Per-and Poly-fluorinated Compounds Analysis Case Study: Cape Fear Drainage Basin

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LAB TECHNOLOGY DAY 2018
THURSDAY – MAY 3, 2018
MCKIMMON CENTER - RALEIGH

ED_005565_00007681-00001

Elevated levels of unregulated chemicals found in Jordan Lake, Cary drinking water

Posted December 21, 2017

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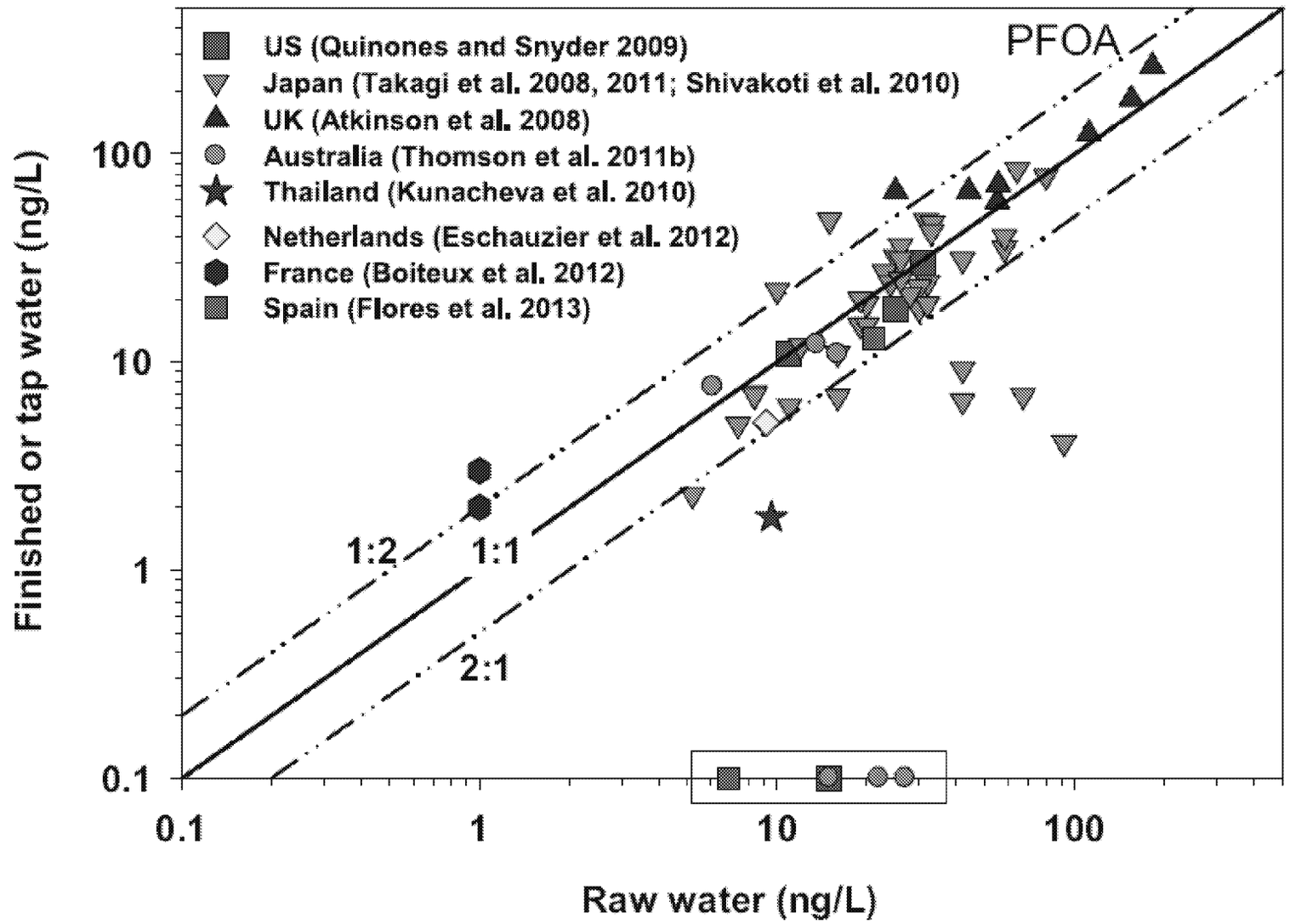
By Tyler Dukes

Recommended Discussed
DRAUGHON DRAWS: Editorial
MAGNET ELEMENTARY
WAKE COUNTY
Looking for something?

PFAS Generally Not Removed During Conventional Drinking Water Treatment



Similar for PFOS, PFHxA and PFHxS

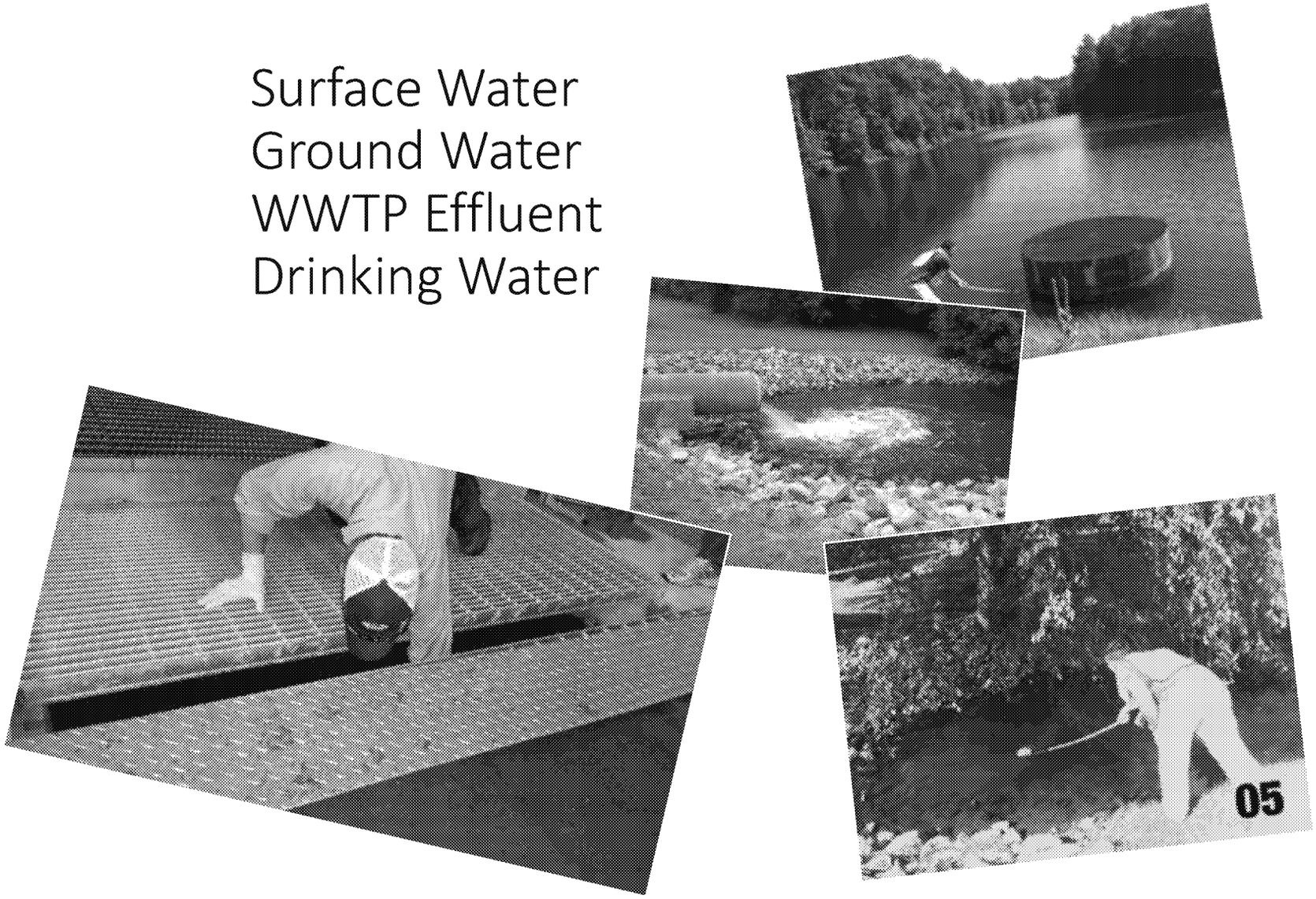
Rahman et al., (2014) *Water Research,* 50:318-340

