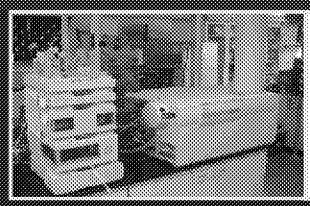
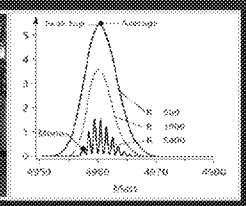
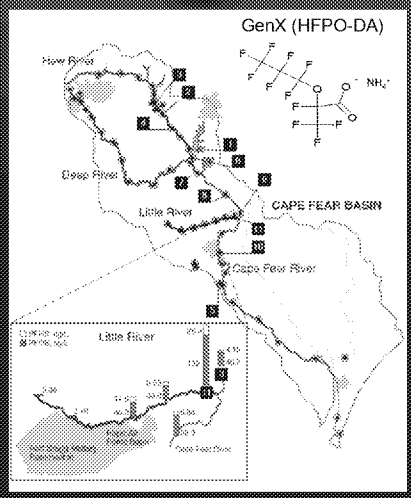
Investigations of per- and polyfluorinated compounds in environmental samples and contemporary products

Mark Strynar USEPA/ORD/NERL/EMMD

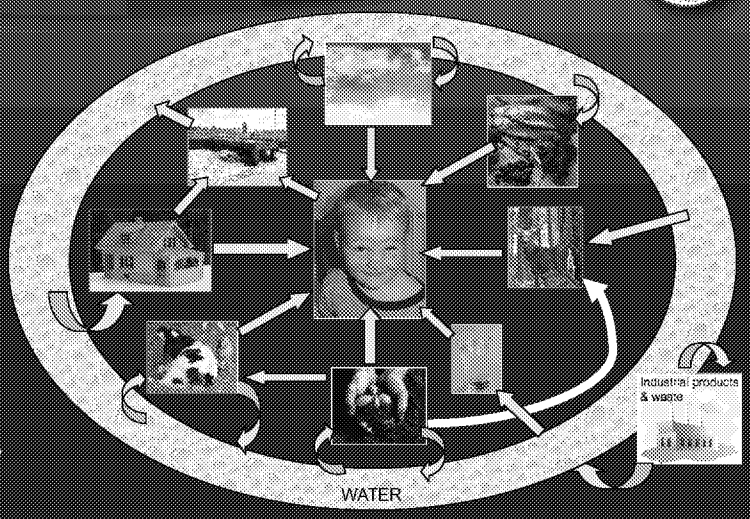




September 5, 2018
NCEH/ATSDR Seminar



Human Exposure Pathways



Many chemicals
Many media
Many sources
Unknown toxicity

U.S. Environmental Protection Agency

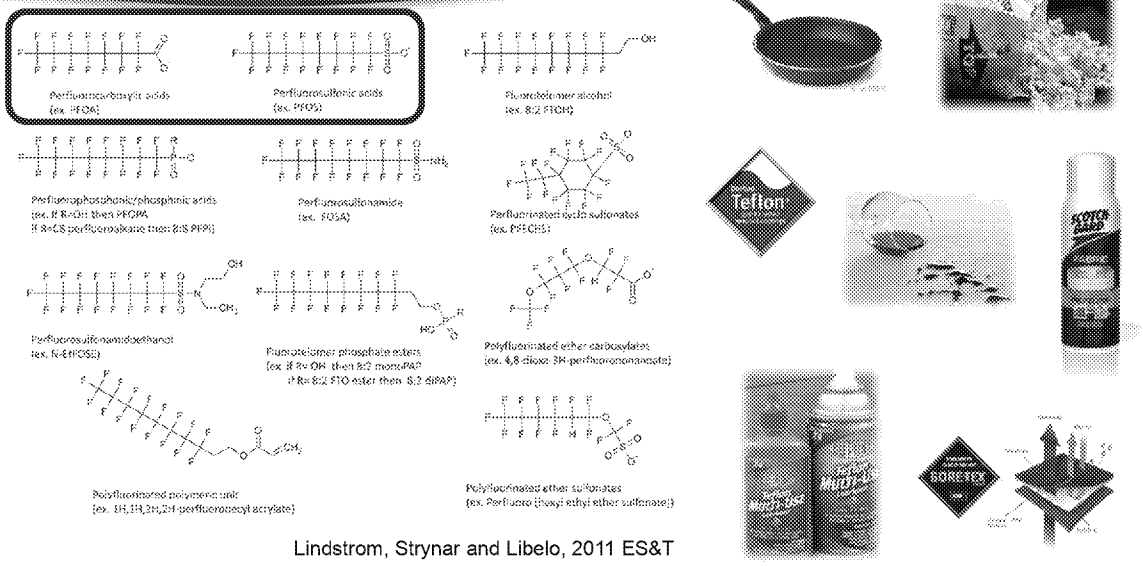
Screening Intention?

Usual Suspects for Elevated Scrutiny

- Large peaks
- Found in many samples)
- Contain halogens (Cl, Br)
- Negative Mass defect
- Related chemicals
- ???

Some Typical PFAS and Products

^ Formerly known as PFCs



Lindstrom, Strynar and Libelo, 2011 ES&T

Fact Sheet: 2010/2015 PFOA Stewardship Program

What is the 2010/2015 PFOA Stewardship Program?
In 2006, EPA invited eight major (PFASs) producers with two goals:

•To commit to achieve, **no later than 2010, a 95 percent reduction**, perfluorooctanoic acid **(PFOA)**, **precursor chemicals** that can break down to PFOA, and related higher homologue chemicals, and product content levels of these chemicals.

•To commit to working toward **the elimination** of these chemicals from **emissions and products by 2015**.

What companies participated in the PFOA Stewardship Program?
Participating companies included:

- Arkema
- Asahi
- BASF Corp. (formerly Ciba)
- Clariant
- Daikin
- 3M/Dyneon
- DuPont/Chemours
- Solvay Solexis

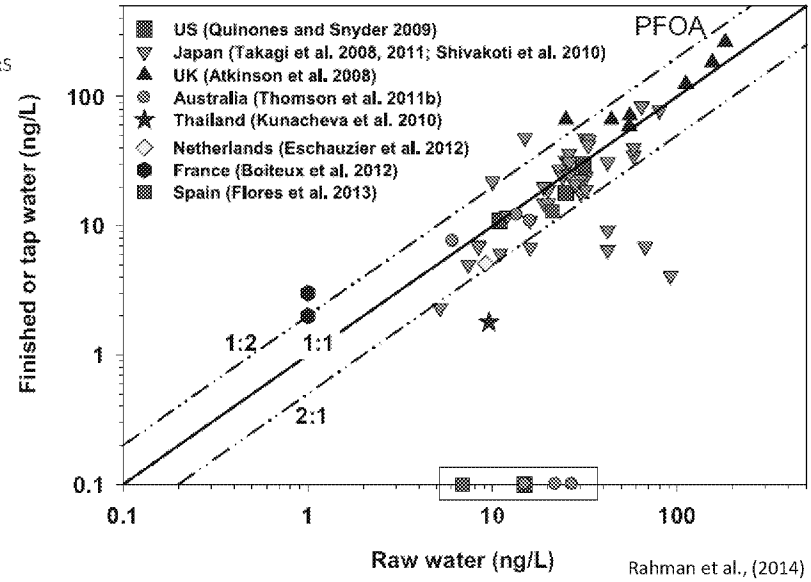
https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program#what

PFAS Generally Not Removed During Conventional Drinking Water Treatment

Similar for PFOS, PFHxA and PFHxS

NC State (Detlef Knappe) Active ongoing research on this:

- Reverse Osmosis
- Under-sink Carbon
- Whole-home Carbon

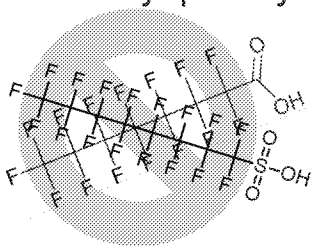


Rahman et al., (2014) *Water Research*, 50:318-340

Work approached for detection not quantification

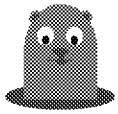
OTHER PFASs: The Era of HRMS & Non-Targeted Analysis

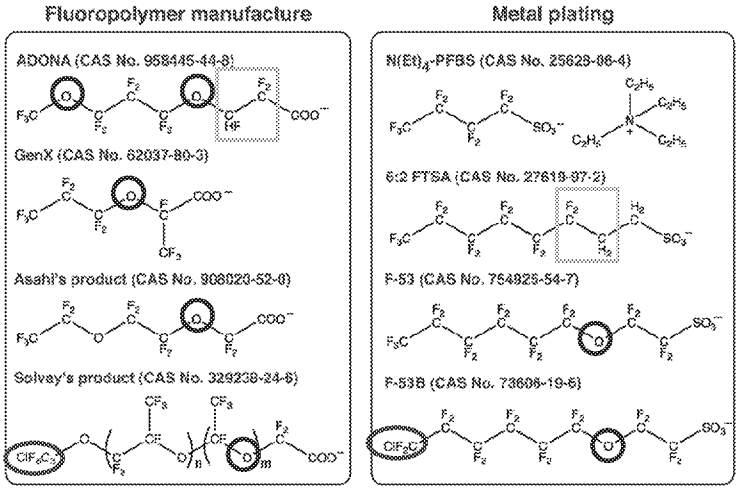
- How do we find compounds without knowing what they are?
- How do we prioritize unknowns for further analysis?
- How do we identify/quantify without analytical standards?

