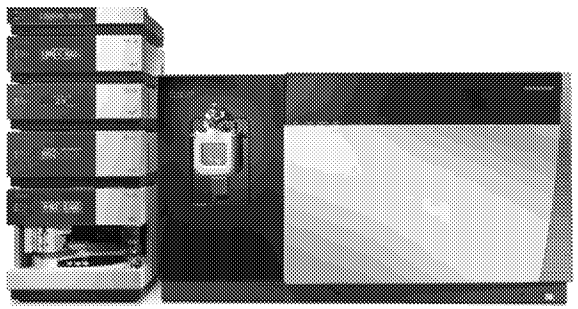
Identification of novel PFAS in environmental samples

Mark Strynar US EPA Office of Research and Development (ORD)



Orbitrap Fusion - HRMS

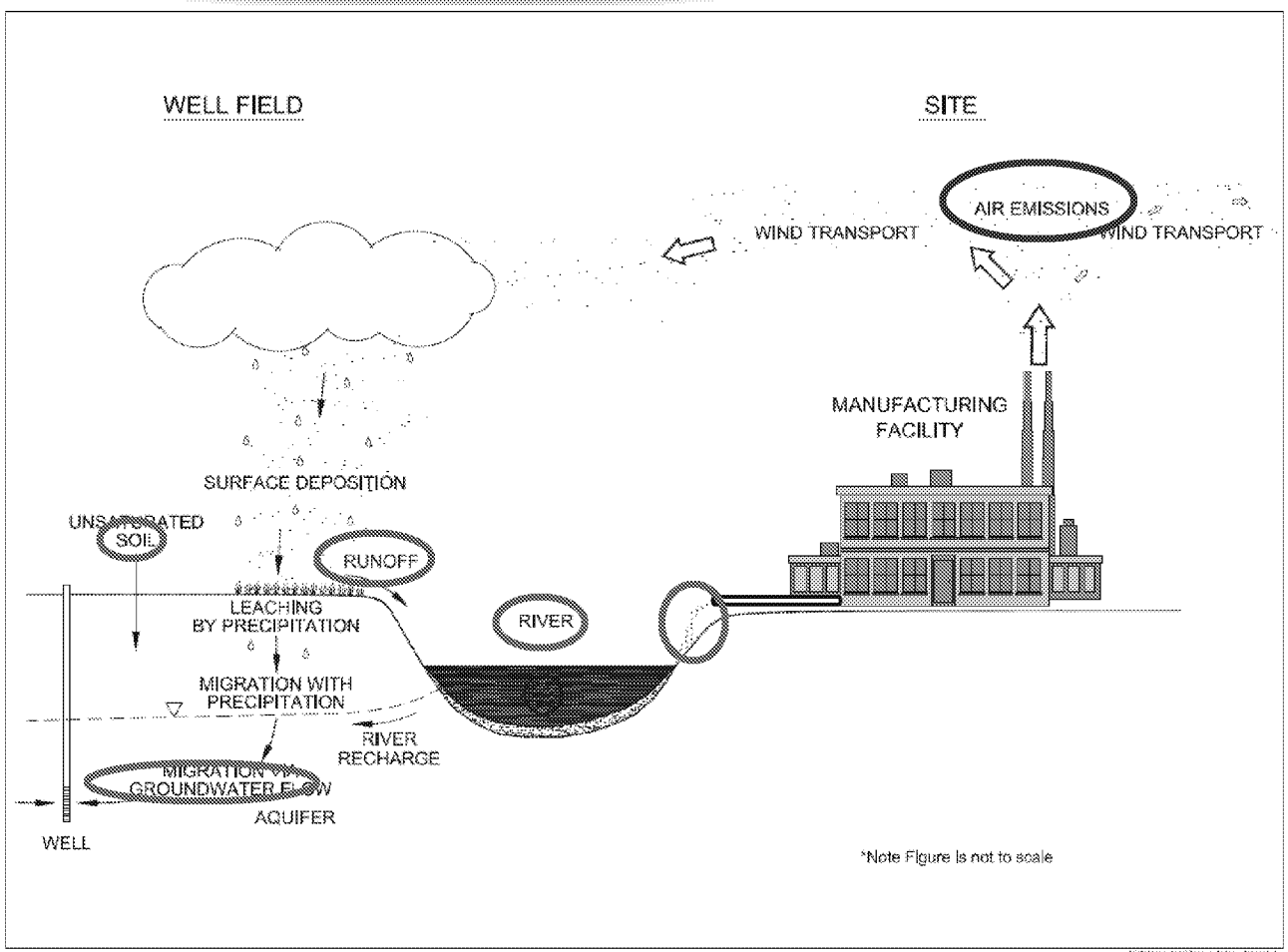
July 23rd,2019
CSS Science Webinar

ED_006086_00126878-00001

Presentation Outline

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

Conceptual Model of APFO Emission

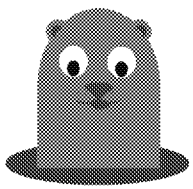


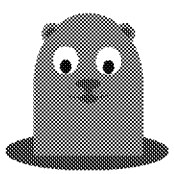
Davis et al., 2007 Chemosphere (67) 2011-2019
"Transport of ammonium perfluorooctanoate in environmental media near a fluoropolymer manufacturing facility"

Dupont/Chemours

Saint-Gobain
Solvay Specialty Polymers
3M
Daikin….

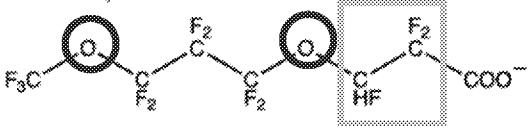
Post PFOA Stewardship Agreement



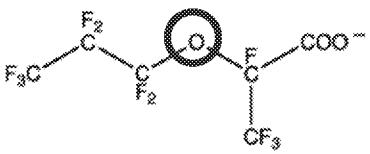


Fluoropolymer manufacture

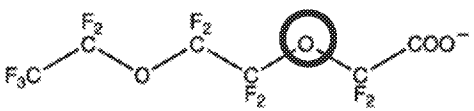
ADONA (CAS No. 958445-44-8)



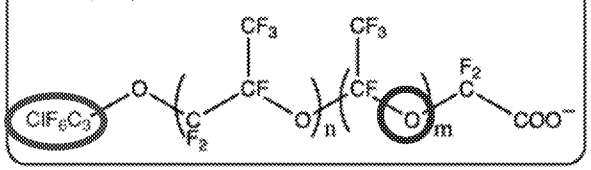
GenX (CAS No. 62037-80-3)



Asahi's product (CAS No. 908020-52-0)

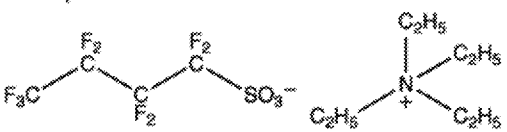


Solvay's product (CAS No. 329238-24-6)

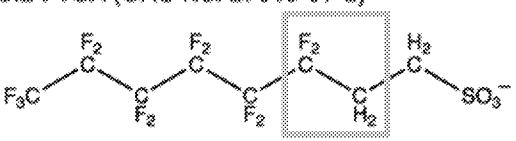


Metal plating

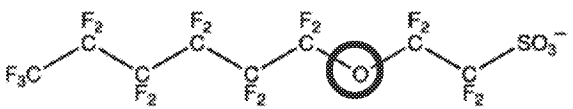
$N(Et)_4$-PFBS (CAS No. 25628-08-4)



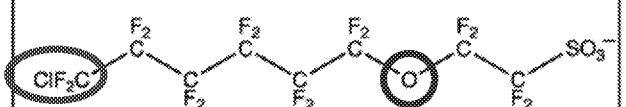
6:2 FTSA (CAS No. 27619-97-2)

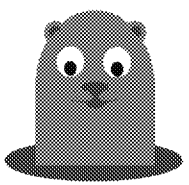


F-53 (CAS No. 754925-54-7)



F-53B (CAS No. 73606-19-6)

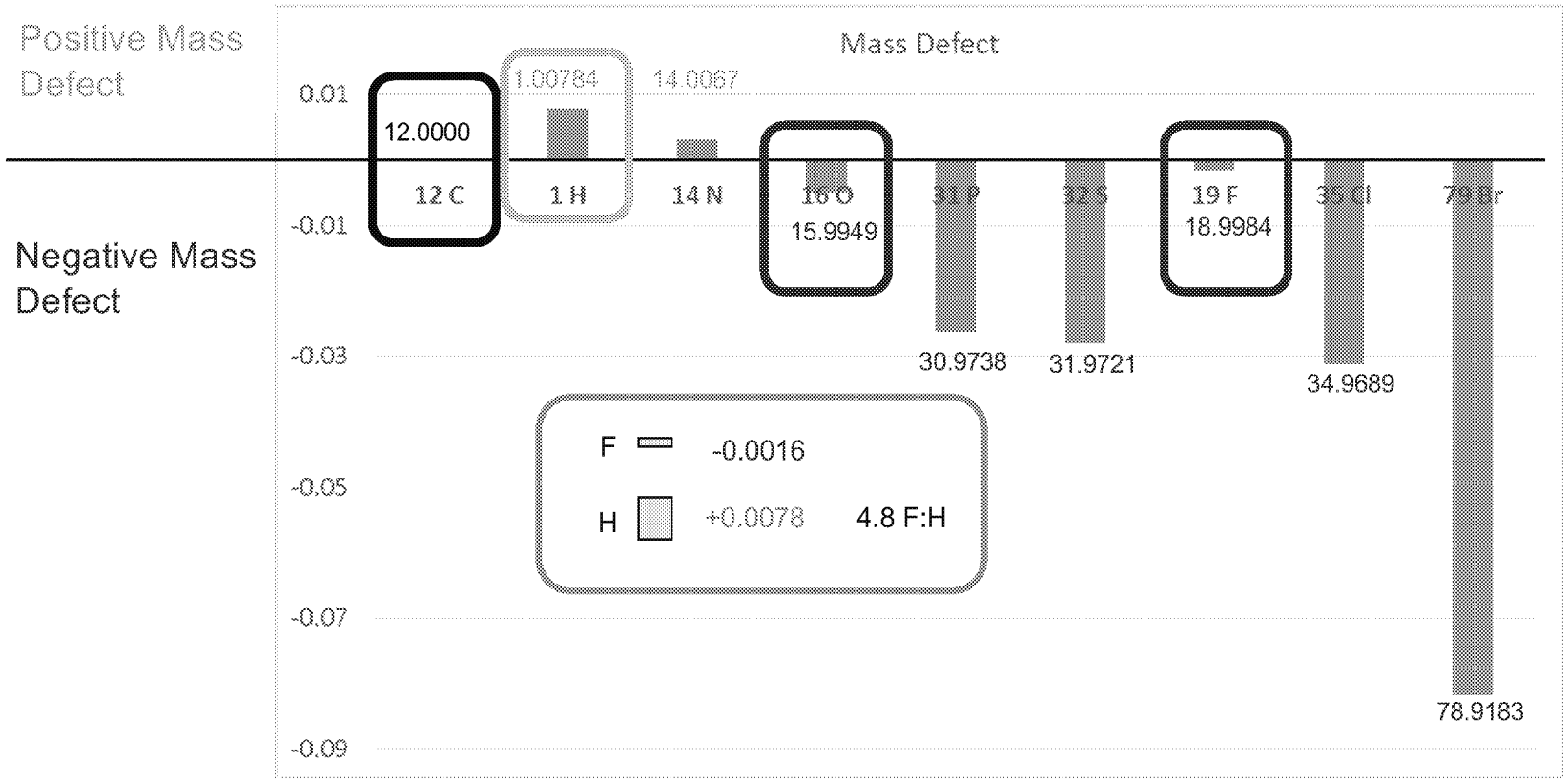




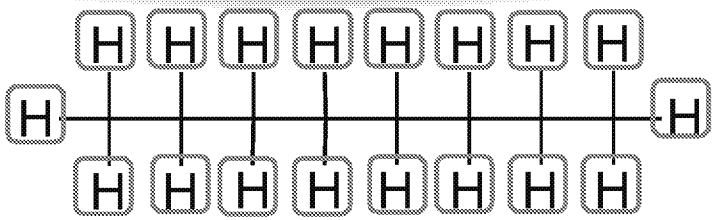
4

Wang et al. *Environment International*, **2013,** *60,* pp 242–248

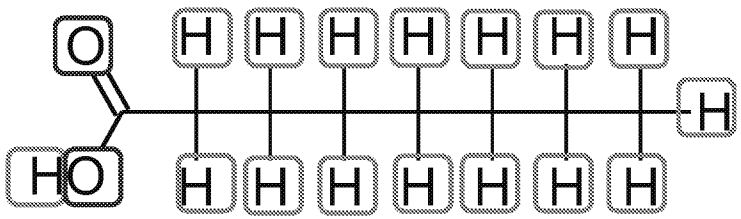
Isotope Signatures: Negative Mass Defect