Timeline: US EPA/NERL Water PFAS Efforts

- 2007 Nakayama et al., PFAS in Cape Fear Watershed
- 2007-2008 Decatur, AL discovery of PFAS in bio-solids, soil, surface water, groundwater
- 2009 (January) Provisional Health Advisory (PHA) for PFOA and PFOS established 400 and 200 ng/L
- 2011-2012 Sampling of Cape Fear River for determination of replacement chemistries
- 2012 (November) Presentation at SETAC Long Beach CA – Identification of novel polyfluorinated compounds in natural waters using accurate mass TOFMS (GenX)
- 2013-2014 Collaborative study with NCSU with sampling of Cape Fear River and three municipalities (Pittsboro, Fayetteville, Wilmington, NC) for legacy and PFECA determination
- 2014 (November) Presentation at SETAC Vancouver, BC - Determination of perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in North Carolina surface water using high resolution mass spectrometry (GenX and eleven other novel chemicals)
- 2015 (August) Publication of Strynar et al., *"Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)"* ES&T
- 2016 (May) OW Health Advisory for PFOS and PFOA set at 70 ng/L
- 2016 (November) Publication of Sun et al., *"Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina" ES&T Letters*
- 2017 (June) Reporting of PFECAs in CFR and Wilmington drinking water – Star News Online

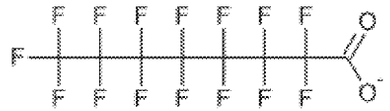
NERL/EMMD Water Analysis Method

Surface Water
Ground Water
WWTP Effluent
Drinking Water

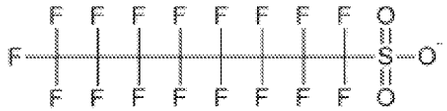


Also methods for:
Soil
Fish tissue
Dosed rodent tissue/fluids
Human Serum/Urine
House Dust

Some Typical PFAS



Perfluorocarboxylic acids
(ex. PFOA)

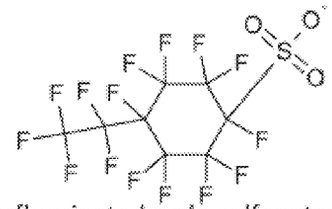


Perfluorosulfonic acids
(ex. PFOS)

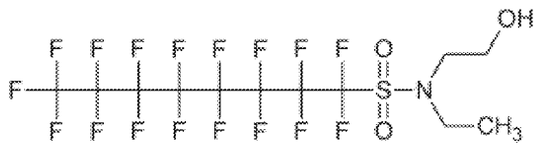
Fluorotelomer alcohol
(ex. 8:2 FTOH)

Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPi)

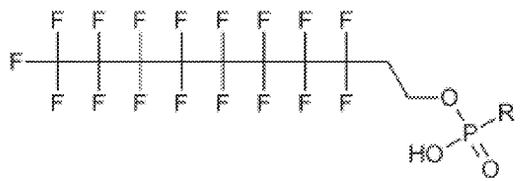
Perfluorosulfonamide
(ex. FOSA)



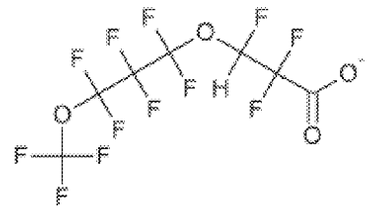
Perfluorinated cyclo sulfonates
(ex. PFECHS)



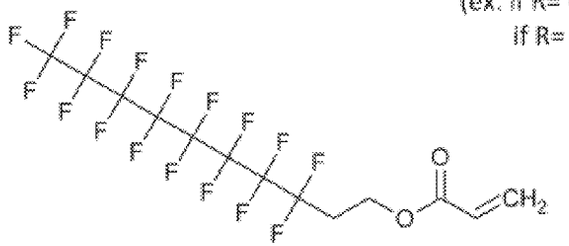
Perfluorosulfonamidoethanol
(ex. N-EtFOSE)



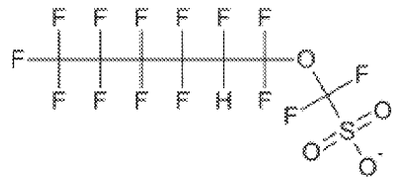
Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated ether carboxylates
(ex. 4,8-dioxa-3H-perfluorononanoate)



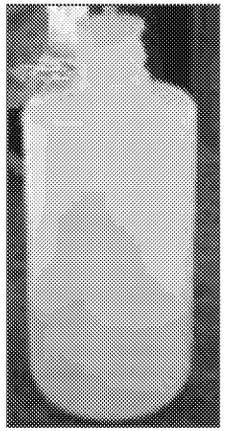
Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)



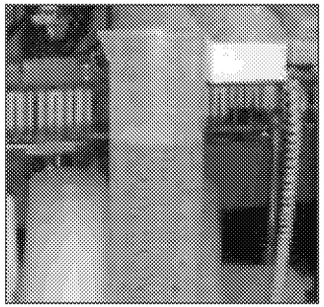
Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

Method Summary – Sample Processing

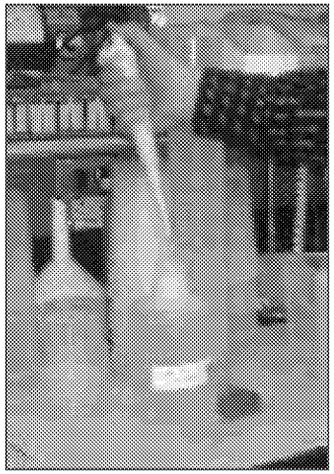
Nakayama et al., 2009, Strynar et al., 2015; Sun et al., 2016, Newton et al., 2017



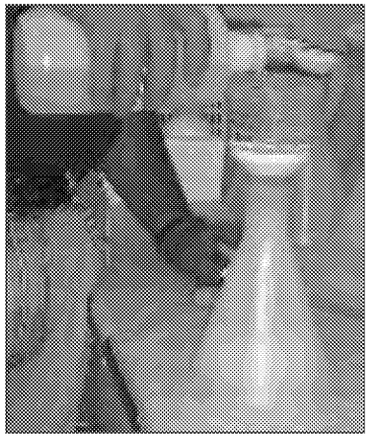
1 L HDPE bottles
5 mL 1:1 HNO_3 (35%):DI
Shipped ambient



Pour water out of sample bottle for volume measurement



Wash bottle with 10 mL MeOH, add water back to bottle, add IS Shake



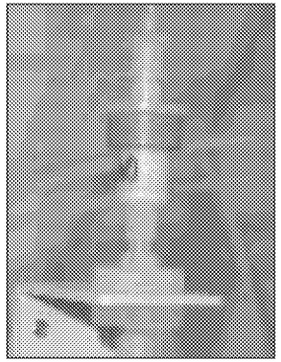
Filter entire contents
Whatman GF/A 1.7 um

