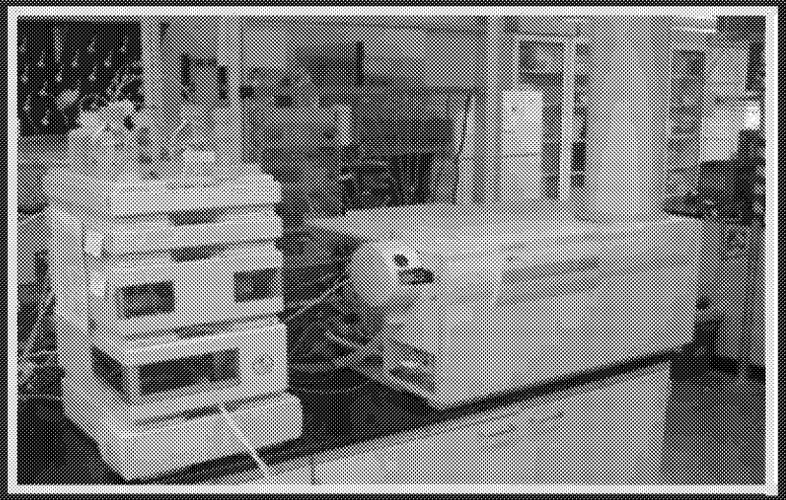
Identification of per- and polyfluoroalkyl substances (PFAS) from samples near US industrial manufacturing and use facilities



Mark Strynar[1], James McCord[1], Andrew Lindstrom[1], John Washington[1], John Offenberg[1], Jeff Ryan[1], Theran Riedel[1], Dennis Tabor[1], Ingrid George[1], Tim Buckley[1], Myriam Medina-Vera[1], Andy Gillespie[1], Erica Bergman[2], Sandra Goodrow[2], Ed Peduto Jr.[3], Brandon Kernen[3], Cathy Beahm[3]

1 US EPA Office of Research and Development (ORD)
2 New Jersey Department of Environmental Protection (NJDEP)
3 New Hampshire Department of Environmental Services (NHDES)

April 1, 2019
Spring 2019 ACS National Meeting
Orlando, FL, March 31 – April 4, 2019

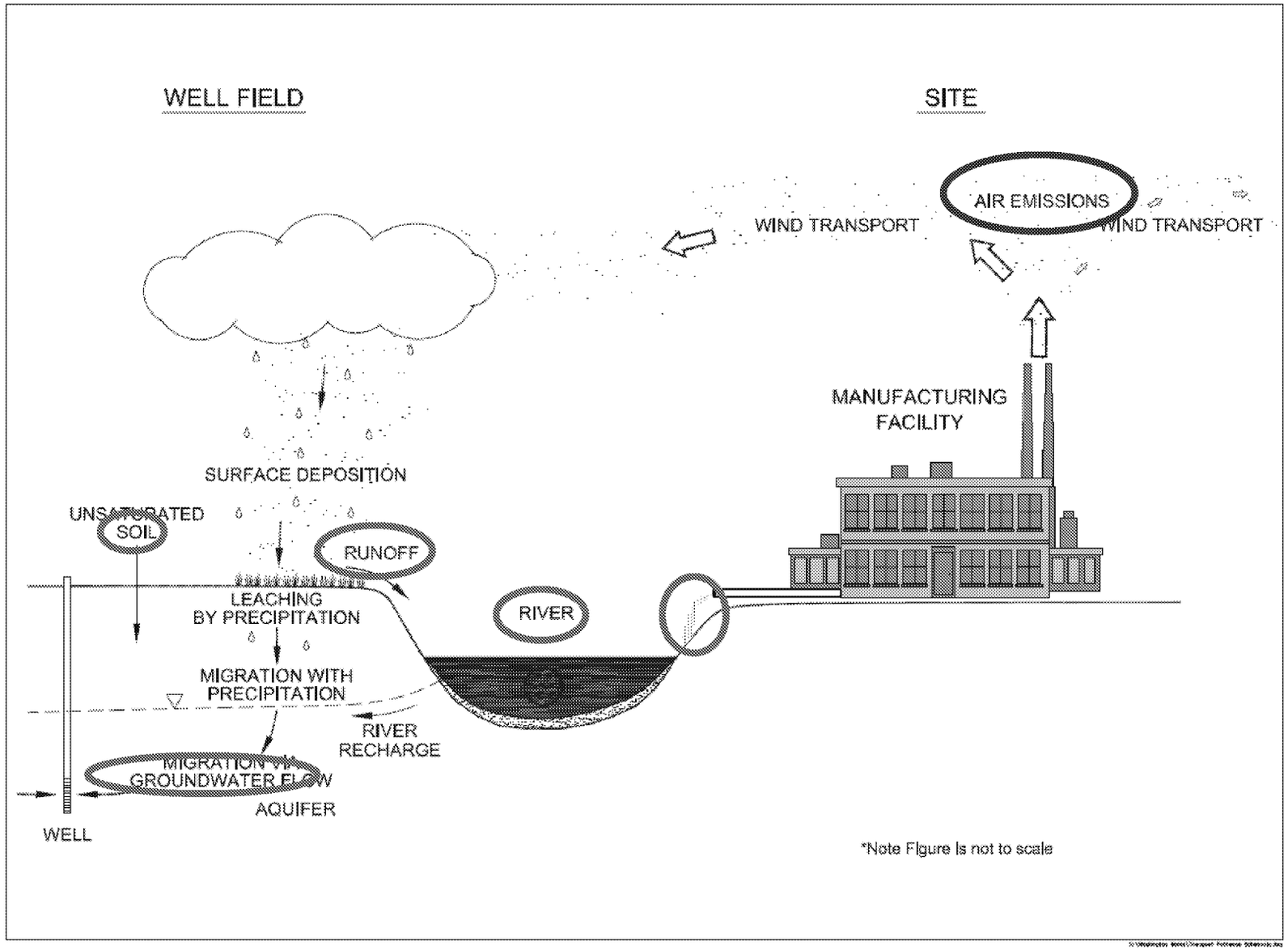
ED_006086_00129255-00001

Presentation Outline

- NTA background/approach
- Documented findings (Cape Fear River, NC)
  - Strynar et al., 2015
  - Sun et al., 2016
  - McCord and Strynar 2019 *in press*
- Documented findings (Tennessee River, AL)
  - Newton et al., 2017
- Merrimack, New Hampshire (NHDES)
- West Deptford, New Jersey (NJDEP)

ED_006086_00129255-00002

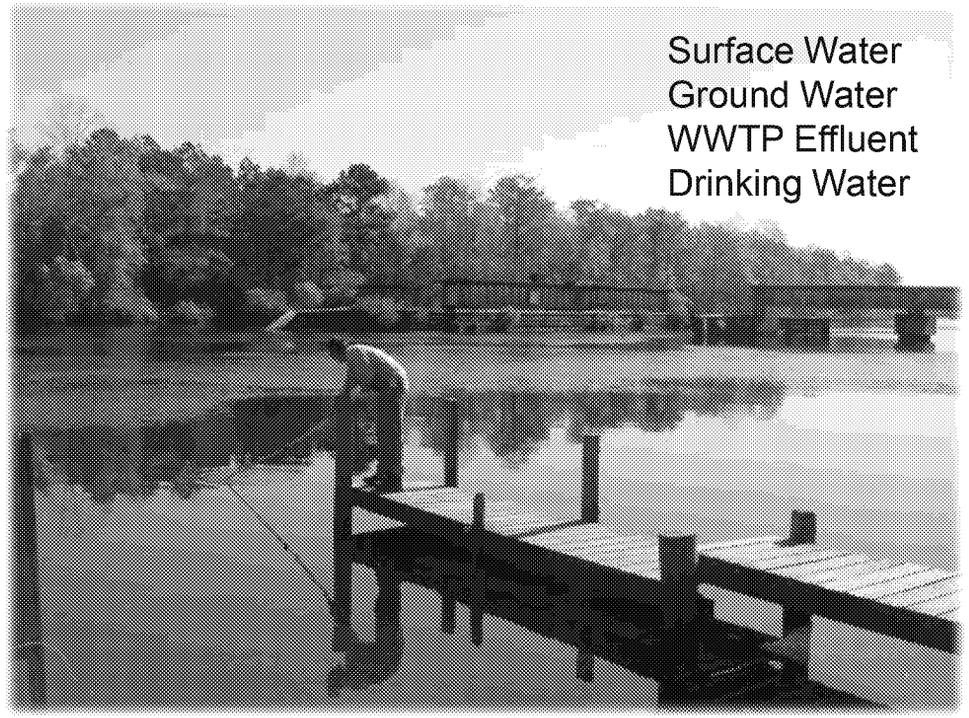
Conceptual Model of APFO Emission

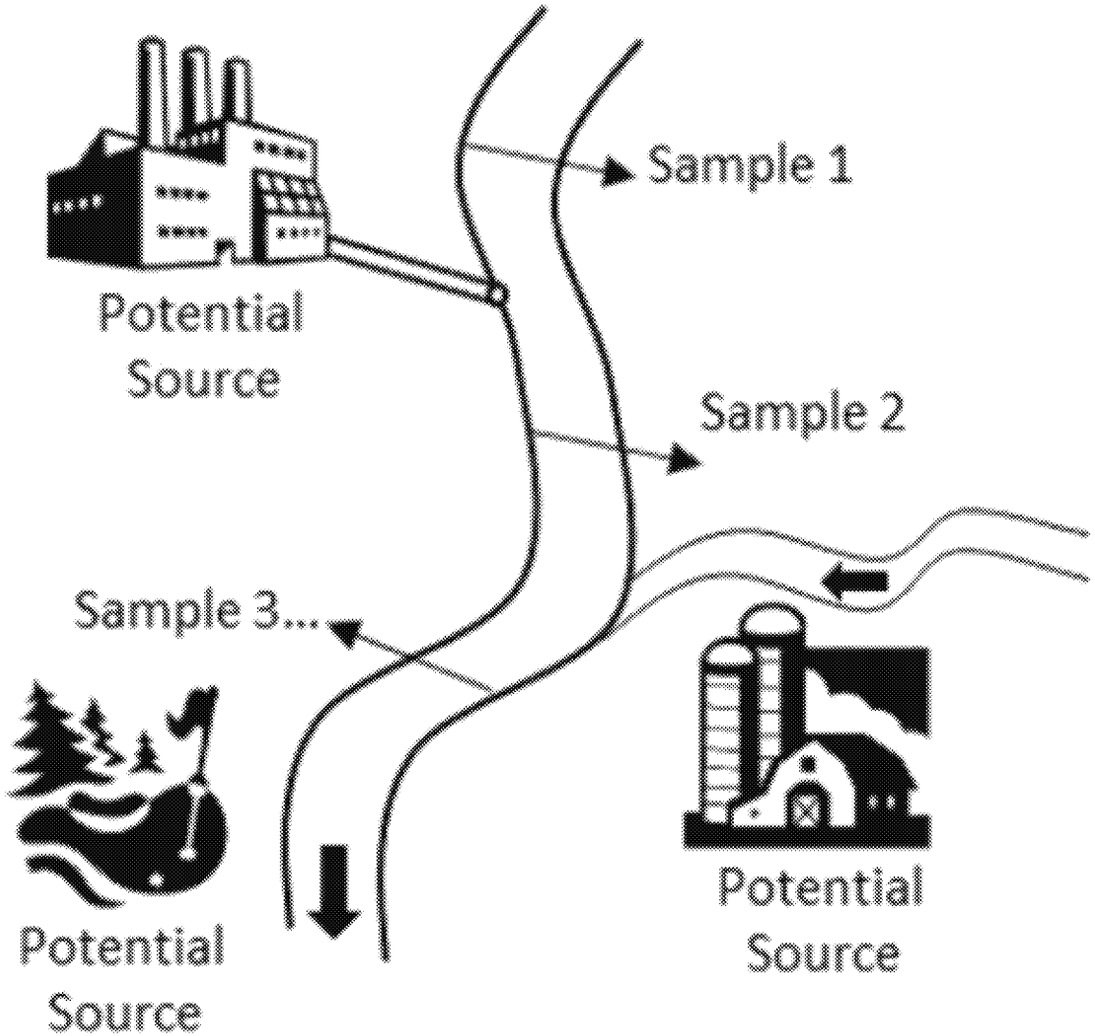


Davis et al., 2007 Chemosphere (67) 2011-2019. "Transport of ammonium perfluorooctanoate (APFO) in environmental media near a fluoropolymer manufacturing facility"