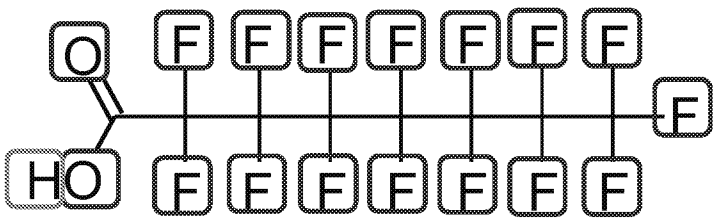
Example of Mass Defect



Octane
MI mass 114.1409



Octanoic Acid
MI mass 144.1150

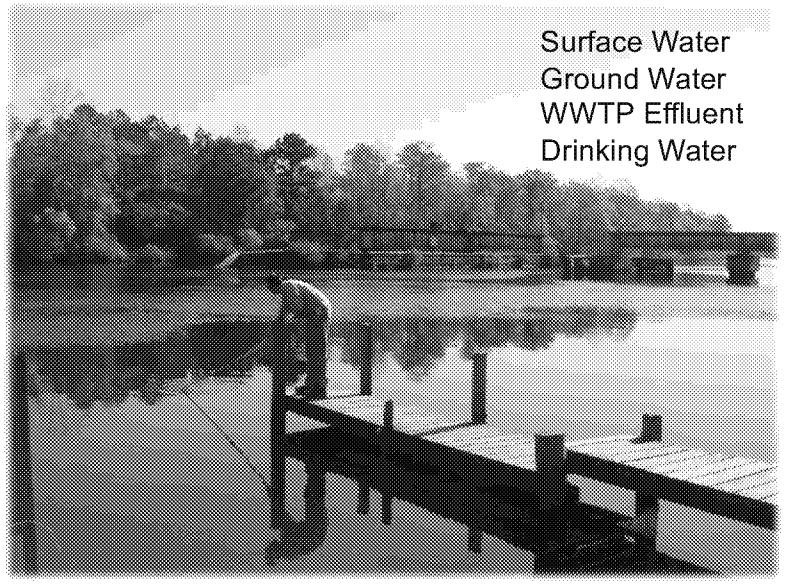


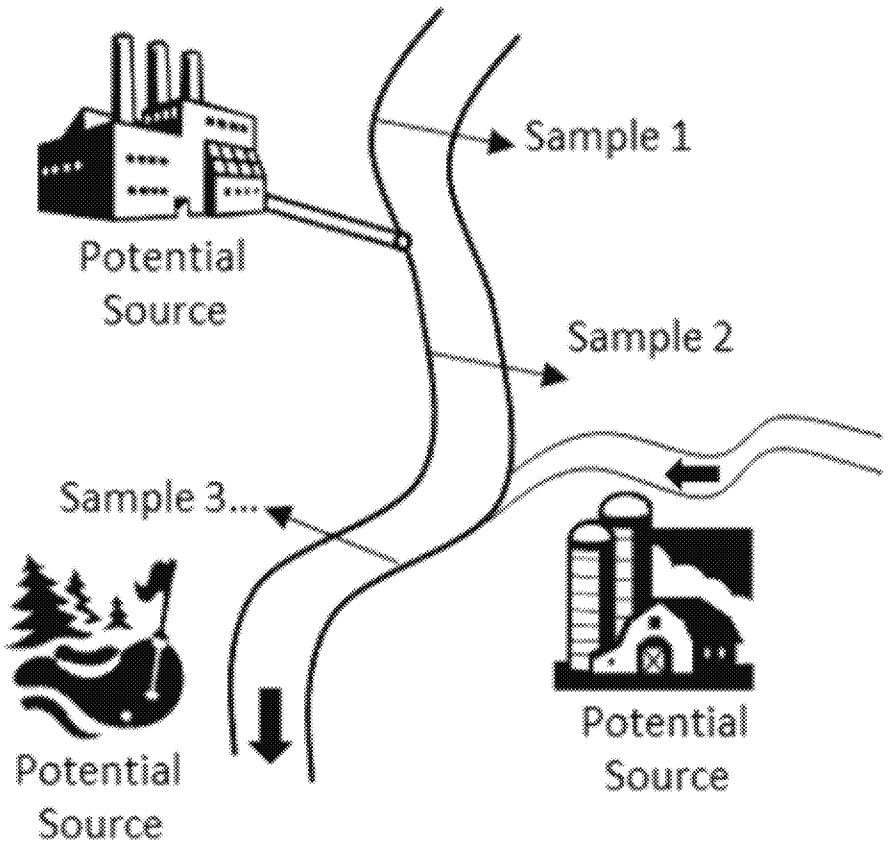
Perfluorooctanoic Acid
MI mass 413.9737

ED_006086_00126878-00006

Data Generation: Source Determination by NTA

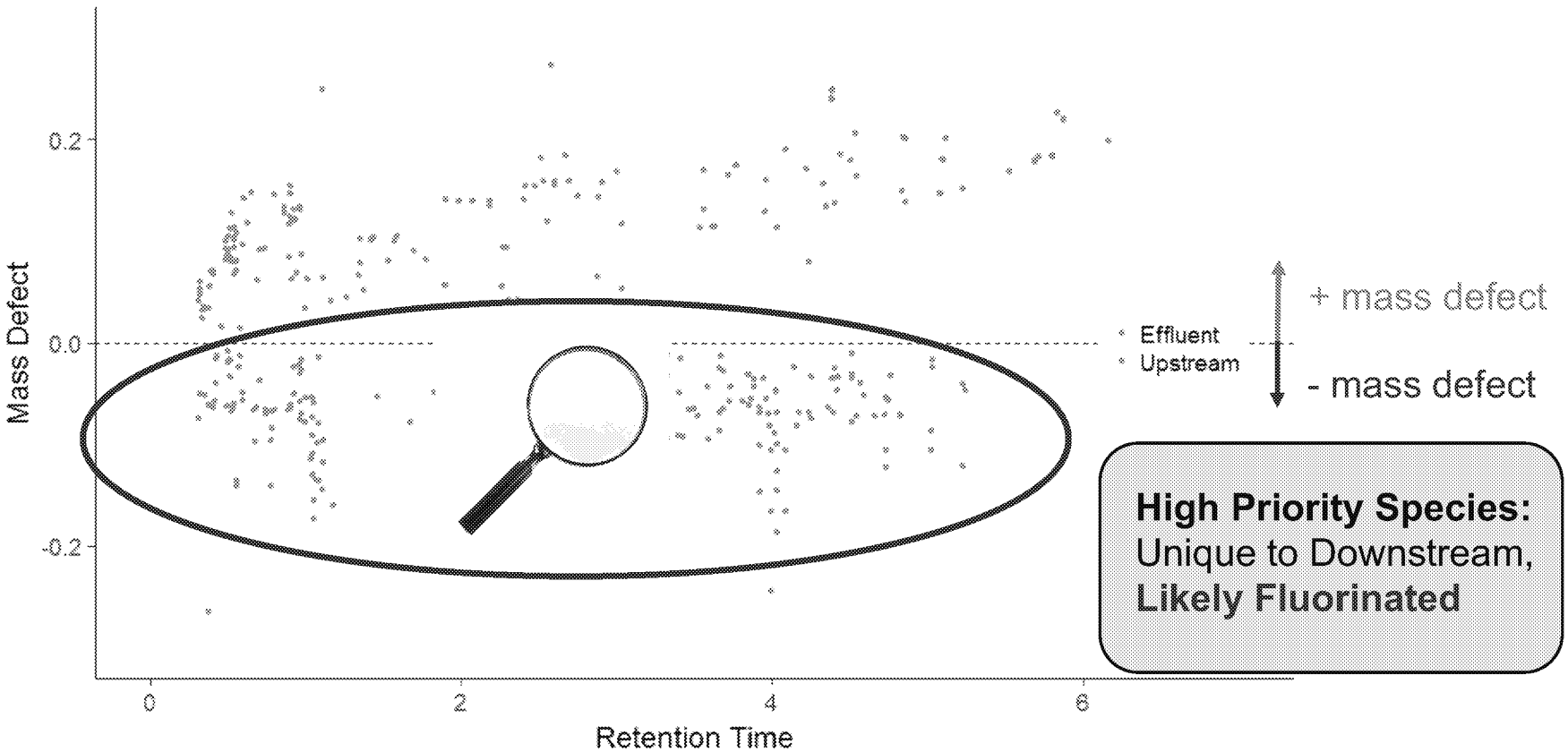
Legacy PFAS are an indicator





Sampling from geographically or temporally displaced locations allows triangulation of sourcing

Mass Defect of Outfall and Cape Fear River Upstream Features



High Priority Species:
Unique to Downstream,
Likely Fluorinated

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)

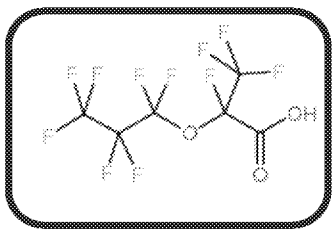
Mark Strynar,[*,†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Liang,[†,‡] Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[∥] Imma Ferrer,[∥] and Carol Ball[⊥]

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

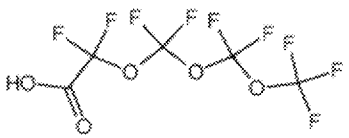
number	formula	CAS no.	name	$[M]^+$	$[M - H]^-$ m/z	$[2M - 2H + Na]^-$ m/z	$[2M - H]^-$ m/z
Monoether PFECAs							
1	$C_3HF_5O_3$			179.9846	178.9773	380.9438	358.9619
2	$C_4HF_7O_3$			229.9813	228.9740	480.9372	458.9553
3	$C_5HF_9O_3$	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	$C_6HF_{11}O_3$	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	$C_7HF_{15}O_3S$	66796-30-3[#]		443.9337	442.9264		
12	$C_7H_2F_{14}O_3S$			463.9399	462.9326		

3 Found in human serum Wilmington, NC 2019 (NCSU Kotlarz/Hoppin)

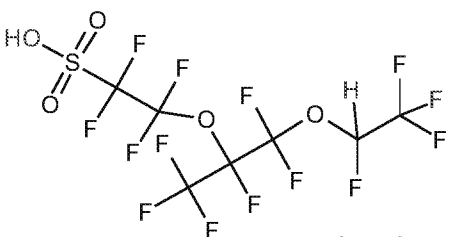
Example Structures



Monoether (6): GenX



Polyethers (4):



Polyethers sulfonates (2):

