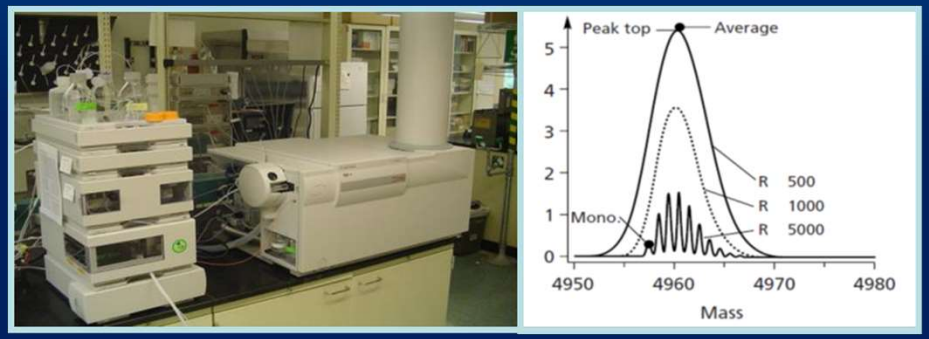
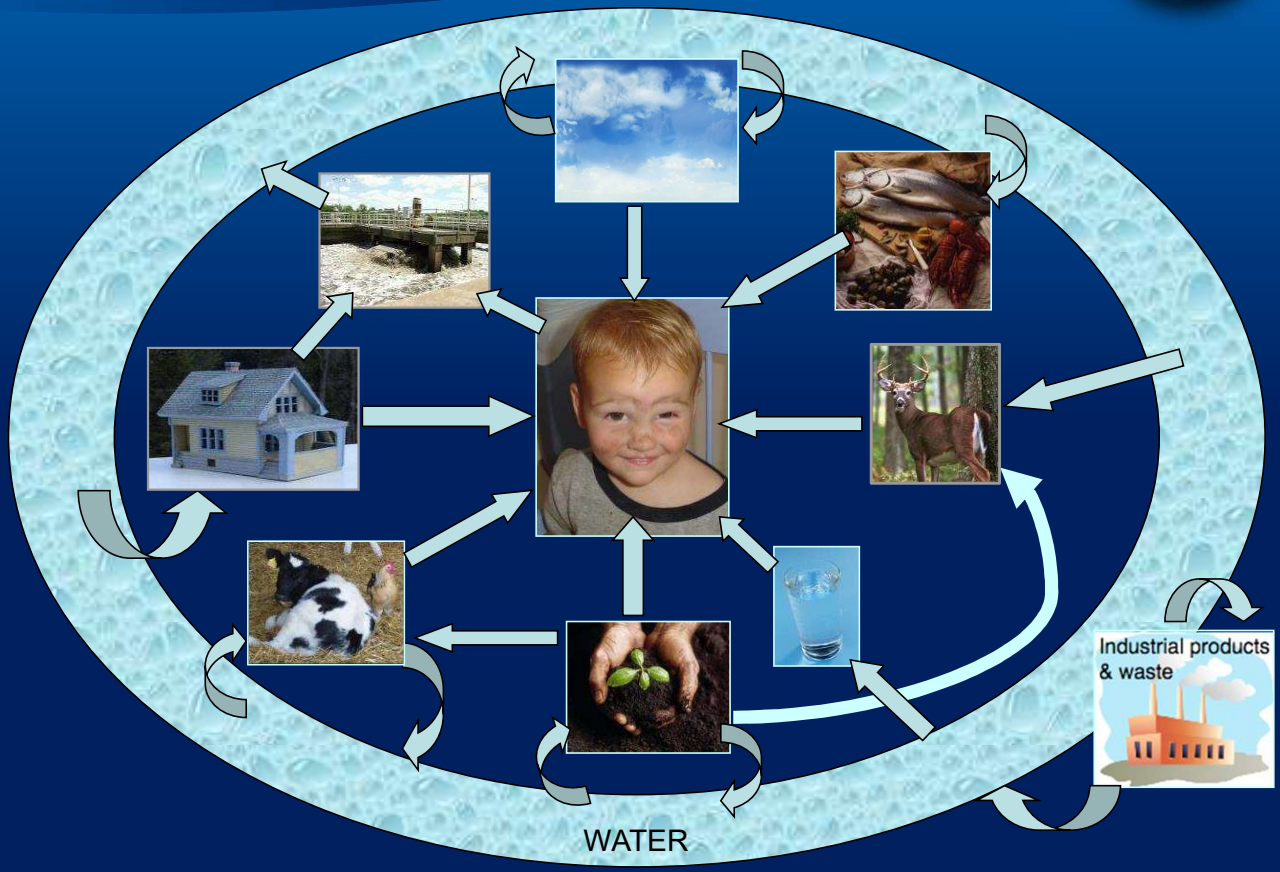
Investigations of per- and polyfluorinated compounds in environmental samples and contemporary products

Mark Strynar USEPA/ORD/NERL/EMMD



December 6th, 2018
Groundwater Professionals of North Carolina (GWPNC) Meeting
NC State Arboretum

Human Exposure Pathways



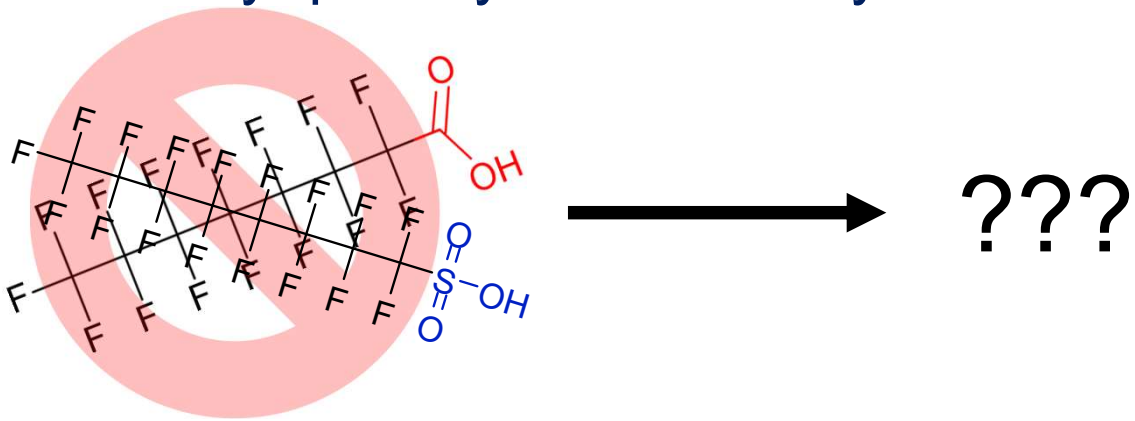
Many chemicals
Many media
Many sources
Unknown toxicity

Usual Suspects for Elevated Scrutiny

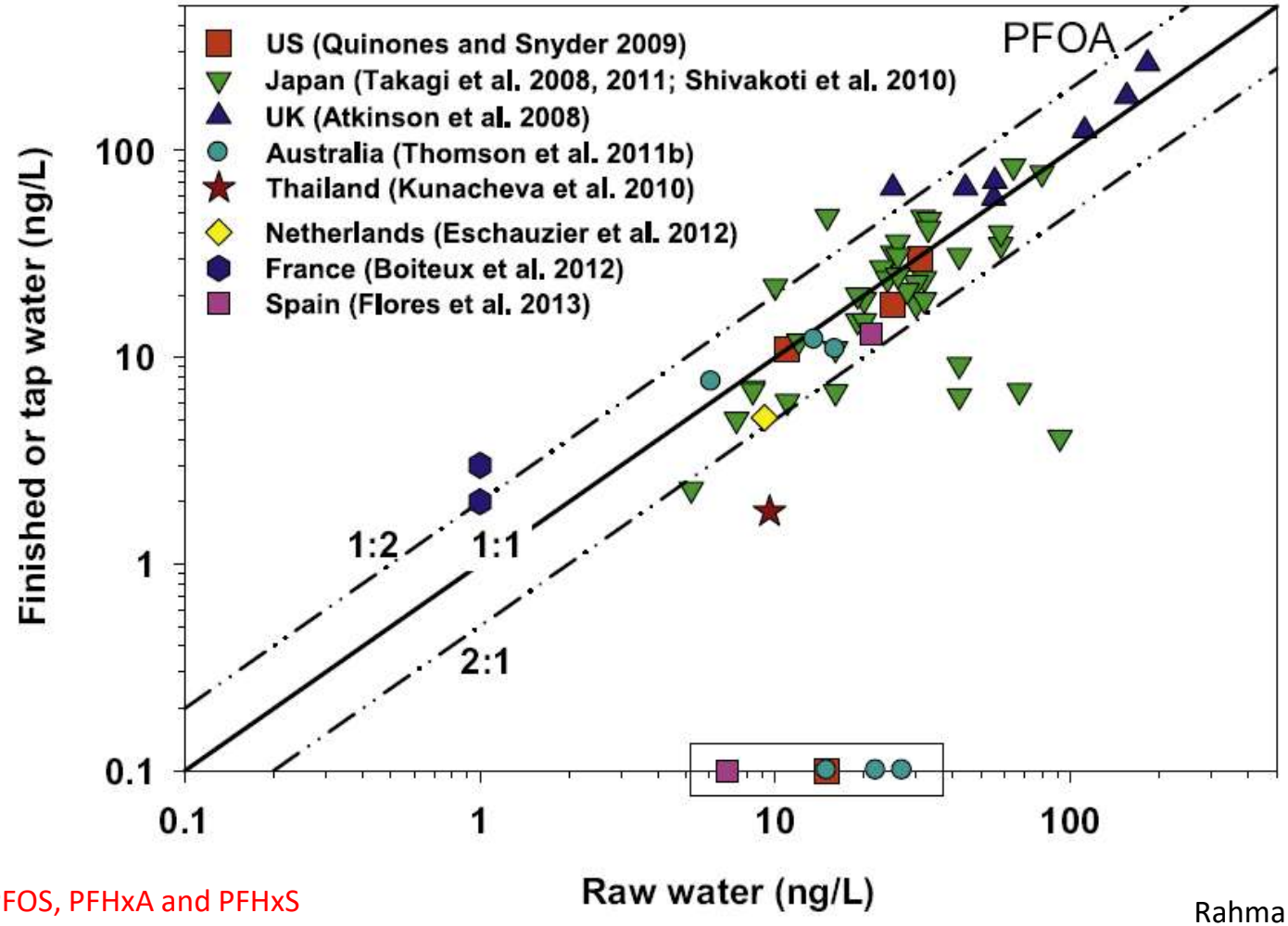
- Large peaks
- Found in many samples)
- Contain halogens (Cl, Br)
- Negative Mass defect
- Related chemicals
- ???

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?



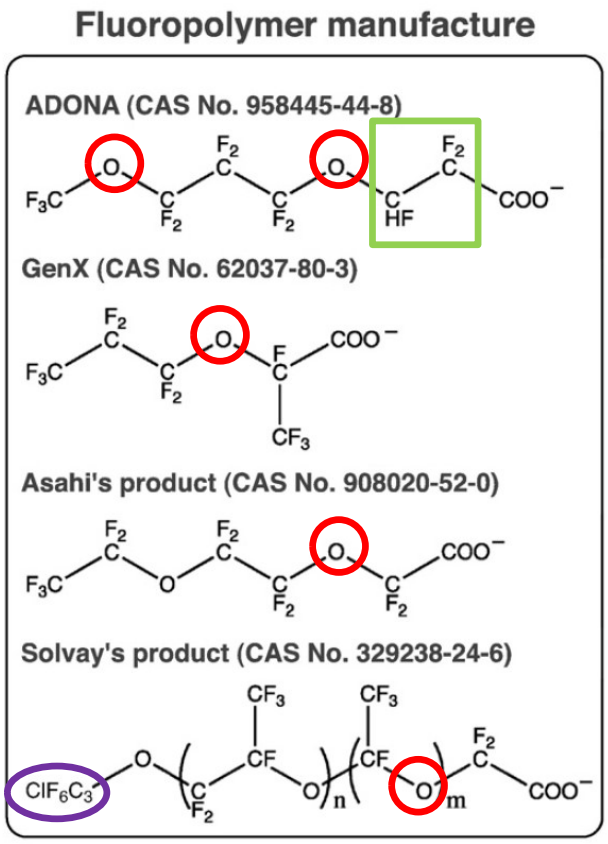
PFAS Generally Not Removed During Conventional Drinking Water Treatment