Data Generation: Source Determination by NTA

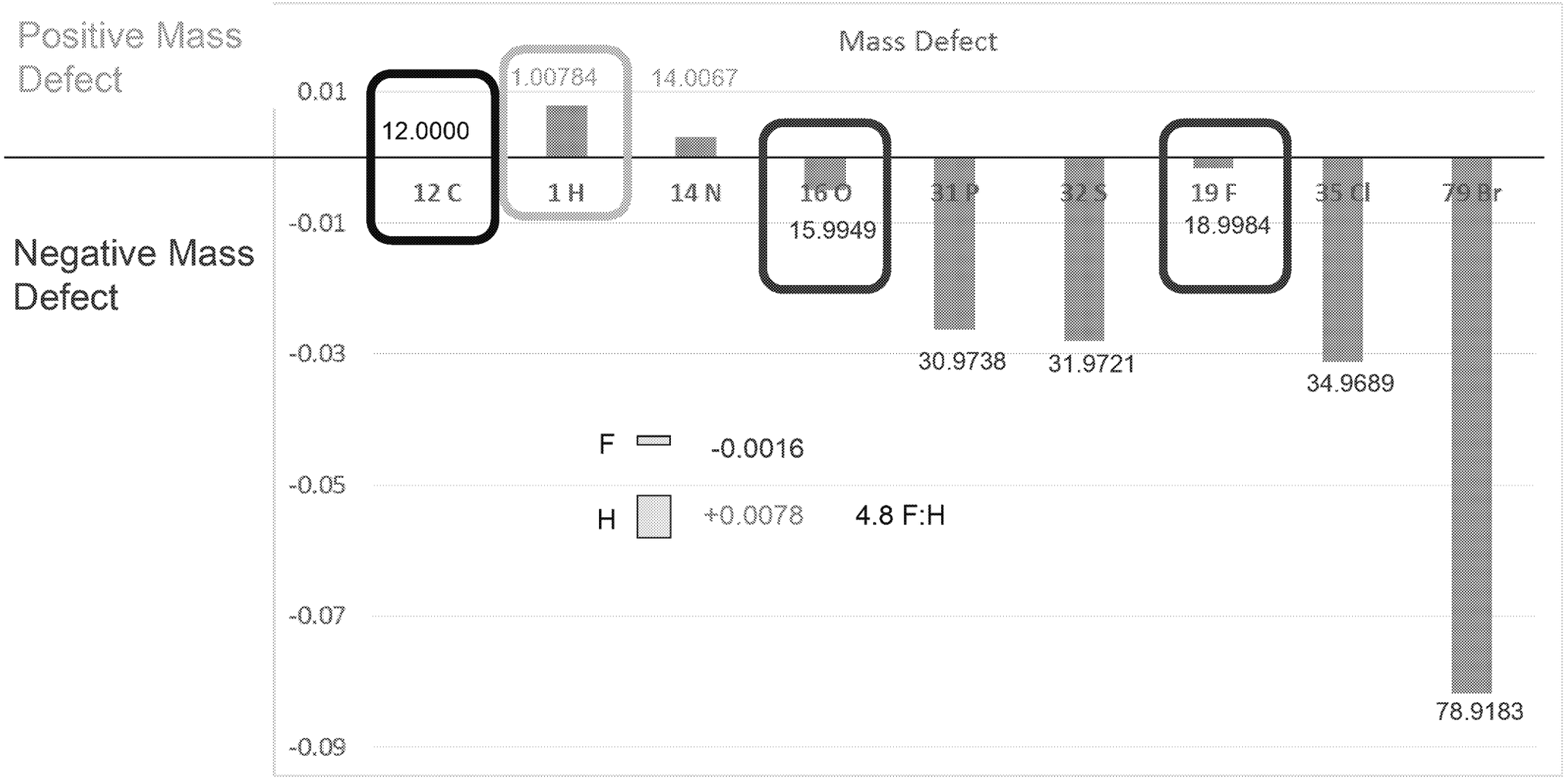
Legacy PFAS are an indicator





Sampling from geographically or temporally displaced locations allows triangulation of sources

Isotope Signatures: Negative Mass Defect



Environmental Science & Technology

November 2015

Article

pubs.acs.org/est

Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

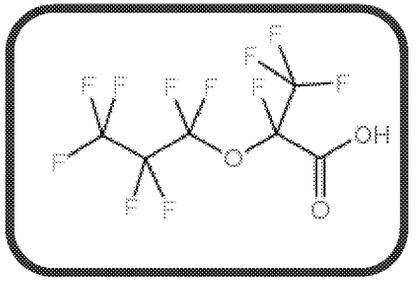
Mark Strynar,*[†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Liang,[†,‡] Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[∥] Imma Ferrer,[∥] and Carol Ball[⊥]

Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

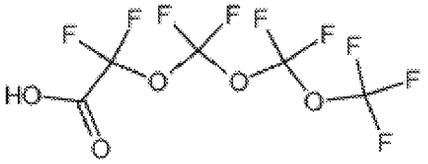
number	formula	CAS no.	name	$[M]^a$	$[M - H]^-$ m/z	$[2M - 2H + Na]^-$ m/z	$[2M - H]^-$ m/z
Monoether PFECAs							
1	$C_3HF_5O_3$			179.9846	178.9773	380.9438	358.9619
2	$C_4HF_7O_3$			229.9813	228.9740	480.9372	458.9553
3	$C_5HF_9O_3$	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	$C_6HF_{11}O_3$	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427
5	$C_7HF_{13}O_3$			379.9718	378.9645	780.9182	758.9363
6	$C_8HF_{15}O_3$			429.9686	428.9613	880.9118	858.9299
Polyether PFECAs							
7	$C_7HF_{13}O_7$	39492-91-6	perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	443.9515	442.9442	908.8776	886.8957
8	$C_6HF_{11}O_6$	39492-90-5	perfluoro-3,5,7,9-butaoxadecanoic acid	377.9598	376.9525	776.8942	754.9123
9	$C_5HF_9O_5$	39492-89-2	perfluoro-3,5,7-propaoxaoctanoic acid	311.9681	310.9608	644.9108	622.9289
10	$C_4HF_7O_4$	39492-88-1	perfluoro-3,5-dioxahexanoic acid	245.9764	244.9691	512.9274	490.9455
PFESAs							
11	$C_7HF_{13}O_5S$	66796-30-3[b]		443.9337	442.9264		
12	$C_7H_2F_{14}O_5S$			463.9399	462.9326		

Three found human serum (Kotlarz/Hoppin/Knappe)
https://chhe.research.ncsu.edu/

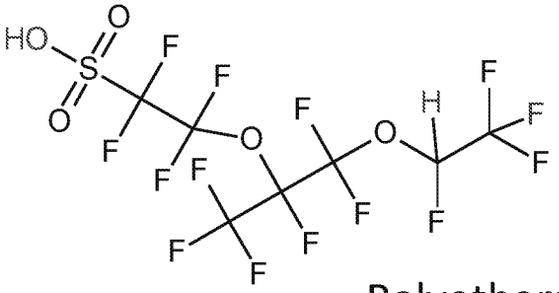
Example Structures



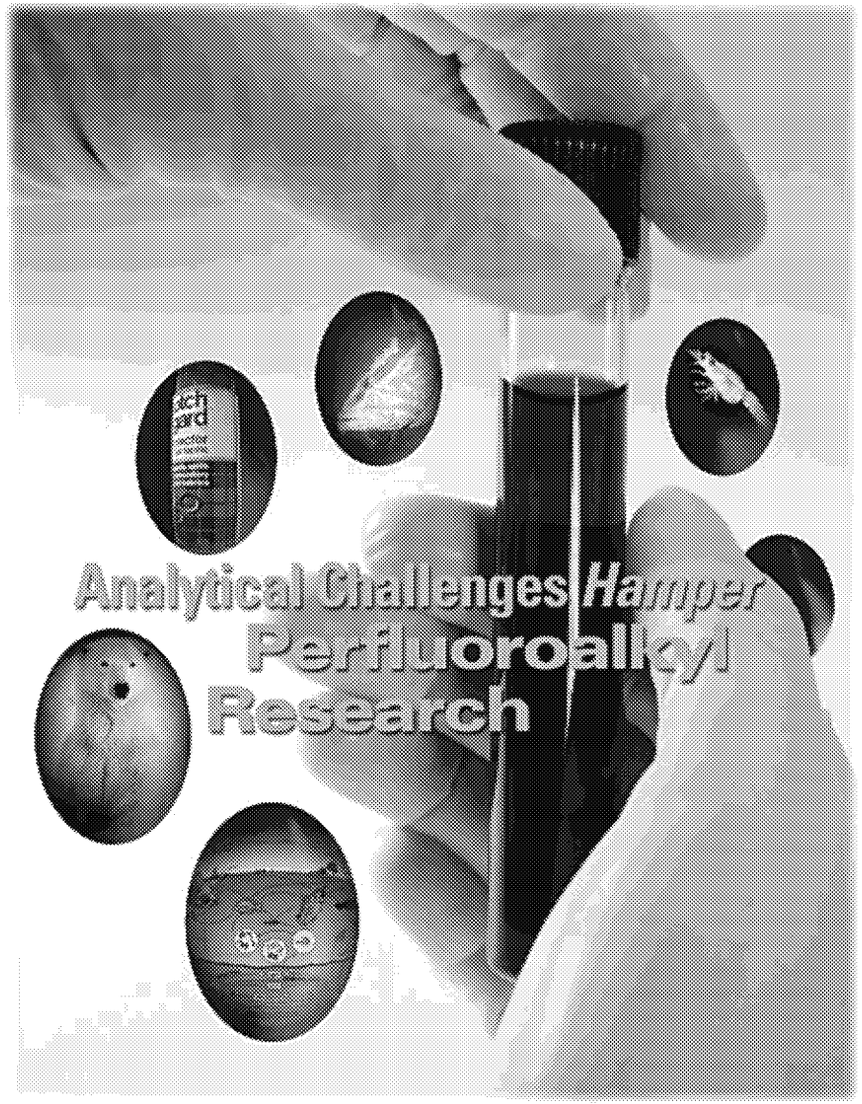
Monoether (6): GenX



Polyethers (4):



Polyethers sulfonates (2):



Martin et al., 2004 ES&T

- Need for authentic standards
- Validated methods
- Isomers
- Blank contamination