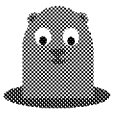


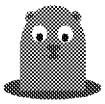
→ ???

Post PFOA Stewardship Agreement



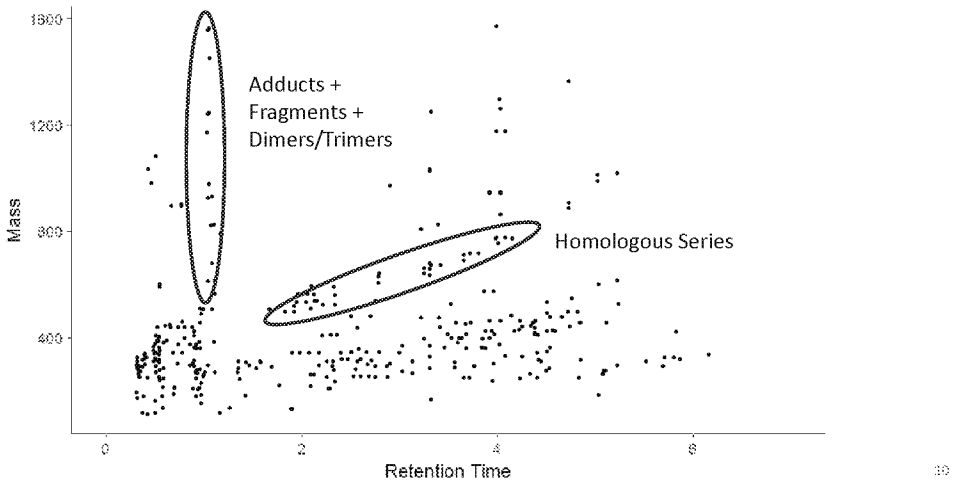




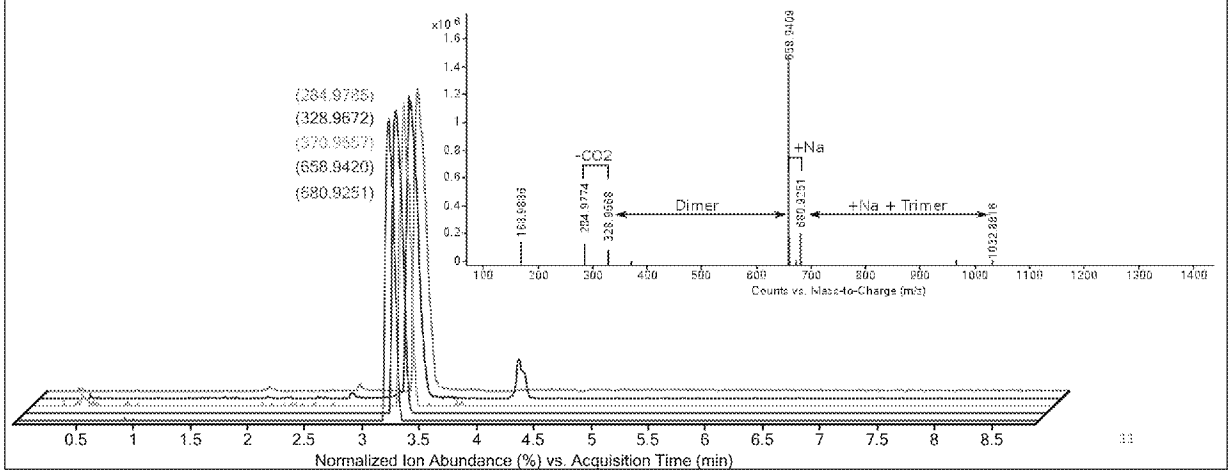


Wang et al. *Environment International*, **2013**, *60*, pp 242–248

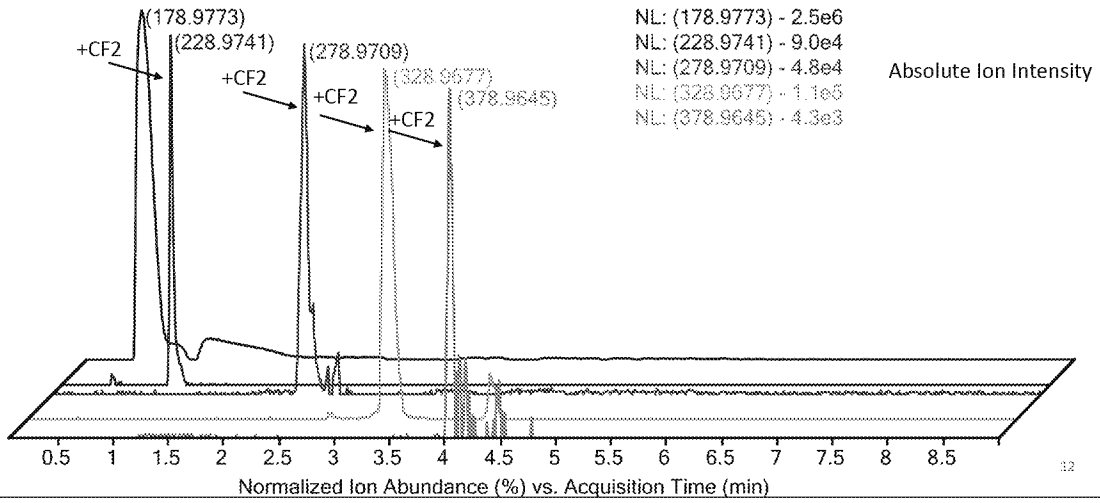
Relationships Reveal Underlying Chemistry



In-Source Related Species



Homologous Series



Feature Finding: Unique & Highly Different Features

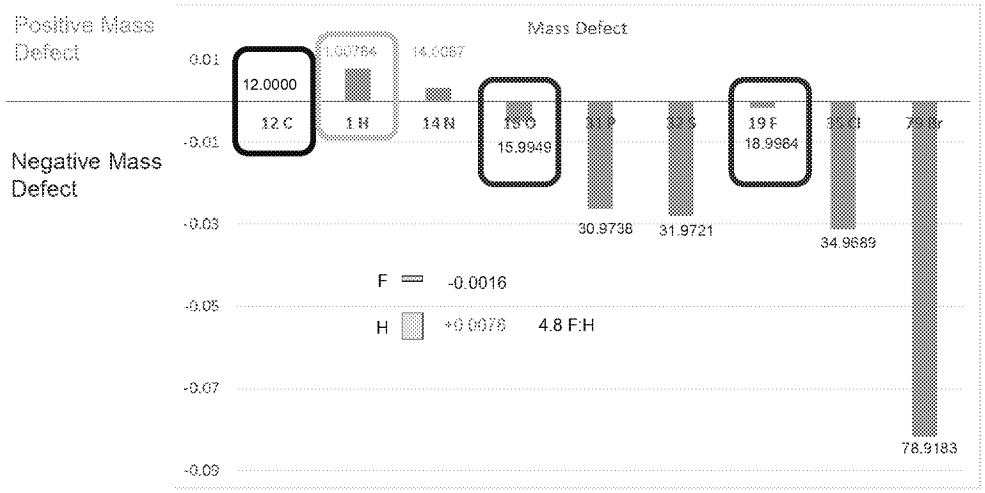
Cmpd	*m/z*	RT	Effluent Peak Area	Upstream Peak Area
1	194.9263	0.31	1277673	NA
2	174.9502	0.32	128095	NA
3	272.9487	0.35	893478	NA
4	290.9396	0.37	82068	NA
5	119.0345	0.37	56430	NA
6	179.0558	0.38	51910	NA
7	340.9372	0.4	1961449	NA
8	324.9428	0.41	75414	NA
9	248.961	0.42	235520	NA
10	112.9856	0.42	9963533	NA
11	1033.987	0.43	185007	NA
12	340.9376	0.49	847790	NA
13	118.9927	0.5	242003	NA
14	162.9821	0.5	1382091	NA
15	1083.984	0.51	14125	NA

Hundreds of Features of Interest

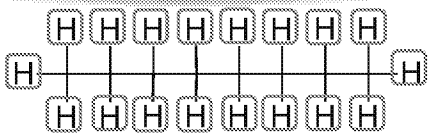
Useful For:

- Identification of increasing/decreasing chemicals
- Features unique to a specific location, time, treatment, etc.