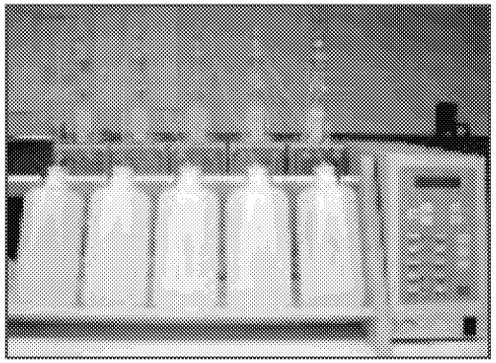
All samples Treated same way

- Trip Spike
- Blanks
- Unknowns
- Calibration

Add filtered water back into original bottle

Subsample 500 mL
Store 500 mL

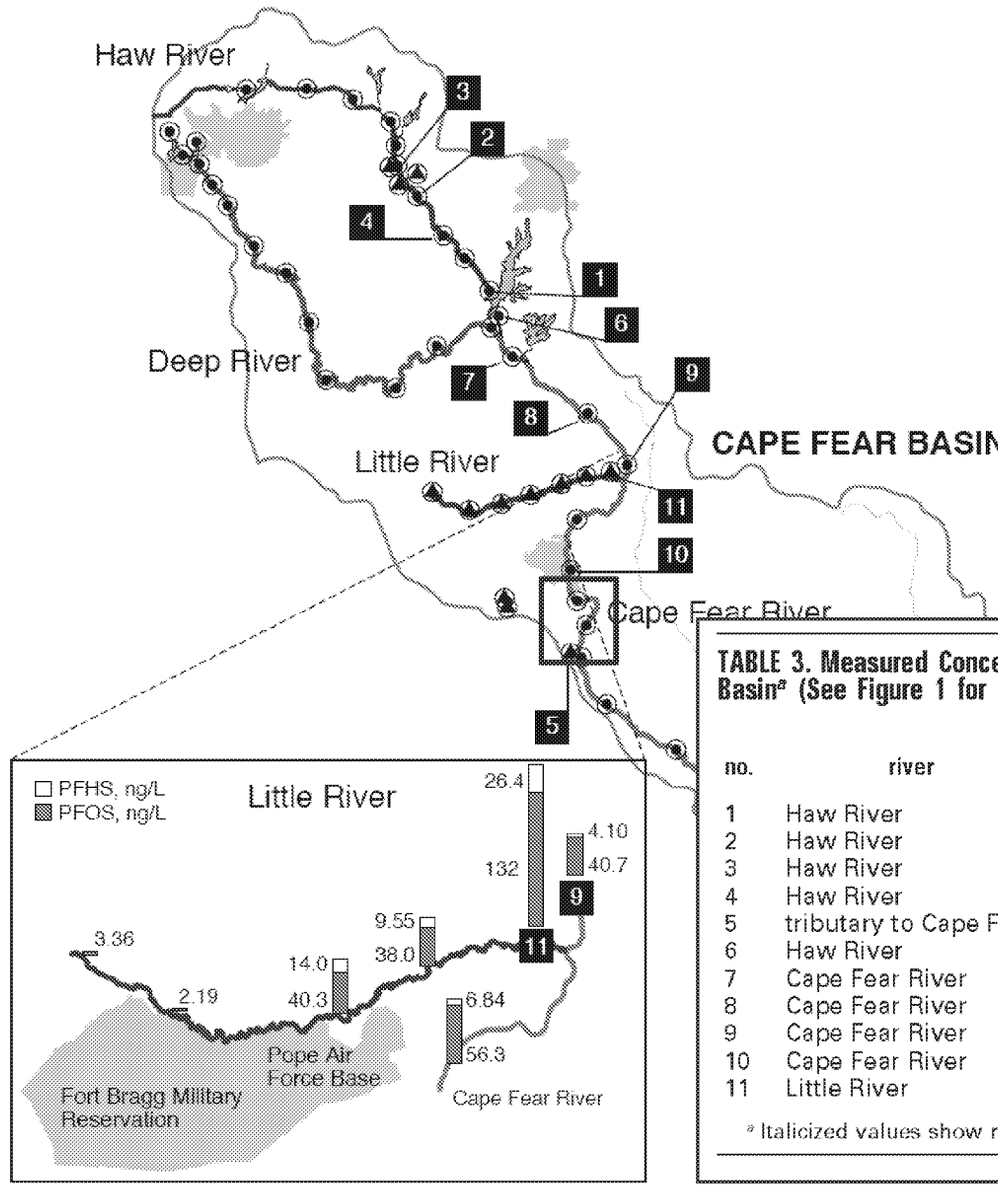




Load onto SPE tube
Waters Plus style WAX

Elute for LC/MS-MS analysis

Water Sampling Cape Fear River, NC
Nakayama et al., 2007



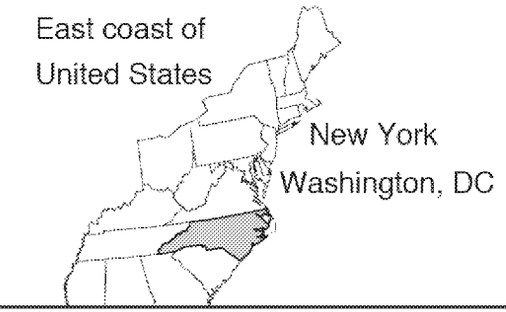


TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin[a] (See Figure 1 for locations)

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.

Fact Sheet: 2010/2015 PFOA Stewardship Program

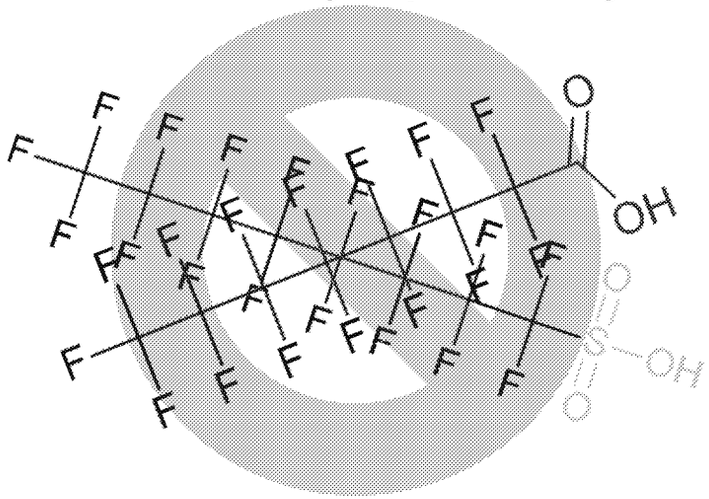
Q1. What is the 2010/2015 PFOA Stewardship Program?
In 2006, EPA invited eight major leading companies in the per- and polyfluoroalkyl substances (PFASs) industry to join in a global stewardship program with two goals:
•To commit to achieve, no later than **2010, a 95 percent reduction,** measured from a year 2000 baseline, in both facility emissions to all media of 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**.

Q4. What companies participated in the PFOA Stewardship Program?
Participating companies included:
•Arkema
•Asahi
•BASF Corporation
•Clariant
•Daikin
•3M/Dyneon
•DuPont
•Solvay Solexis

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

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

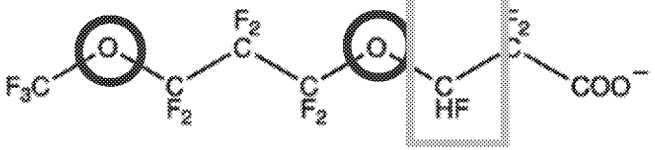
- How do we find compounds without knowing what they are?
- How do we prioritize unknowns for further analysis?
- How do we identify/quantify without analytical standards?