Environmental Science & Technology Letters

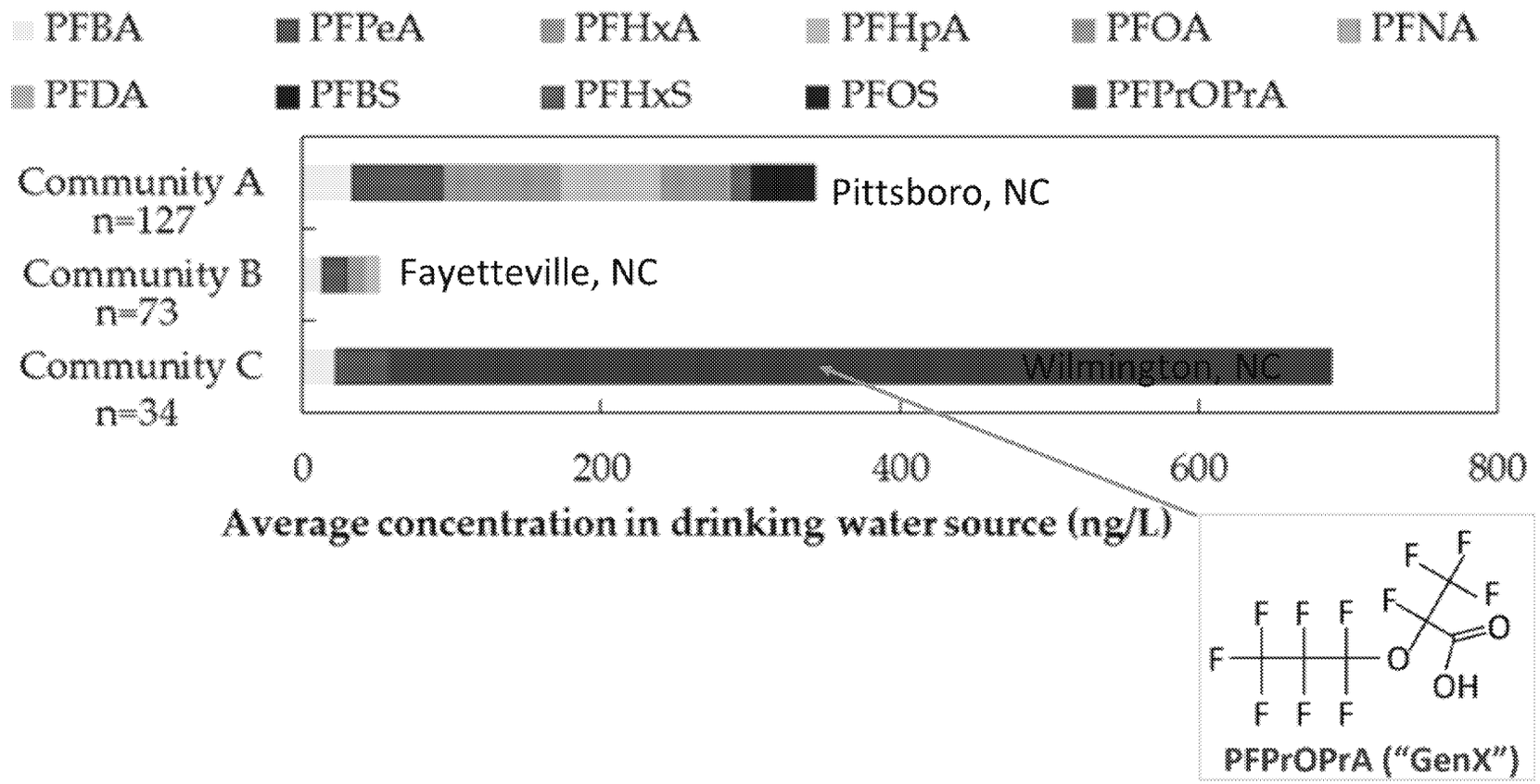
November 2016

Letter

pubs.acs.org/journal/estlcu

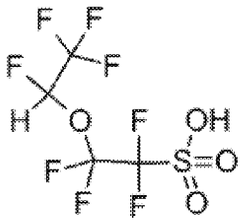
Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,[*,†,‡,⊗] Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,[∥] Ben Kearns,[∥] Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]



Retrospective Analysis (McCord and Strynar 2019 *in press ES&T*)

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	×	×	×
	1-26-12	✓	×	×	✓	✓	×	×	×
2012	2-1-12	✓	×	×	✓	✓	×	✓	×
	2-9-12	✓	✓	✓	✓	✓	✓	×	×
	5-4-12	✓	×	×	✓	×	×	×	×
	5-4-12	✓	×	×			×	×	×
2014	11-24-14	✓	×	×			×	×	×
2015	5-12-15	✓	✓	✓			✓	✓	✓
	5-12-15	✓	✓	✓			✓	✓	✓
	8-6-15	✓	✓	✓			✓	✓	✓
2017	5-12-17	✓	×	✓			✓	✓	✓
	6-20-17	✓	✓	✓			×	✓	✓
	6-27-17	✓	✓	✓			×	×	×
	7-4-17	✓	✓	✓	✓	✓	×	×	×
	7-11-17	✓	✓	✓	✓	✓	×	×	×
	7-18-17	✓	✓	✓	✓	✓	×	×	×
	7-25-17	✓	✓	✓	✓	✓	×	×	×
	8-3-17	✓	✓	✓	✓	✓	×	×	×



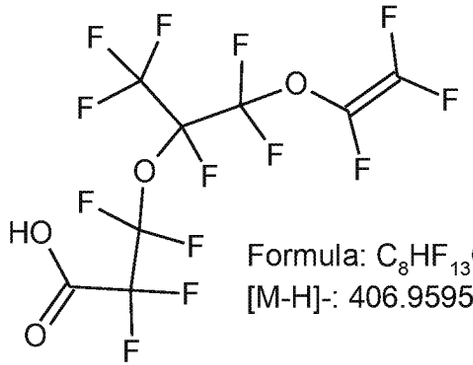
Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

NVHOS

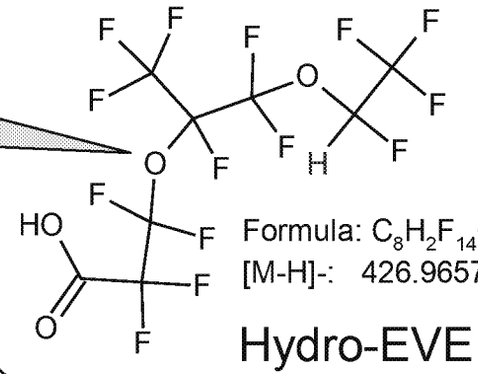
Retrospective Analysis (McCord and Strynar 2019 *in press ES&T*)

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	×	×	×
	1-26-12	✓	×	×	✓	✓	×	×	×
2012	2-1-12	✓	×	×	✓	✓			
	2-9-12	✓	✓	✓	✓	✓			
	5-4-12	✓	×	×	✓	×			
	5-4-12	✓	×	×	×	✓			
2014	11-24-14	✓	×	×	✓	×			
2015	5-12-15	✓	✓	✓	✓	✓			
	5-12-15	✓	✓	✓	×	✓			
	8-6-15	✓	✓						
2017	5-12-17	✓	×						
	6-20-17	✓	✓						
	6-27-17	✓	✓	✓	✓	✓			
	7-4-17	✓	✓	✓	✓	✓			
	7-11-17	✓	✓	✓	✓	✓			
	7-18-17	✓	✓	✓	✓	✓			
	7-25-17	✓	✓	✓	✓	✓	×	×	×
	8-3-17	✓	✓	✓	✓	✓	×	×	×

found human serum
(Kotlarz/Hoppin/Knappe)
https://chhe.research.ncsu.edu/



Formula: $C_8HF_{13}O_4$
[M-H]-: 406.9595 Da

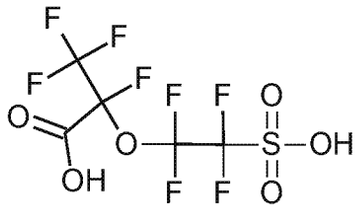


Formula: $C_8H_2F_{14}O_4$
[M-H]-: 426.9657 Da

Hydro-EVE

Retrospective Analysis (McCord and Strynar 2019 *in press ES&T*)

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	×	×	×
	1-26-12	✓	×	×	✓	✓	×	×	×
2012	2-1-12	✓	×	[illegible]	[illegible]	[illegible]	×	✓	×
	2-9-12	✓	✓	[illegible]	[illegible]	[illegible]	✓	×	×
	5-4-12	✓	×	[illegible]	[illegible]	[illegible]	×	×	×
	5-4-12	✓	×	[illegible]	[illegible]	[illegible]	×	×	×
2014	11-24-14	✓	×	[illegible]	[illegible]	[illegible]	×	×	×
2015	5-12-15	✓	✓	[illegible]	[illegible]	[illegible]	✓	✓	✓
	5-12-15	✓	✓	[illegible]	[illegible]	[illegible]	✓	✓	✓
	8-6-15	✓	✓	[illegible]	[illegible]	[illegible]	✓	✓	✓
2017	5-12-17	✓	×	[illegible]	[illegible]	[illegible]	✓	✓	✓
	6-20-17	✓	✓	✓	✓	✓	×	✓	✓
	6-27-17	✓	✓	✓	✓	✓	×	×	×
	7-4-17	✓	✓	✓	✓	✓	×	×	×
	7-11-17	✓	✓	✓	✓	✓	×	×	×
	7-18-17	✓	✓	✓	✓	✓	×	×	×
	7-25-17	✓	✓	✓	✓	✓	×	×	×
	8-3-17	✓	✓	✓	✓	✓	×	×	×



Formula: $C_5H_2F_8O_6S$
[M-H]-: 340.9372 Da

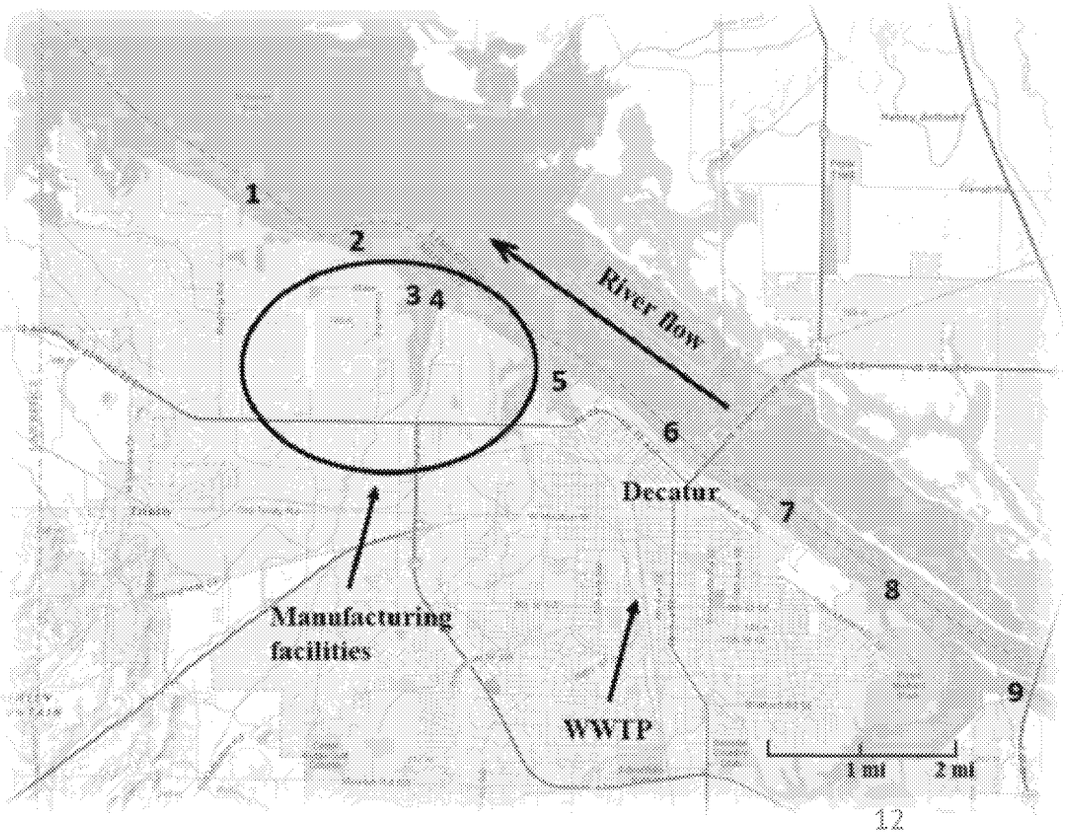
Environmental Science & Technology

2017 Article

pubs.acs.org/est

Novel Polyfluorinated Compounds Identified Using High Resolution Mass Spectrometry Downstream of Manufacturing Facilities near Decatur, Alabama

Seth Newton,[†] Rebecca McMahen,[‡] James A. Stoeckel,[§] Michael Chislock,[§] Andrew Lindstrom,[†] and Mark Strynar[*,†]