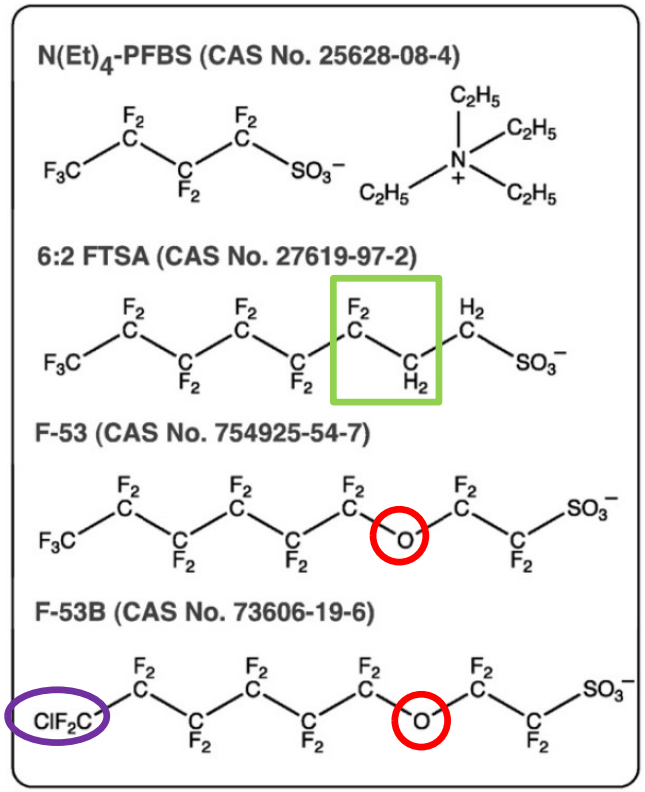


Similar for PFOS, PFHxA and PFHxS

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

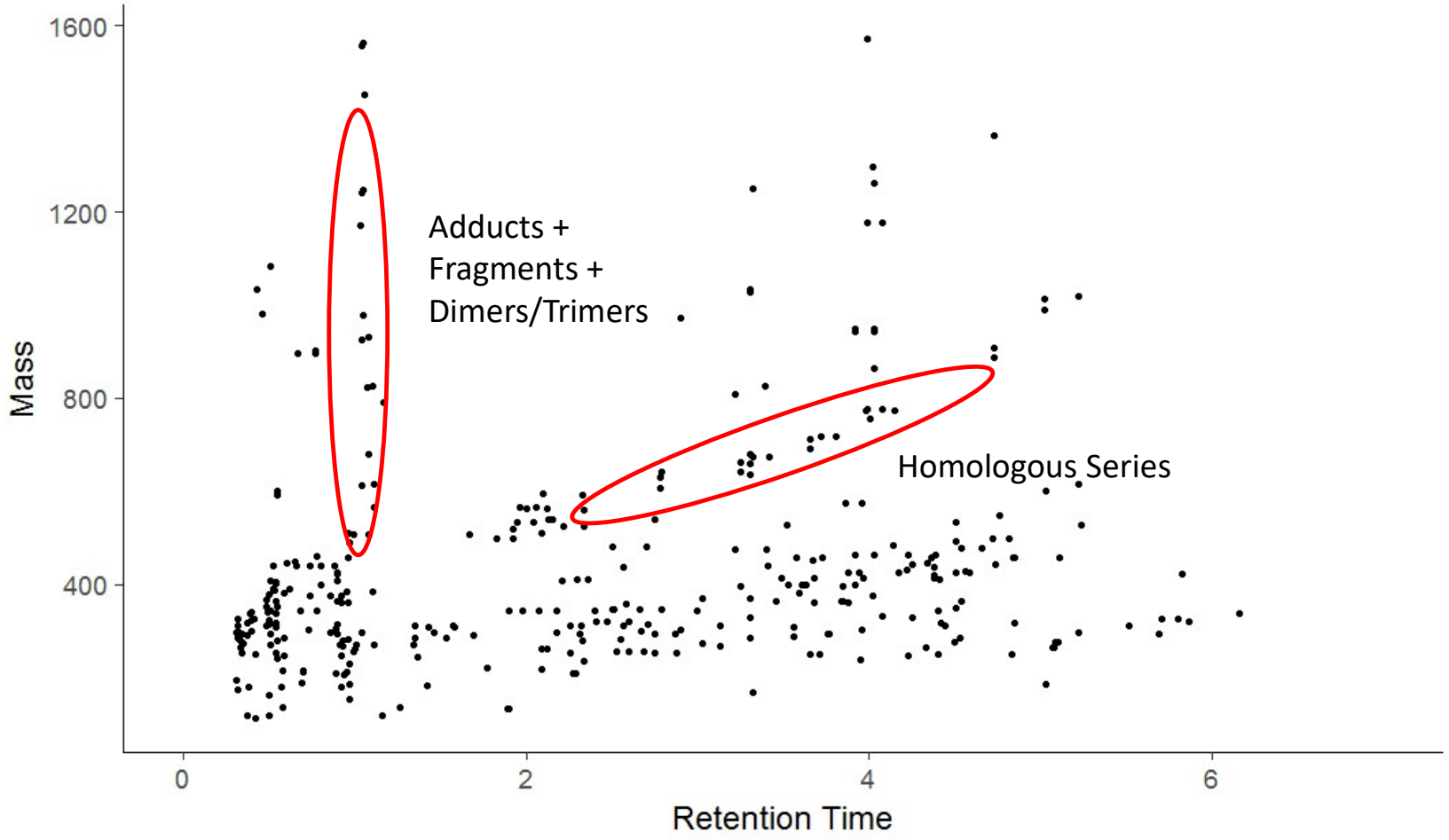
Post PFOA Stewardship Agreement



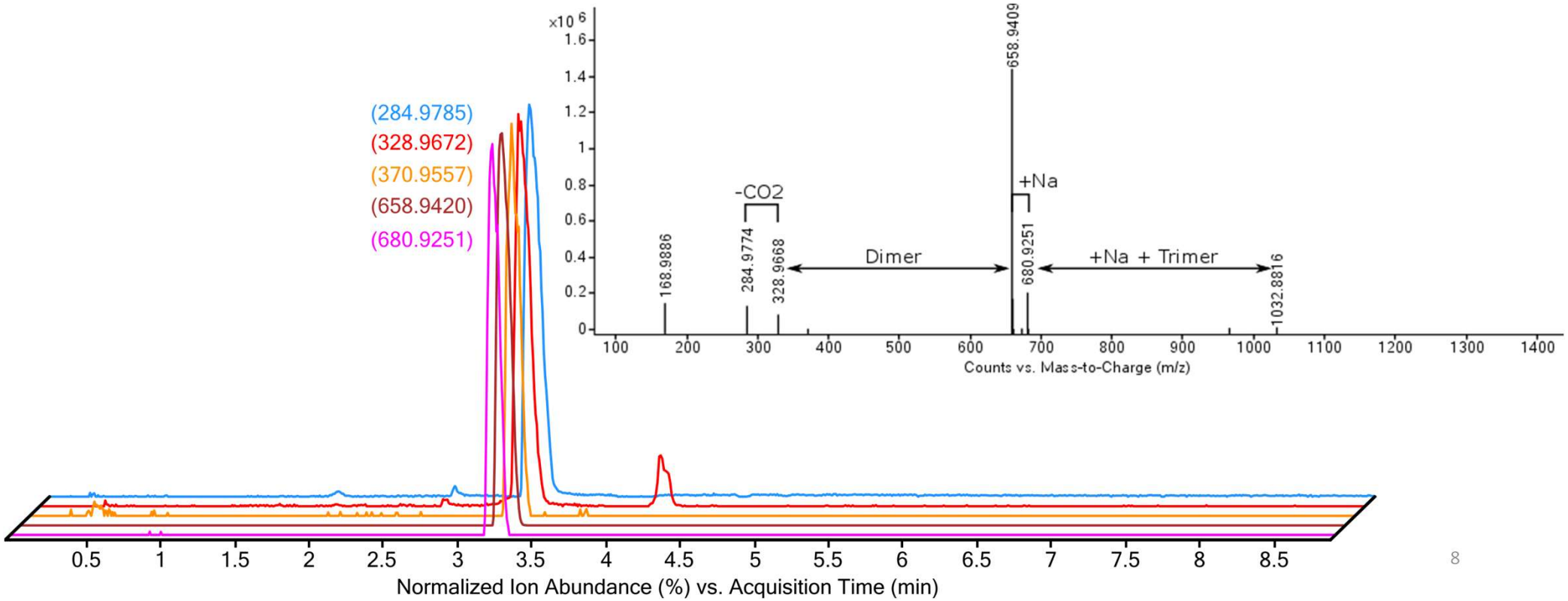


Wang et al. *Environment International*, **2013,** *60,* pp 242–248

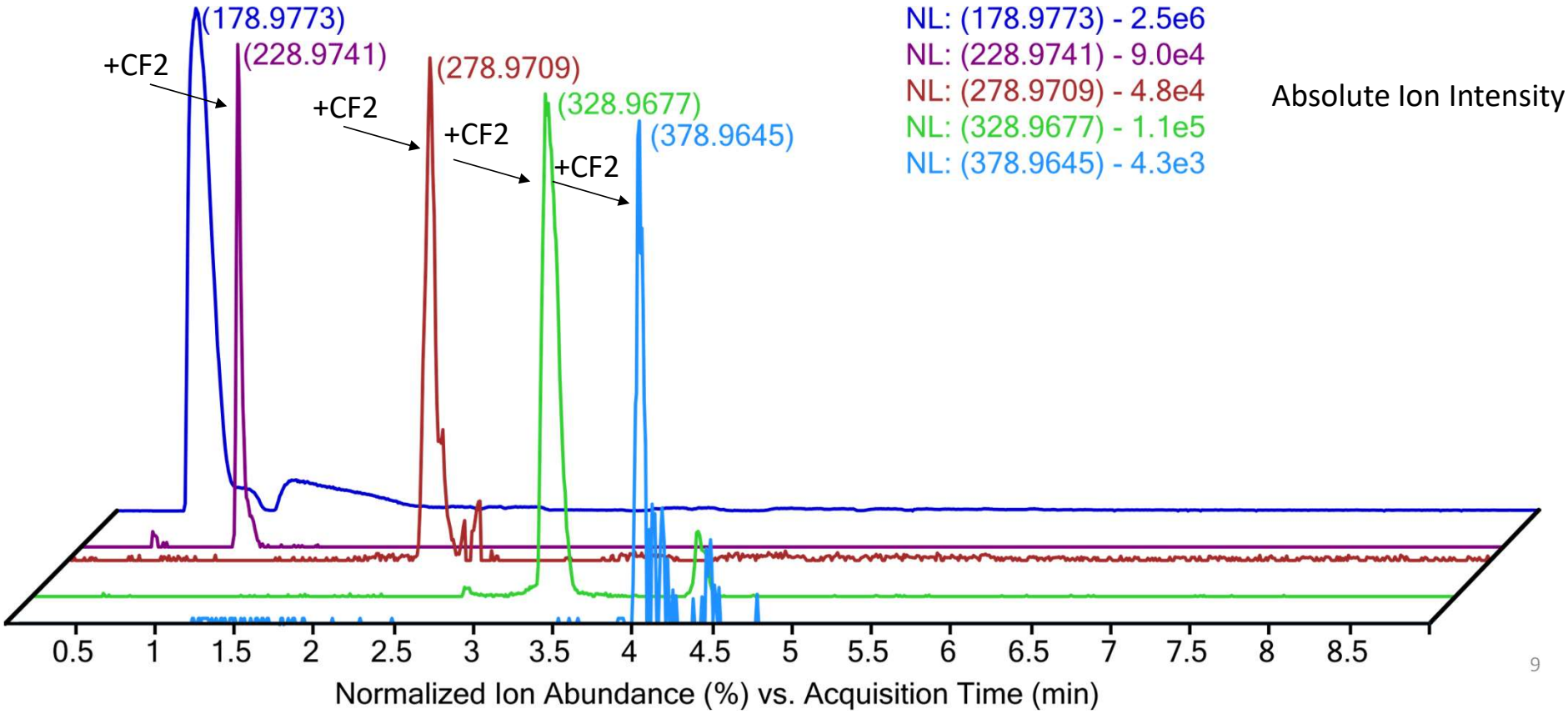
Relationships Reveal Underlying Chemistry