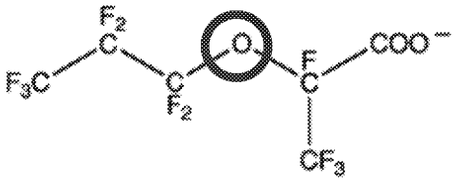
→ ???

Fluoropolymer manufacture

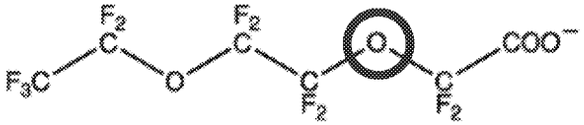
ADONA (CAS No. 958445-44-8)



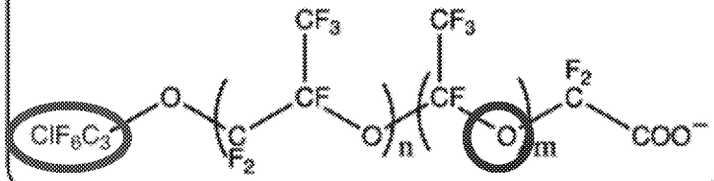
GenX (CAS No. 62037-80-3)



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

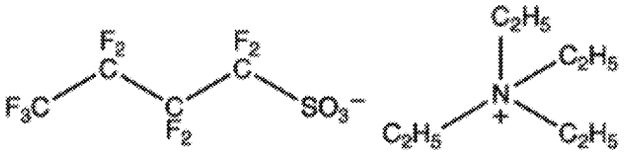


Solvay's product (CAS No. 329238-24-6)

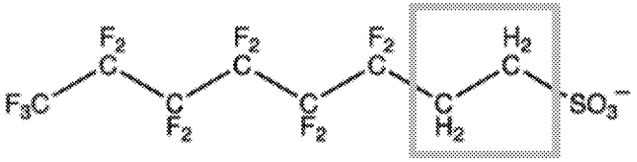


Metal plating

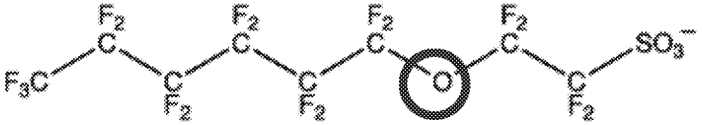
$N(Et)_4$-PFBS (CAS No. 25628-08-4)



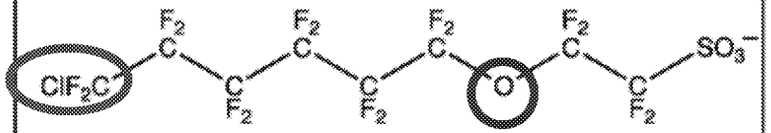
6:2 FTSA (CAS No. 27619-97-2)



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



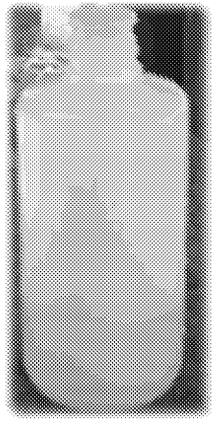
F-53B (CAS No. 73606-19-6)



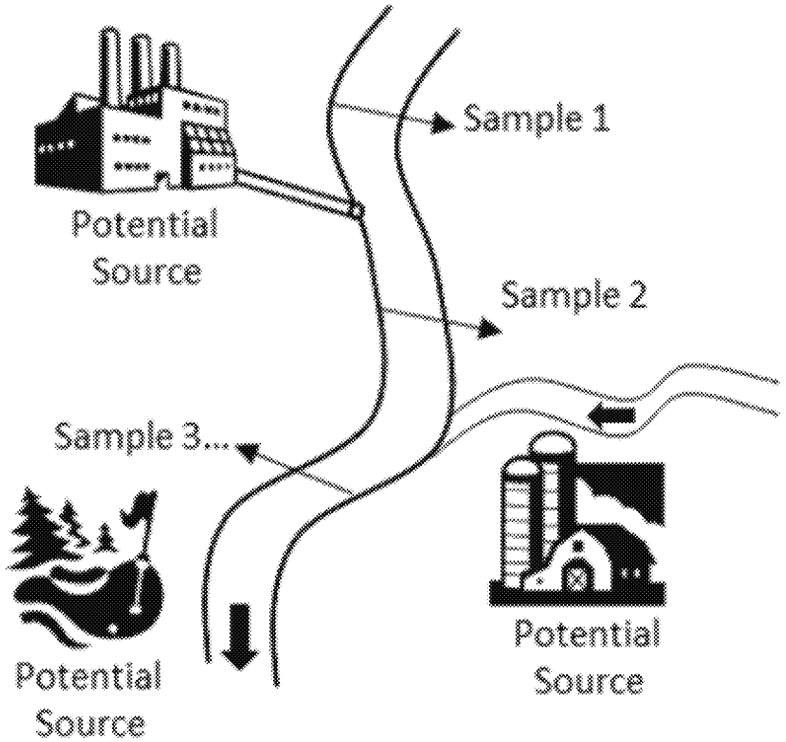
Wang et al. *Environment International*, **2013,** *60,* pp 242–248

Data Generation: Source Determination by NTA

Surface Water
Ground Water
WWTP Effluent
Drinking Water



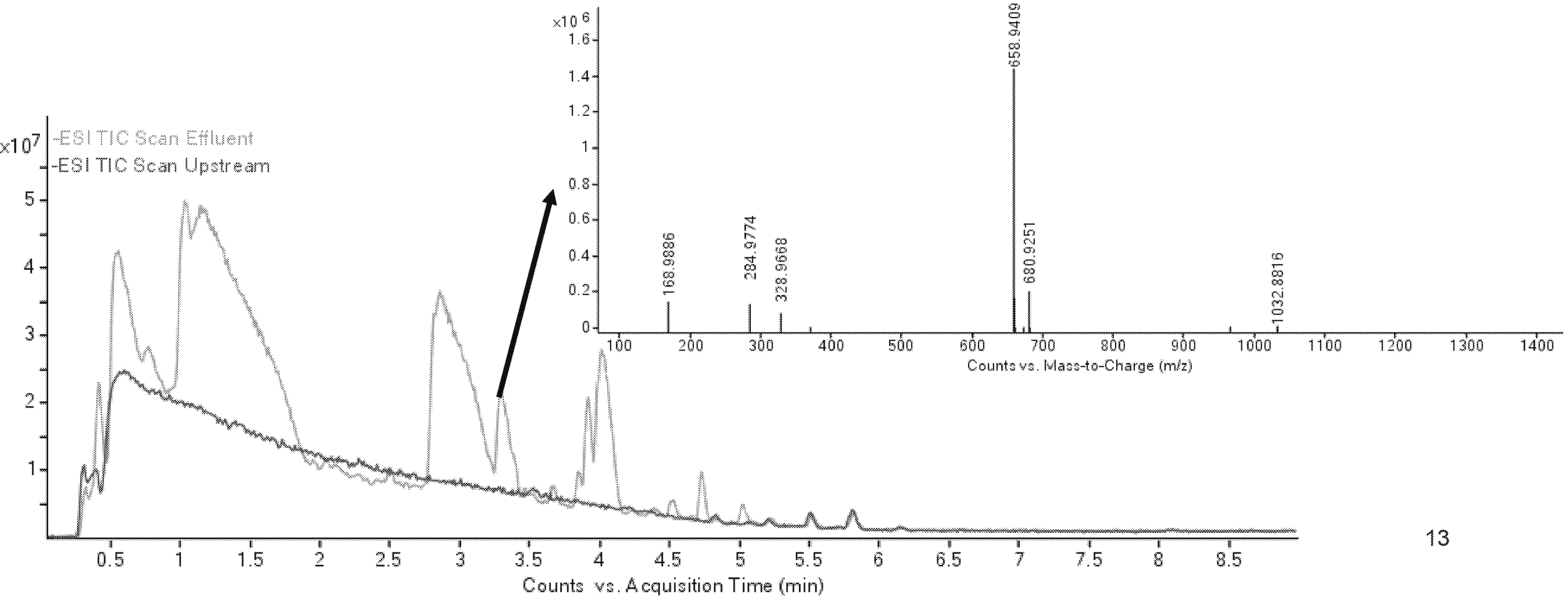
HDPE Bottles



Sampling from geographically or temporally displaced locations allows triangulation of sourcing