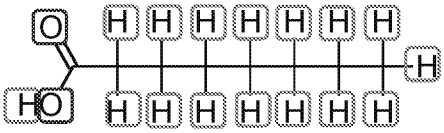
Isotope Signatures: Negative Mass Defect



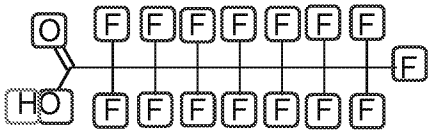
Example of Mass Defect



Octane
MI mass 114.1409



Octanoic Acid
MI mass 144.1150



Perfluorooctanoic Acid
MI mass 413.9737

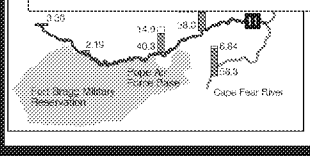
Past Work: PFAS in NC Water

Nakayama et al. 2007 *ES&T* 41:5271-5276

TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin[a] (See Figure 1 for locations)

no.	river	C12 (ng/L)	C11 (ng/L)	C10 (ng/L)	C9 (ng/L)	C8 (ng/L)	C7 (ng/L)	C6 (ng/L)	PFOS (ng/L)	PFHS (ng/L)	PFBS (ng/L)	total (ng/L)
1	Haw River	***4.46***	***52.1***	***120***	***194***	***287***	118	21.7	127	8.43	***9.41***	942
2	Haw River	3.20	28.7	112	157	200	66.8	14.5	33.4	7.87	2.61	626
3	Haw River	3.29	27.6	109	157	191	59.2	13.7	36.4	9.49	3.04	609
4	Haw River	1.98	20.0	88.2	151	201	58.2	13.2	31.5	7.49	2.88	574
5	tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	***329***	***23.0***	30.0	3.36	ND	531
6	Haw River	1.18	8.87	31.0	72.1	152	58.3	13.5	31.2	7.70	ND	376
7	Cape Fear River	< LOQ	3.34	13.2	34.8	70.3	24.0	7.84	66.7	5.59	ND	227
8	Cape Fear River	1.14	6.39	17.2	35.7	71.5	26.9	9.35	50.4	4.82	ND	223
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.10	ND	211
10	Cape Fear River	< LOQ	7.55	19.3	31.2	46.8	13.9	4.62	56.3	6.84	2.12	189
11	Little River	< LOQ	< LOQ	2.17	2.24	12.6	3.38	3.23	***132***	***26.4***	3.20	185

[a] Italicized values show maximal concentrations of each compound.



performance fabrics, bio-solids, AFFF, industrial waste

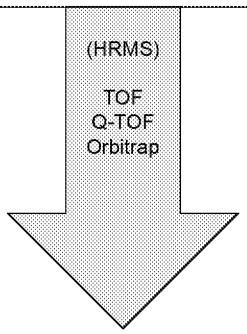
onmental Protection Agency

Framed talk in terms of defining the problem
Why this is important at NERL

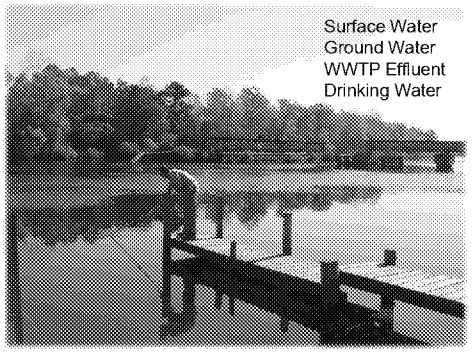
What is Non-Targeted Analysis?

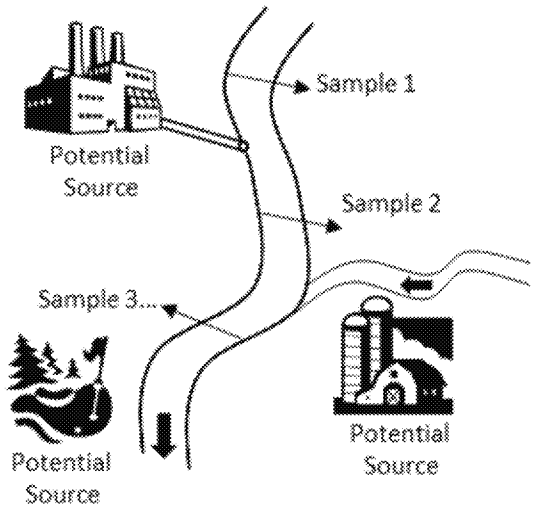
- Targeted Analysis
  - How much PFOA is in my sample?

- Suspect Screening
  - Which chemicals in this database are in my sample?
- Non-Targeted Screening
  - What are the chemicals in my sample?

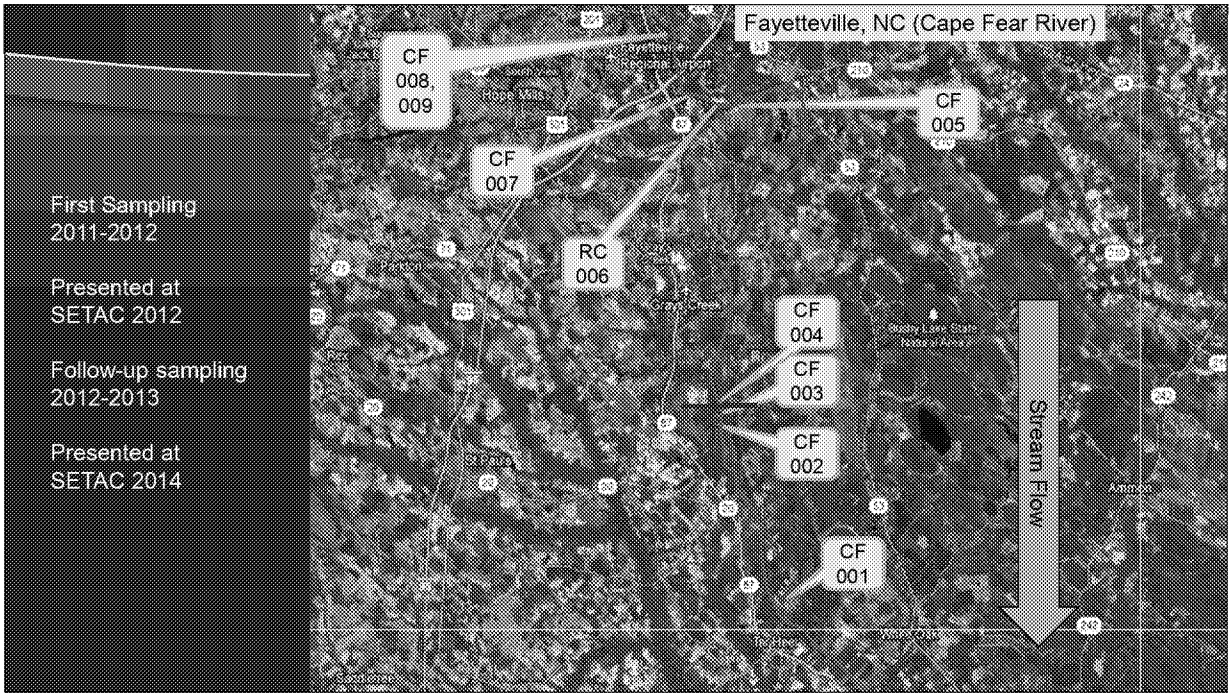


Data Generation: Source Determination by NTA





Sampling from geographically or temporally displaced locations allows triangulation of sourcing


Fayetteville, NC (Cape Fear River)
First Sampling
2011-2012
Presented at
SETAC 2012
Follow-up sampling
2012-2013
Presented at
SETAC 2014
CF
008,
009
CF
007
RC
006
CF
005
CF
004
CF
003
CF
002
CF
001
Stream Flow

