomer sulfonate at 250 ng/l

PFCA	ELLE	Houtz
PFBA	21.6	22
PFPeA	43.6	27
PFHxA	16.1	22
PFHpA	2.4	2
PFOA	0.3	0
PFNA	0.0	0
PFDA	0.0	0
PFUnDA	0.0	0

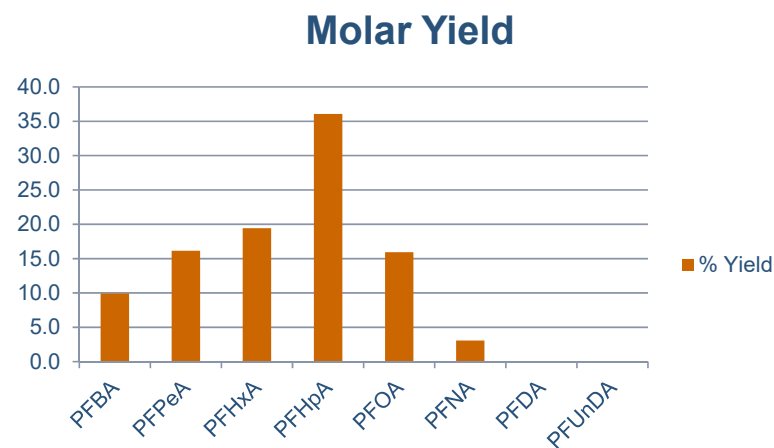


TOP Assay – 8:2 FTS



Results of oxidation of 8:2 Fluorotelomer sulfonate at 250 ng/l

PFCA	ELLE	Houtz
PFBA	9.9	11
PFPeA	16.1	12
PFHxA	19.4	19
PFHpA	36.1	27
PFOA	15.9	21
PFNA	3.1	3
PFDA	0.0	
PFUnDA	0.0	

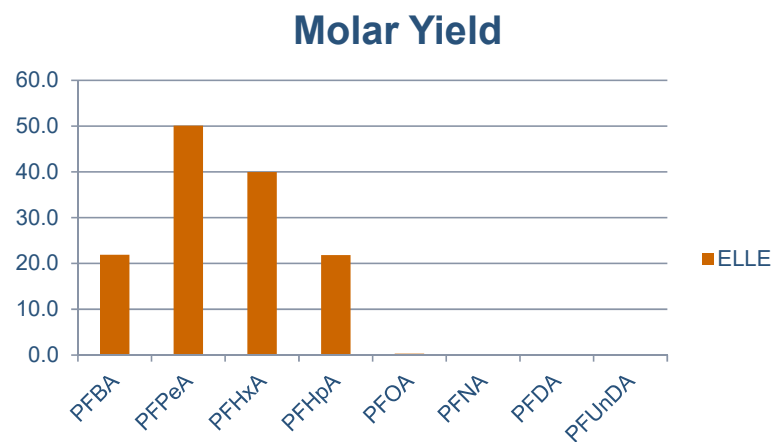


TOP Assay – 6:2 diPAP



Results of oxidation of 6:2 Perfluoroalkyl phosphate diester at 250 ng/l

PFCA	ELLE	Houtz
PFBA	21.9	27
PFPeA	50.1	47
PFHxA	40.0	33
PFHpA	21.8	15
PFOA	0.3	
PFNA	0.0	
PFDA	0.0	
PFUnDA	0.0	

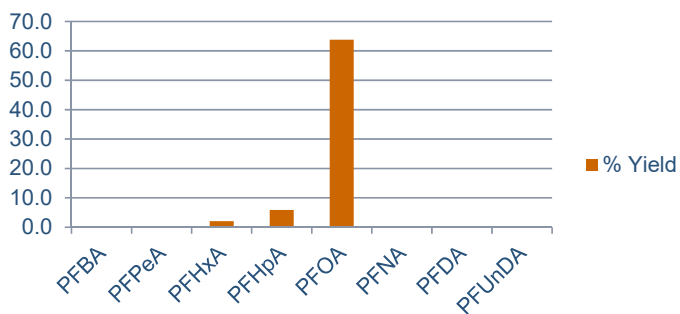


TOP Assay – other precursors



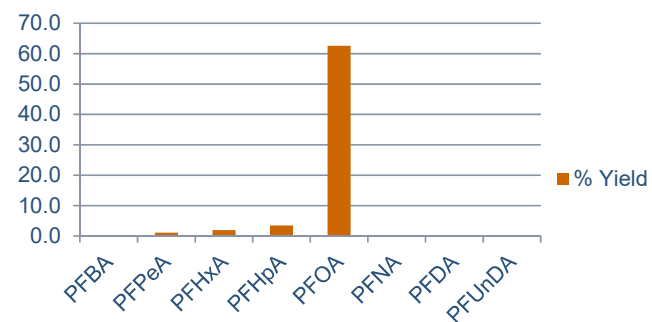
NETFOSAA

Molar Yield



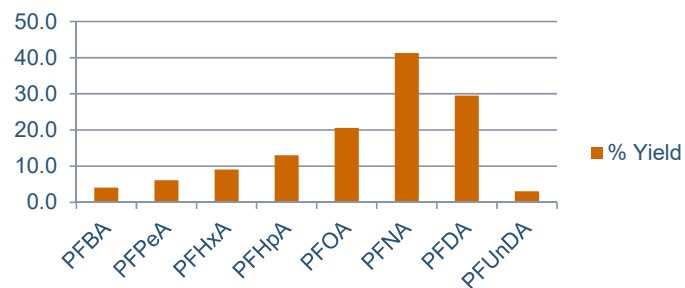
NETPFOSAE

Molar Yield



10:2 FTS

Molar Yield



Incomplete Oxidation



Compound	Units	Sample Pre-Ox	Sample Post-Ox
PFBA	ng/l	N.D.	370 000
PFPeA	ng/l	N.D.	590 000
PFBS	ng/l	N.D.	280
4:2-FTS	ng/l	N.D.	N.D.
PFHxA	ng/l	250 000	470 000
PFPeS	ng/l	N.D.	620
PFHxS	ng/l	51 000	6 800
PFHpA	ng/l	240 000	120 000
6:2-FTS	ng/l	7 000 000	37 000
PFHpS	ng/l	N.D.	360
PFOA	ng/l	140 000	33 000
PFOS	ng/l	75 000	14 000
PFNA	ng/l	16 000	5 300
PFOSA	ng/l	N.D.	N.D.
PFNS	ng/l	N.D.	N.D.
PFDA	ng/l	N.D.	500
8:2-FTS	ng/l	110 000	1 800