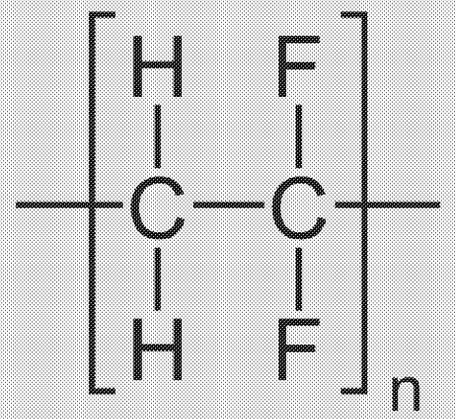


Tennessee River, Decatur, AL

- Basis of PFOA/PFOS PHA (2009)
- Co-mingled industrial/municipal waste; biosolids
- 3M, Daikin America, Toray Fluorofibers

Hansen et al., 2002 Quantitative Characterization of Trace Levels of PFOS and PFOA in the Tennessee River

Newton et al., 2017



Polyvinylidene fluoride (PVDF)

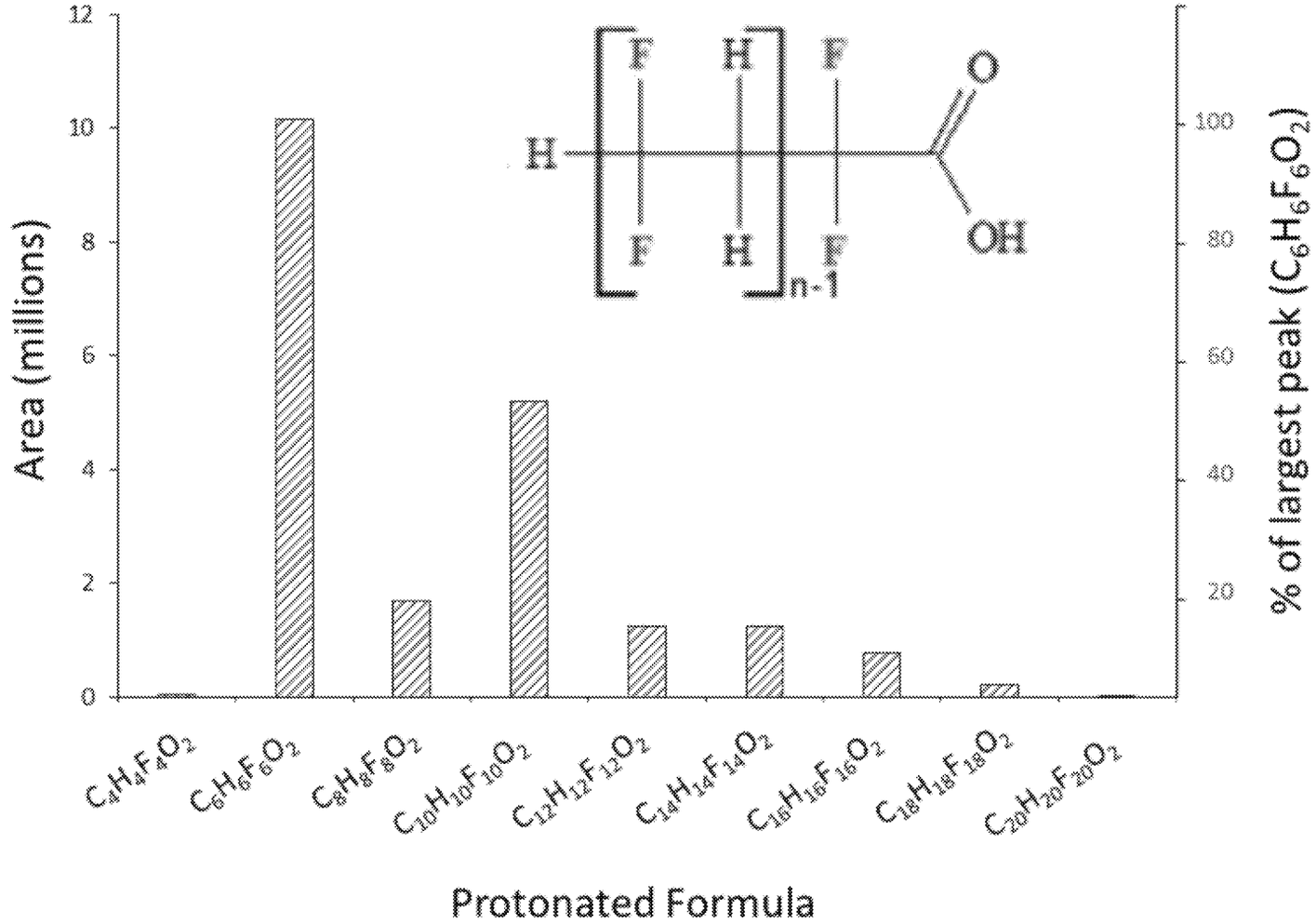
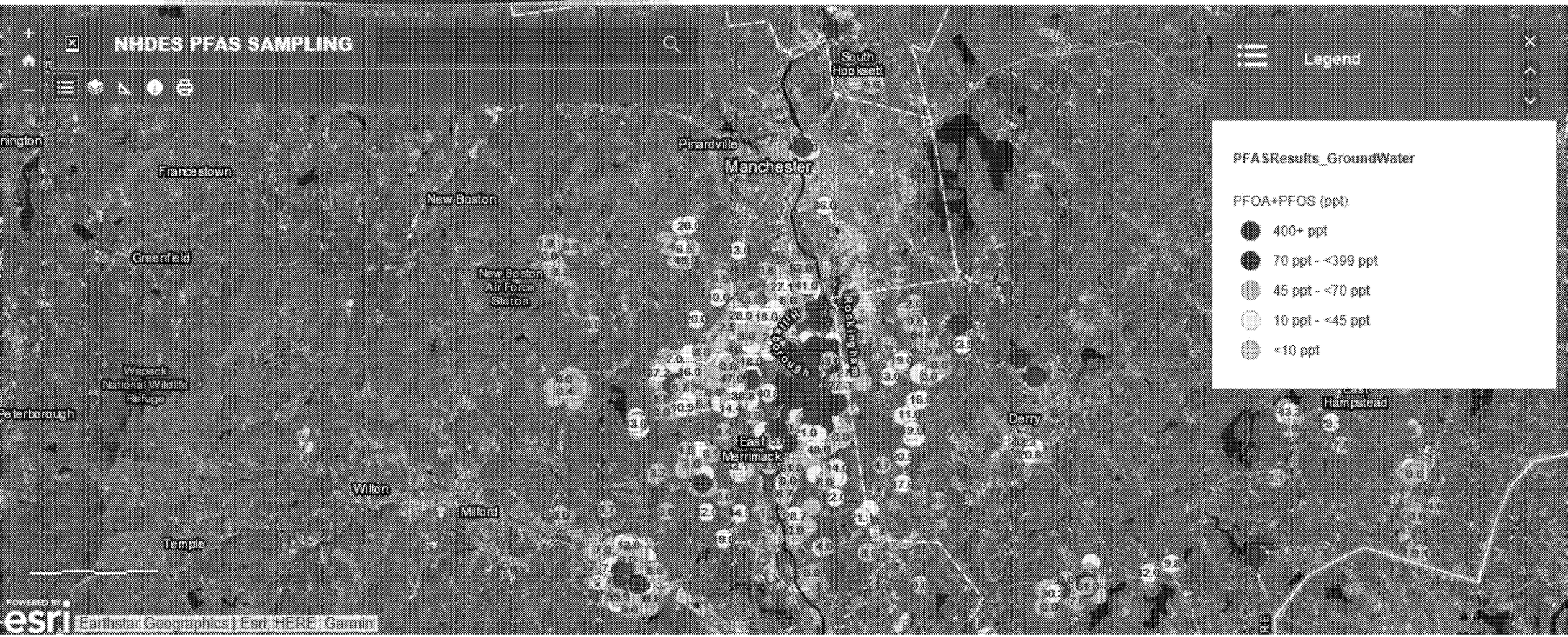


Figure S3 - Total area (sum of all isomers) of different species and their relative percentages in related series at Site 2.

Work with New Hampshire Department of Environmental Services (NHDES)

ED_006086_00129255-00014

Background NHDES Merrimack, NH



http://nhdes.maps.arcgis.com/apps/View/index.html?appid=66770bef141c43a98a445c54a17720e2&extent=-73.5743,42.5413,-69.6852,45.4489

Background NHDES Merrimack, NH

PER- AND POLYFLUOROALKYL SUBSTANCES

The Social Discovery of a Class of Emerging Contaminants

HOME | ABOUT | PUBLICATIONS & PRESENTATIONS | TIMELINES | CONTAMINATION SITE TRACKER

Hoosick Falls, New York

Suspected contamination source: Saint-Gobain Performance Plastics and Honeywell manufacturing plant (Lyons, 2016)

Village of Hoosick Falls and Town of Hoosick Private Well Sampling

https://pfasproject.com/hoosick-falls-new-york/

PER- AND POLYFLUOROALKYL SUBSTANCES

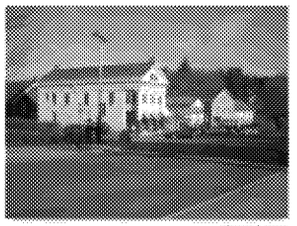
The Social Discovery of a Class of Emerging Contaminants

HOME | ABOUT | PUBLICATIONS & PRESENTATIONS | TIMELINES | CONTAMINATION SITE TRACKER

North Bennington, Vermont

Suspected contamination source: Former Chemfab manufacturing plant, later purchased by Saint-Gobain and H.C. White Company (Lyons, 2017)

NORTH BENNINGTON, VERMONT: PFAS CONTAMINATION



Click here to view our interactive timeline of PFAS contamination in North Bennington.