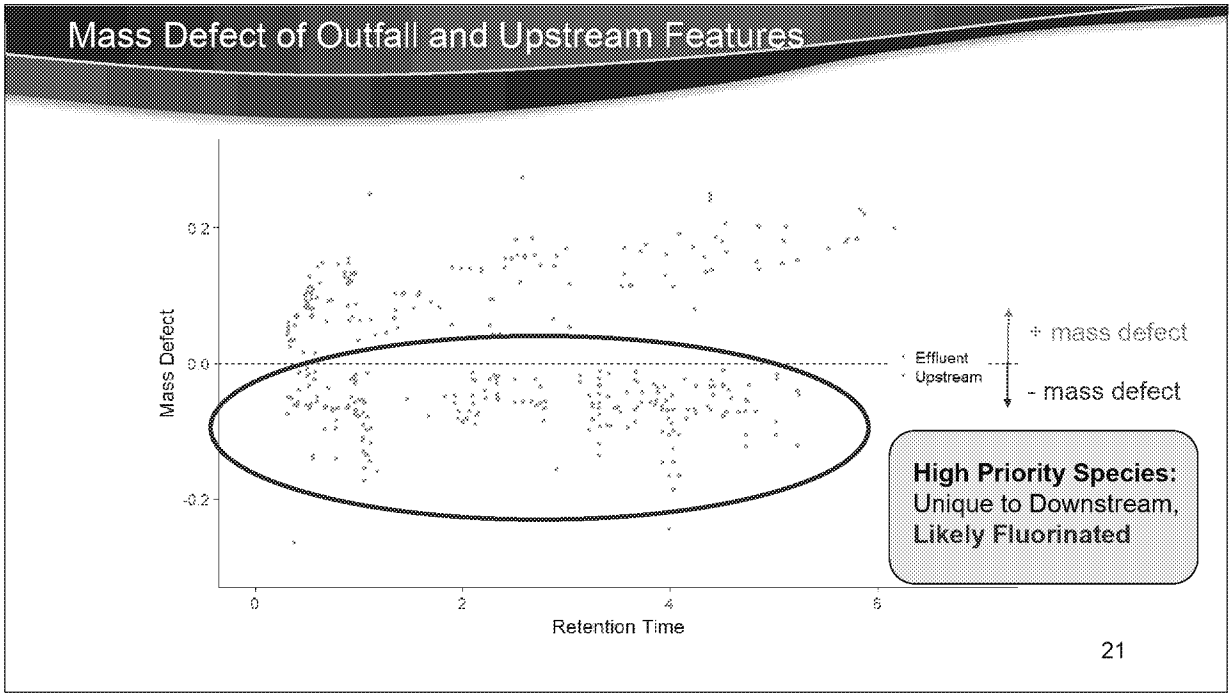
Legacy PFAS found in Cape Fear Water circa 2012

Stream Flow

Analyte	001	002	003	004	005	006	007	008	008	009
C4	23	502	3761	6	4	0	8	7	5	3
C5	441	5607	43590*	17	9	1	32	46	12	9
PFBS	4	5	3	4	5	2	9	5	6	4
C6	17	90	434	18	12	2	27	16	18	14
C7	37	599	3873	14	17	0	11	20	21	9
PFHS	7	12	10	9	7	4	9	10	9	22
C8	32	39	71	33	25	2	38	36	41	18
C9	13	34	127	7	11	1	6	8	11	5
PFOS	19	27	26	17	23	0	0	16	18	14
C10	10	17	12	11	0	3	3	8	10	5

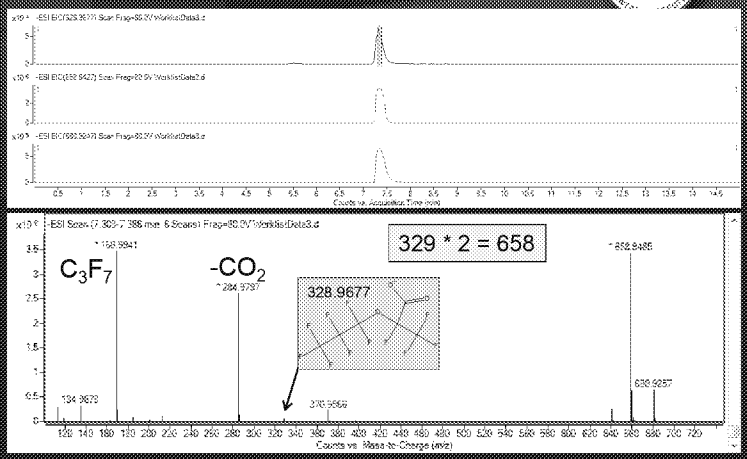
Increase in PFAS below site 003

Legacy PFAS in Cape Fear River



MAKE ONE OF THESE FOR OUR DATA

m/z Extracted Ion Chromatograph (EIC)

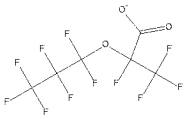


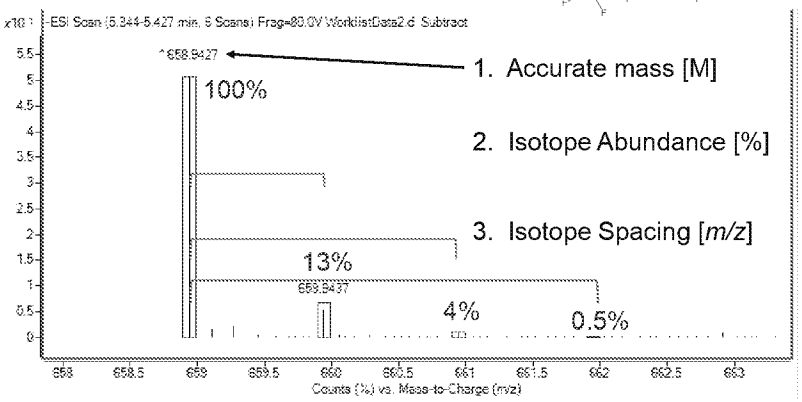
Standard or extracted water, same spectra. *m/z* 328 LOW

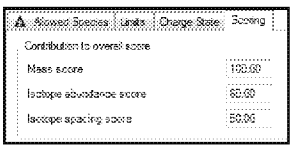
United States Environmental Protection Agency

Isotope Cluster Scoring

Ex. $C_{12}H F_{22} O_6$





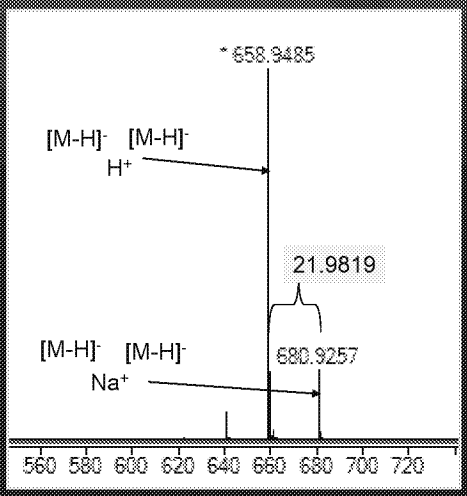


Office of Research and Development
National Exposure Research Lab/ Human Exposure and Atmospheric Science Division

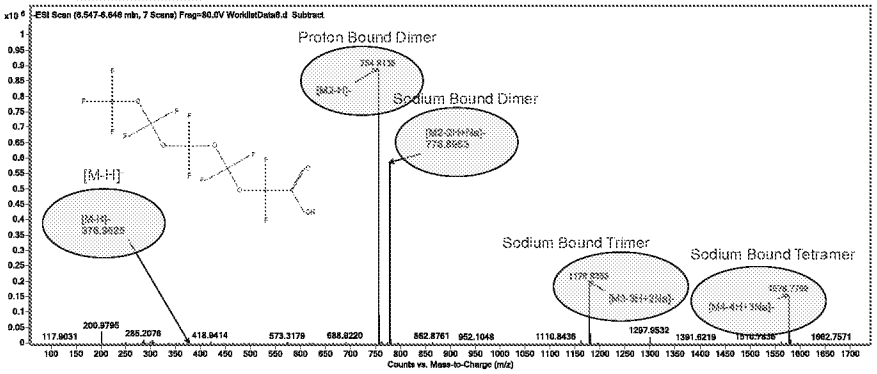
Key TOFMS Information

Difference Between Peaks

Na^+ (22.9892)
$-H^+$ (1.0073)
= **21.9819**



Additional *n*-mers*



* Trier, X.; Granby, K.; Christensen, J. H., Tools to discover anionic and nonionic polyfluorinated alkyl surfactants by liquid chromatography electrospray ionisation mass spectrometry. *J. Chromatogr. A* **2011,** *1218*, (40), 7094-104.