Incomplete Oxidation



Compound	Units	Sample Pre-Ox	Sample Post-Ox	Sample Post-Ox 1/10 Volume
PFBA	ng/l	N.D.	370 000	390 000
PFPeA	ng/l	N.D.	590 000	760 000
PFBS	ng/l	N.D.	280	N.D.
4:2-FTS	ng/l	N.D.	N.D.	N.D.
PFHxA	ng/l	250 000	470 000	330 000
PFPeS	ng/l	N.D.	620	N.D.
PFHxS	ng/l	51 000	6 800	7 500
PFHpA	ng/l	240 000	120 000	110 000
6:2-FTS	ng/l	7 000 000	37 000	1 700
PFHpS	ng/l	N.D.	360	N.D.
PFOA	ng/l	140 000	33 000	33 000
PFOS	ng/l	75 000	14 000	16 000
PFNA	ng/l	16 000	5 300	5 500
PFOSA	ng/l	N.D.	N.D.	N.D.
PFNS	ng/l	N.D.	N.D.	N.D.
PFDA	ng/l	N.D.	500	640
8:2-FTS	ng/l	110 000	1 800	N.D.

Incomplete Oxidation



Compound	Units	Sample Pre-Ox	Sample Post-Ox	Sample Post-Ox 1/10 Volume	Sample Post-Ox w/2X Persulfate
PFBA	ng/l	N.D.	370 000	390 000	380 000
PFPeA	ng/l	N.D.	590 000	760 000	700 000
PFBS	ng/l	N.D.	280	N.D.	N.D.
4:2-FTS	ng/l	N.D.	N.D.	N.D.	N.D.
PFHxA	ng/l	250 000	470 000	330 000	290 000
PFPeS	ng/l	N.D.	620	N.D.	N.D.
PFHxS	ng/l	51 000	6 800	7 500	7 600
PFHpA	ng/l	240 000	120 000	110 000	110 000
6:2-FTS	ng/l	7 000 000	37 000	1 700	N.D.
PFHpS	ng/l	N.D.	360	N.D.	N.D.
PFOA	ng/l	140 000	33 000	33 000	30 000
PFOS	ng/l	75 000	14 000	16 000	16 000
PFNA	ng/l	16 000	5 300	5 500	5 300
PFOSA	ng/l	N.D.	N.D.	N.D.	N.D.
PFNS	ng/l	N.D.	N.D.	N.D.	N.D.
PFDA	ng/l	N.D.	500	640	580
8:2-FTS	ng/l	110 000	1 800	N.D.	N.D.