https://pfasproject.com/north-bennington-vermont/

MM5 Impinger Schematic/Industrial Process

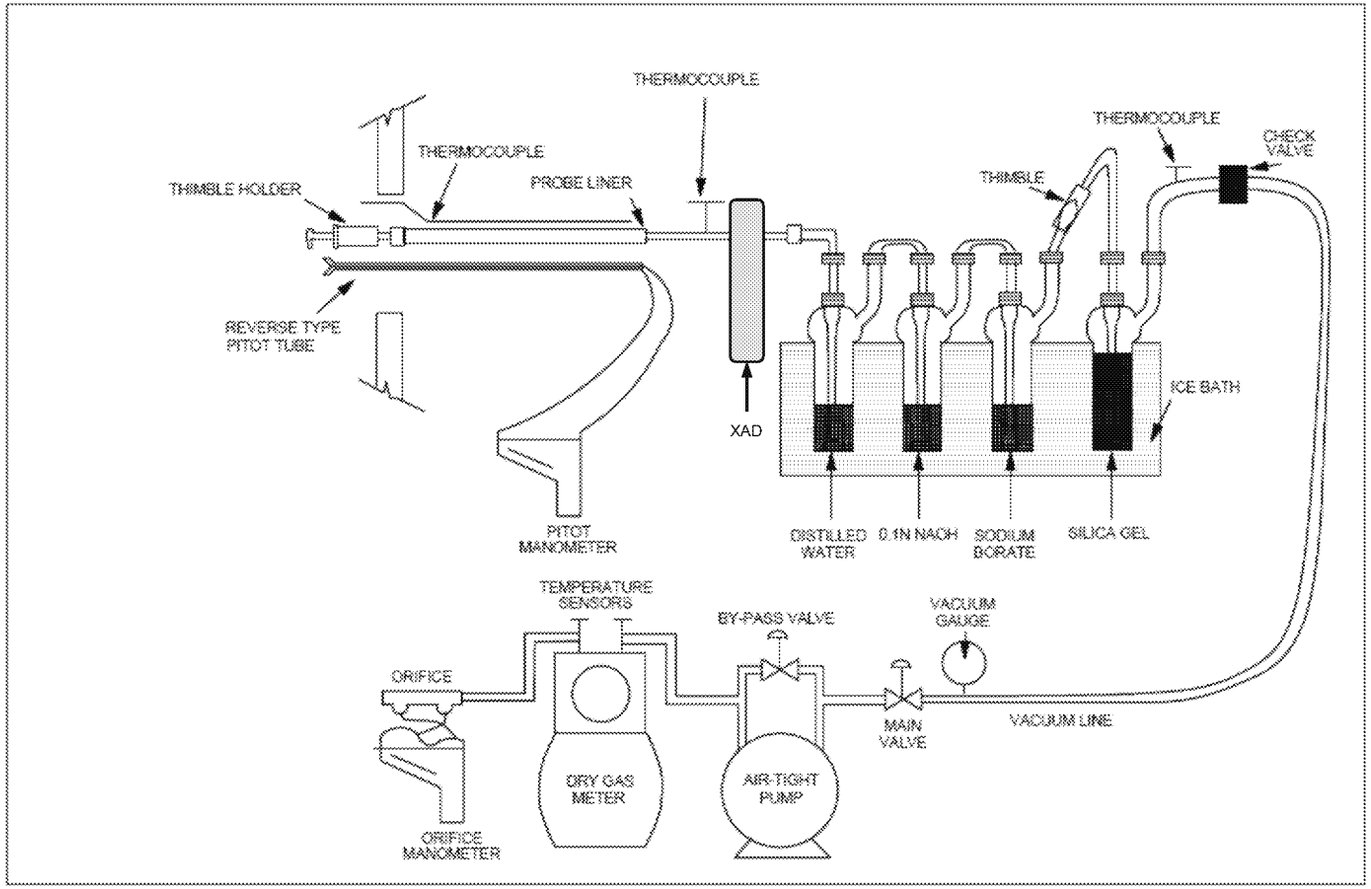
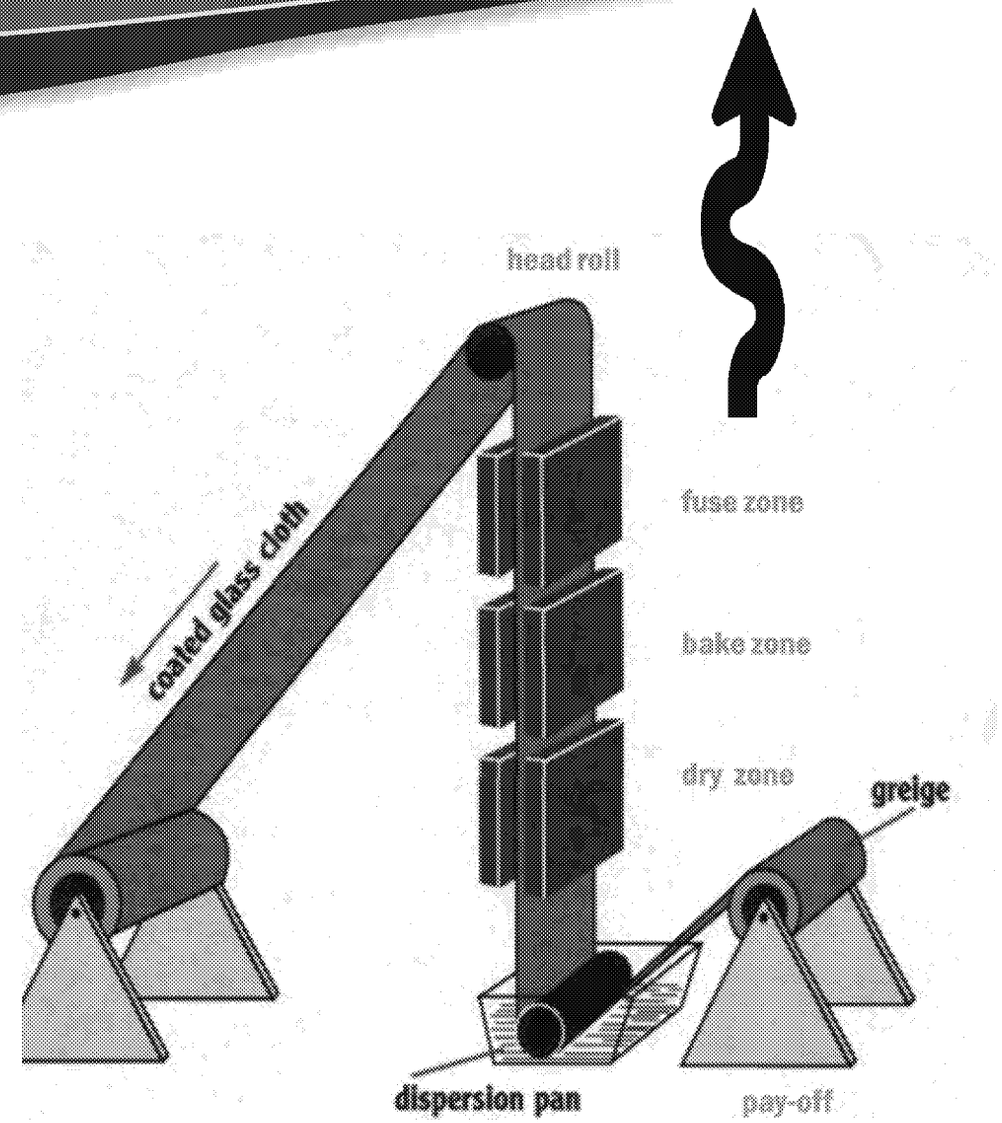
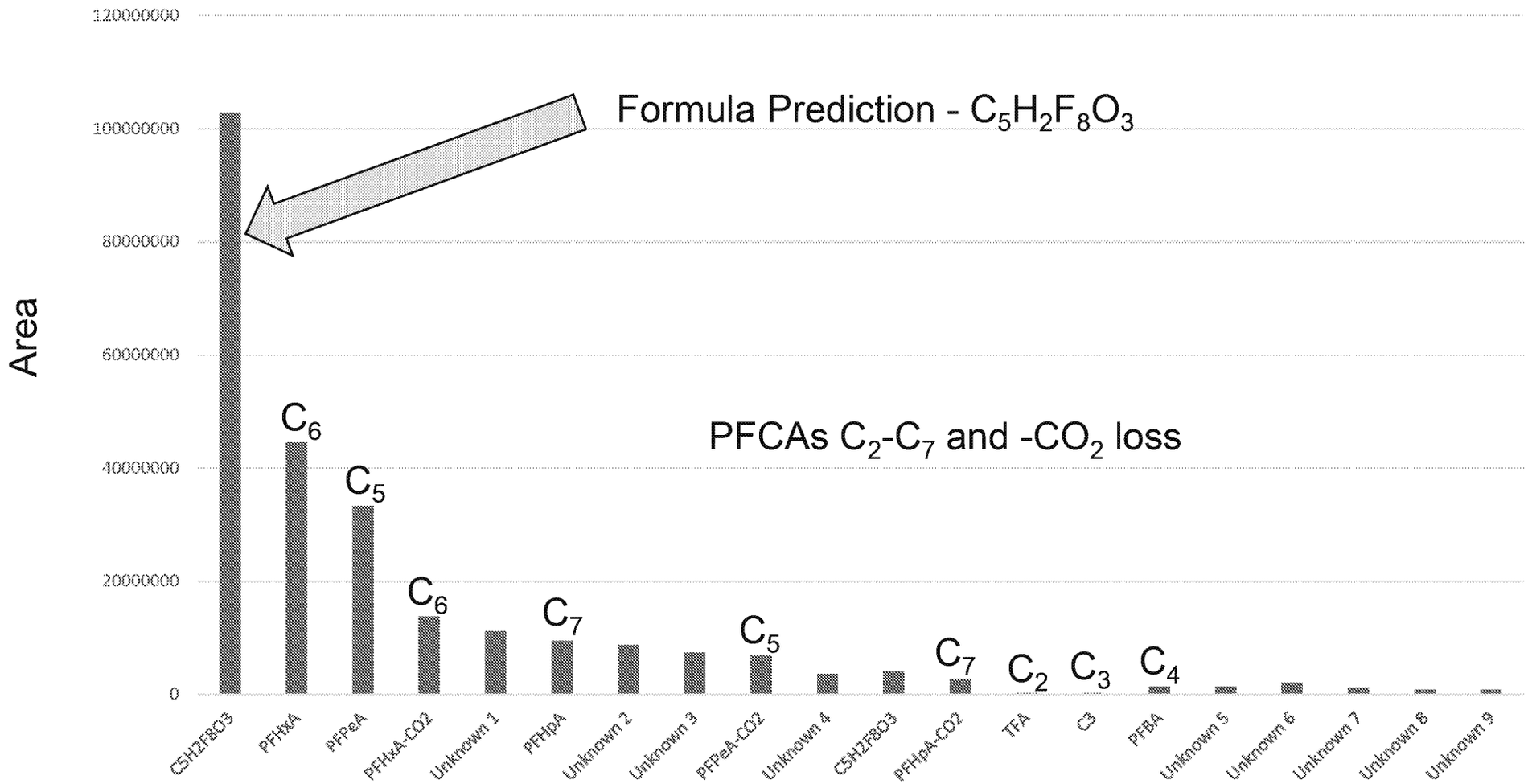


FIGURE 3-1
MODIFIED EPA METHOD 5
PFOA SAMPLING TRAIN



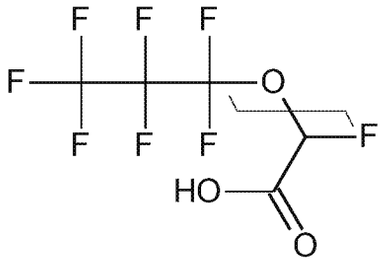
Slide courtesy Jeff Ryan (EPA/ORD/NRMRL)

Control Technology Sump Water Analytes

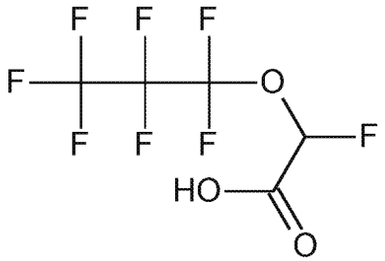


Additional PFAS beyond Legacy

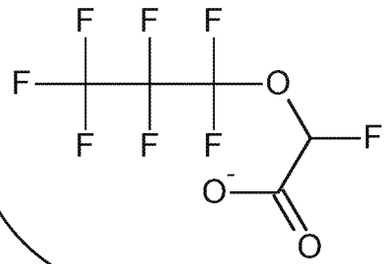
C_3F_7O
184.9837 Da



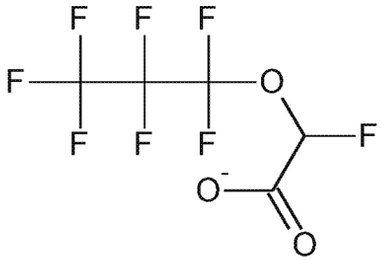
$C_2H_2FO_2$
77.0039 Da



Molecular Formula: $C_5H_2F_8O_3$
Monoisotopic Mass: 261.98762 Da
[M+H]+: 262.994896 Da
[M-H]-: 260.980343 Da

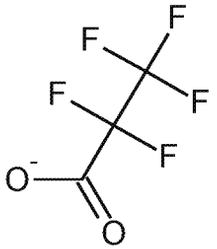


H^+



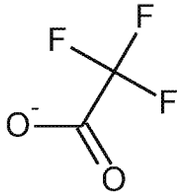
Monoisotopic Mass: 522.967963 Da

C3



Molecular Formula: $C_3F_5O_2^-$
Monoisotopic Mass: 162.9824

TFA



Molecular Formula: $C_2F_3O_2^-$
Monoisotopic Mass: 112.9856

In dispersion #6, control technology, XAD inlet/outlet, filters inlet/outlet

Assessment of industrial dispersions/surfactants

NHDES collected:

8 industrially used PTFE dispersions
5 industrially used surfactants
near Merrimack, NH region