Kendrick Mass Defect Transformations

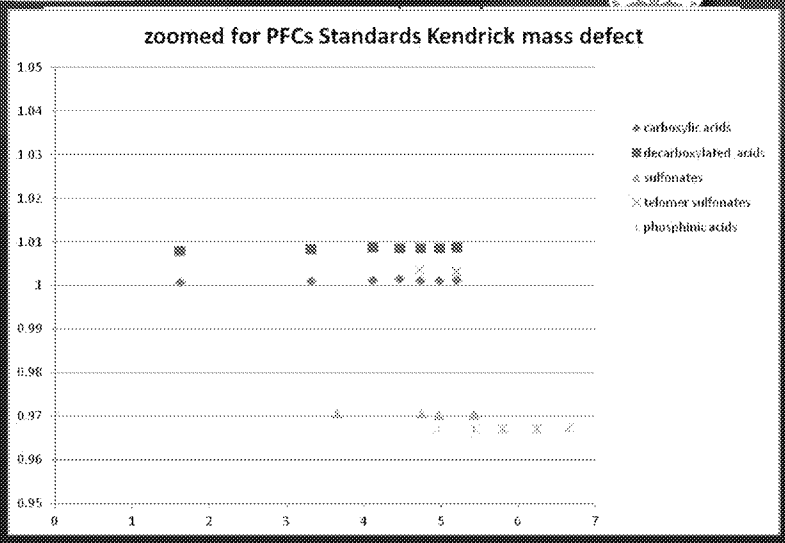
$$\text{Kendrick Mass (F)} = (\text{observed mass}) \times \frac{\text{Nominal mass F}}{\text{Exact mass F}}$$

$$\text{If (F)} = CF_2 \qquad \frac{\text{Nominal mass F}}{\text{Exact mass F}} = \frac{50}{49.99681}$$

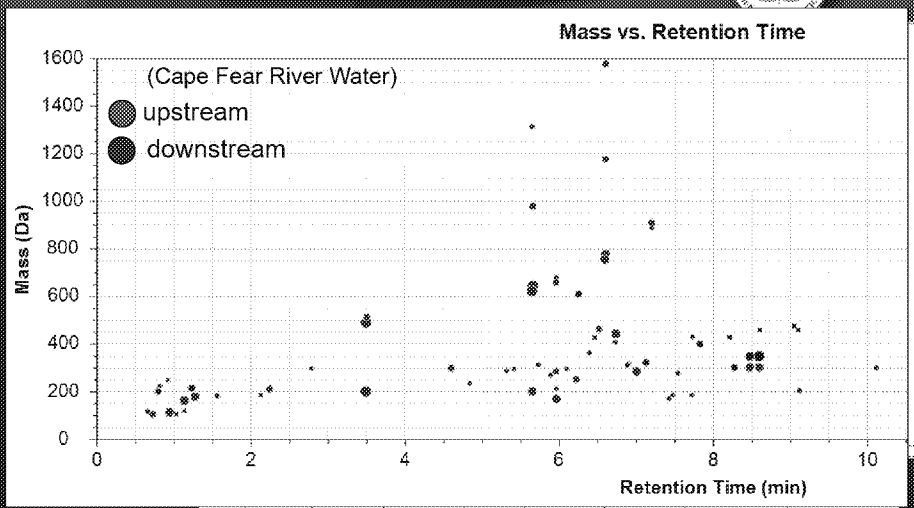
http://en.wikipedia.org/wiki/Kendrick_mass

Kendrick, Edward (1963) Anal. Chem. 35 (13) 2146-2154

Kendrick Mass Defect Standards Example



Kendrick Mass Defect Water Example



1.268	179.9849	4011200	178.97706	179	179.9963838	180.0075373	0.996383769	1.007537312

Environmental Science & Technology

November 2015

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)

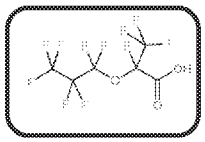
Mark Strynar,[*,†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Liang,[†,∥] Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[⊥] Imma Ferrer,[⊥] and Carol Ball[‡]

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

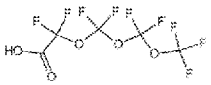
number	formula	CAS no.	name	$[M - H]^-$ m/z	$[M - H]^-$ m/z	$[2M - 2H + Na]^-$ m/z	$[2M - H]^-$ m/z
Monoether PFECAs							
1	$C_4HF_7O_3$			179.9846	175.9773	389.9438	359.9619
2	$C_6HF_9O_3$			229.9813	225.9740	489.9372	459.9553
3	$C_7HF_{11}O_3$	865090-89-5		279.9779	275.9706	589.9310	559.9491
4	$C_8HF_{13}O_3$	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	325.9677	689.9247	659.9427
5	$C_8HF_{13}O_4$	39693-90-5	perfluoro-3,6,7,9-butanoxidecanoic acid	377.9988	373.9925	776.8962	754.9123
9	$C_9HF_{15}O_5$	39492-89-2	perfluoro-3,6,7-propoxooctanoic acid	411.9881	410.9808	644.9168	622.9289
10	$C_{12}HF_{23}O_4$	39492-88-1	perfluoro-3,6-dioxadecanoic acid	545.9764	544.9691	512.9274	490.9455
PFESAs							
11	$C_6HF_{13}O_4S$	66796-30-3[b]		445.9337	442.9264		
12	$C_8HF_{17}O_4S$			465.9399	462.9326		

Undecafluoro-2-methyl-3-oxahexanoic acid

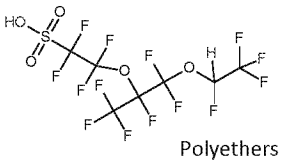
Example Structures



Monoether (6): GenX

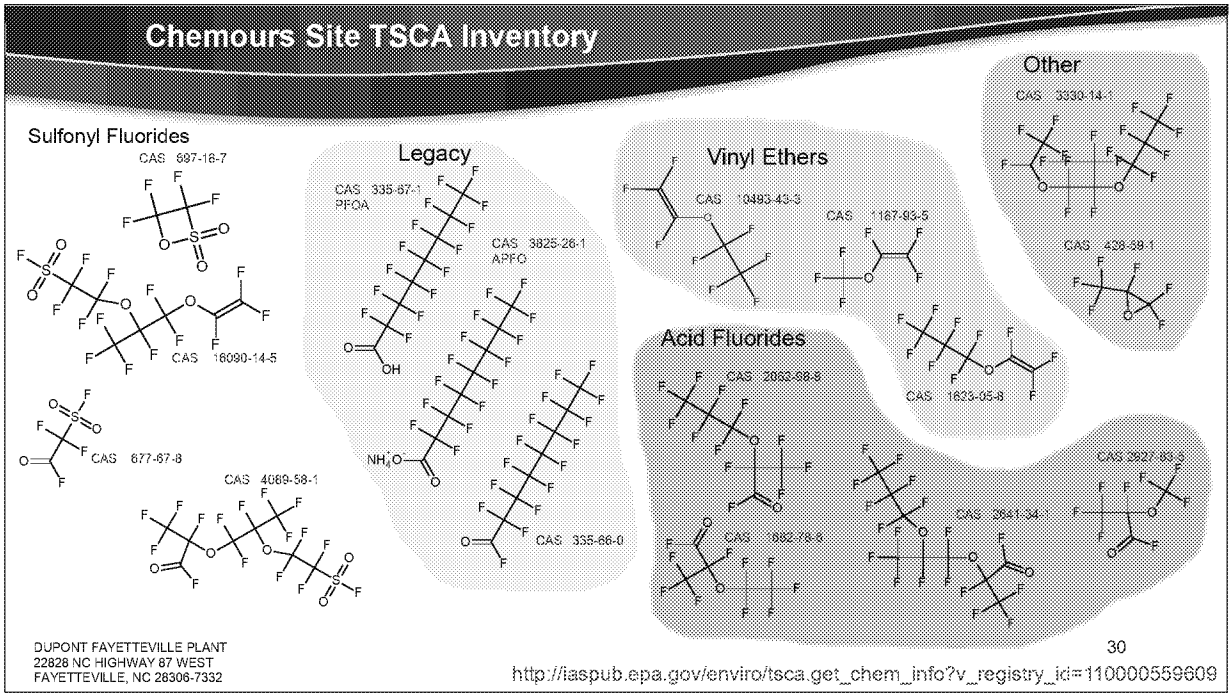


Polyethers (4):



Polyethers sulfonates (2):