Preliminary Conclusions



- Houtz and Sedlak paper evaluated precursor concentrations up to 25 ug/l
- Approach in paper not sufficient for higher concentrations of precursors
- Need consistent tactic for high organics (Envi-Carb) and high concentrations of precursors
- Need criteria for identifying when technique is at it's limit of practicality

3% Solution AFFF Foam



<u>Compound</u>	<u>CAS Number</u>	<u>Pre-Oxidation Analysis Result</u>	<u>Post-Oxidation Analysis Result</u>	<u>Net Difference</u>	<u>Units</u>
10:2-fluorotelomersulfonate	120226-60-0	ND	ND		ng/l
4:2-fluorotelomersulfonate	757124-72-4	ND	ND		ng/l
6:2-fluorotelomersulfonate	27619-97-2	1800	54000	52200	ng/l
8:2-fluorotelomersulfonate	39108-34-4	ND	5100	5100	ng/l
NEtFOSAA	2991-50-6	ND	ND		ng/l
NEtPFOSA	4151-50-2	ND	ND		ng/l
NEtPFOSAE	1691-99-2	ND	ND		ng/l
NMeFOSAA	2355-31-9	ND	ND		ng/l
NMePFOSA	31506-32-8	ND	ND		ng/l
NMePFOSAE	24448-09-7	ND	ND		ng/l
Perfluoro-octanesulfonate	1763-23-1	ND	ND		ng/l
Perfluorobutanesulfonate	375-73-5	ND	ND		ng/l
Perfluorobutanoic acid	375-22-4	1000	11000	10000	ng/l
Perfluorodecanesulfonate	335-77-3	ND	ND		ng/l
Perfluorodecanoic acid	335-76-2	ND	ND		ng/l
Perfluorododecanesulfonate	79780-39-5	ND	ND		ng/l
Perfluorododecanoic acid	307-55-1	ND	ND		ng/l
Perfluoroheptanesulfonate	375-92-8	ND	ND		ng/l
Perfluoroheptanoic acid	375-85-9	ND	1700	1700	ng/l
Perfluorohexadecanoic acid	67905-19-5	ND	ND		ng/l
Perfluorohexanesulfonate	355-46-4	ND	ND		ng/l
Perfluorohexanoic acid	307-24-4	1000	2900	1900	ng/l
Perfluorononanesulfonate	68259-12-1	ND	ND		ng/l
Perfluorononanoic acid	375-95-1	ND	ND		ng/l
Perfluorooctadecanoic acid	16517-11-6	ND	ND		ng/l
Perfluorooctanesulfonamide	754-91-6	ND	ND		ng/l
Perfluorooctanoic acid	335-67-1	ND	ND		ng/l
Perfluoropentanesulfonate	2706-91-4	ND	ND		ng/l
Perfluoropentanoic acid	2706-90-3	ND	14000	14000	ng/l
Perfluorotetradecanoic acid	376-06-7	ND	ND		ng/l
Perfluorotridecanoic acid	72629-94-8	ND	ND		ng/l
Perfluoroundecanoic acid	2058-94-8	ND	ND		ng/l
Total PFCA		2000	29600	27600	ng/l
Total PFSA		0	0	0	ng/l

Observations



- Houtz and Sedlak may not have anticipated applying principles of 2012 paper to AFFF
- Oxidation process has created fluorotelomer sulfonates. Indicating presence of betaines and other amines?
- What determines the endpoint of the process/method? Only net increase in PFCAs?

Observations



In Australia, under an ALGA research grant, performed a study to assess measurement reliability of the TOP Assay. Three laboratories participated and based on the results, they proposed the following “QA Guidance”;

- Validate the method using detectable (C13 labeled) oxidizable precursors
- Total PFAS Post-Ox should be \geq Total PFAS Pre-Ox
- Sum of PFCAs Post-Ox should be \geq Sum of PFCAs Pre-Ox
- Sum of PFSA Post-Ox should approximate Sum of PFSA Pre-Ox
- For situations where near complete oxidation is acceptable, allow for acceptable amounts of precursors to be present Post-Ox

Conclusions



- TOP Assay useful tool for assessing total potential impact on site from PFAS contamination
- TOP Assay should not be considered to have mimicked the oxidation process in the environment
- The relative change in PFAAs can be used as an indicator of additional PFAS mass
- The TOP Assay needs to be standardized with expected QA/QC measures and expectations
- The ruggedness and thoroughness of the TOP Assay need to be more thoroughly evaluated.

Thank you



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