Environmental Science & Technology Letters

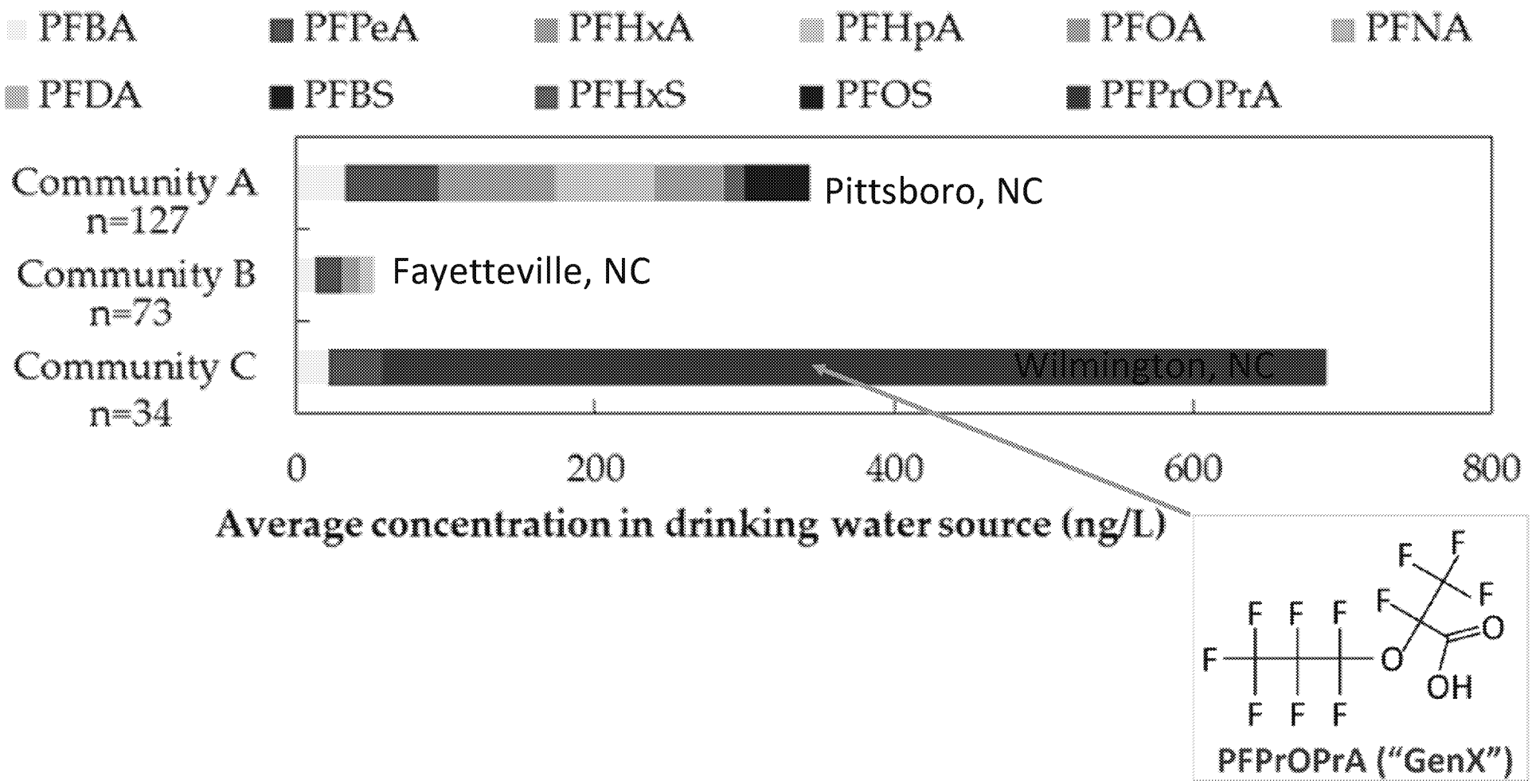
November 2016

Letter

pubs.acs.org/journal/estlcu

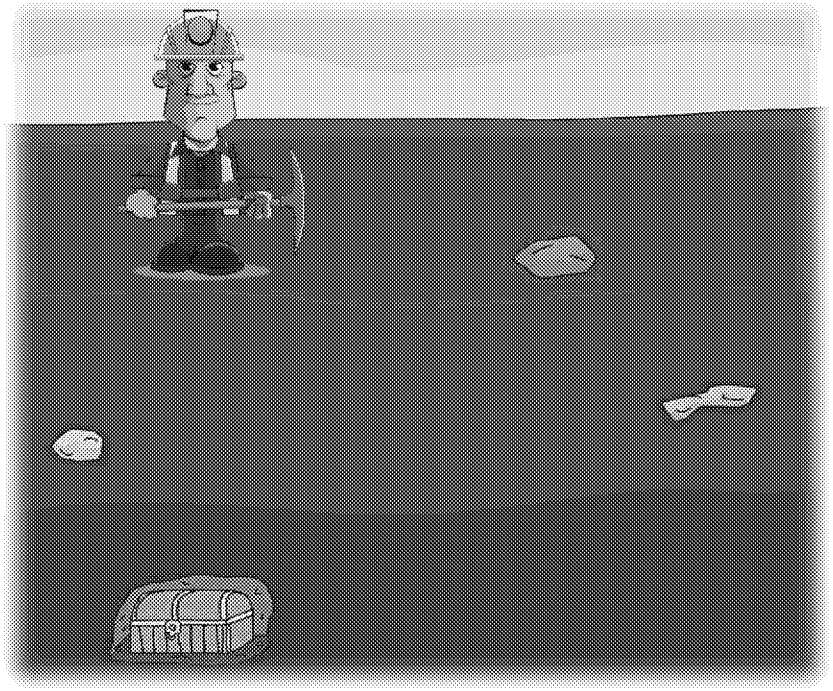
Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

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


PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFBS
PFHxS
PFOS
PFPrOPrA
Community A
n=127
Pittsboro, NC
Community B
n=73
Fayetteville, NC
Community C
n=34
Wilmington, NC
0
200
400
600
800
Average concentration in drinking water source (ng/L)
PFPrOPrA ("GenX")

Data Mining -NTA

- Lots of overburden (stuff) to sift through
- A lot of work
- Some hidden gems
- Only possible with NTA and, HRMS works best

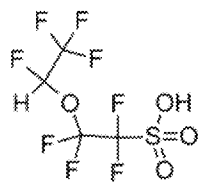


Retrospective Analysis (McCord 2019)

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	✓	✓	✓	✓	✓	×	×	×

Retrospective Analysis (McCord 2019)

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	✓	✓	✓	✓	✓	×	×	×

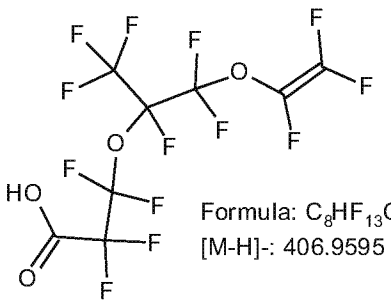


Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

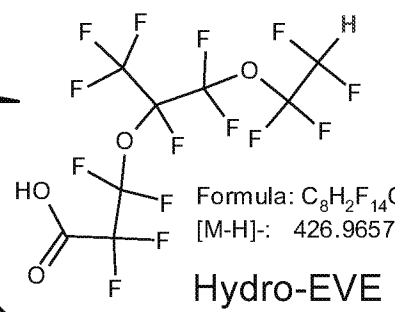
NVHOS

Retrospective Analysis (McCord 2019)

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



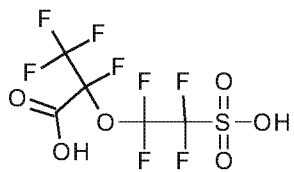
Formula: $C_8H_2F_{14}O_4$
[M-H]-: 426.9657 Da

Hydro-EVE

Also found in Wilmington, NC serum (NCSU Kotlarz/Hoppin)

Retrospective Analysis (McCord 2019 *in review*)

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

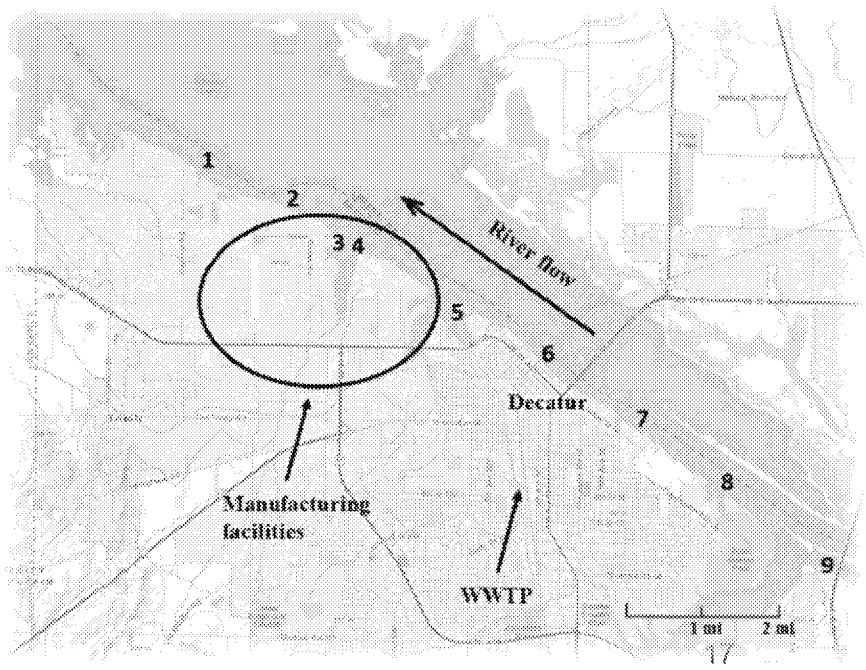
pubs.acs.org/est

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

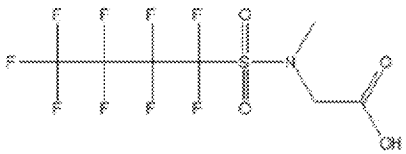
Seth Newton,[†] Rebecca McMahen,[‡] James A. Stoeckel,[§] Michael Chislock,[§] Andrew Lindstrom,[†] and Mark Strynar*[,†]

Tennessee River, Decatur, AL

- Basis of PFOA/PFOS PHA (2009)

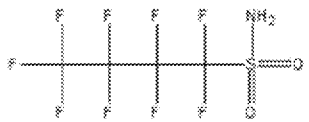


Newton et al., 2017



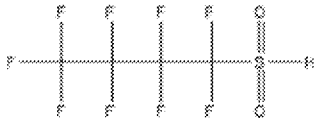
N-methyl perfluorobutane sulfonamidoacetic acid

(MeFBSAA)

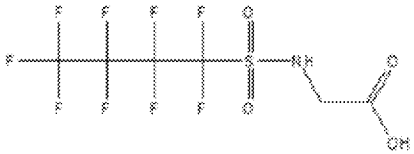


perfluorobutane sulfonamide

(FBSA)

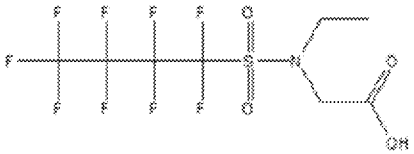


perfluorobutane sulfinic acid



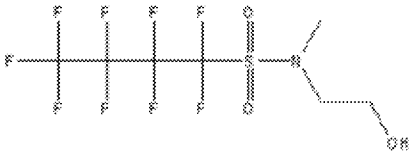
perfluorobutane sulfonamidoacetic acid

(FBSAA)



N-ethyl perfluorobutane sulfonamidoacetic acid

(EtFBSAA)



N-methyl perfluorobutane sulfonamdoethanol

(MeFBSE)

Figure S7 – Structures, names, and abbreviations for perfluorobutane sulfonamides (PBSAs)

June 25th, 2019

Chu et al. 2016
Fish - Canada and Great Lakes

c&en TOPICS MAGAZINE COLLECTIONS VIDEOS JOBS

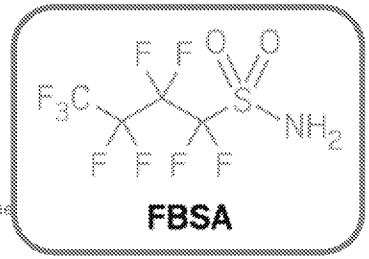
3M admits to unlawful release of PFAS in Alabama

US EPA barred company from discharging two substances to water

by Cheryl Hogue

JUNE 26, 2019 | APPEARS IN VOLUME 97, ISSUE 26

3M has voluntarily acknowledged to regulators that its Decatur, Alabama, plant illegally released a perfluorinated chemical to the Tennessee River, which supplies drinking water to hundreds of thousands of people.