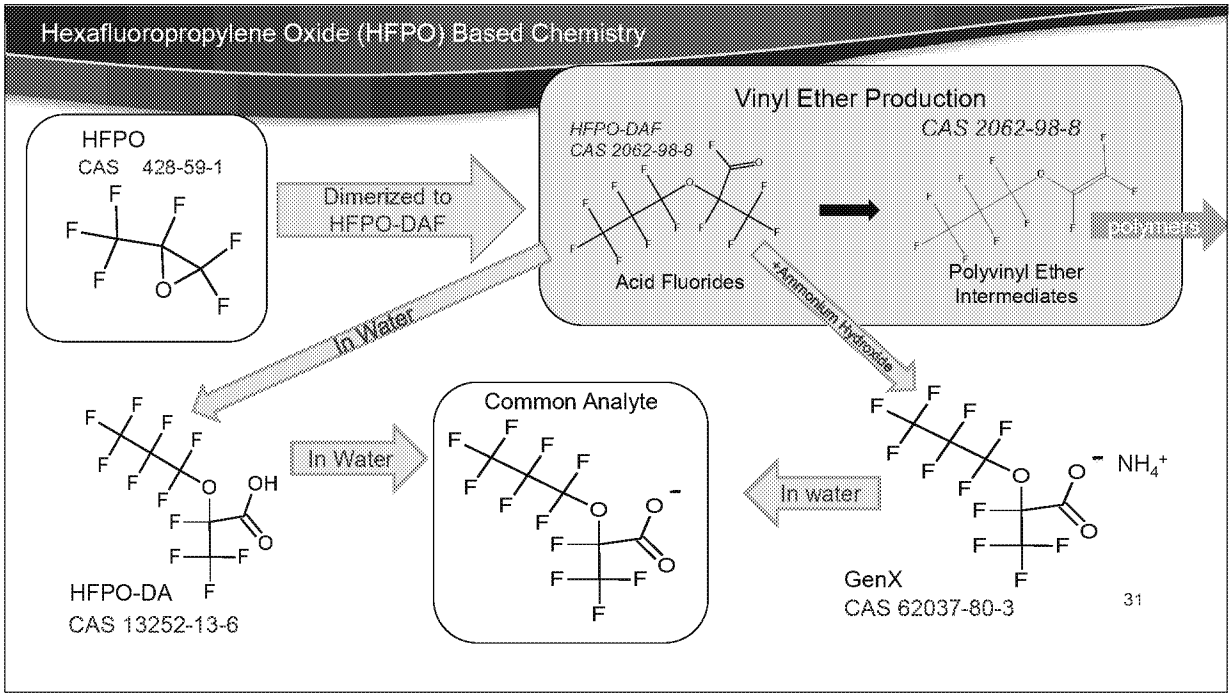
Chemours Site TSCA Inventory



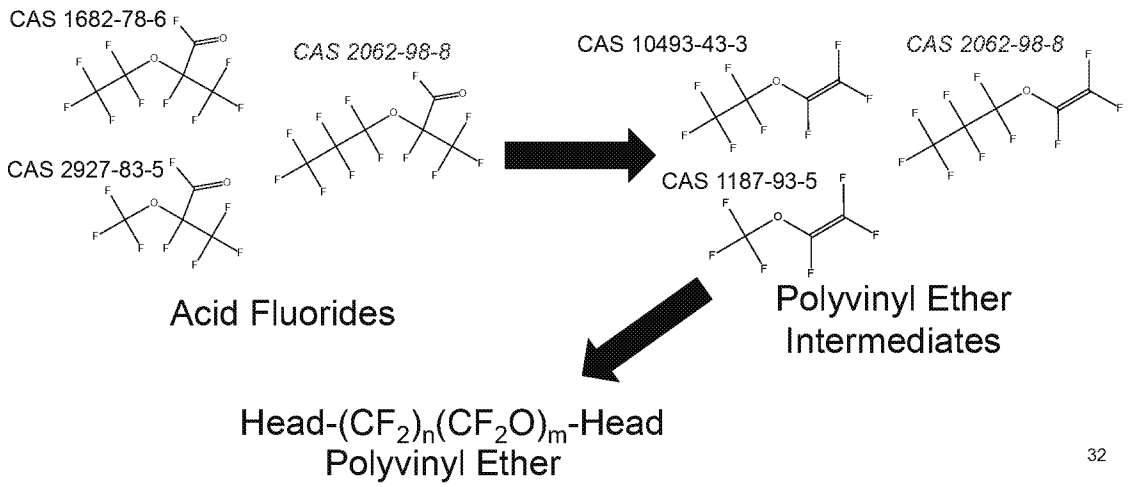
DUPONT FAYETTEVILLE PLANT
22828 NC HIGHWAY 87 WEST
FAYETTEVILLE, NC 28306-7332

30

http://iaspub.epa.gov/enviro/tsca.get_chem_info?v_registry_id=110000559609

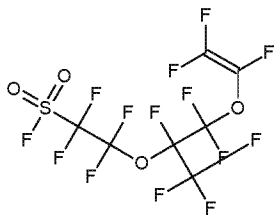

Hexafluoropropylene Oxide (HFPO) Based Chemistry
HFPO
CAS 428-59-1
Dimerized to HFPO-DAF
Vinyl Ether Production
HFPO-DAF
CAS 2062-98-8
CAS 2062-98-8
Acid Fluorides
Polyvinyl Ether Intermediates
polymerize
+Ammonium Hydroxide
In Water
In Water
Common Analyte
In water
HFPO-DA
CAS 13252-13-6
GenX
CAS 62037-80-3
31

Polyvinyl Ether Production



Nafion Polymer

- Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer
- Proton conductor for proton exchange membrane (PEM) fuel cells



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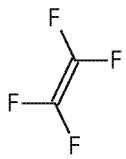
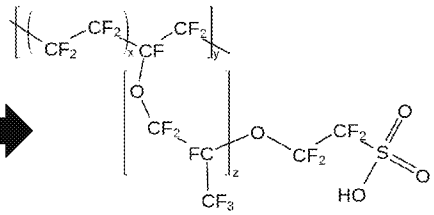


CAS 116-14-3



CAS 66796-30-3

Environmental Science & Technology Letters

November 2016

pubs.acs.org/journal/estlet

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[∇]

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StarNews

Toxin taints CFPUA drinking water

June 7th, 2017

Cape Fear River Fayetteville to Wilmington, NC

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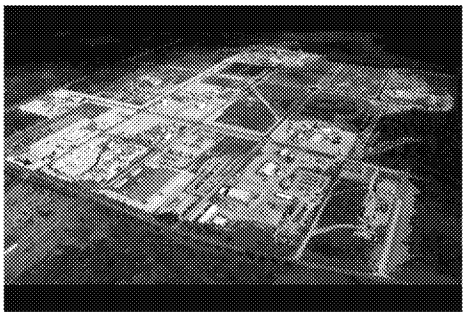
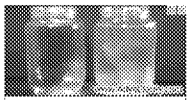
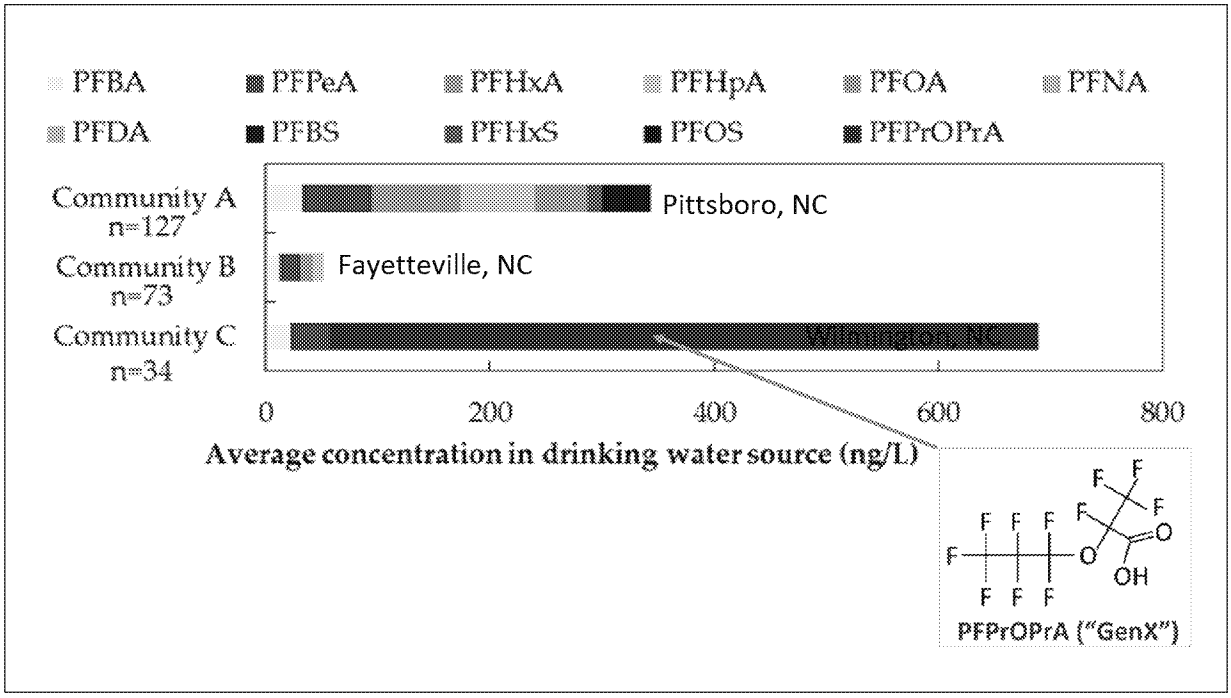
OUR PICKS