In-Source Related Species



Homologous Series

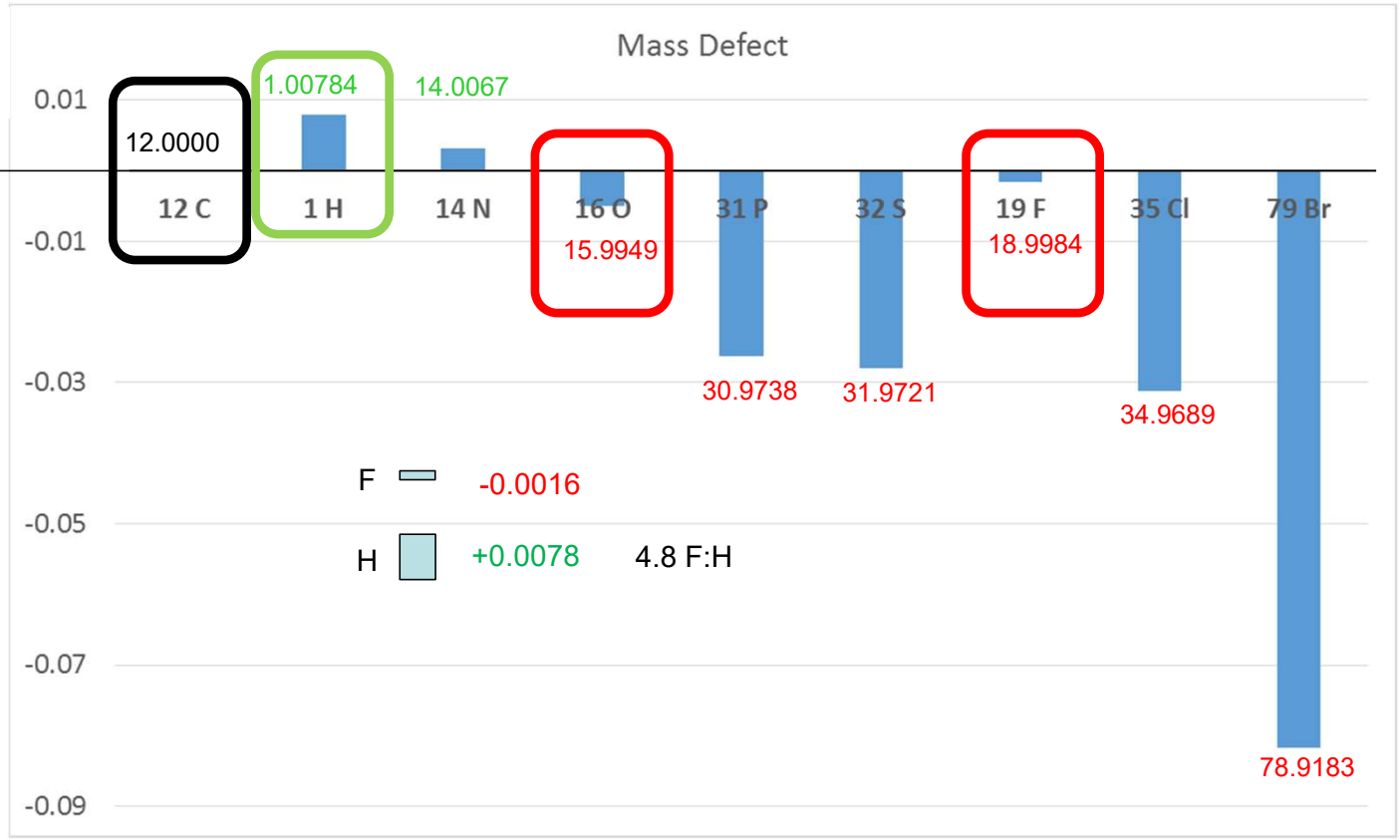


Absolute Ion Intensity

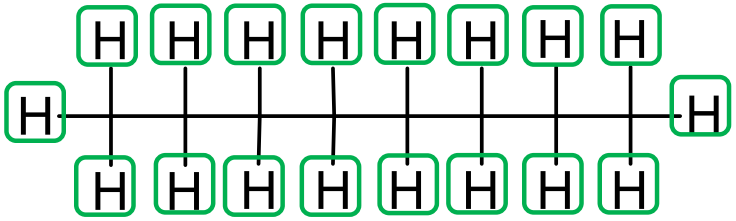
Isotope Signatures: Negative Mass Defect

Positive Mass Defect

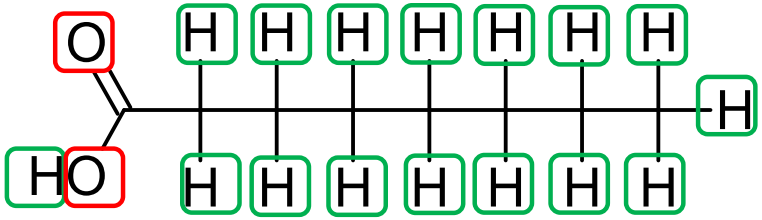
Negative Mass Defect



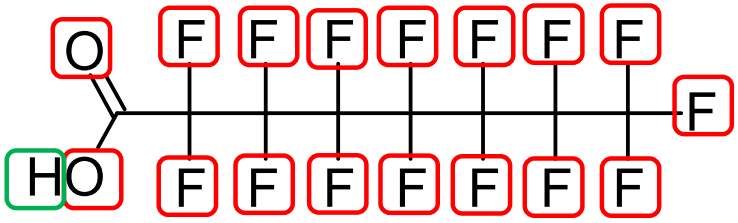
Example of Mass Defect



Octane
MI mass 114.**1409**



Octanoic Acid
MI mass 144.**1150**



Perfluorooctanoic Acid
MI mass 413.**9737**

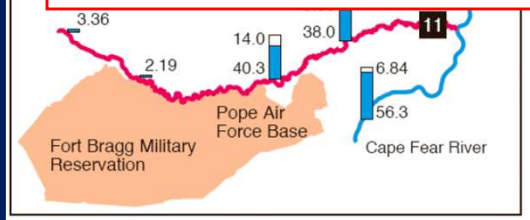
Past Work:
PFAS in NC Water

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.

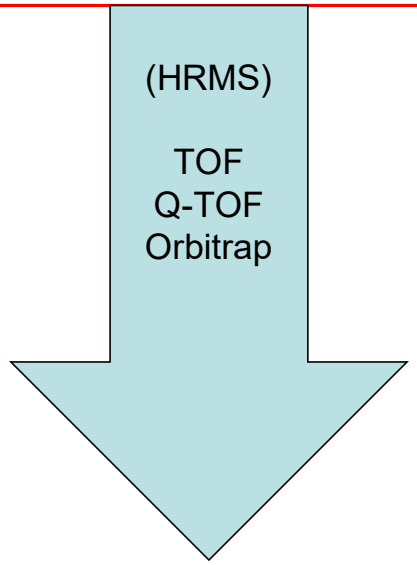


performance fabrics, bio-solids, AFFF, industrial waste

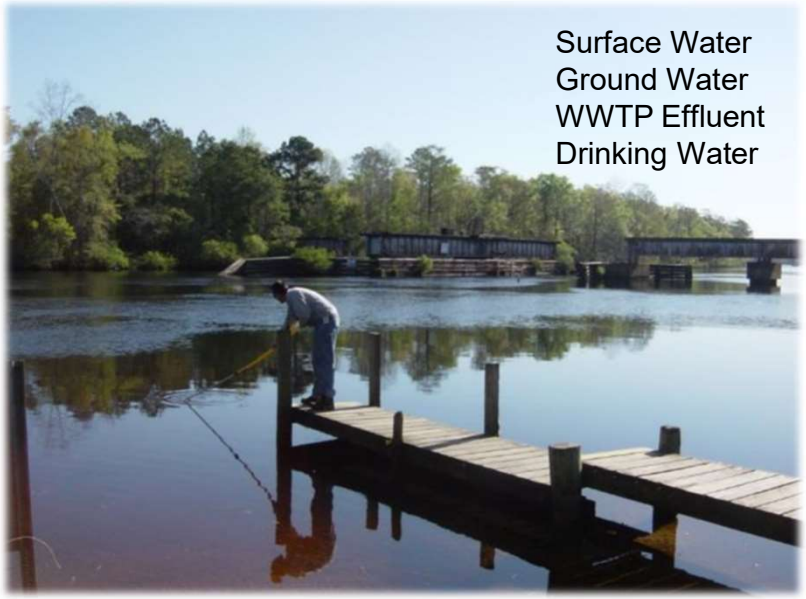
What is Non-Targeted Analysis?

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

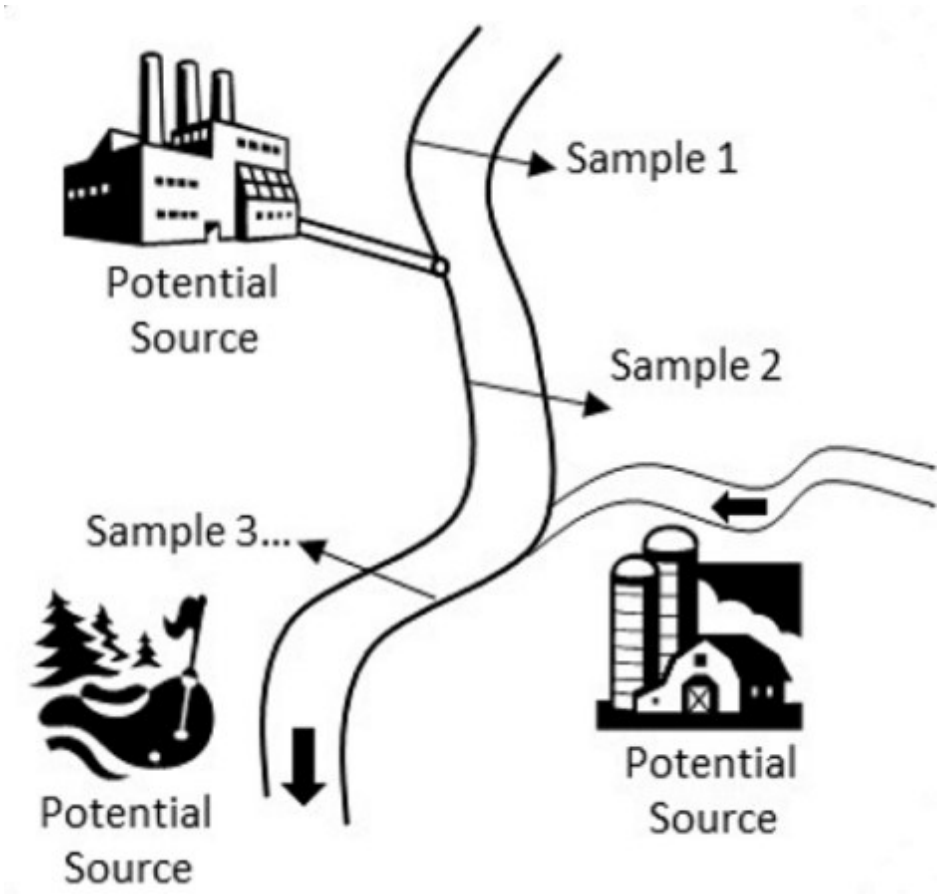
- Suspect Screening
  - Which chemicals in this database are in my sample?
- Non-Targeted Screening
  - What are the chemicals in my sample?



Data Generation:
Source Determination by NTA



Sampling from geographically or temporally displaced locations allows triangulation of sourcing