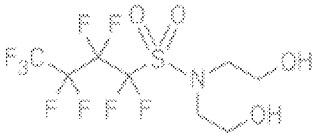
FBSA

The chemical is perfluorobutane sulfonamide (FBSA), which the company began to manufacture and use at the Decatur facility in 2009. As a condition of allowing manufacture of the substance under the US Toxic Substances Control Act, the Environmental Protection Agency prohibited 3M from releasing FBSA into US waterways.

3M says its Decatur plant may also have released a related chemical, a polyfluorinated sulfonamide alcohol, to the river as well. That substance, which 3M calls FBSEE, is a derivative of FBSA. It is also covered by the 2009 EPA order prohibiting release to water.

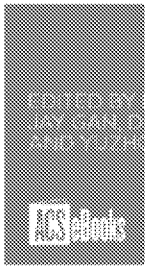
"We shut down the identified manufacturing operations and are completing internal changes to fully address the issue," 3M says in a statement.

FBSA and FBSEE are intermediates used to make fluorochemical products, according to 3M, including water- and stain-resistant coatings. Data on the toxicity of FBSA and FBSEE wasn't immediately available. The chemicals are in a class of environmentally persistent pollutants known as per- and polyfluorinated substances (PFAS).



FBSEE

In late April, 3M settled a lawsuit brought by a Decatur area water utility over longstanding PFAS contamination in the Tennessee River, agreeing to pay $35 million to fund a new filtration facility. Weeks earlier, 3M told the EPA about its failure to comply with the agency's no-release requirement following an internal check of the plant's



MOST POPUL
ENVIRONME

Periodic Graphics
reef damage

Sulfoxaflor pestic
market

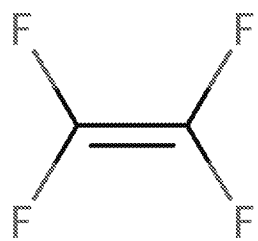
Periodic Graphics
reef damage

Plastics recycling
worms is further

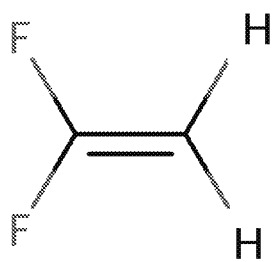
3M admits to unla
in Alabama

Chemours sues D
environmental lia

Newton et al., 2017



TFE – PTFE (Telfon)



DFE (Vinylidene fluoride) – (PVDF)

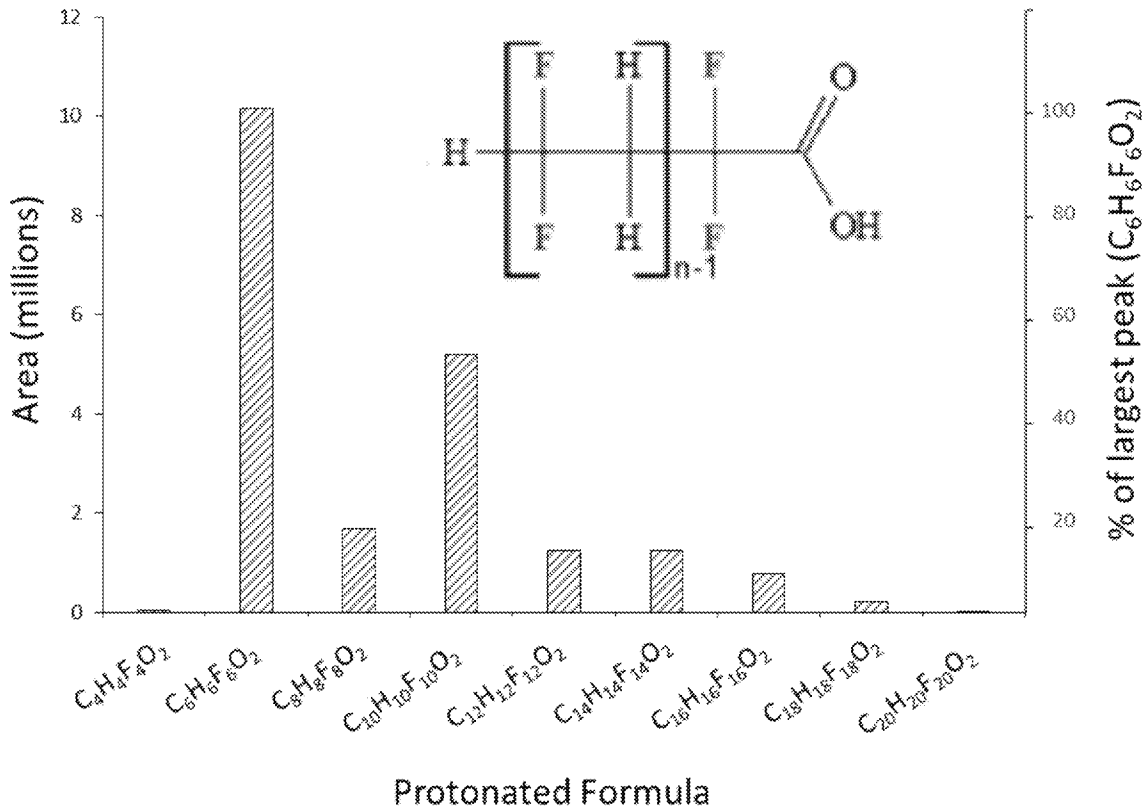
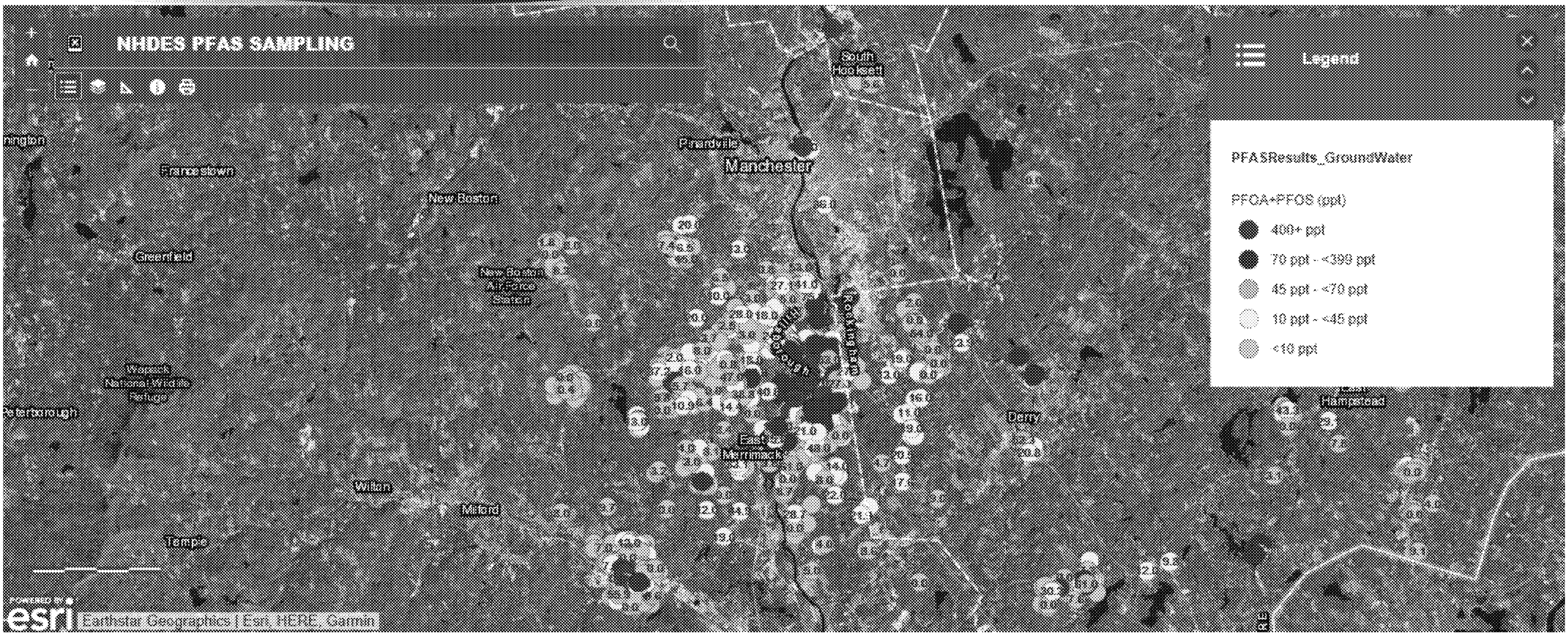


Figure S3 - Total area (sum of all isomers) of different species and their relative percentages in related series at Site 2.