Strynar et al. Environ. Sci. Technol., 2015, 49 (19), pp 11622–11630

Chromatographic and MS Data



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

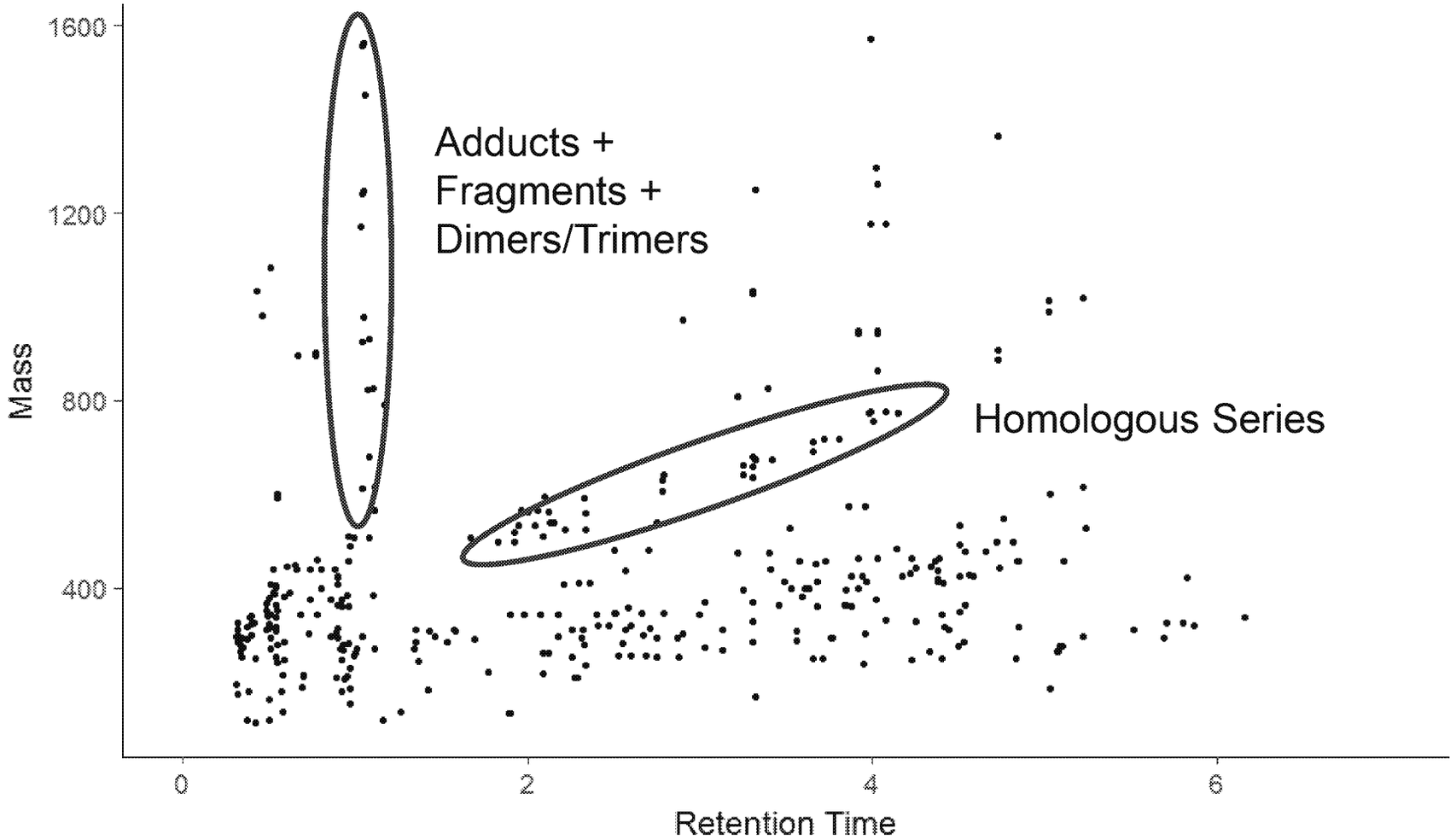
Hundreds of Features of Interest

Useful For:

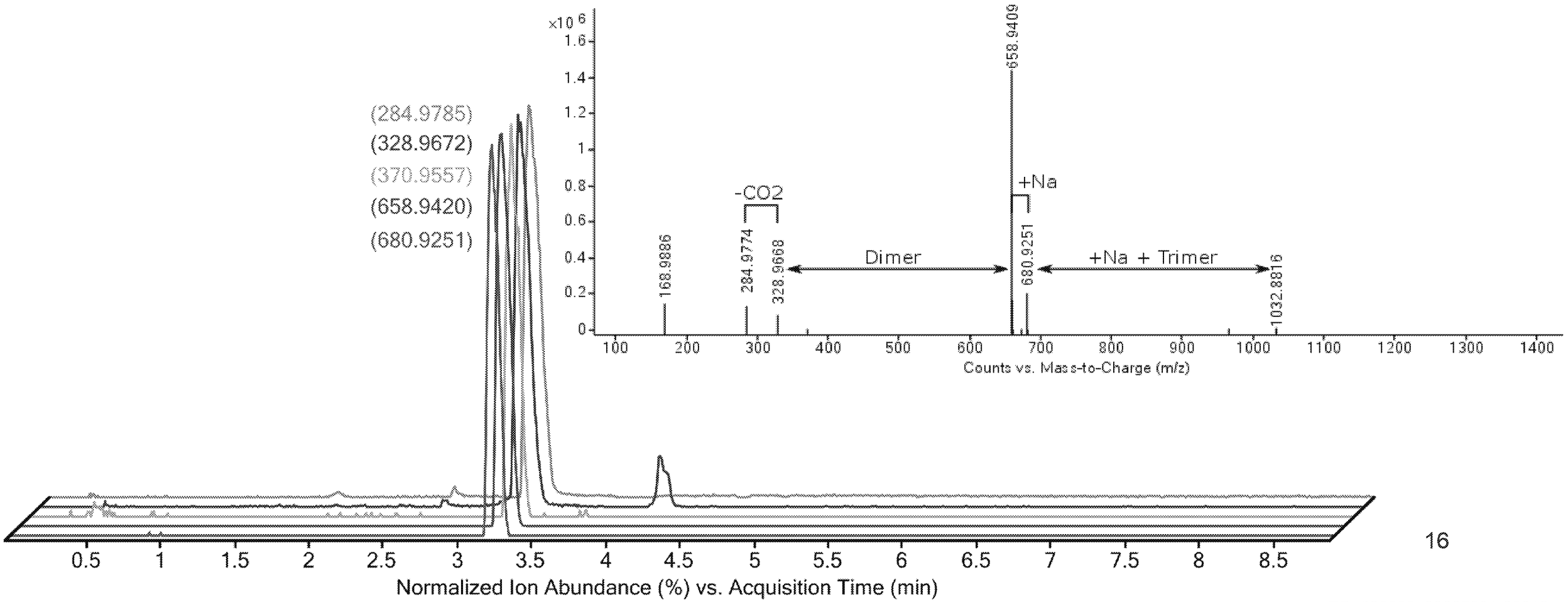
- Identification of increasing/decreasing chemicals
- Features unique to a specific location, time, treatment, etc.