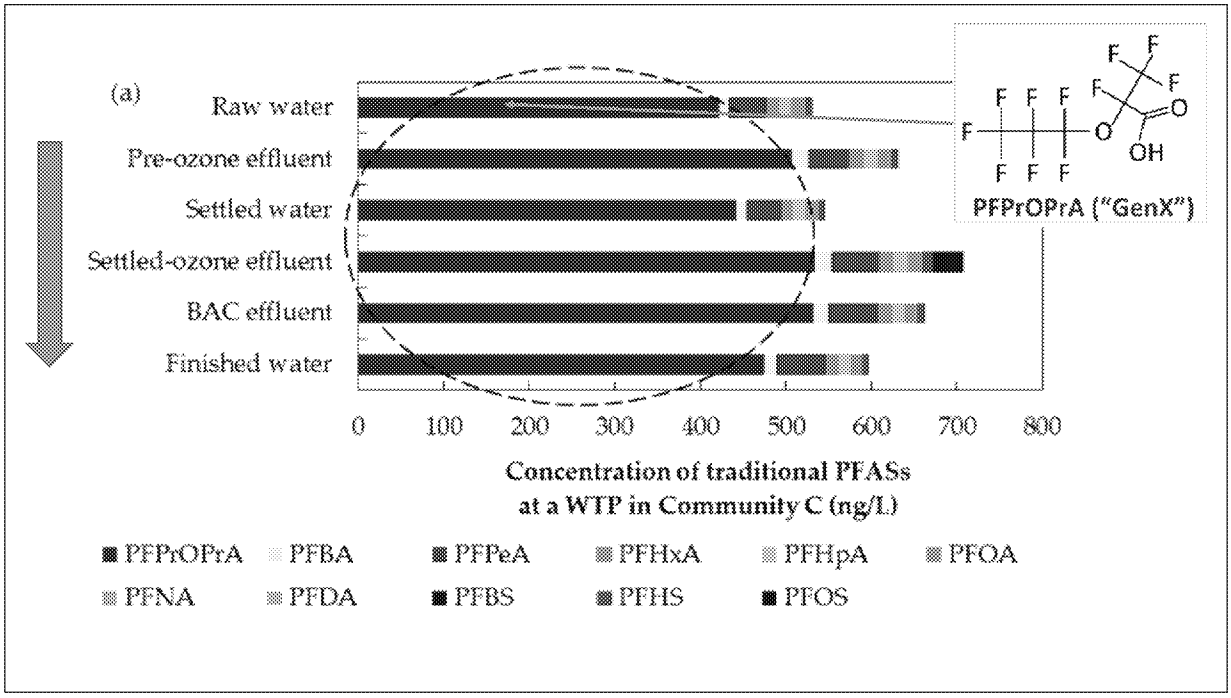


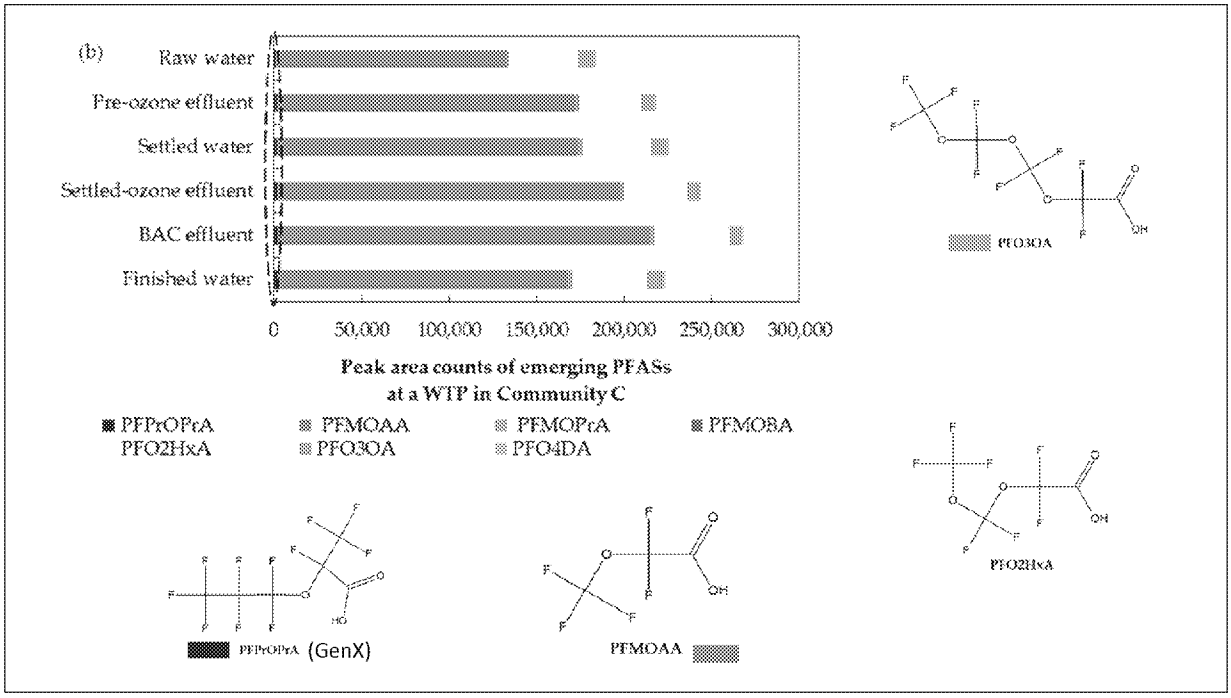
By Vaughn Hagerty Staff Reporter

Utility can't filter out chemical produced upriver

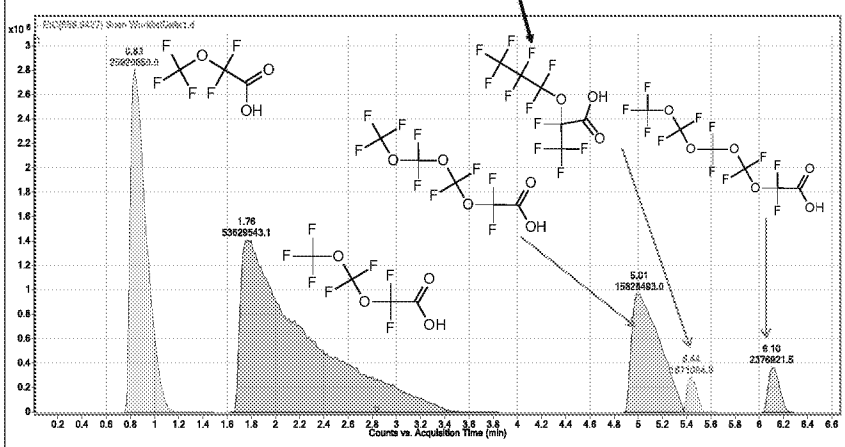


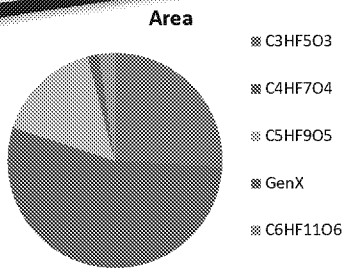

PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFBS
PFHxS
PFOS
PFPrOPrA
Community A
n=127
Pittsboro, NC
Community B
n=73
Fayetteville, NC
Community C
n=34
Wilmington, NC
0
200
400
600
800
Average concentration in drinking water source (ng/L)
PFPrOPrA ("GenX")


(a)
Raw water
Pre-ozone effluent
Settled water
Settled-ozone effluent
BAC effluent
Finished water
0
100
200
300
400
500
600
700
800
Concentration of traditional PFASs
at a WTP in Community C (ng/L)
PFPrOPrA ("GenX")
PFPrOPrA
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFBS
PFHS
PFOS


(b)
Raw water
Pre-ozone effluent
Settled water
Settled-ozone effluent
BAC effluent
Finished water
0
50,000
100,000
150,000
200,000
250,000
300,000
Peak area counts of emerging PFASs
at a WTP in Community C
PFPrOPrA
PFMOAA
PFMOPrA
PFMOBA
PFO2HxA
PFO3OA
PFO4DA
PFO3OA
PFO2HxA
PFPrOPrA (GenX)
PFMOAA

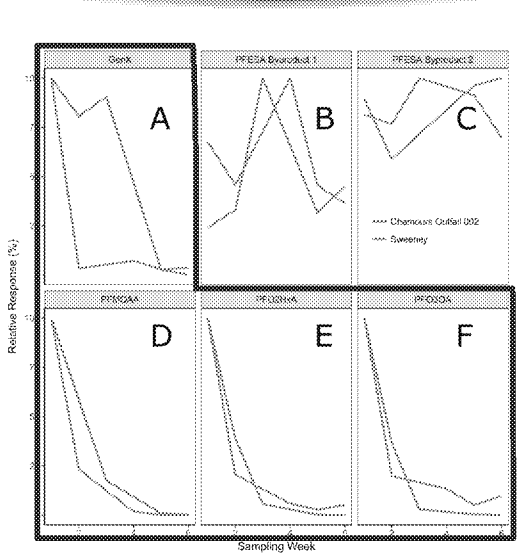
PFECAs in 5-15-17 Cape Fear River Sample