Work with NHDES near Manchester NH



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

MM5 Impinger Schematic/Industrial Process

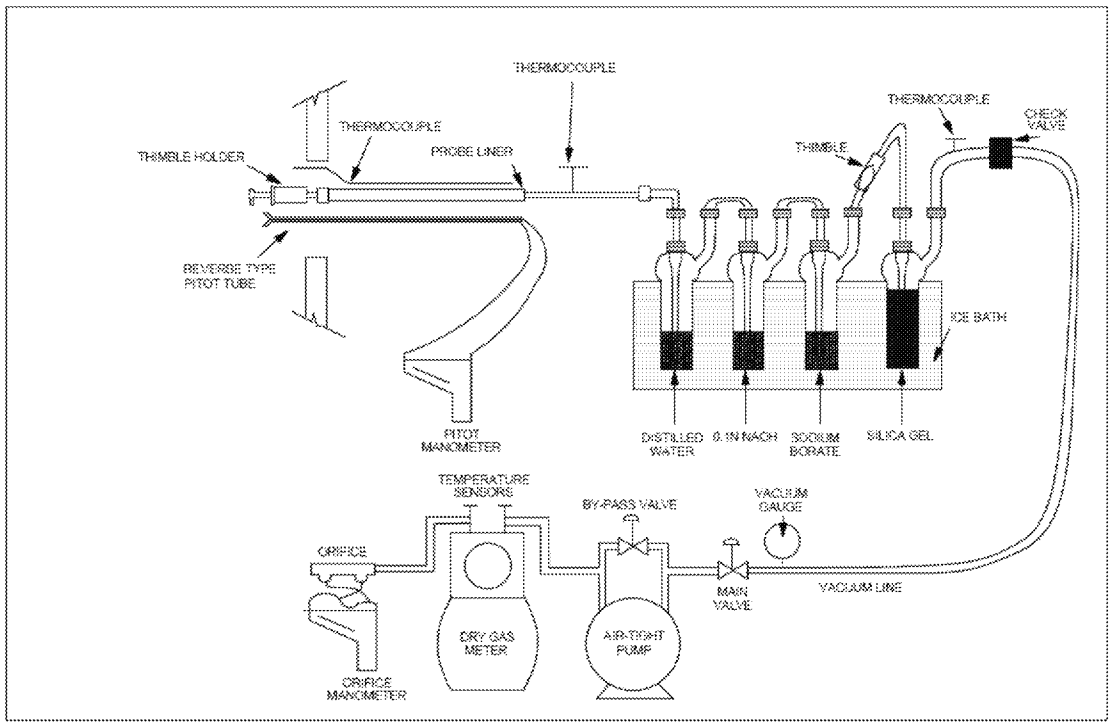
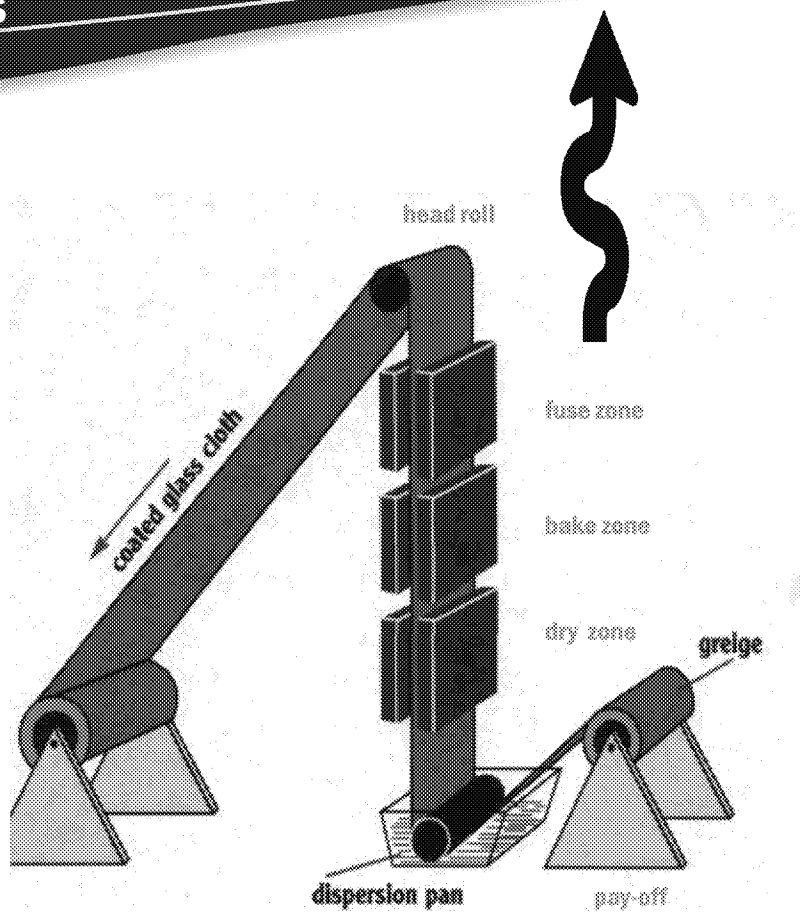
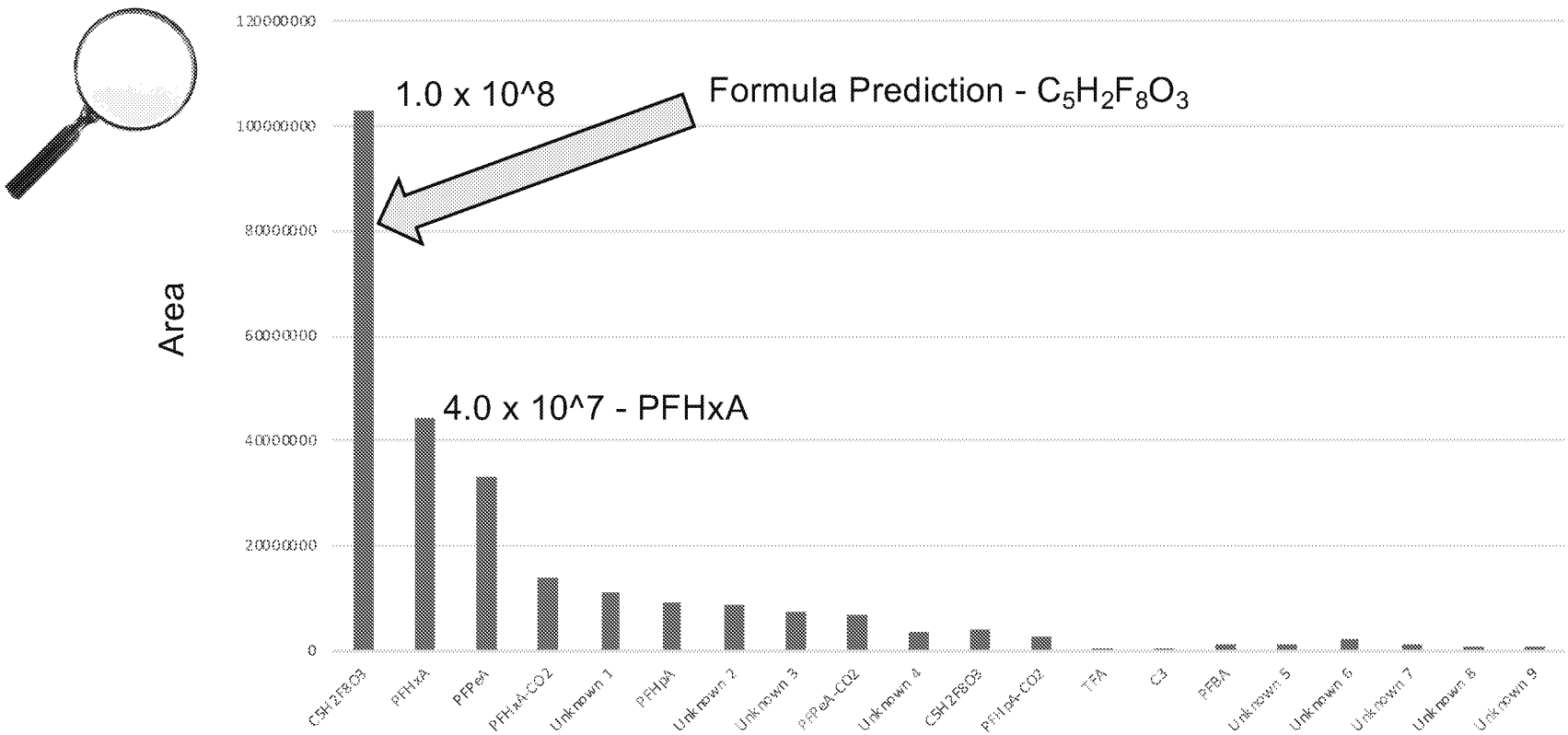


FIGURE 3-1
MODIFIED EPA METHOD 5
PFOA SAMPLING TRAIN



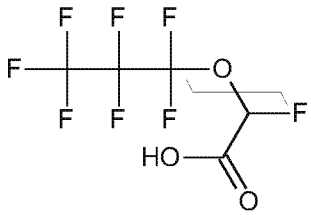
Slide courtesy of Jeff Ryan NRMRL

Control Technology Sump Water Analyte Breakdown

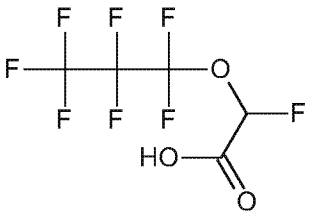


Additional PFAS beyond Legacy

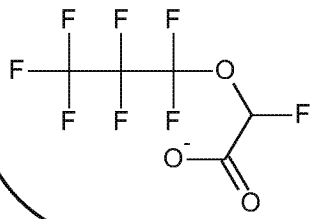
C_3F_7O
184.9837 Da



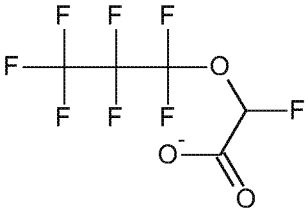
$C_2H_2FO_2$
77.0039 Da



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

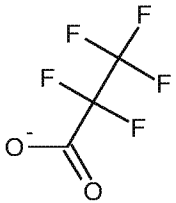


H^+



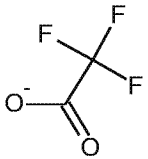
Monoisotopic Mass: 522.967963 Da

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, drip pan 1, sump water, XAD inlet/outlet, filters inlet/outlet

Assessment of industrial dispersions/surfactants

NHDES collected:

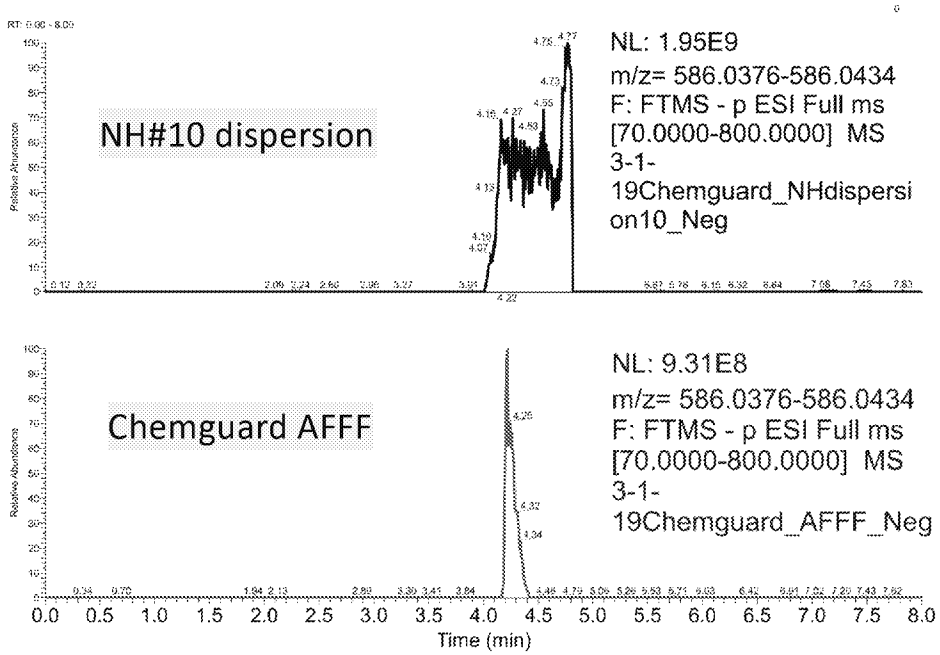
10 industrially used PTFE dispersions
4 industrially used surfactants
near Manchester, NH region

EPA ORD NERL:

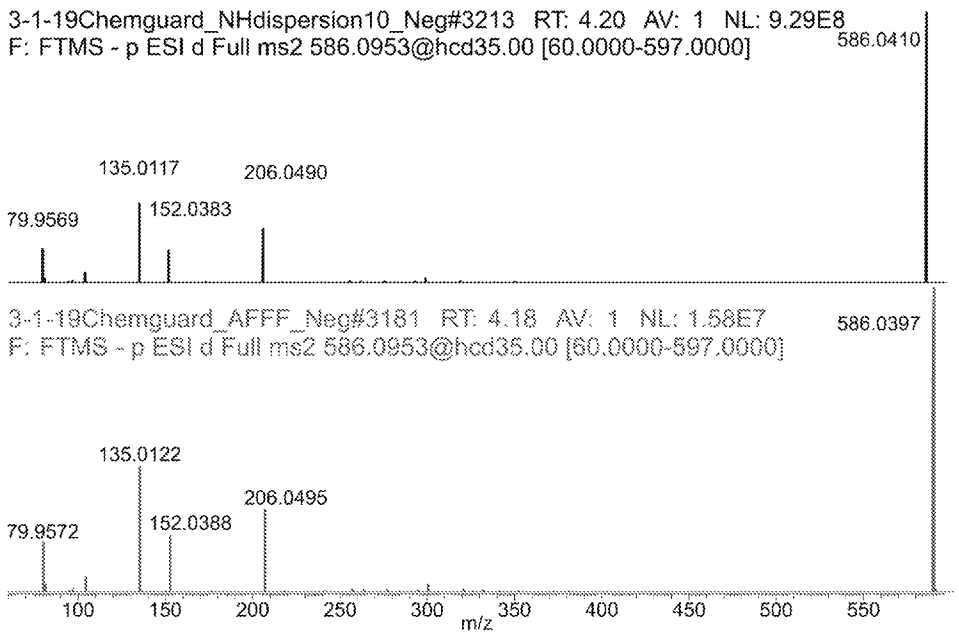
assessed via QTOFMS and Orbitrap MS

6:2 Fluorotelomer thioether amido sulfonate

Chromatograms



MS/MS spectra

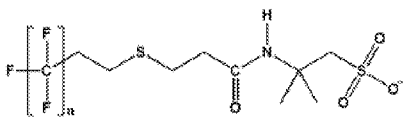


Slide courtesy of James McCord NERL

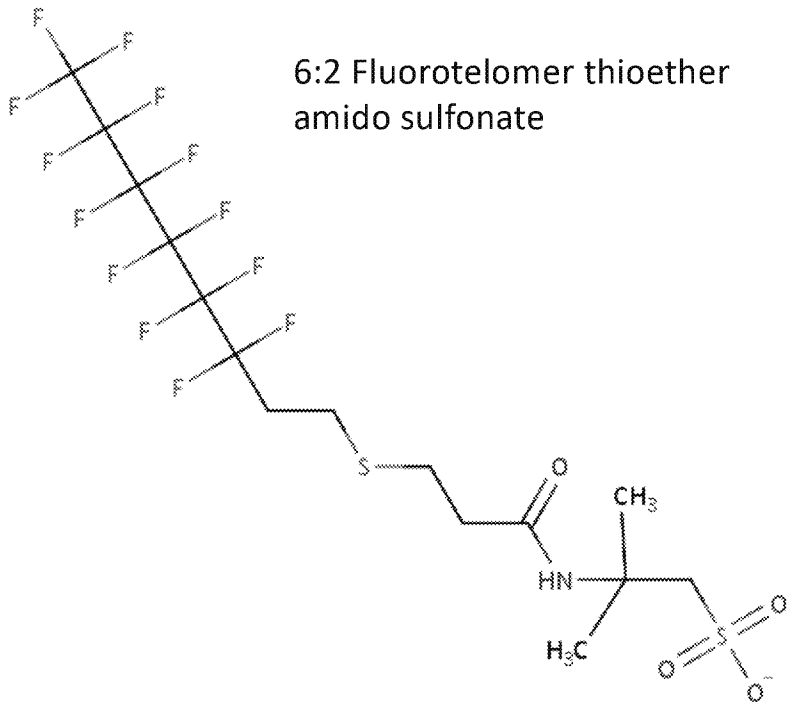
Select PFAS found in dispersions/surfactants collected