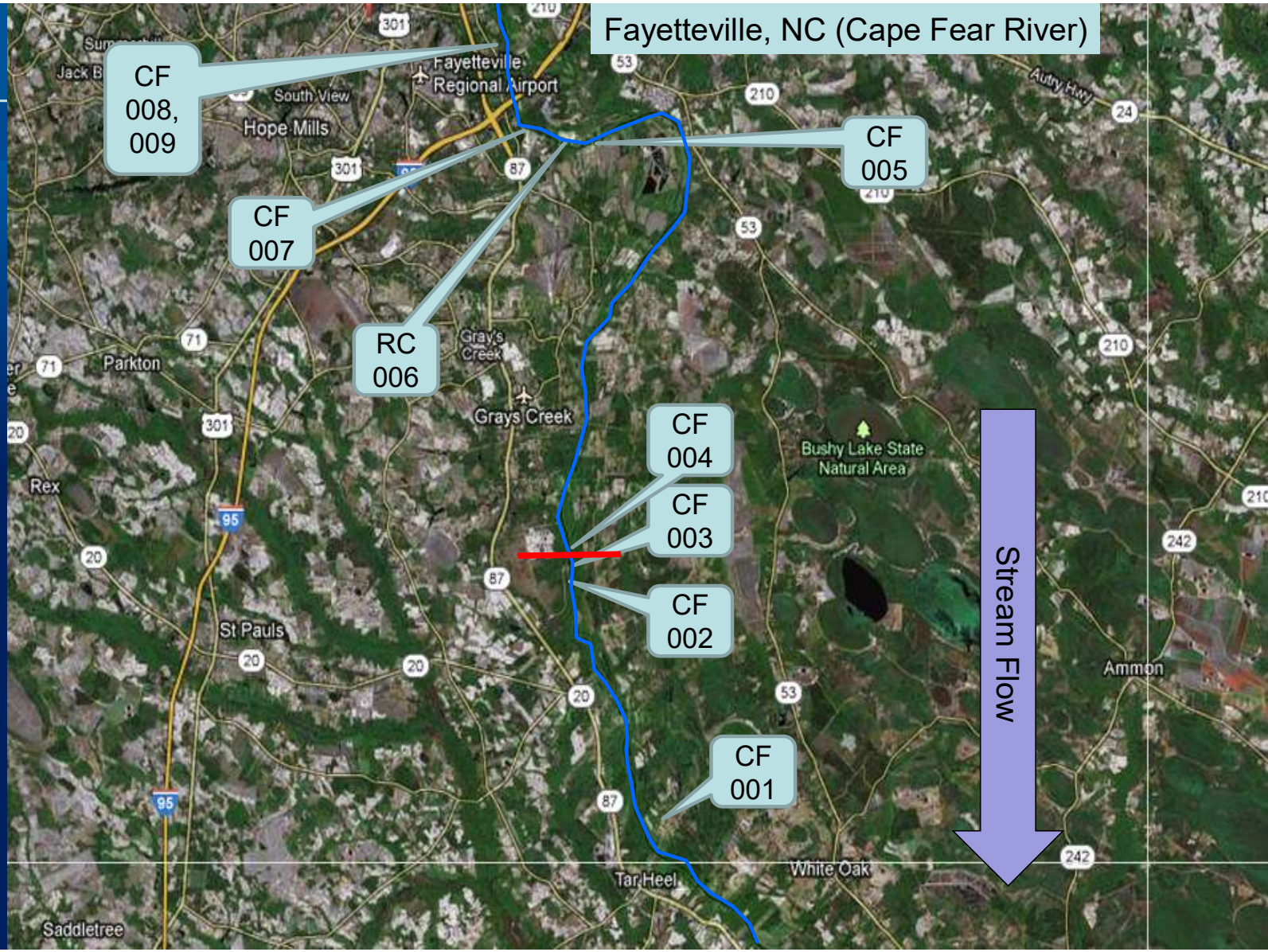


First Sampling
2011-2012

Presented at
SETAC 2012

Follow-up sampling
2012-2013

Presented at
SETAC 2014



Legacy PFAS found in Cape Fear Water circa 2012

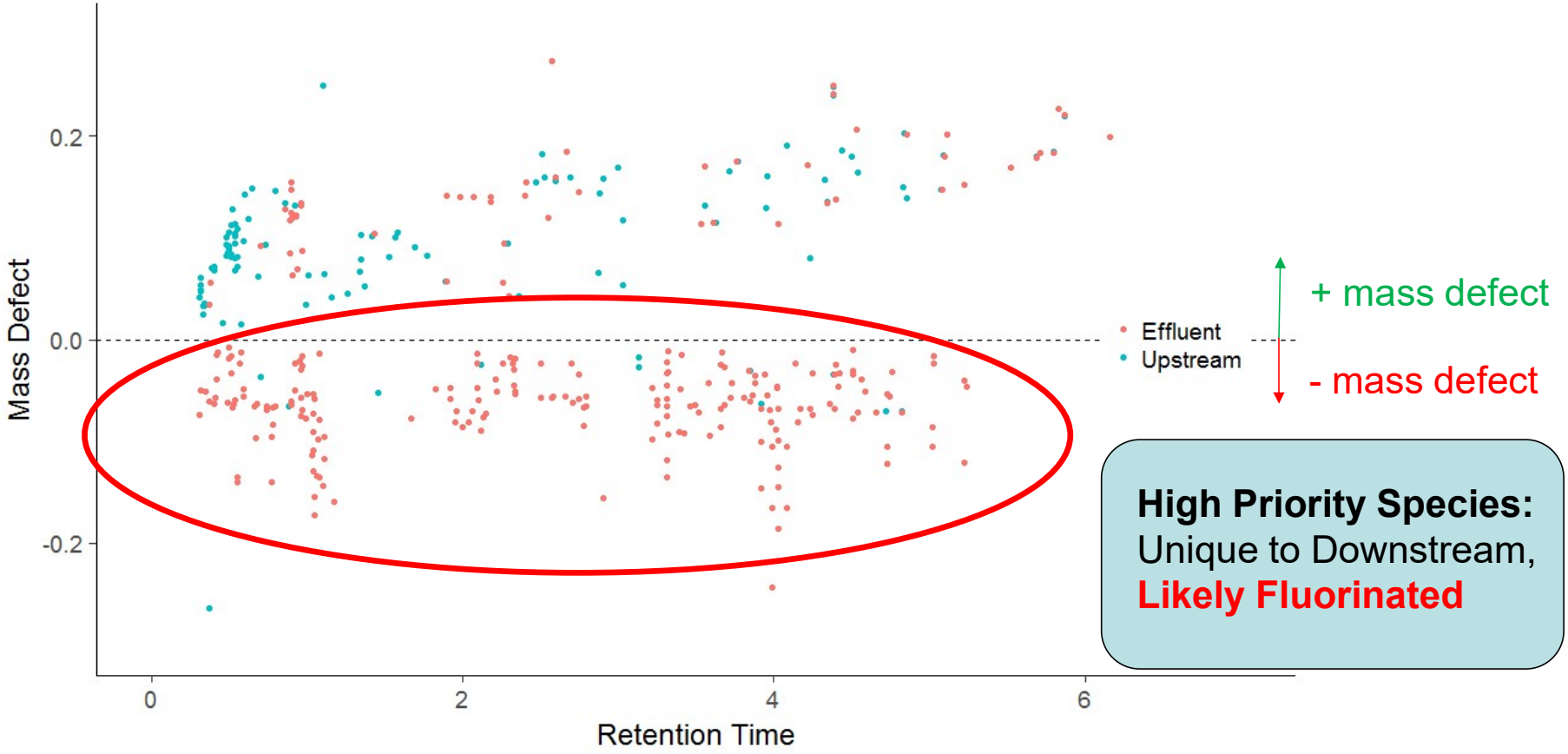
Stream Flow

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

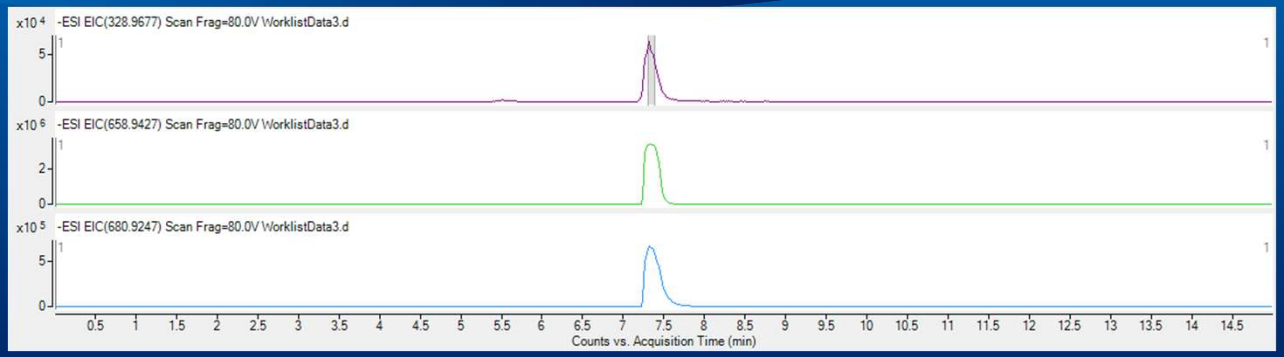
Legacy PFAS in Cape Fear River

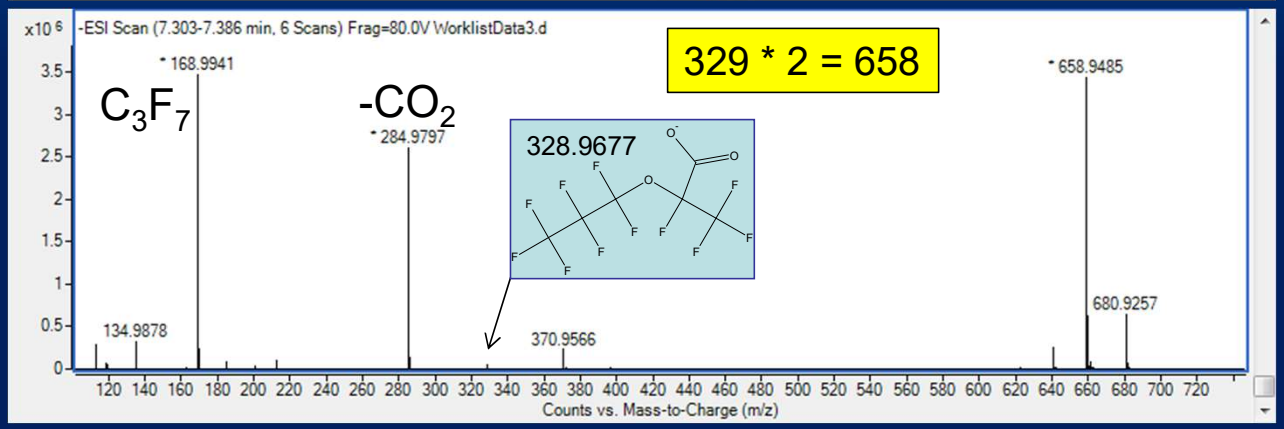
Mass Defect of Outfall and Upstream Features



High Priority Species:
Unique to Downstream,
Likely Fluorinated

m/z Extracted Ion Chromatograph (EIC)