ED_005565_00007681-00014

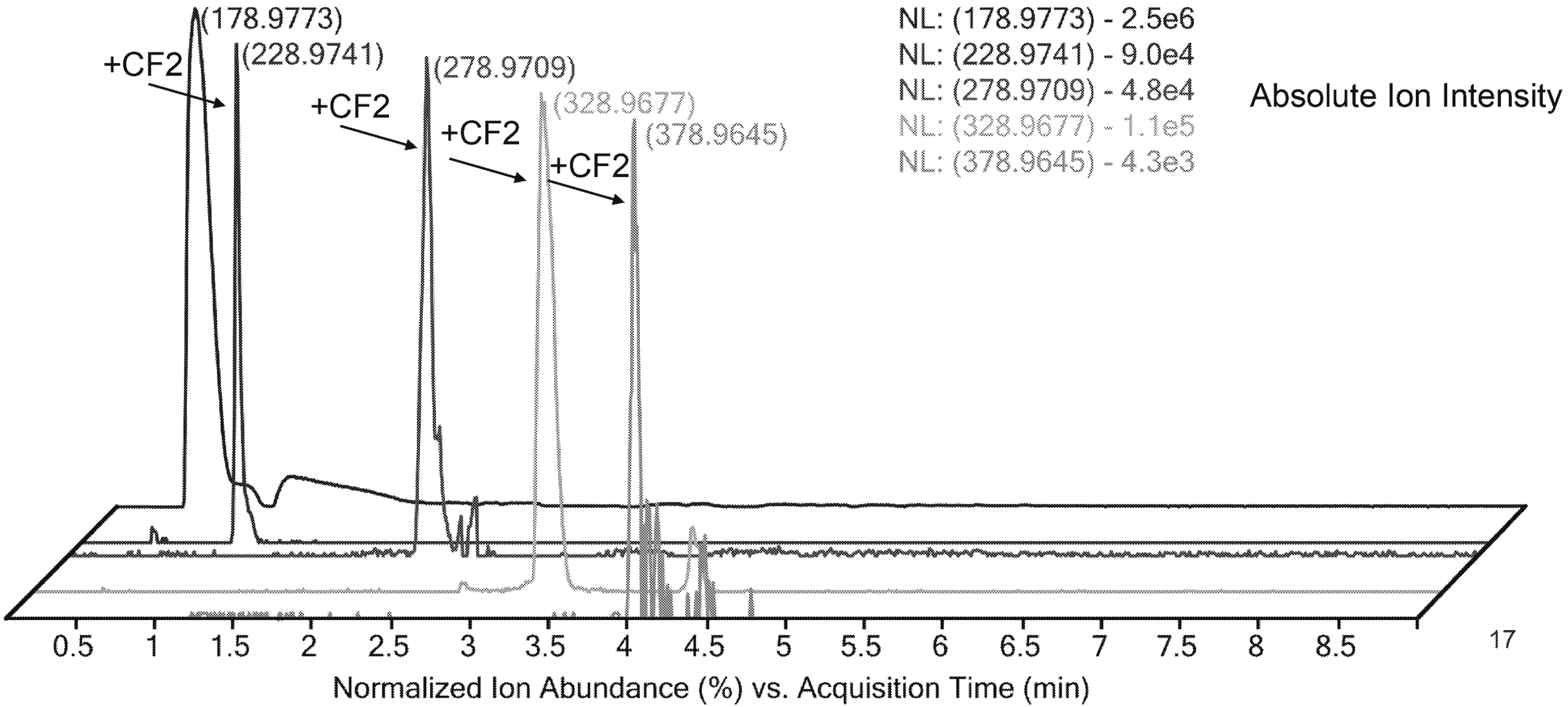
Relationships Reveal Underlying Chemistry