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

Fluorotelomermercaptoalkylamido sulfonate (FTSAS)

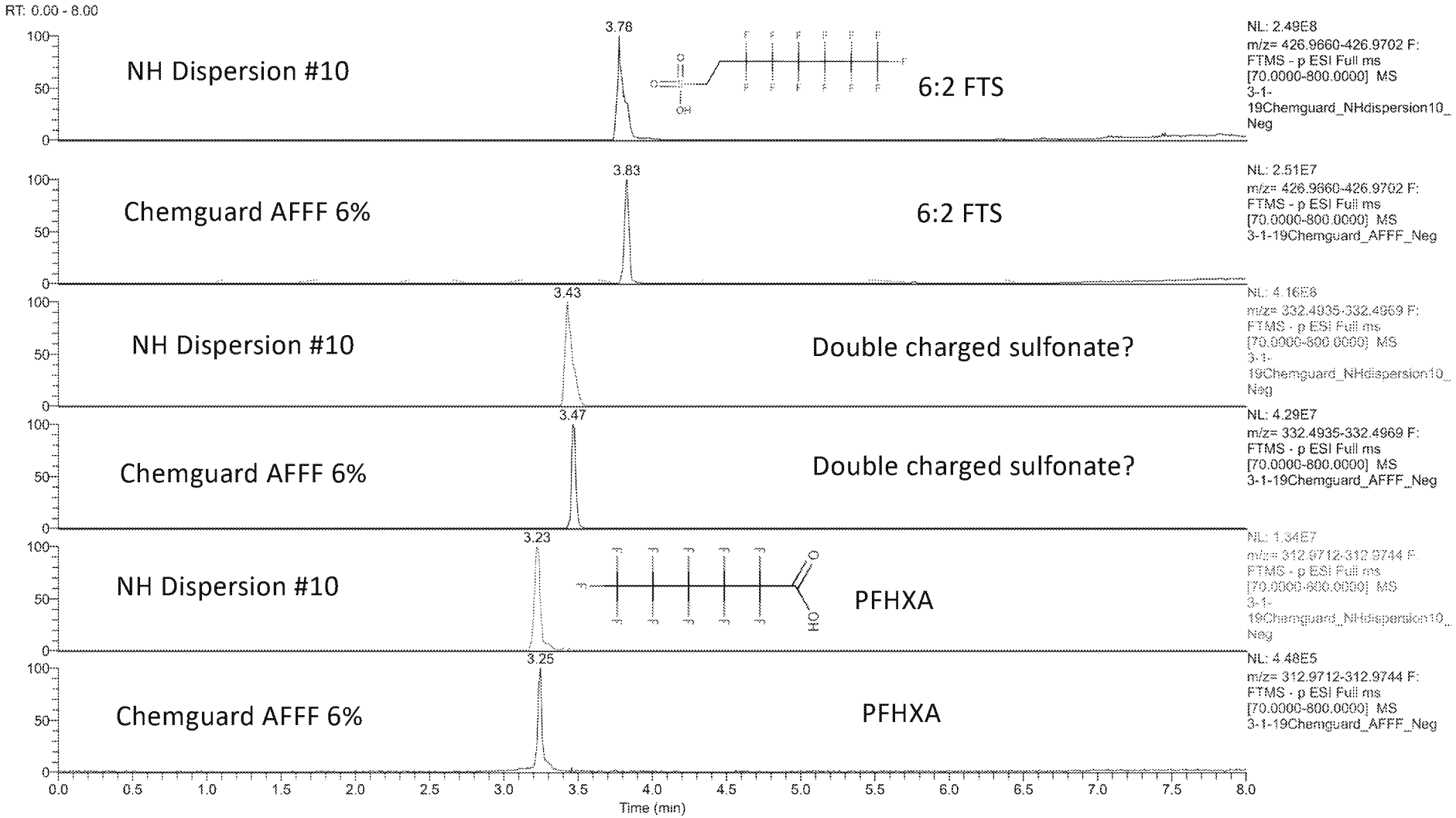


4:2 FTSAS	n = 4	Sc
6:2 FTSAS	n = 6	Sc
8:2 FTSAS	n = 8	Sc
10:2 FTSAS	n = 10	Sc
12:2 FTSAS	n = 12	Sc
14:2 FTSAS	n = 14	Sc



6:2 Fluorotelomer thioether amido sulfonate

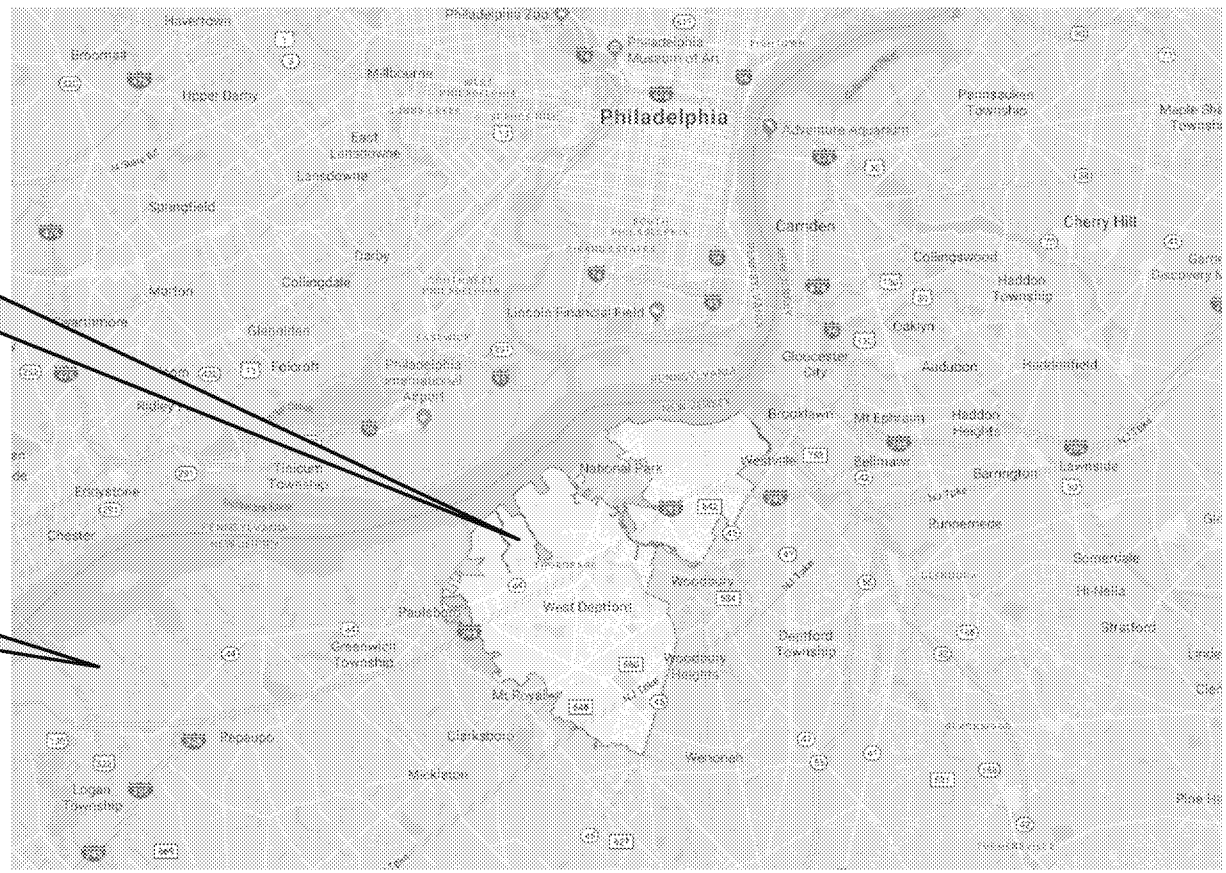
https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID70892333


RT: 0.00 - 8.00
NH Dispersion #10
3.78
6:2 FTS
NL: 2.49E8
m/z= 426.9660-426.9702 F: FTMS - p ESI Full ms [70.0000-800.0000] MS 3-1-19Chemguard_NHdispersion10_Neg
Chemguard AFFF 6%
3.83
6:2 FTS
NL: 2.51E7
m/z= 426.9660-426.9702 F: FTMS - p ESI Full ms [70.0000-800.0000] MS 3-1-19Chemguard_AFFF_Neg
NH Dispersion #10
3.43
Double charged sulfonate?
NL: 4.16E6
m/z= 332.4935-332.4969 F: FTMS - p ESI Full ms [70.0000-800.0000] MS 3-1-19Chemguard_NHdispersion10_Neg
Chemguard AFFF 6%
3.47
Double charged sulfonate?
NL: 4.29E7
m/z= 332.4935-332.4969 F: FTMS - p ESI Full ms [70.0000-800.0000] MS 3-1-19Chemguard_AFFF_Neg
NH Dispersion #10
3.23
PFHXA
NL: 1.34E7
m/z= 312.9712-312.9744 F: FTMS - p ESI Full ms [70.0000-800.0000] MS 3-1-19Chemguard_NHdispersion10_Neg
Chemguard AFFF 6%
3.25
PFHXA
NL: 4.48E5
m/z= 312.9712-312.9744 F: FTMS - p ESI Full ms [70.0000-800.0000] MS 3-1-19Chemguard_AFFF_Neg
Time (min)

Work with NJDEP West Deptford, NJ

Solvay Specialty Polymers

Chemours - Chambers Works



Work with NJDEP West Deptford, NJ

Table 1. New Jersey versus national PFNA detections (≥20 ng/L) in public water supplies in initial UCMR3 results

New Jersey (as of 1/22/15)		*National (other than NJ) (as of January 2015)*	
Number of PWS	*% of PWS*	*Number of PWS*	*% of PWS*
3/122	2.5%	6/3483	0.2%

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

Work with NJDEP West Deptford, NJ

In private well testing results reported to NJDEP (July 18, 2014),

- PFNA (at > 2.5 ng/L) was detected in wells at 26 of 94 (28%) of residences tested in the vicinity of the West Deptford industrial facility.
- Fifteen of the wells had PFNA levels above 20 ng/L
- highest concentration found was 1,500 ng/L

PFNA is the primary component of Surflon S-111 (a polymer processing aid (PPA)) (CAS # 72968-3-88), a commercial mixture of linear perfluorinated carboxylic acids. Prevedouros et al. (2006)