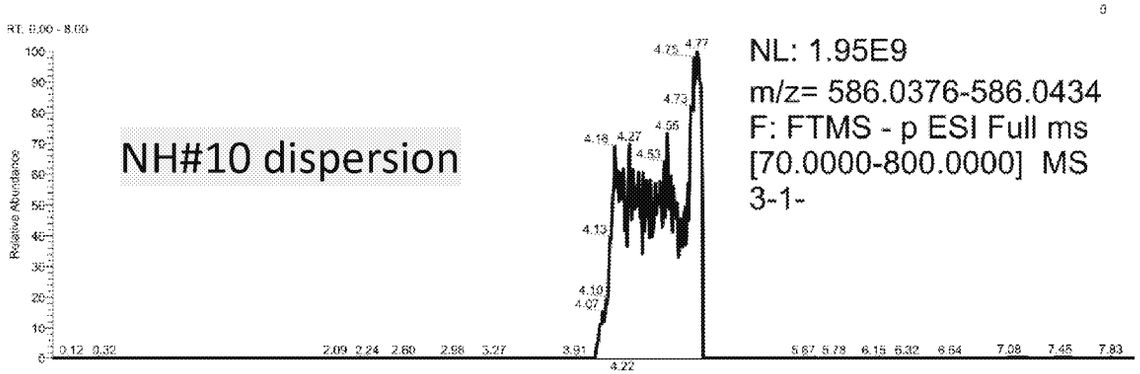
EPA ORD NERL:

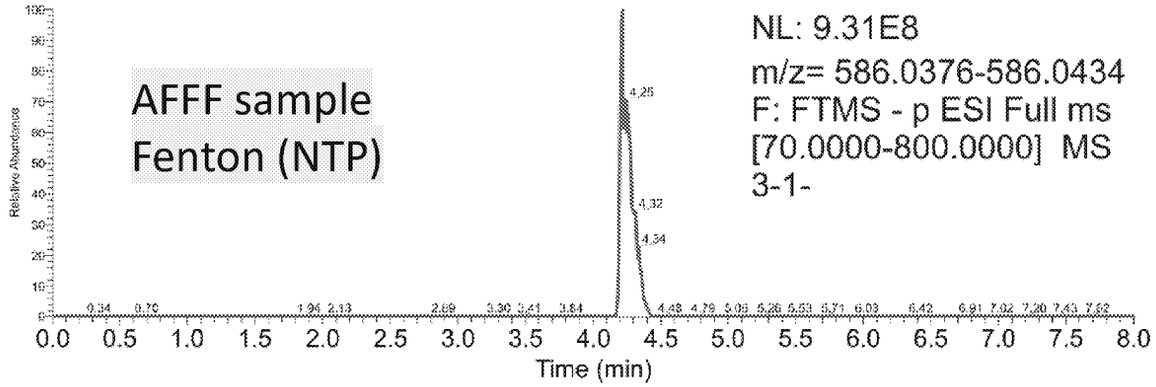
assessed via QTOFMS and Orbitrap MS

ED_006086_00129255-00020

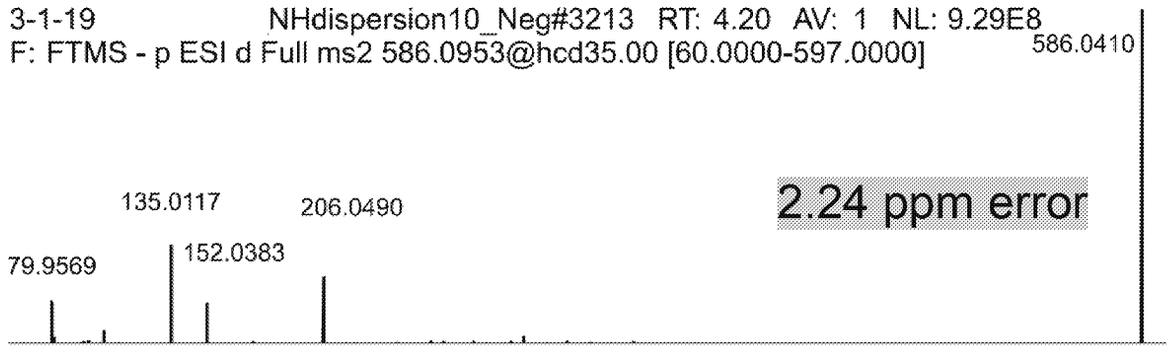
6:2 Fluorotelomer thioether amido sulfonate

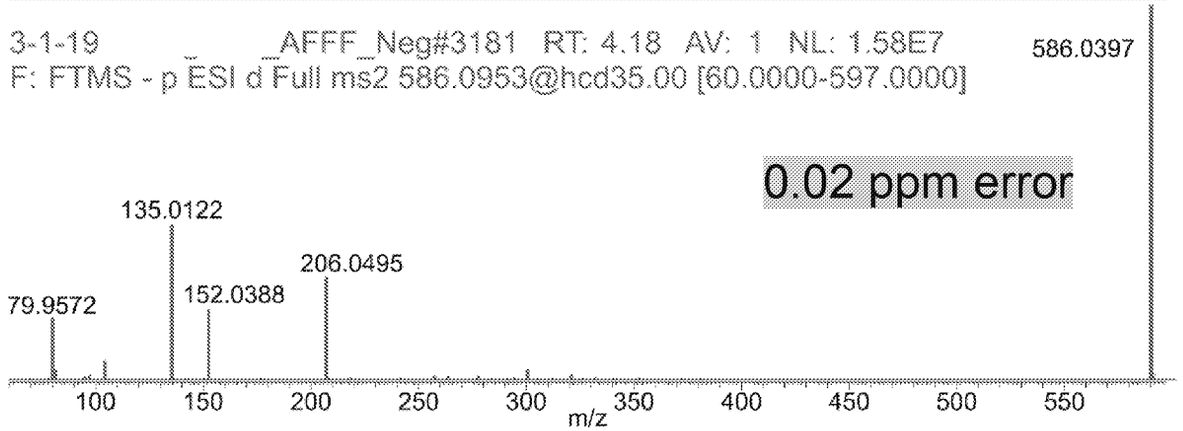
Chromatograms





MS/MS spectra

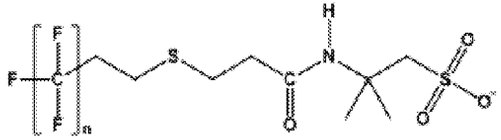




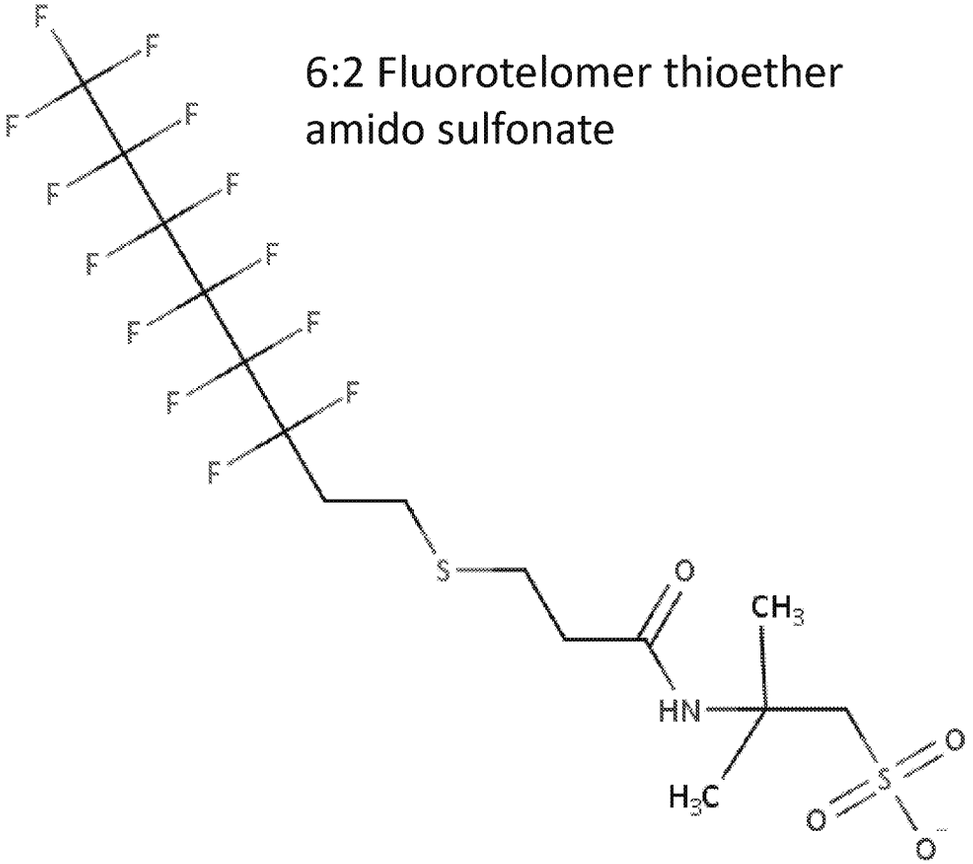
Select PFAS found in dispersions/surfactants collected

Munoz et al., 2017 Environ. Sci. Technol.
AFFF deployment Lac-Mégantic railway accident Québec, Canada

Fluorotelomermercaptoalkylamido sulfonate (FTSAS)



4:2 FTSAS	n = 4	Sc
6:2 FTSAS	n = 6	Sc
6:2 FTSAS	n = 8	Sc
10:2 FTSAS	n = 10	Sc
12:2 FTSAS	n = 12	Sc
14:2 FTSAS	n = 14	Sc

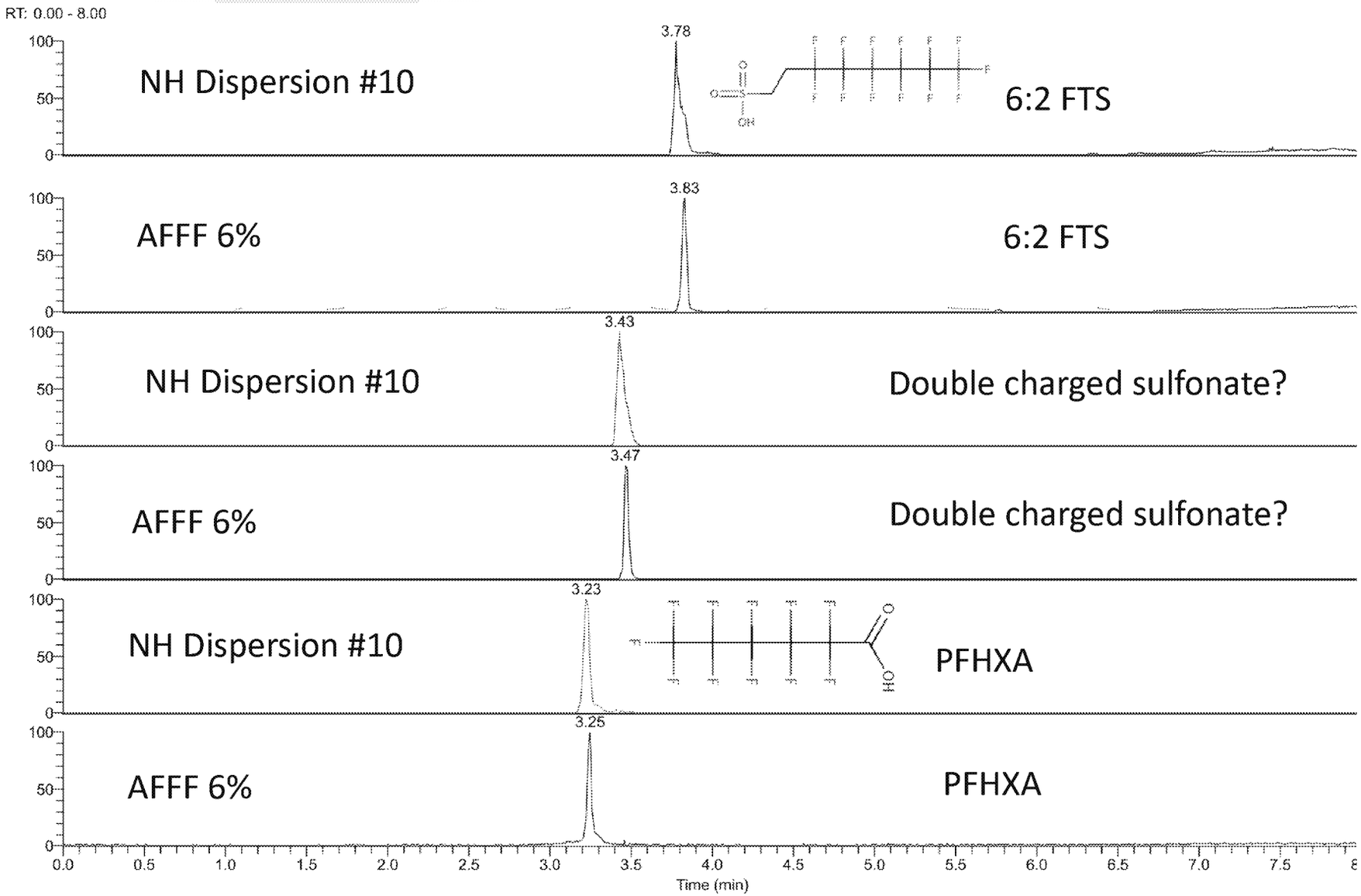


6:2 Fluorotelomer thioether amido sulfonate

https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID70892333

ED_006086_00129255-00022

Select PFAS found in dispersions/surfactants collected



Work with New Jersey Department of Environmental Protection (NJDEP)