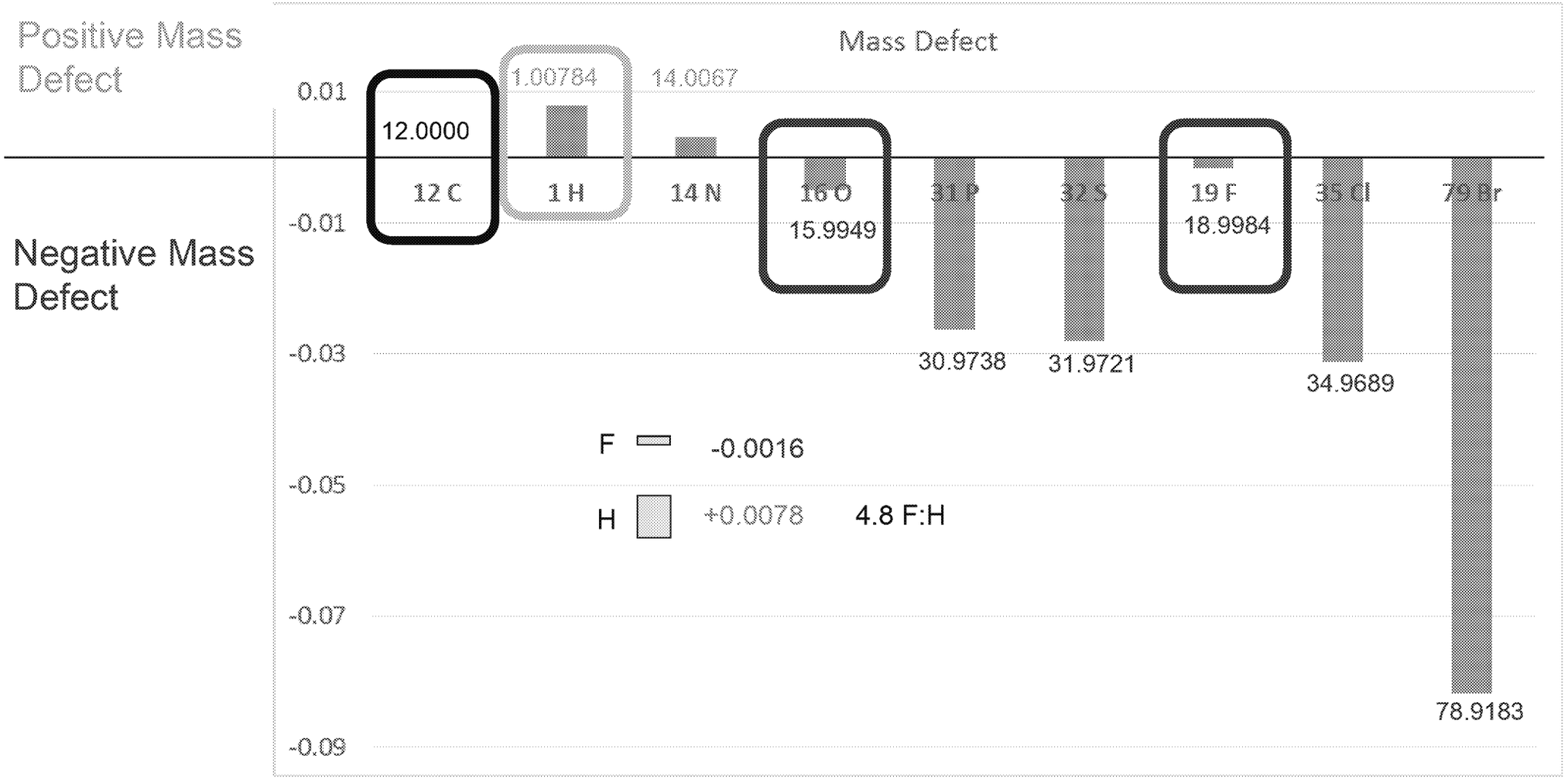
In-Source Related Species



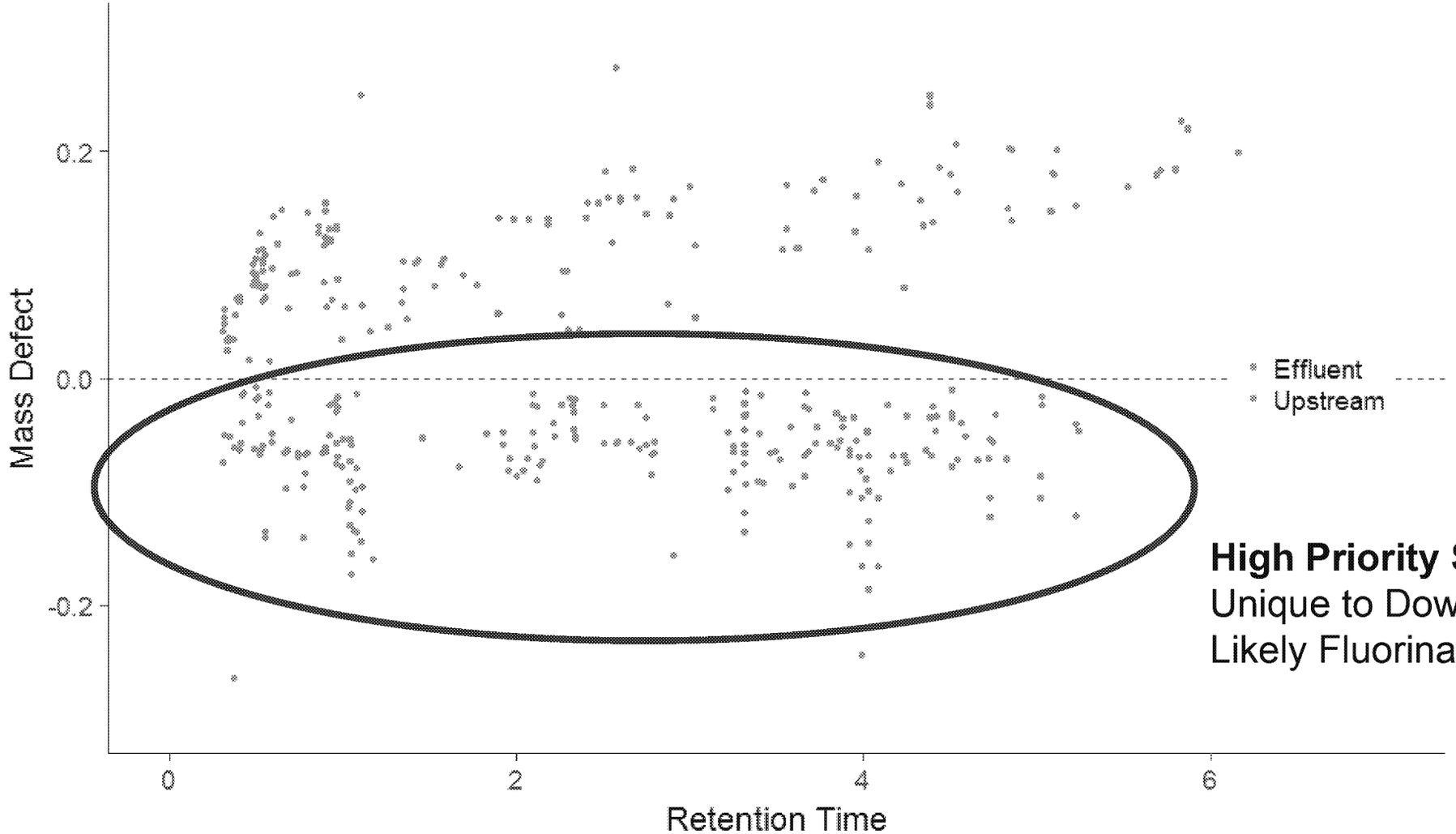
Homologous Series



Isotope Signatures: Negative Mass Defect



Mass Defect of Outfall and Upstream Features



High Priority Species:
Unique to Downstream,
Likely Fluorinated

First Sampling 2011-2012

Presented at SETAC 2012

Follow-up sampling 2013-2013

Presented at SETAC 2014

Water Intake
Current Outfall
Former Outfall
The Chemours Company
Kuraray
US Lock & Dam
William O Huske
Clear Fear River
Map
Google
Imagery ©2017 DigitalGlobe, USDA Farm Service Agency, Map data ©2017 Google
3D Earth view is not available
Terms
Send feedbac

Legacy PFAS found in Cape Fear Water

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

items in red exceed the standard curve high end of 500 ng/L; 10x diluted and re-analyzed; * still exceed curve and are estimated

Environmental Science & Technology

November 2015

Article

pubs.acs.org/est

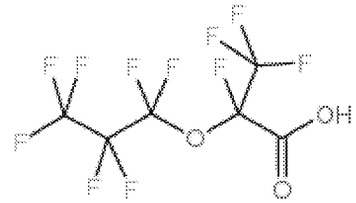
Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

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

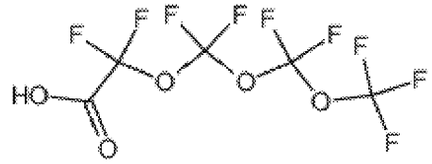
Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

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	$C_7HF_{13}O_5S$	66796-30-3[b]		443.9337	442.9264		
12	$C_7H_2F_{14}O_5S$			463.9399	462.9326		

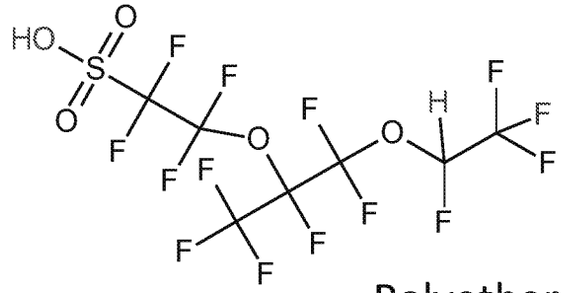
Example Structures



Monoether (6): GenX



polyethers (4):



Polyethers sulfonates (2):