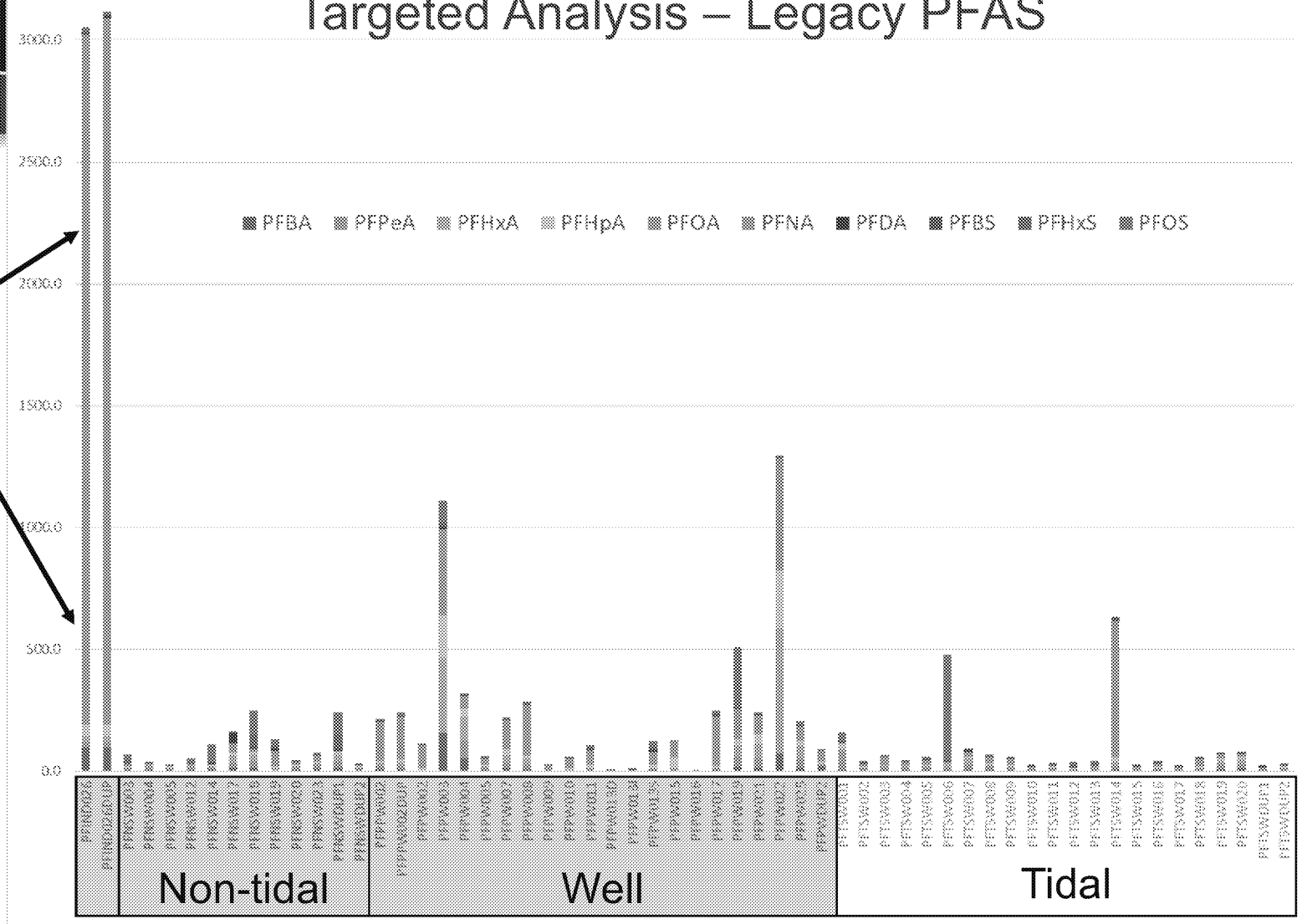
composition of Surflon S-111 by weight as

PFNA perfluornonanoic acid (C9), 74%;
PFUnDA perfluoroundecanoic acid (C11), 20%;
PFTrDA perfluorotridecanoic acid (C13), 5%;

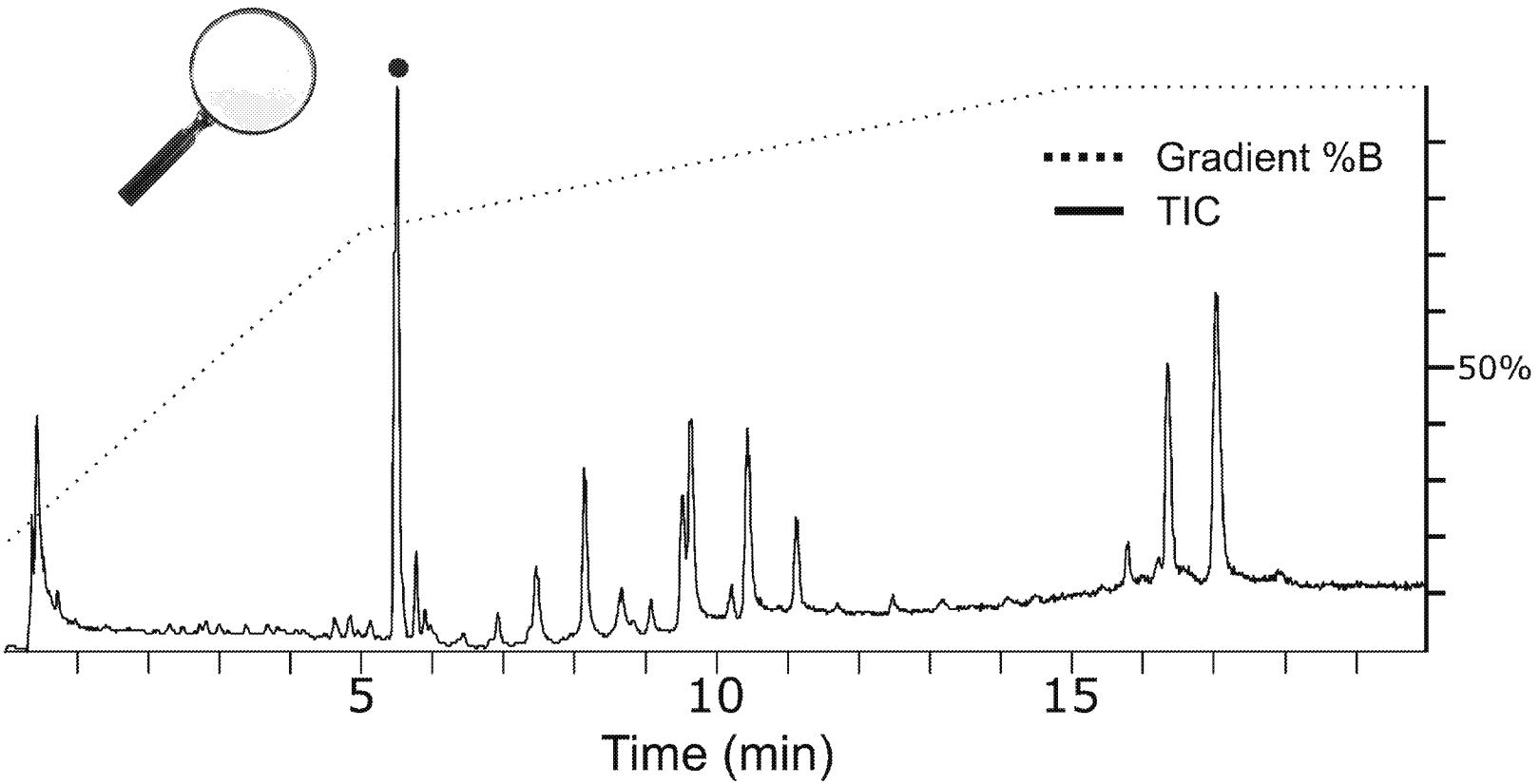
https://www.state.nj.us/dep/watersupply/pdf/pfna-health-effects.pdf

Targeted Analysis – Legacy PFAS

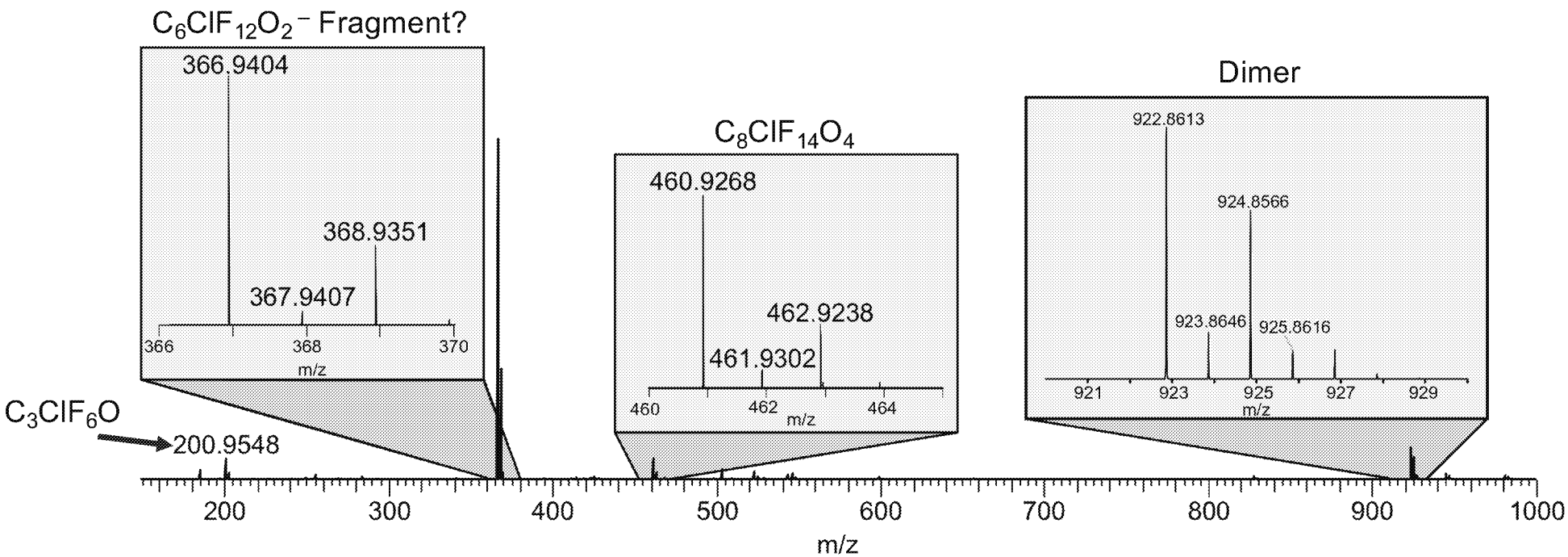
PFIND26; DUP
PFNA ~2,250 ng/L
PFOA ~ 600 ng/L