ED_006086_00129255-00024

New Jersey vs. National PFAA Detections in 2013-15
USEPA Unregulated Contaminated Monitoring Rule 3 (UCMR3)

Compound	Reporting Level (ng/L)	New Jersey PWS		National PWS other than NJ	
		# Detects*	% Detects	# Detects**	% Detects
PFOA (C8)	20	**19/175**	**10.9%**	**98/4745**	**2.1%**
PFNA (C9)	20	**4/175**	**2.3%**	**10/4745**	**0.2%**
PFOS (C8-S)	40	6/175	3.4%	89/4745	1.9%
PFHxS (C6-S)	30	2/175	1.1%	53/4745	1.1%
PFBS (C4-S)	90	0/175	0%	8/4745	0.2%
PFHpA (C7)	10	6/175	3.4%	80/4745	1.7%

** Final New Jersey UCMR3 data. **USEPA data posted online as of 1/17.*

Slide courtesy of Sandra Goodrow NJDEP

Background NJDEP West Deptford, NJ

PFNA is the primary component of Surflon S-111 (CAS # 72968-3-88), a commercial mixture of perfluorinated carboxylic acids.

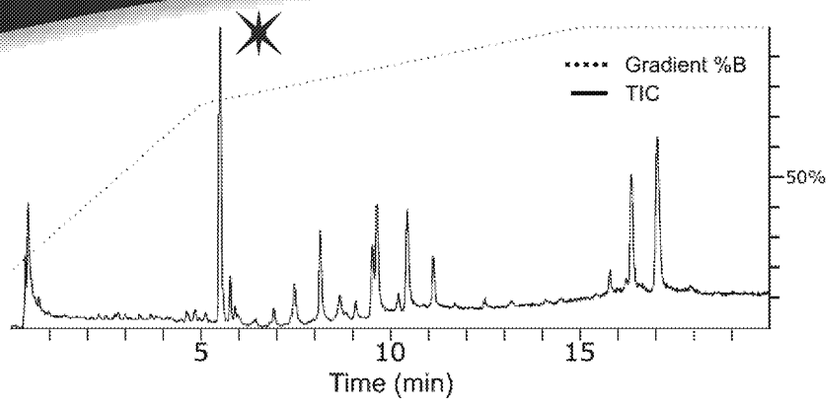
Prevedouros et al. (2006)

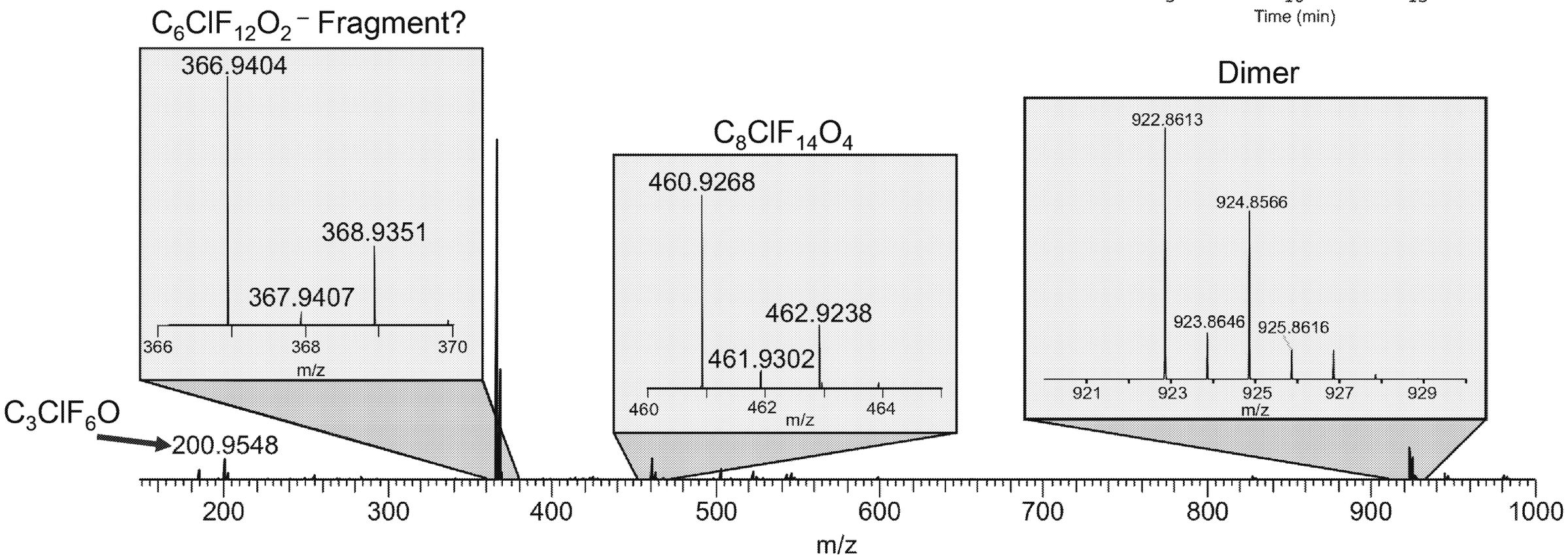
Composition of Surflon S-111 by weight:

- PFNA-C9 (74%)
- PFUnDA-C11 (20%)
- PFTrDA-C13 (5%)

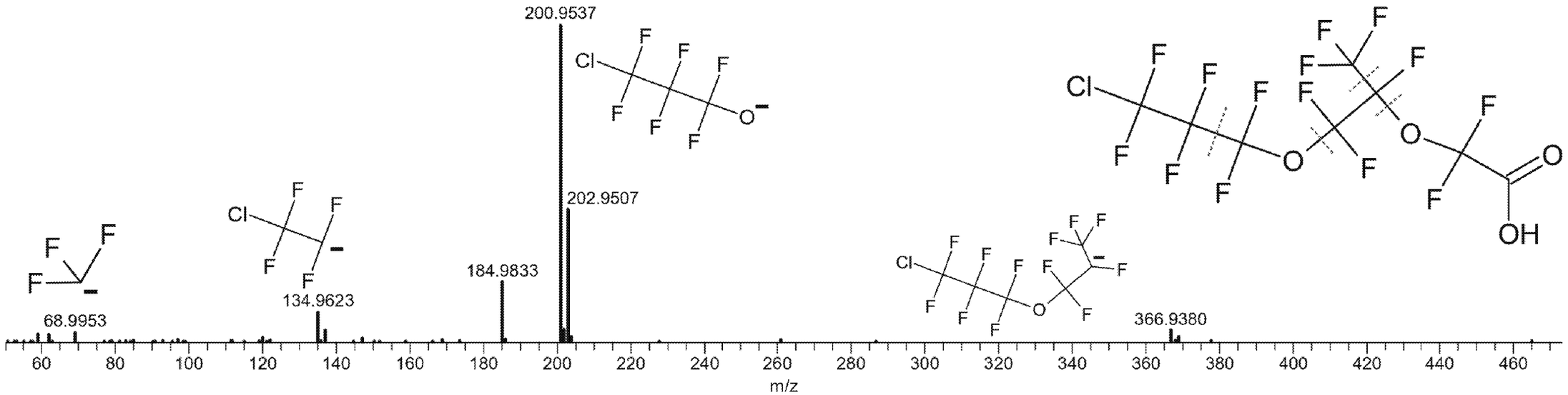
https://www.state.nj.us/dep/watersupply/pdf/pfna-health-effects.pdf

Major Peak Constituents Predicted Formula



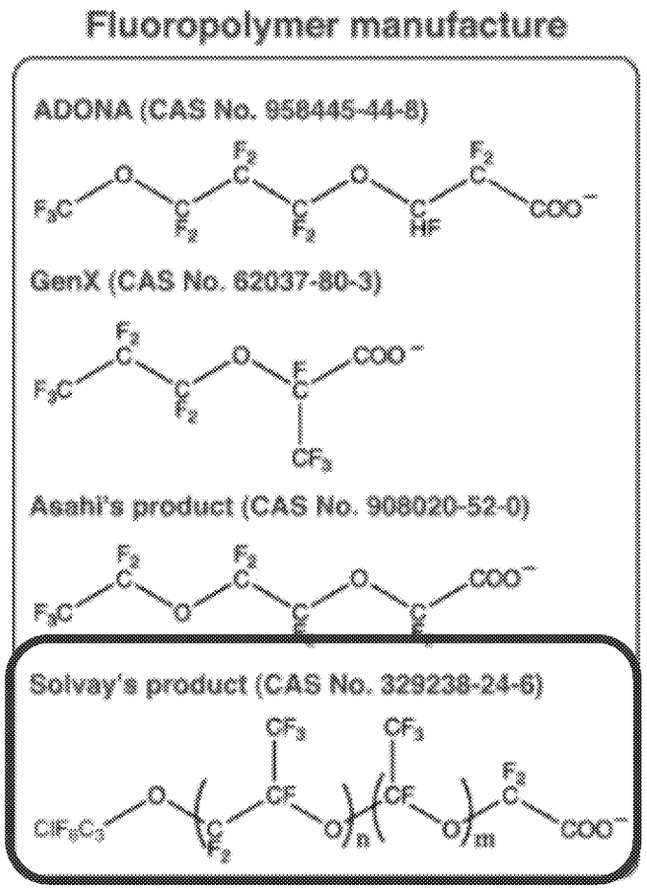


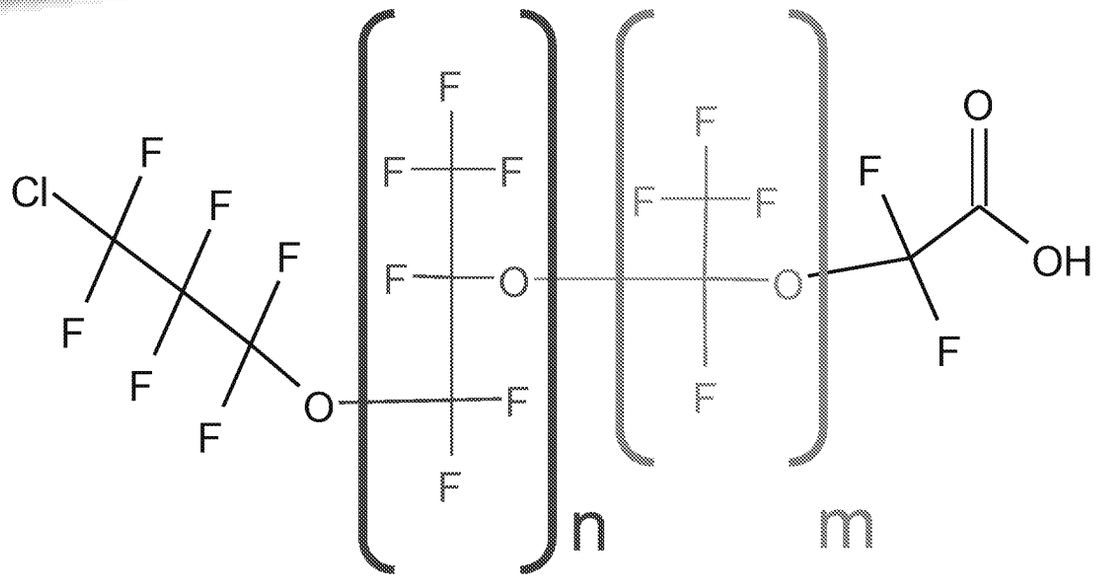
Structural Elucidation by MS/MS



- Unequivocal assignment of terminal Cl and ether positions based on MS/MS experiments
- Confirmation of dimers and in-source fragments from prior slide, with additional experiments (not shown)