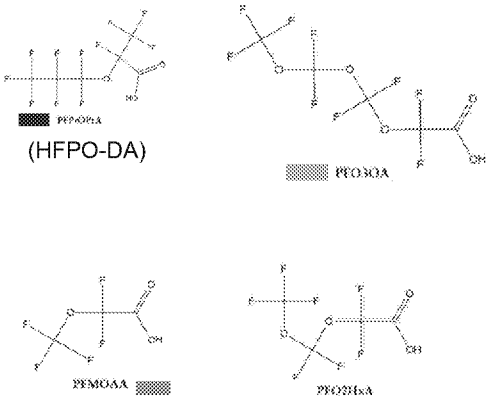




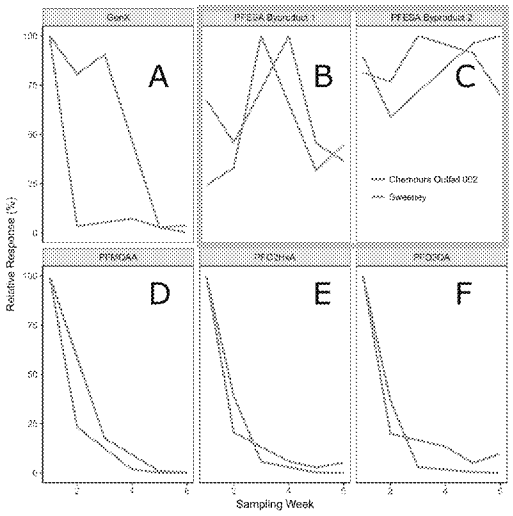
Relative Quantitation Time Trends

6 weeks mid June – early August

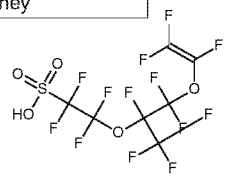




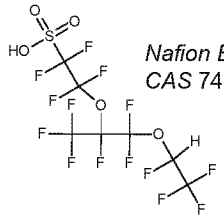
Relative Quantitation Time Trends



Chemours Outfall 002
Sweeney



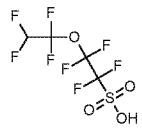
Nafion BP1
CAS 29311-67-9



Nafion BP2
CAS 749836-20-2

Retrospective Analysis (McCord *in prep*)

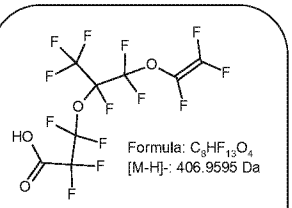
Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	×	×	×
	1-26-12	✓	×	×	✓	✓	×	×	×
2012	2-1-12	✓	×	×	✓	✓	×	✓	×
	2-9-12	✓	✓	✓	✓	✓	✓	×	×
	5-4-12	✓	×	×		×	×	×	×
	5-4-12	✓	×	×			×	×	×
2014	11-24-14	✓	×	×			×	×	×
2015	5-12-15	✓	✓	✓			✓	✓	✓
	5-12-15	✓	✓	✓			✓	✓	✓
	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	✓	✓	✓	✓	✓	×	×	×



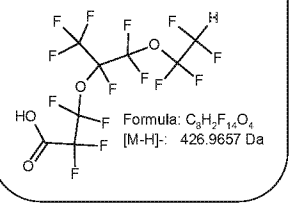
Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

Retrospective Analysis (McCord *in prep*)

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	✓	✓	✓	✓	✓	×	×	×



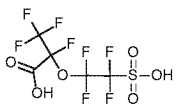
Formula: $C_8HF_{13}O_4$
[M-H]-: 406.9595 Da



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

Retrospective Analysis (McCord *in prep*)

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	✓	✓	✓	✓	✓	×	×	×

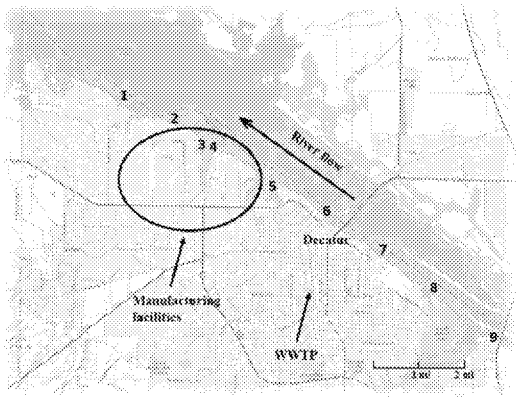


Formula: $C_5H_2F_8O_6S$
[M-H]-: 340.9372 Da

Environmental Science & Technology

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*[,‡]



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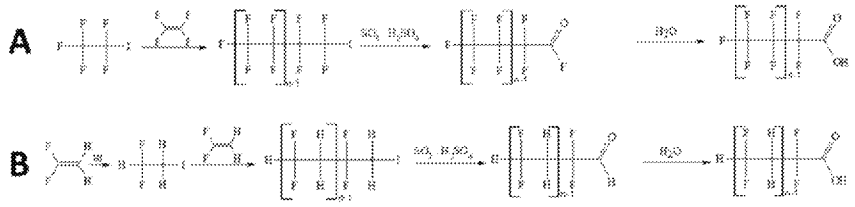
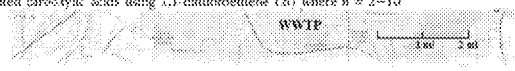


Figure 3. Synthesis reaction for the production of a traditional perfluorinated carboxylic acid using tetrafluoroethene (A) and the hypothesized synthesis of the proposed polyfluorinated carboxylic acids using 1,1-difluoroethene (B) where $n = 2-10$



ENVIRONMENTAL Science & Technology LETTERS

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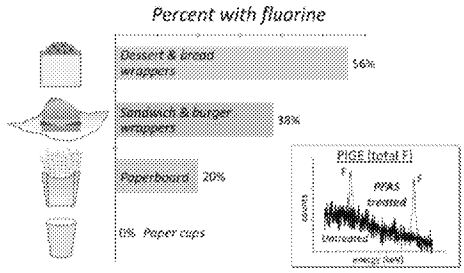
Fluorinated Compounds in U.S. Fast Food Packaging

Laurel A. Schaider,[*,†,⊗] Simona A. Balan,[‡] Arlene Blum,[§,∥] David Q. Andrews,[⊥] Mark J. Strynar,[#,⊗] Margaret E. Dickinson,[∇] David M. Lunderberg,[∇] Johnsie R. Lang,[○] and Graham F. Peaslee[◆]



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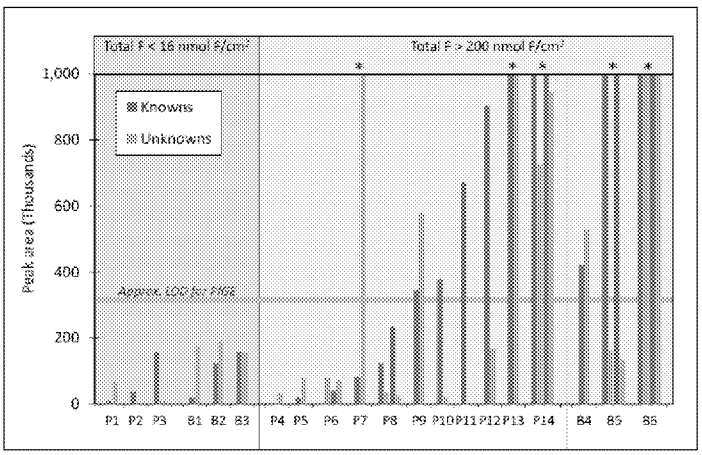

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  - Rebecca McMahen
  - Sonia Dagnino
  - Shuang Liang
  - Erik Andersen
  - Larry McMillan
- University of Colorado Boulder
  - Mike Thurman
  - Imma Ferrer
- Agilent
  - Carol Ball
- NC State
  - Detlef Knappe
  - Zack Hopkins
- UNC Charlotte
  - Mei Sun
- NC DEQ
  - Chris Johnson
  - Linda Culpepper
- Public Utilities
  - Michael Richardson and Ben Kearns (CFPUA)
  - Adam Pickett (Town of Pittsboro)
  - Chris Smith (Fayetteville Public Works Commission)
- People I forgot

Questions?

Contact Information
strynar.mark@epa.gov

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