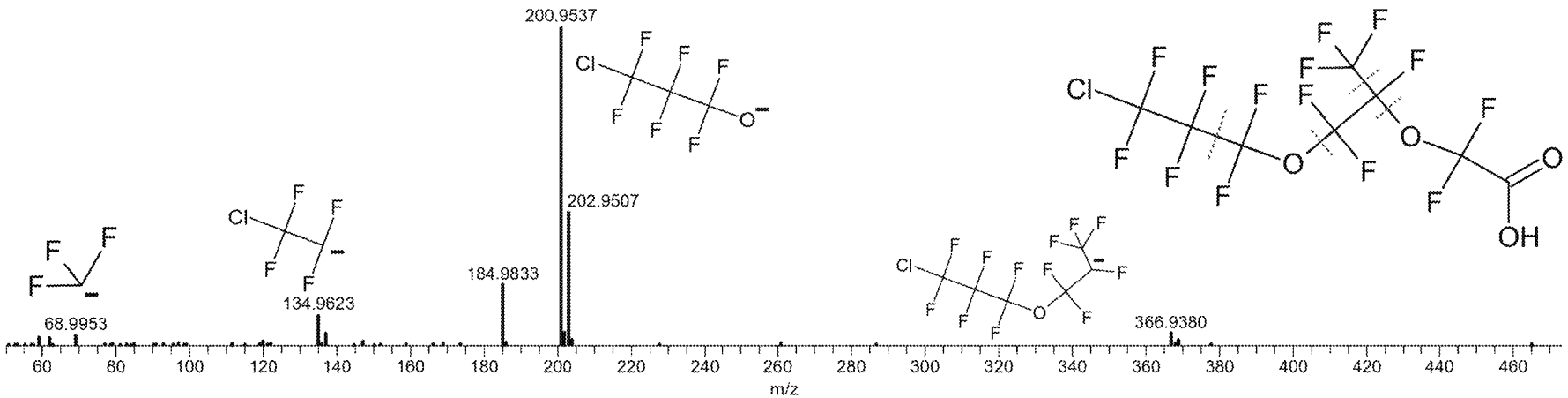
Representative Chromatography NTA



Major Peak Constituents Predicted Formula

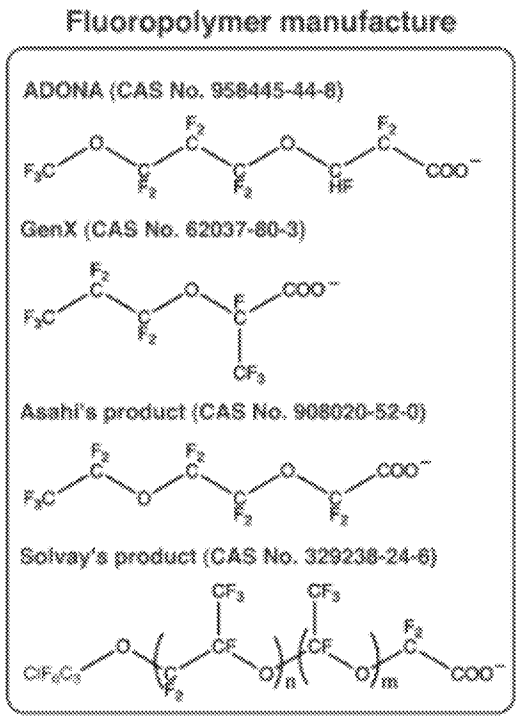


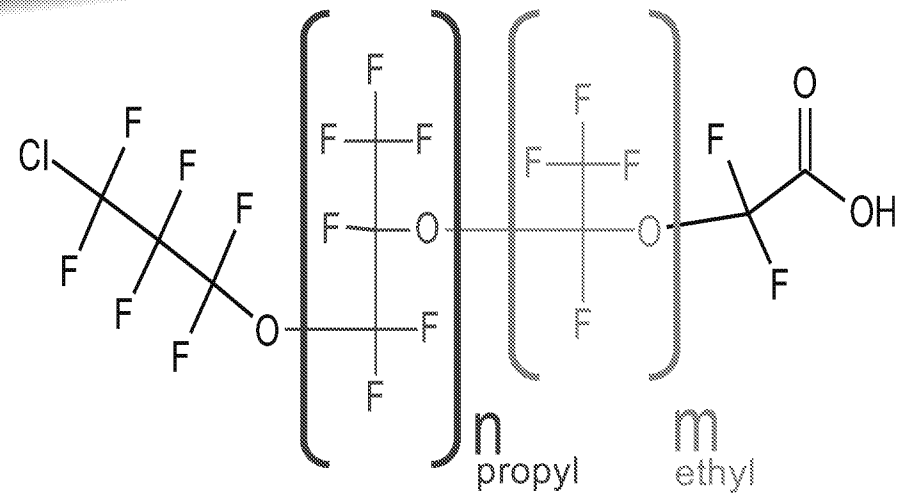
Structural Elucidation by MS/MS



- 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 show)

Literature Support

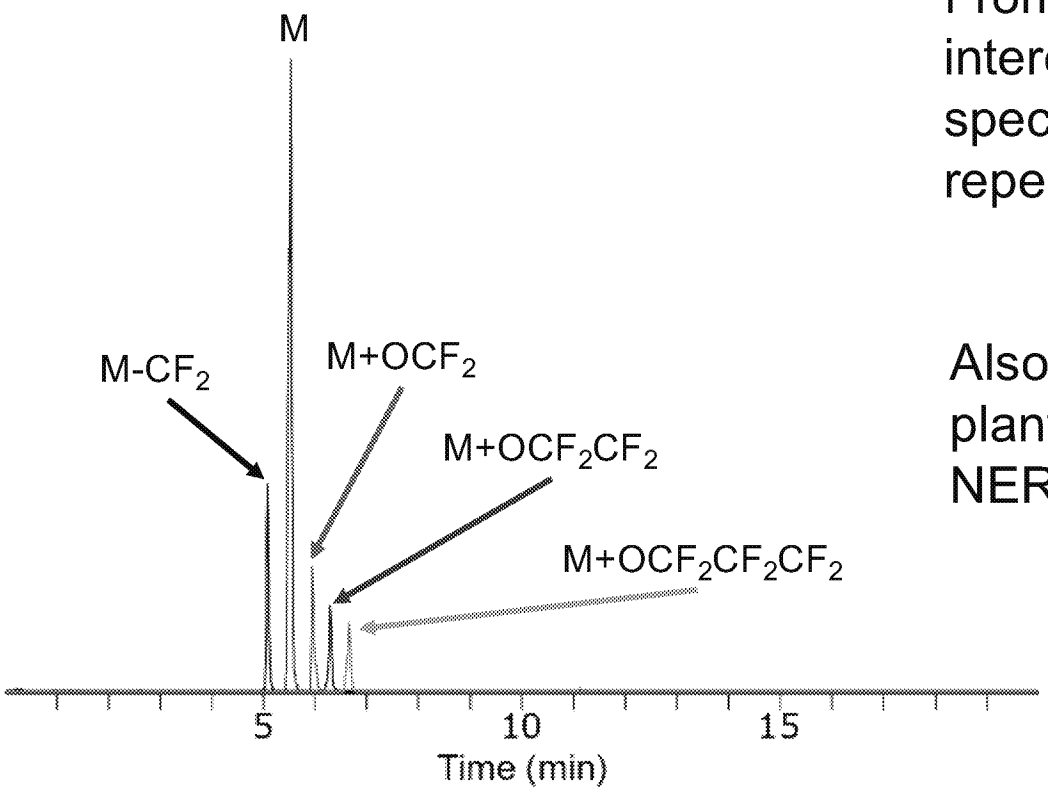




Chloro perfluoro polyether carboxylic acids ClPFPECAs(n,m)

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

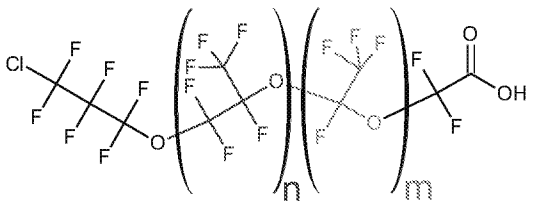


From single identified mass of interest we identified additional species related by CF_2 repeating units

Also found in soil, sediment and plant material (John Washington – NERL Athens)

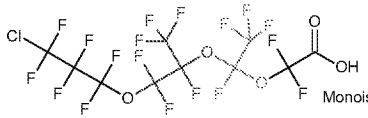
Structural Homologs

Solvay
CAS 329238-24-6



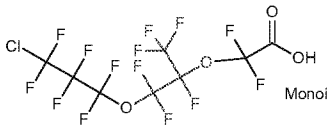
propyl, ethyl

Solvay 1,1



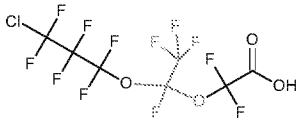
Monoisotopic Mass: 577.922508 Da

Solvay 1,0



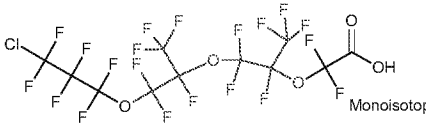
Monoisotopic Mass: 461.933981 Da

Solvay 0,1



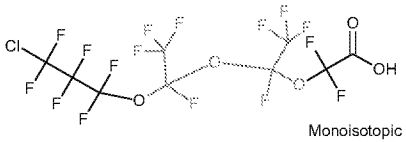
Monoisotopic Mass: 411.937175 Da

Solvay 2,0



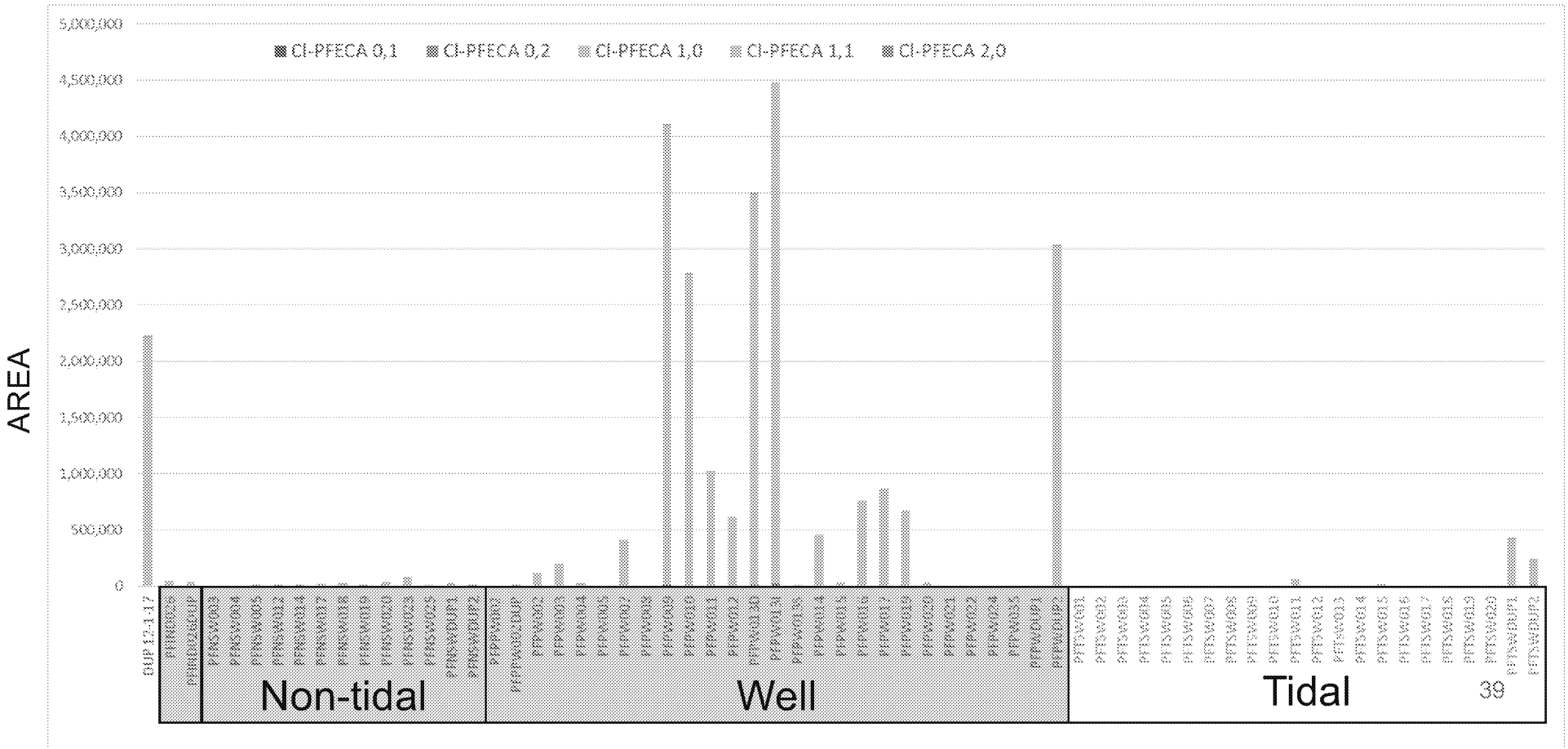
Monoisotopic Mass: 627.919315 Da

Solvay 0,2



Monoisotopic Mass: 527.925702 Da

Nontargeted Analysis – Cl-PFECAs



Additional Ongoing efforts:

- R3 State of West Virginia DAQ – stack emissions for Chemours Washington Works plant

- R5 state of Michigan Department of Environment, Great Lakes and Energy - Identification of PFAS in Fume Suppressants in Chromium Electroplating Facilities

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Questions?

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