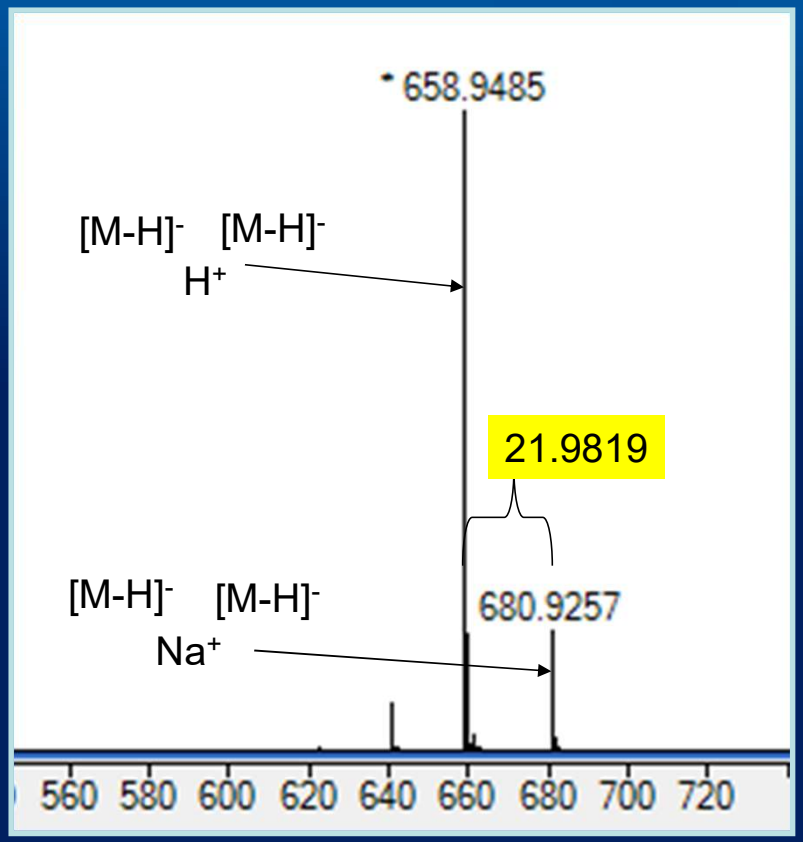


In a standard or extracted water, same spectra. *m/z* 328 LOW

Key TOFMS Information

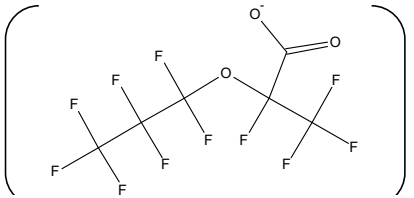
Difference Between Peaks

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

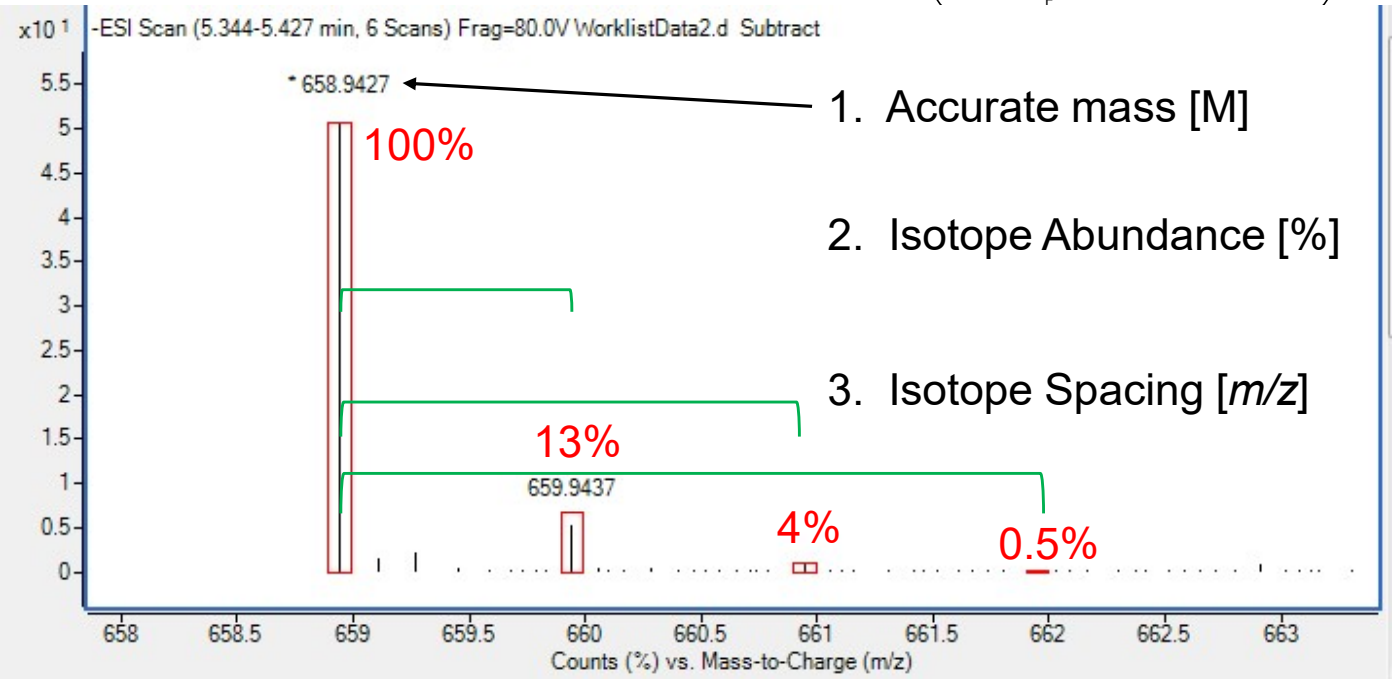


Isotope Cluster Scoring

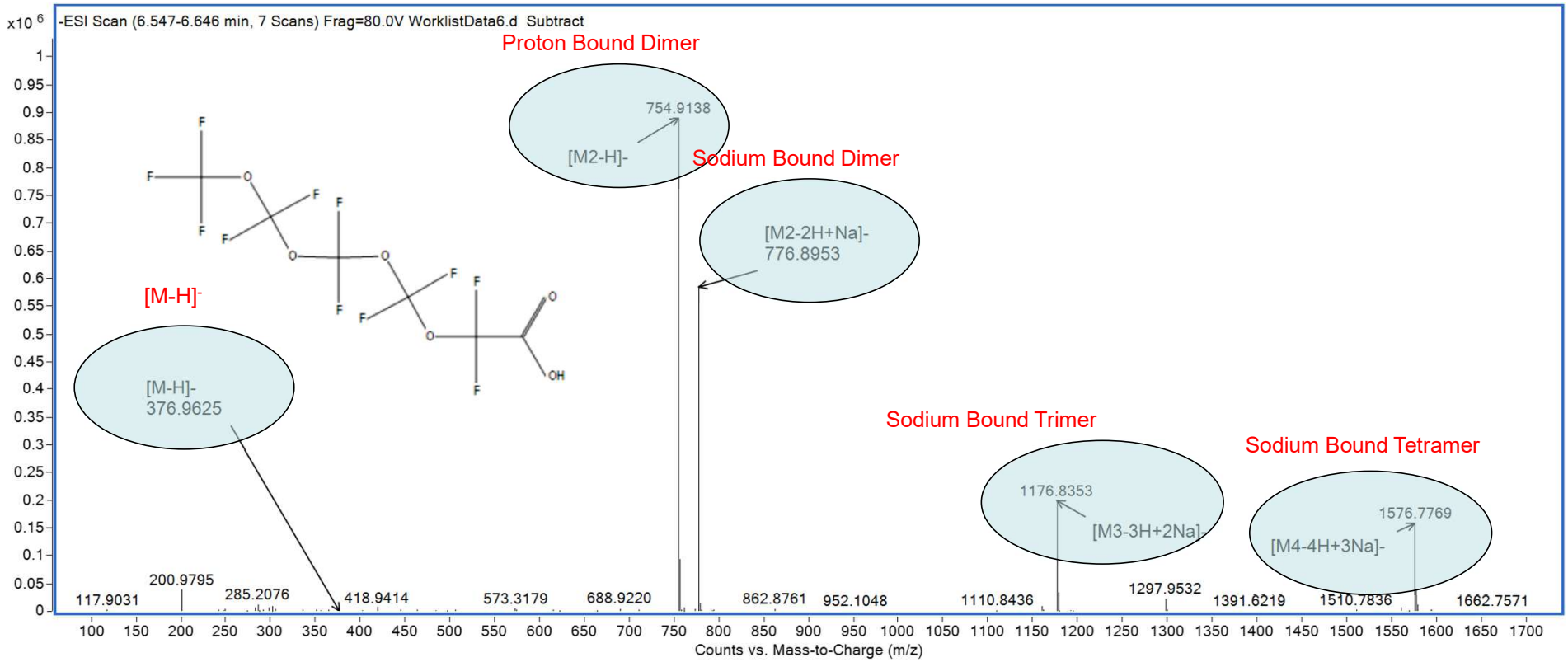
Ex. C_{12} H F_{22} O_6



+ H^+



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

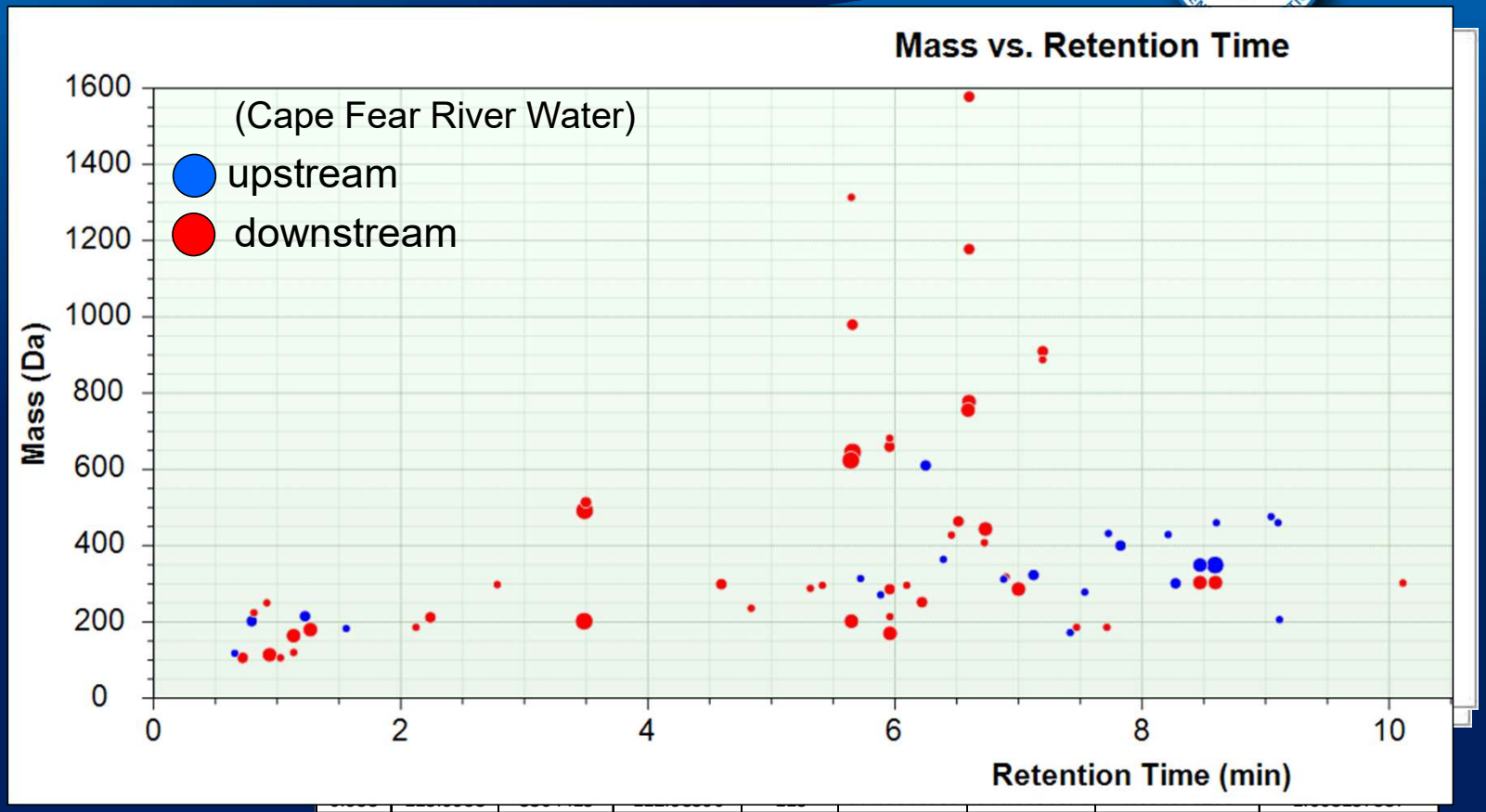
$$\text{Kendrick Mass (F)} = (\text{observed mass}) \times \frac{\text{Nominal mass F}}{\text{Exact mass F}}$$

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

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

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

Kendrick Mass Defect Water Example



1.268	179.9849	4011200	178.97706	179	179.9963838	180.0075373	0.996383769	1.007537312

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)

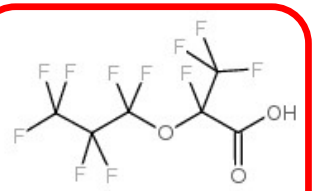
Mark Strynar,[*,†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Liang,[†,‡] Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[∥] Imma Ferrer,[∥] and Carol Ball[⊥]

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

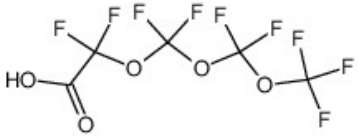
number	formula	CAS no.	name	$[M]^a$	$[M-H]^-$ m/z	$[2M-2H+Na]^-$ m/z	$[2M-H]^-$ m/z
Monoether PFECAs							
1	$C_3HF_5O_3$			179.9846	178.9773	380.9438	358.9619
2	$C_4HF_7O_3$			229.9813	228.9740	480.9372	458.9553
3	$C_5HF_9O_3$	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	$C_6HF_{11}O_3$	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427
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		

Undecafluoro-2-methyl-3-oxahexanoic acid

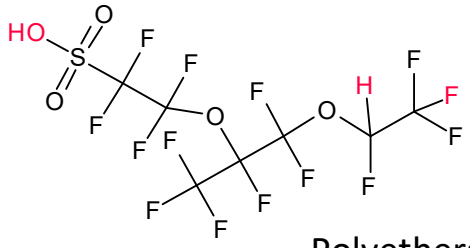
Example Structures



Monoether (6): HFPO-DA;GenX



Polyethers (4):

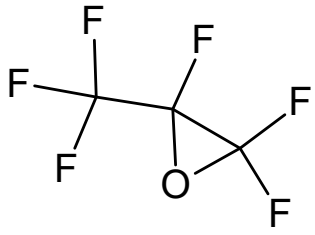


Polyethers sulfonates (2):

Hexafluoropropylene Oxide (HFPO) Based Chemistry

HFPO

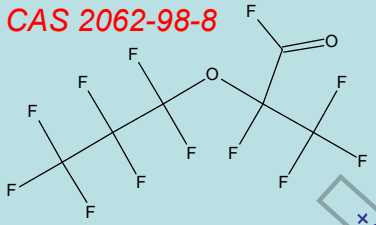
CAS 428-59-1



Dimerized to HFPO-DAF

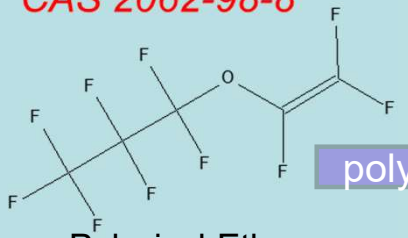
Vinyl Ether Production

HFPO-DAF
CAS 2062-98-8



Acid Fluorides

CAS 2062-98-8

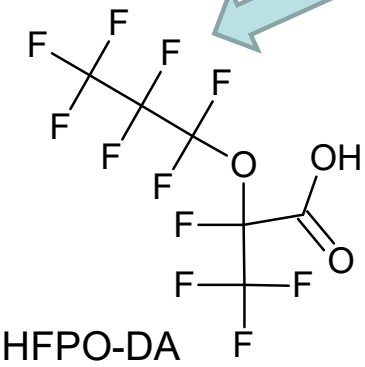


Polyvinyl Ether Intermediates

polymers

In Water

+Ammonium Hydroxide

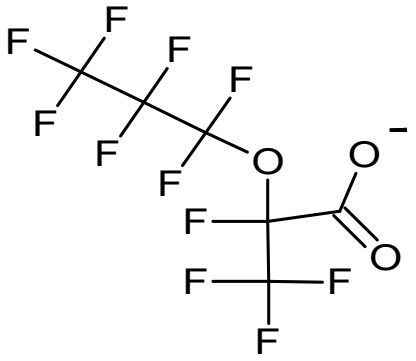


HFPO-DA

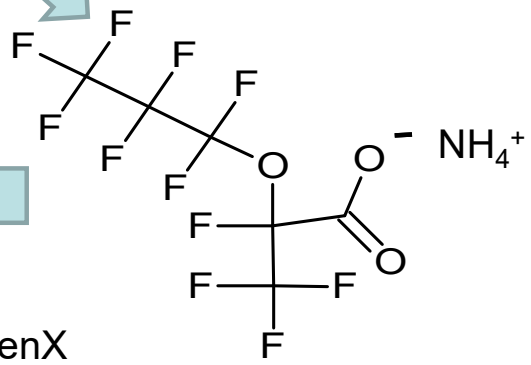
CAS 13252-13-6

In Water

Common Analyte



In water

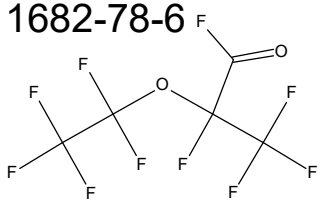


GenX

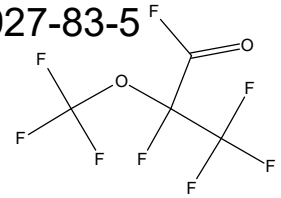
CAS 62037-80-3

Polyvinyl Ether Production

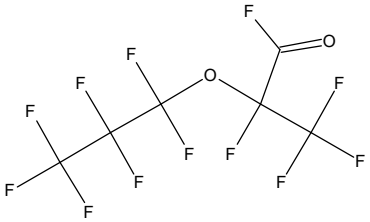
CAS 1682-78-6



CAS 2927-83-5

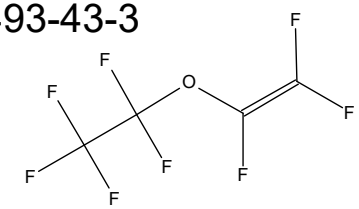


CAS 2062-98-8



Acid Fluorides

CAS 10493-43-3



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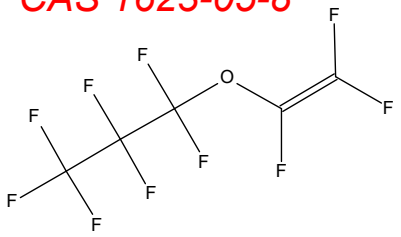
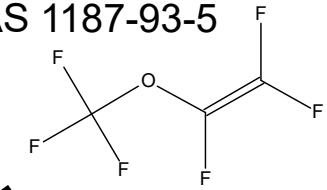