Literature Support

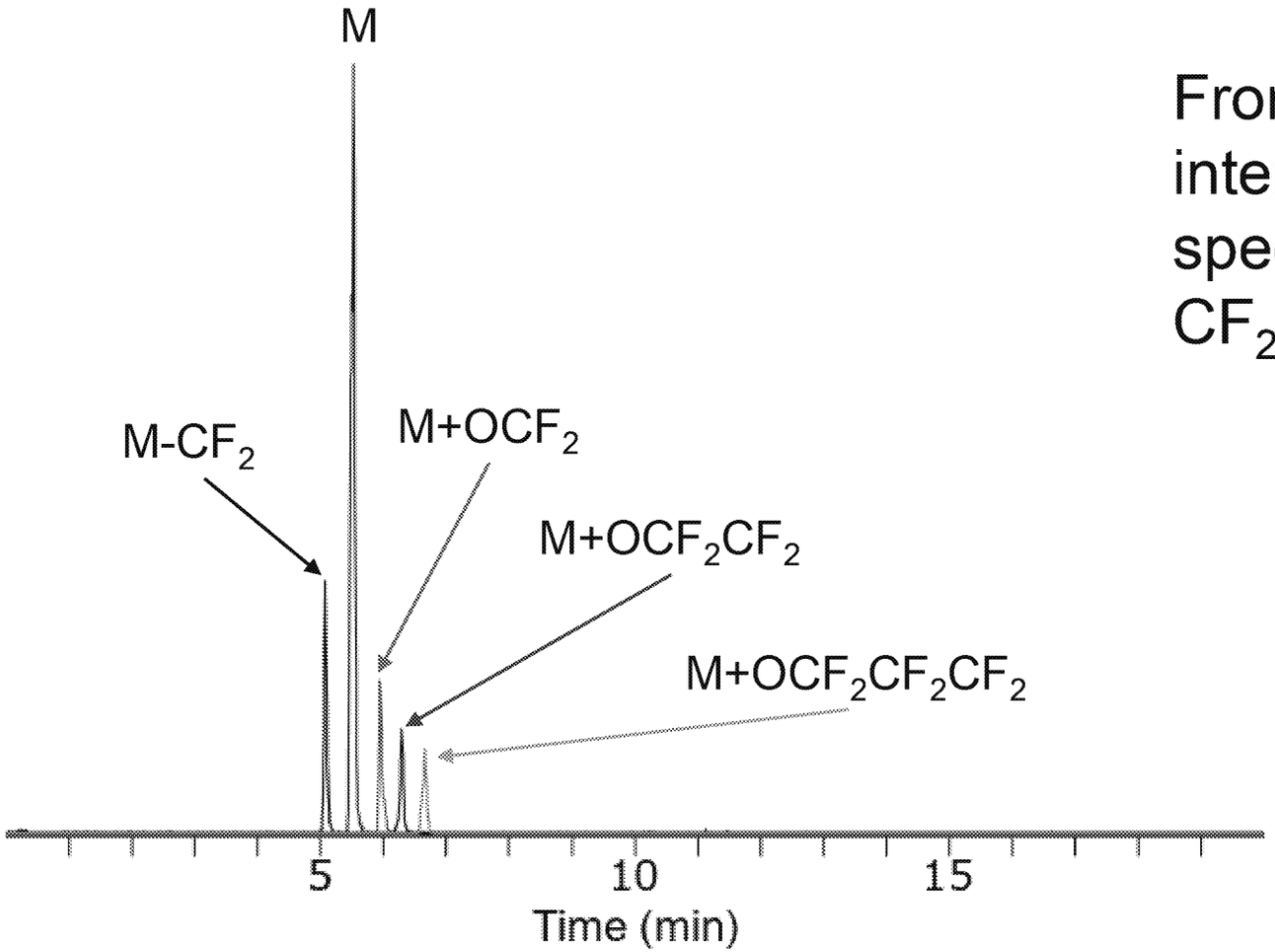




Chloro perfluoro polyether carboxylic acids Cl-PFPECAs(n,m)

Wang, Z., et al. (2013). Environ. Int. **60: 242.**
EFSA J, 8 (2) (2010), p. 1519, 10.2903/j.efsa.2010.1519

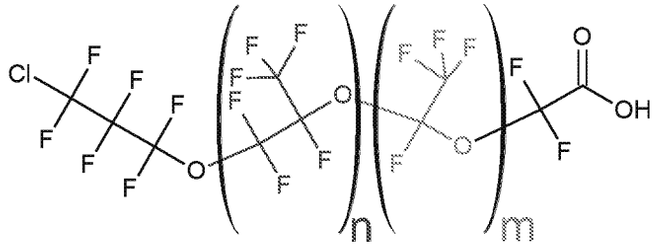
Homologous Fluoropolymer Series



From single identified mass of interest we identified additional species related by OCF_2 and/or CF_2 repeating units

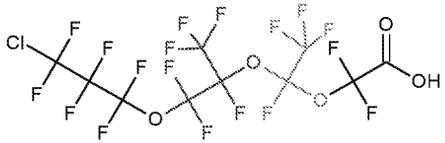
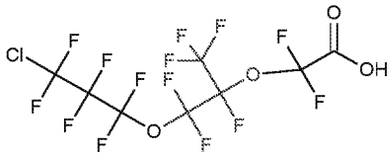
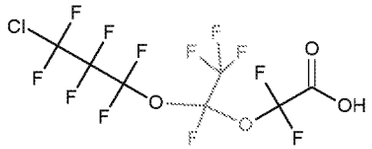
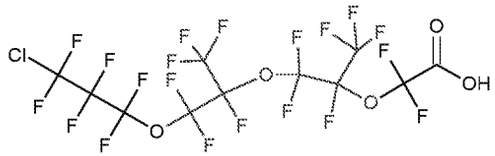
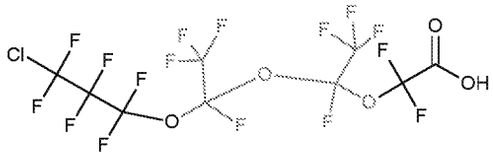
Structural Homologs

Wang et al., 2013
Solvay
CAS 329238-24-6

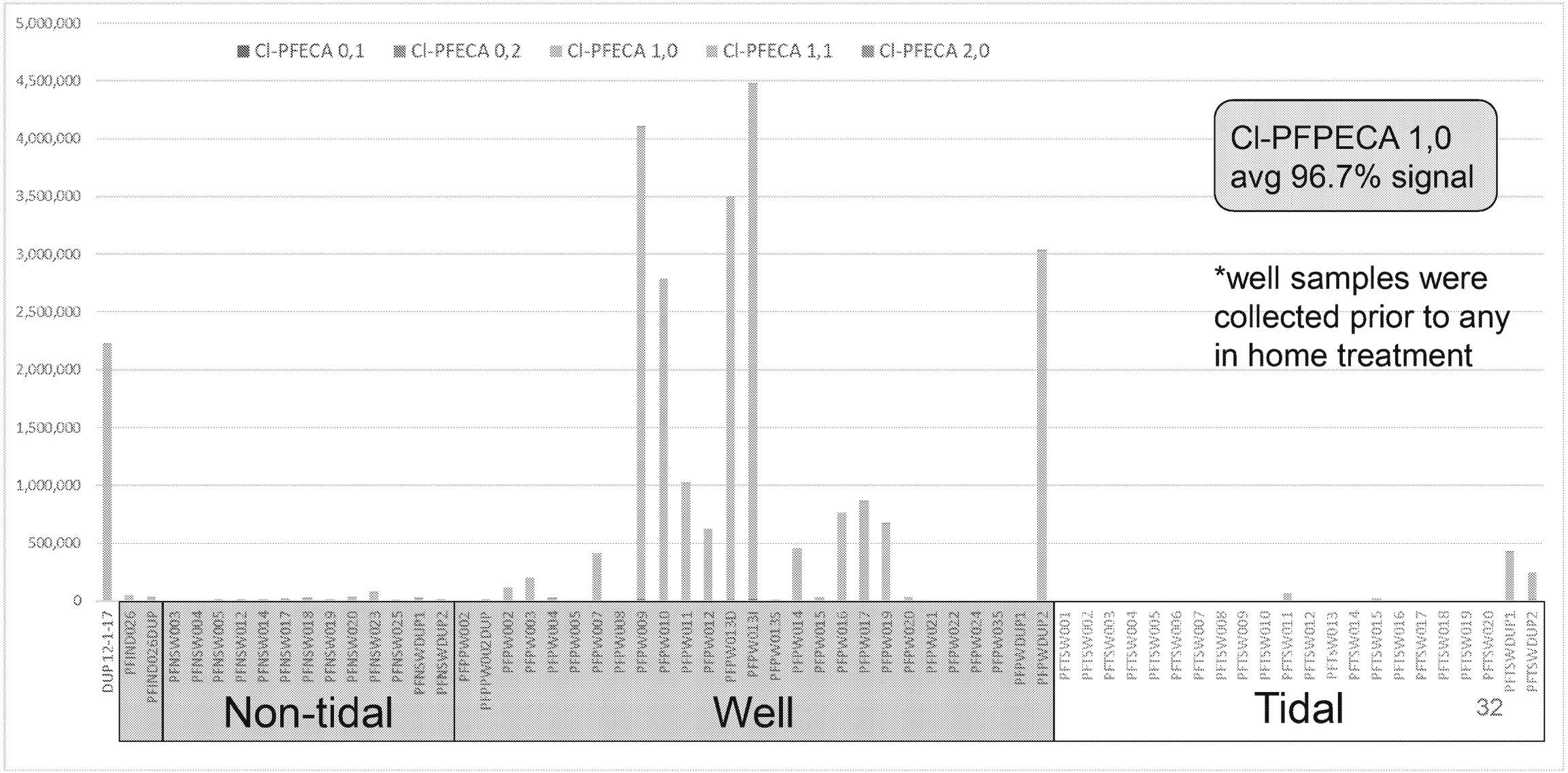


propyl, ethyl

10 congeners also detected in regional soil and plant samples (John Washington EPA/ORD/NERL)

		Monoisotopic Mass (Da)
Cl-PFPECA 1,1		577.9225
Cl-PFPECA 1,0		461.9340
Cl-PFPECA 0,1		411.9372
Cl-PFPECA 2,0		627.9193
Cl-PFPECA 0,2		527.9257

Water Nontargeted Analysis – Cl-PFPECAs



Post-doc Wanted:
EPA-ORD-NERL-EMMD-2019-01

https://www.zintellect.com/Opportunity/Details/EPA-ORD-NERL-EMMD-2019-01.

Questions?

Contact Information
strynar.mark@epa.gov

The views expressed in this presentation are those of the author(s) and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

ED_006086_00129255-00033