CAS 1187-93-5

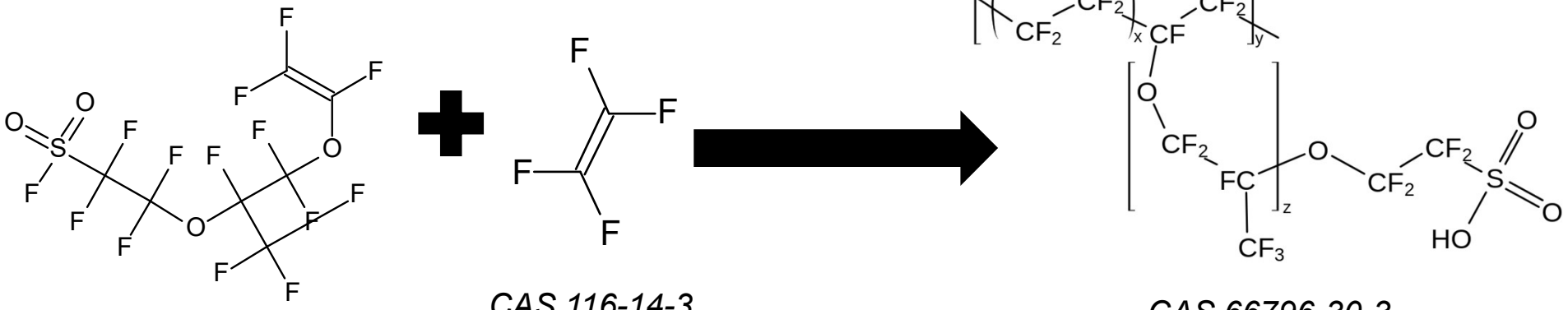


Polyvinyl Ether Intermediates

Head-$(CF_2)_n(CF_2O)_m$-Head
Polyvinyl Ether

Nafion Polymer

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



CAS 16090-14-5

CAS 116-14-3

CAS 66796-30-3

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[‡]

SECTIONS ☰ NEWS SPORTS ENTERTAINMENT LIFE OBITUARIES E-EDITION CARS JOBS HOMES CLASSIFIEDS MEMBER REWARDS

StarNews 150th 1867 • 2017

Toxin taints CFPUA drinking water

MOST POPULAR

1 Carolina Surf condos - in danger of collapse - condemned, evacuated
Jul 2 at 5:50 AM

2 Man injured by hook, not bit by shark at Wrightsville Beach
Jun 30 at 1:43 PM

3 Murder suspect had other charges pending
Jul 2 at 5:44 AM

4 Residents not allowed back into Carolina Surf condos
Jul 4 at 7:33 AM

OUR PICKS

▲ HIDE CAPTION

A 2000 aerial photo of Fayetteville Works on the Cumberland-Bladen county line. The site, home to several plants, one of which makes GenX, is about 100 miles upstream from Wilmington. [COURTESY OF THE FAYETTEVILLE OBSERVER]

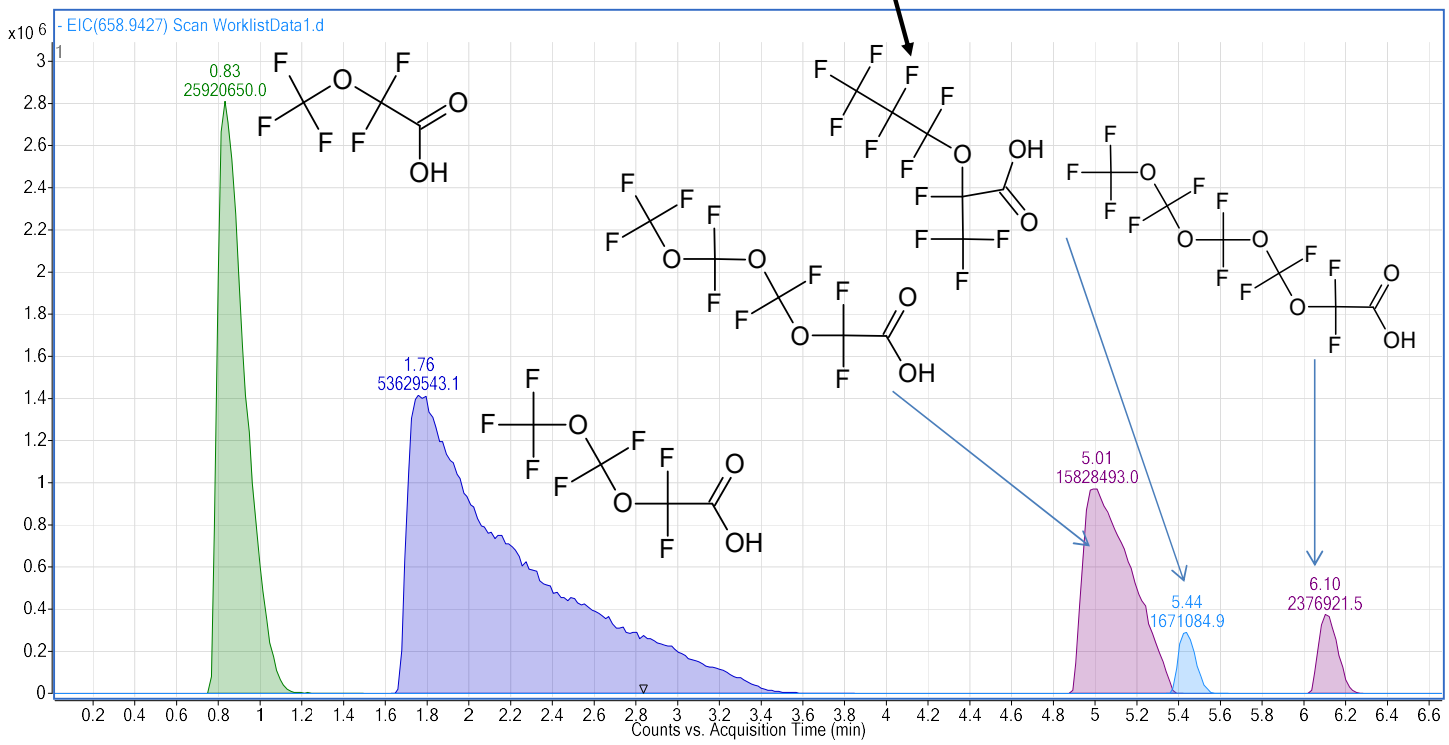
By Vaughn Hagerty StarNews Correspondent
Posted Jun 7, 2017 at 10:31 AM
Updated Jun 8, 2017 at 10:38 AM

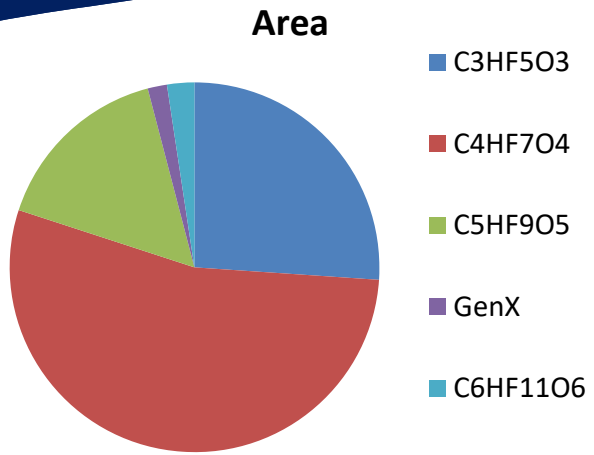
Utility can't filter out chemical produced upriver

June 7th, 2017

Cape Fear River Fayetteville to Wilmington, NC

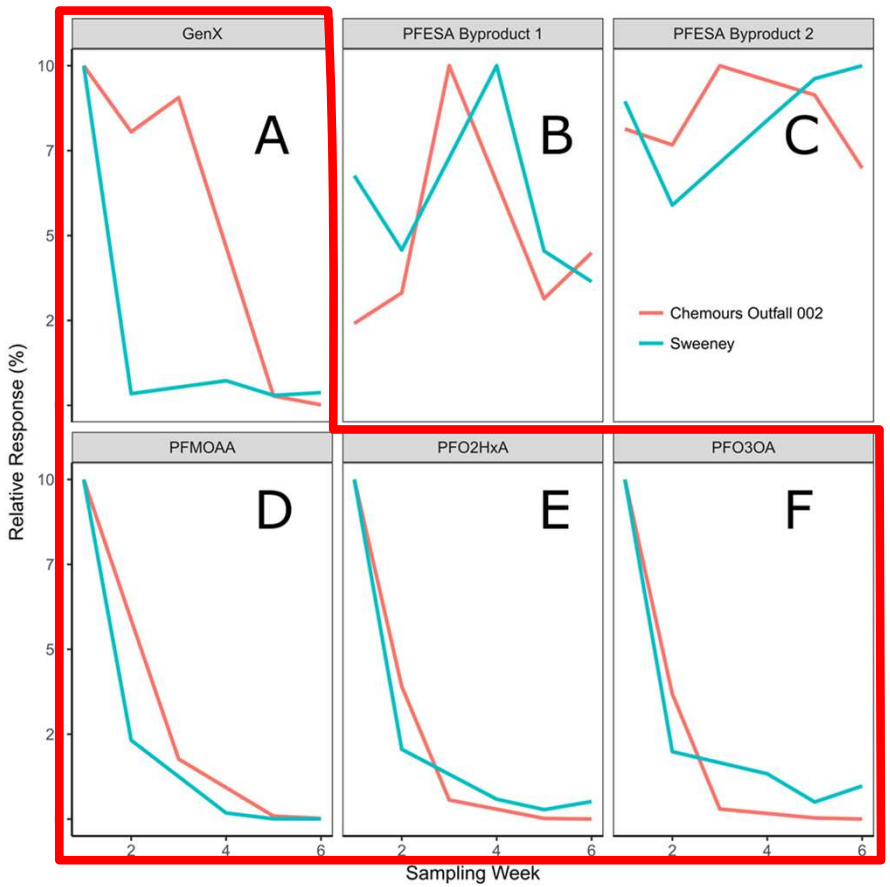
PFECAs in 5-15-17 Cape Fear River Sample

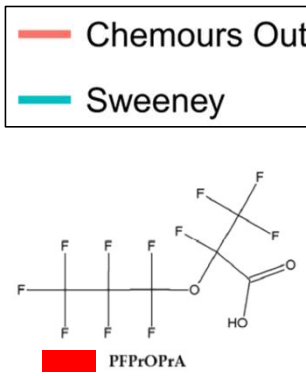




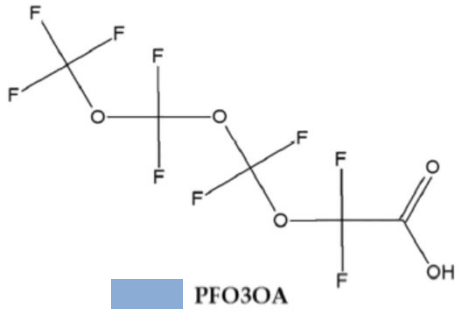
Relative Quantitation Time Trends

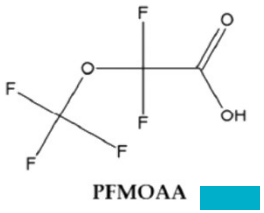
6 weeks mid June – early August

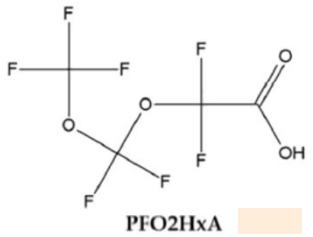




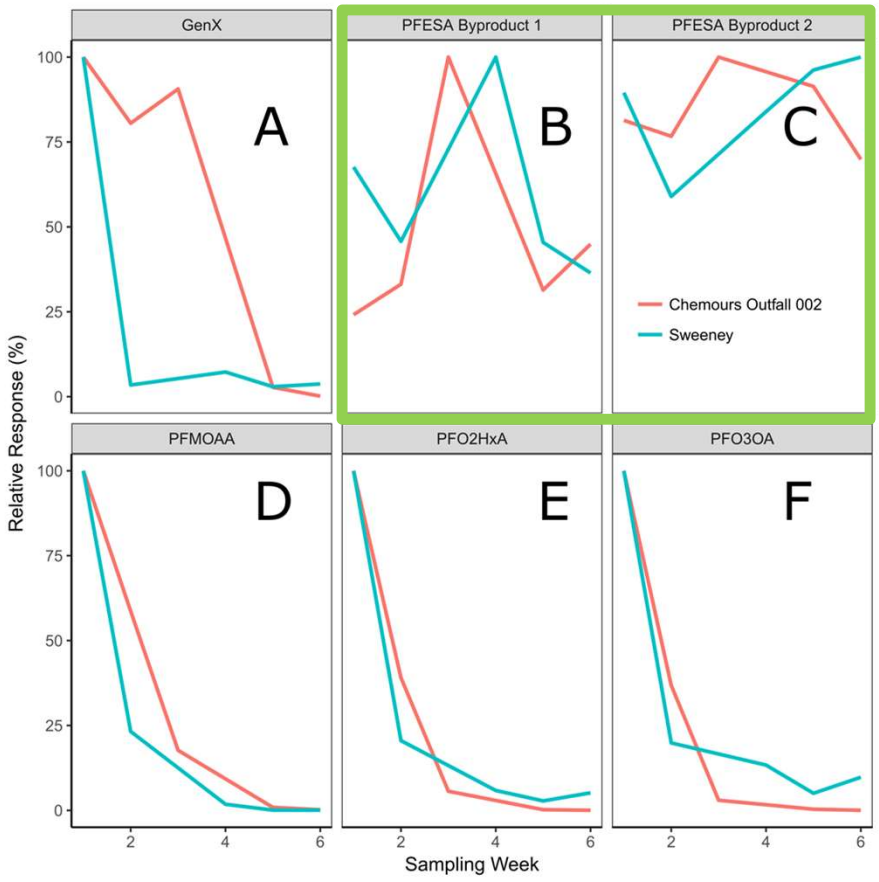
(HFPO-DA)

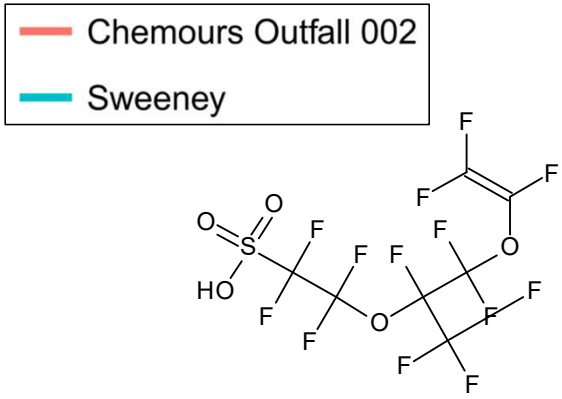




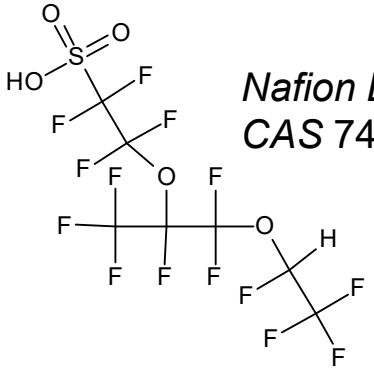


Relative Quantitation Time Trends





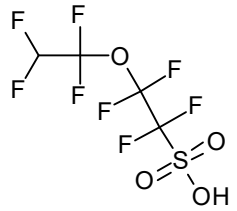
Nafion BP1
CAS 29311-67-9



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	✓	✓	✓	✓	✓	×	×	×

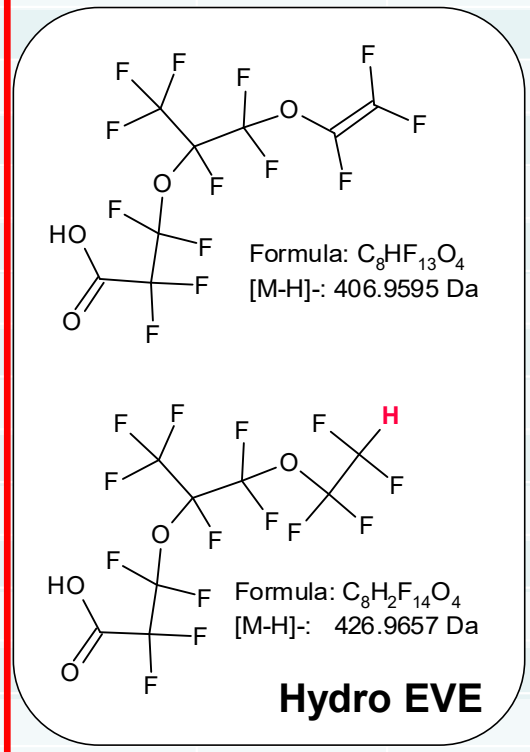


Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

NVHOS

Retrospective Analysis (McCord *in prep*)

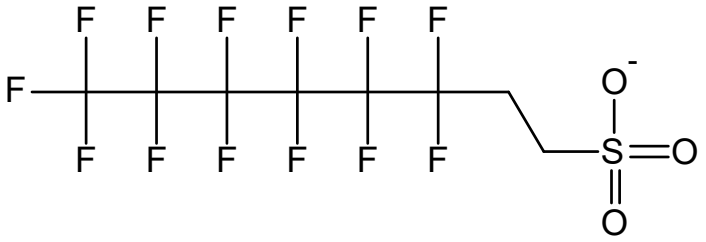
Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	×	×	×
	1-26-12	✓	×	×	✓	✓	×	×	×
2012	2-1-12	✓	×	×	✓	✓			
	2-9-12	✓	✓	✓	✓	✓			
	5-4-12	✓	×	×	✓	×			
	5-4-12	✓	×	×	×	✓			
2014	11-24-14	✓	×	×	✓	×			
2015	5-12-15	✓	✓	✓	✓	✓			
	5-12-15	✓	✓	✓	×	✓			
	8-6-15	✓	✓	✓	×	✓			
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	✓	✓	✓	✓	✓	×	×	×



EIC Confusion

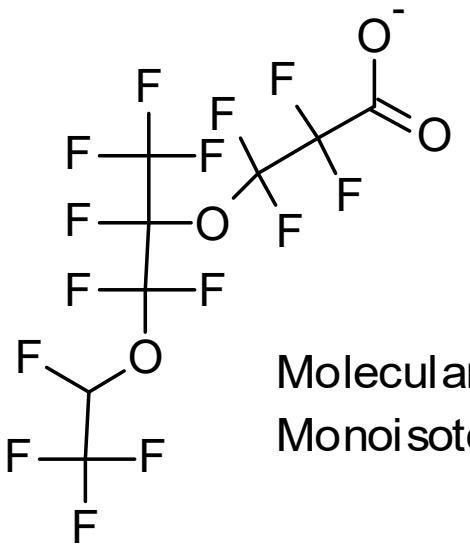
Small ppm difference

426.9679-426.9657/426.9679 *
1000000 = +/- 5.15 ppm



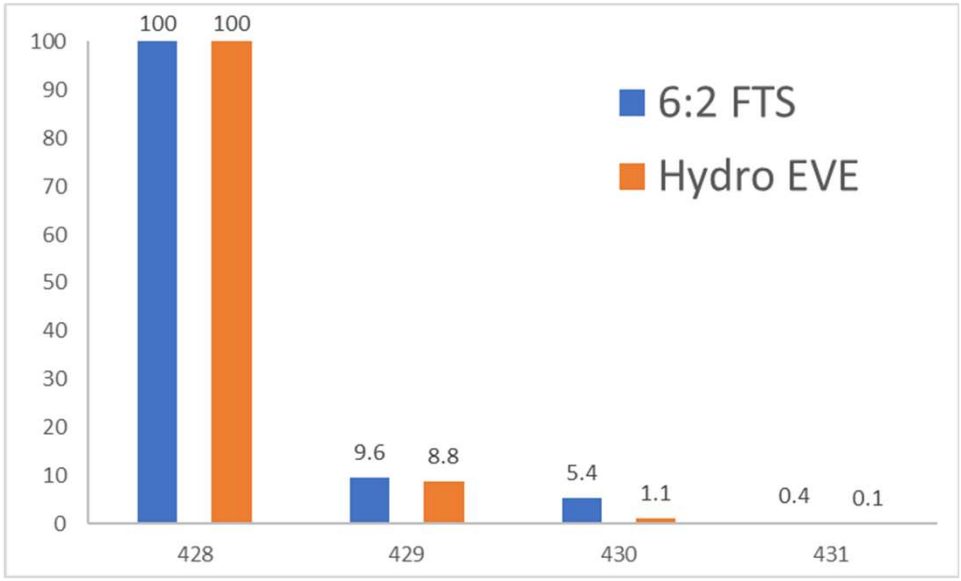
6:2 FTS

Molecular Formula: $C_8H_4F_{13}O_3S^-$
Monoisotopic Mass: 426.9679 Da



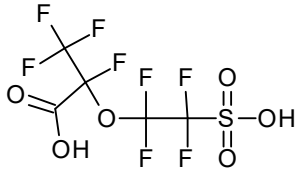
Hydro EVE

Molecular Formula: $C_8HF_{14}O_4^-$
Monoisotopic Mass: 426.9657 Da



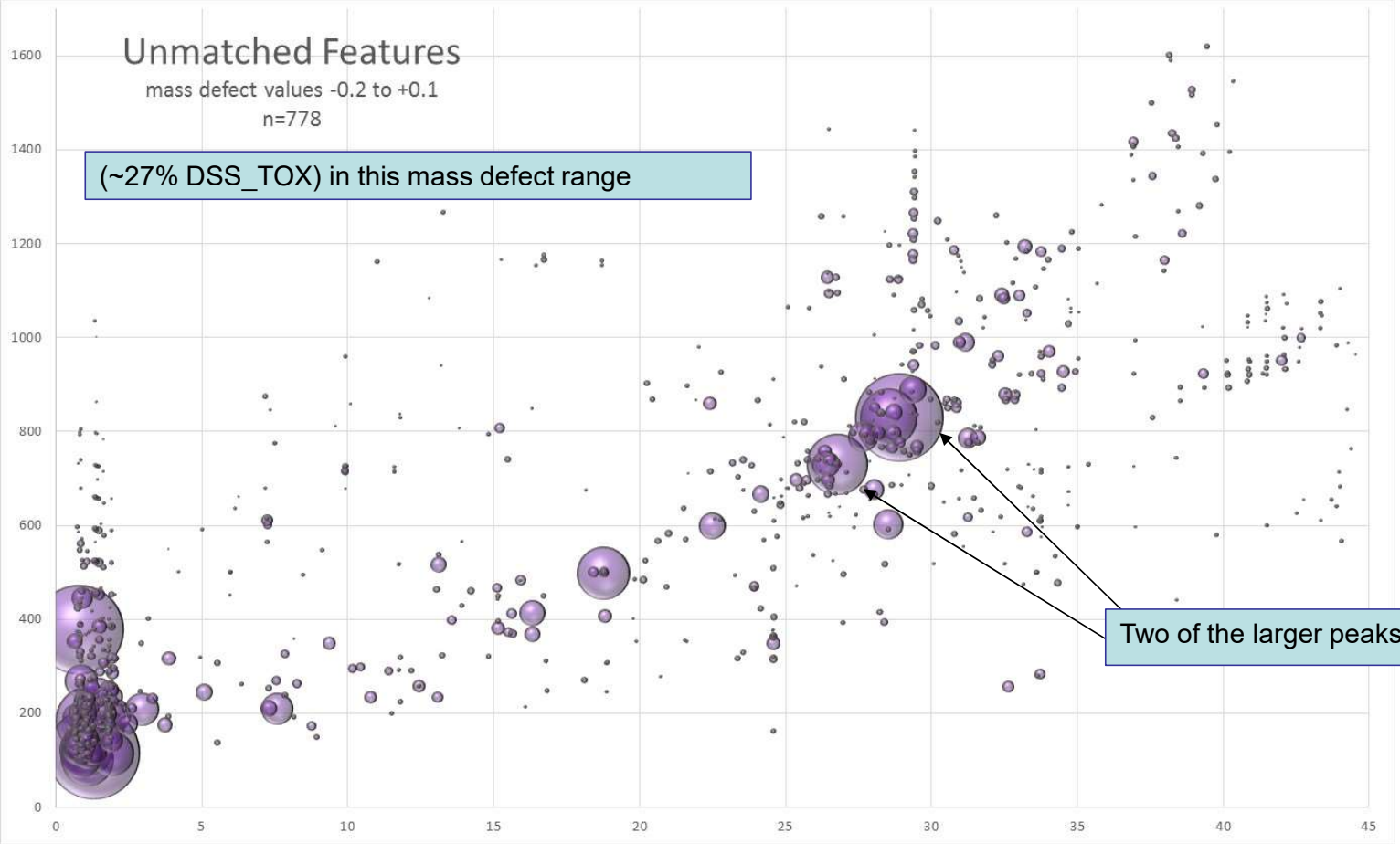
Retrospective Analysis (McCord *in prep*)

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	✓	✓	✓	✓	✓	×	×	×

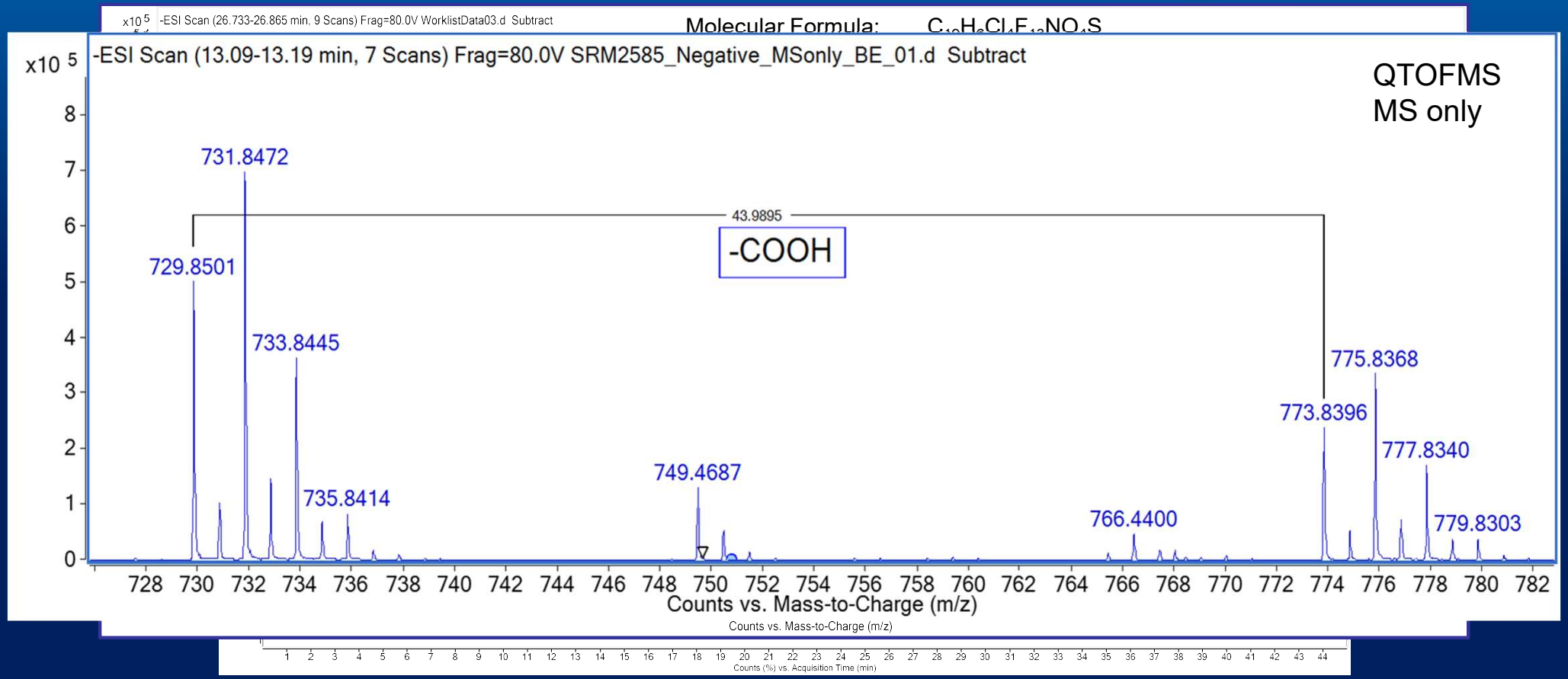


Formula: $C_5H_2F_8O_6S$
[M-H]-: 340.9372 Da

NIST SRM 2585 Organic Compounds in Hose Dust

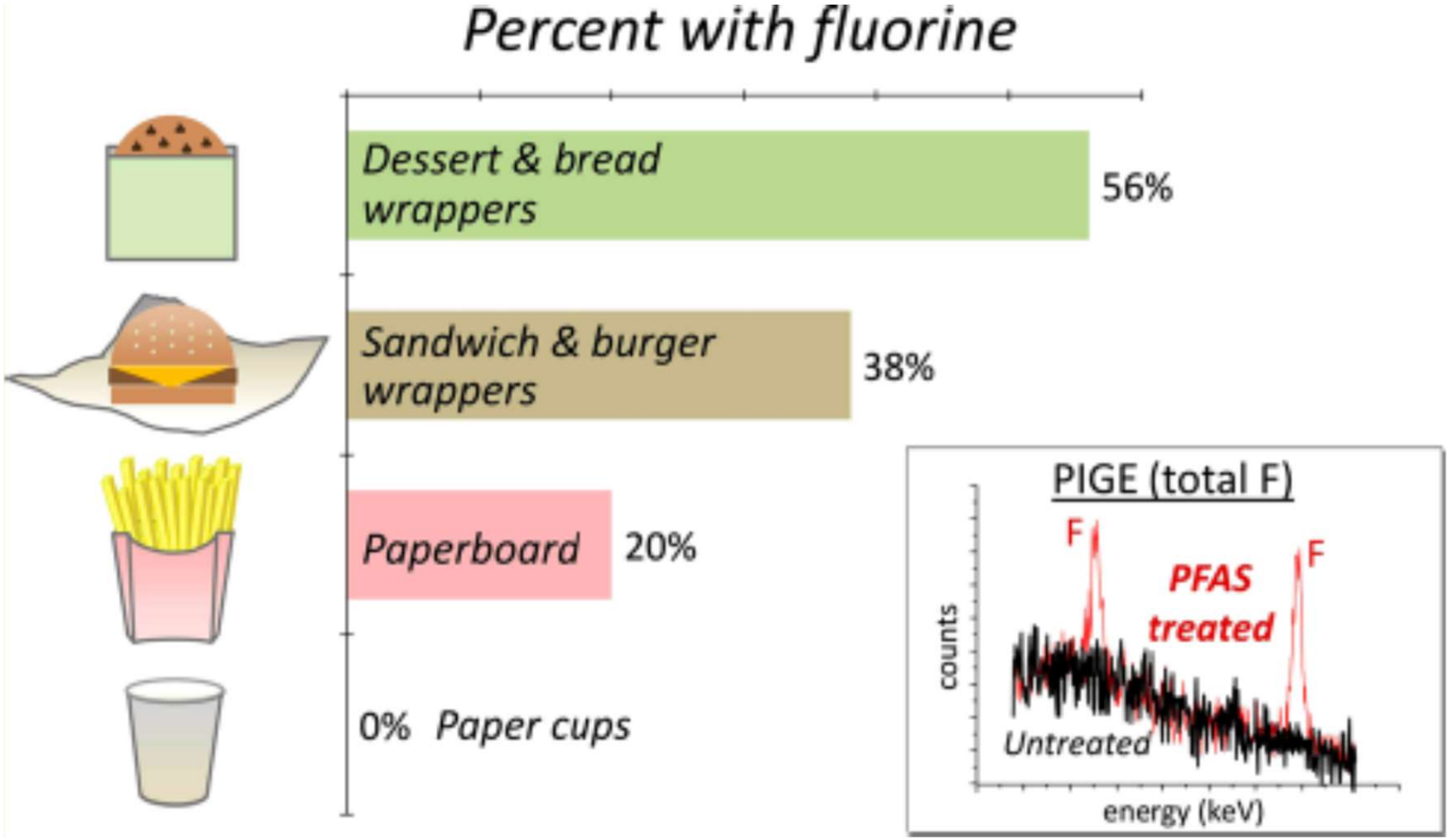


Chromatogram and Spectral Evidence

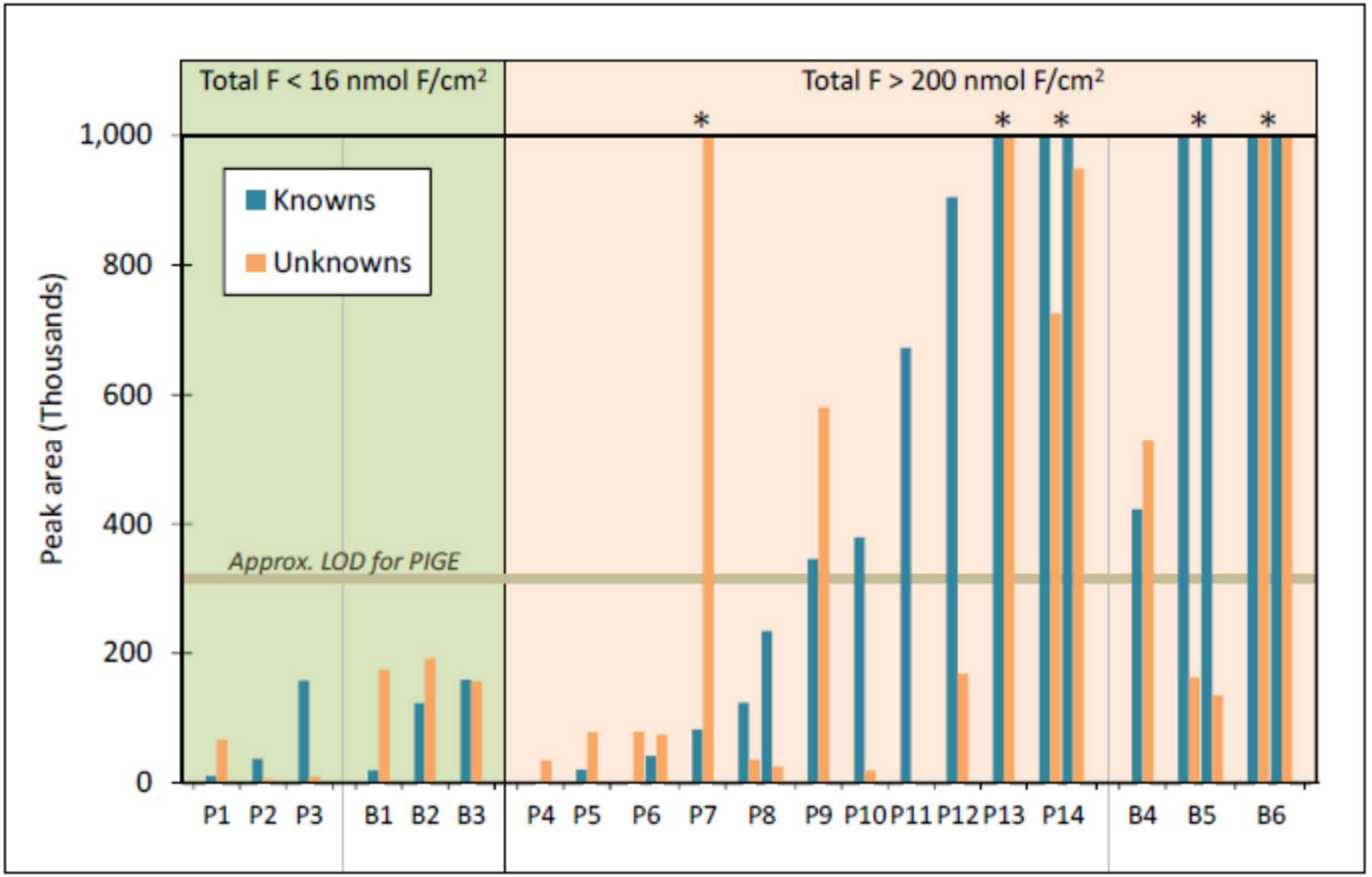


Fluorinated Compounds in U.S. Fast Food Packaging

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[@]



PIGE vs. HRMS


Total F < 16 nmol F/cm²
Total F > 200 nmol F/cm²
Knowns
Unknowns
Approx. LOD for PIGE
Peak area (Thousands)
1,000
800
600
400
200
0
P1 P2 P3 B1 B2 B3 P4 P5 P6 P7 P8 P9 P10 P11 P12 P13 P14 B4 B5 B6

NIH Exploratory/Developmental Research Grant (R21): Hoppin/Knappe

Assessing impact of drinking water exposure to GenX (hexafluoropropylene oxide dimer acid) in the Cape Fear River Basin, North Carolina

Aim 1) Community engagement and interaction to ensure community needs are addressed throughout the study.

Aim 2) Characterize human exposure to GenX in the lower Cape Fear Region through the collection and storage of biological specimens (blood and urine) and drinking water for individuals who consume water from the Cape Fear River.

Aim 3) Perform clinical chemistry tests in blood. Using the blood samples collected, we will analyze lipid profiles, thyroid hormone, and a metabolic panel to detect differences in liver enzymes.

ORDNERL/PHCB serum method

- 50 uL of serum (n=450)
- 100 uL 0.1 M formic acid
- 450 uL acetonitrile crash
- Vortex mix, centrifguge
- Prep 50:50 ACN:buffer
- 25 uL injection analysis
  via Orbitrap Fusion

Method Performance

CHEMICAL	Keller et al., 2010 SRM 1957 (ng/g)	Mean (ng/mL)	SD (ng/mL)
PFHpA	0.305 ± 0.036	0.31	0.10
PFHxS	4.00 ± 0.75	4.22	0.30
PFOA	5.00 ± 0.40	5.25	0.51
PFNA	0.880 ± 0.068	0.90	0.09
PFOS	21.1 ± 1.2	24.1	1.80
PFDA	0.39 ± 0.10	0.18	0.01

Suite of Analytes
-(PFAC MXA) from Wellington
-all PFESAs/PFECAs in Cape Fear River

Acknowledgements:

- ORD/NERL
  - Andy Lindstrom
  - Seth Newton
  - James McCord
  - Johnsie Lang
  - 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
  - Jane Hoppin
- 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

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.