StarNews 150th 1867 • 2017

Toxin taints CFPUA drinking water

MOST POPULAR

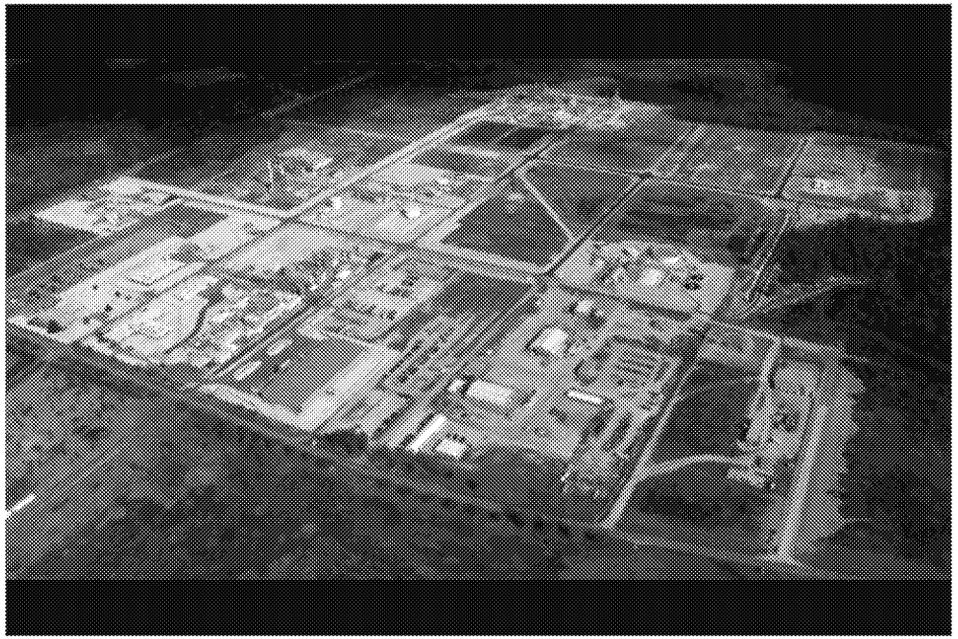
1 Carolina Surf condos - in danger of collapse - condemned, evacuated
Jul 3 at 5:50 AM

2 Man injured by hook, not bit by shark at Wrightsville Beach
Jun 30 at 1:40 PM

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

4 Residents not allowed back into Carolina Surf condos
Jul 4 at 7:30 AM

OUR PICKS

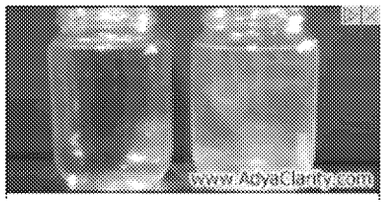


HIDE CAPTION

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 10:05 AM

Utility can't filter out chemical produced upriver



Cape Fear River
Fayetteville to Wilmington, NC

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[‡]

June 7, 2017 story on in Wilmington Star Online News basis

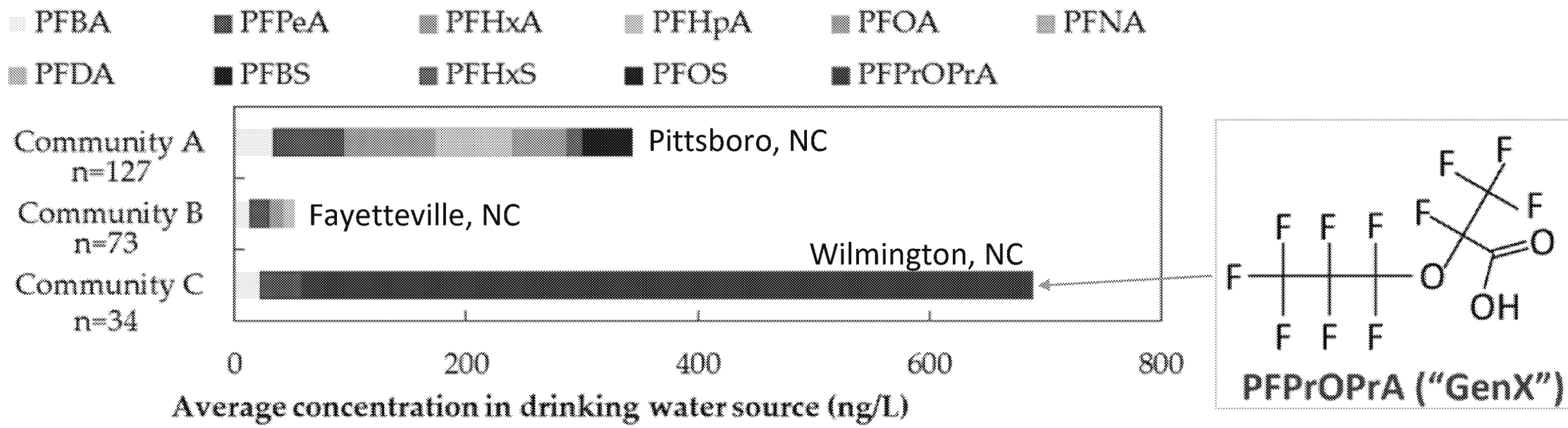
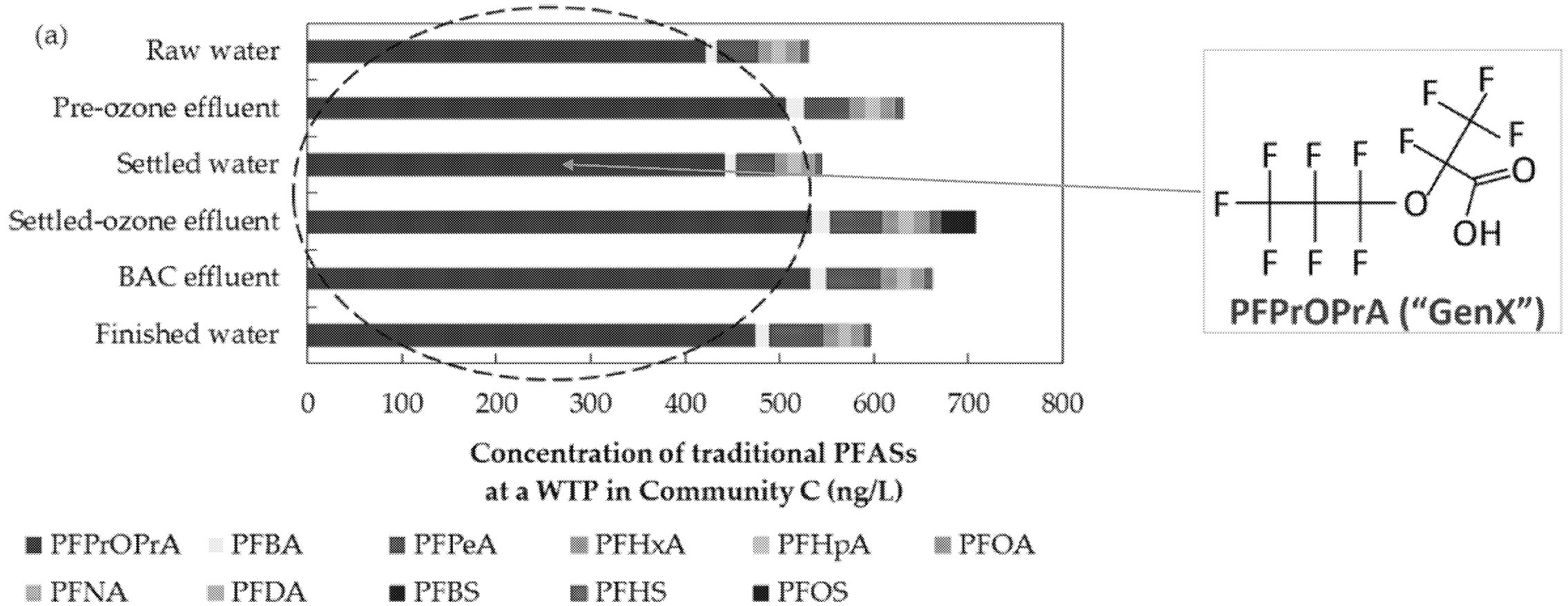


Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

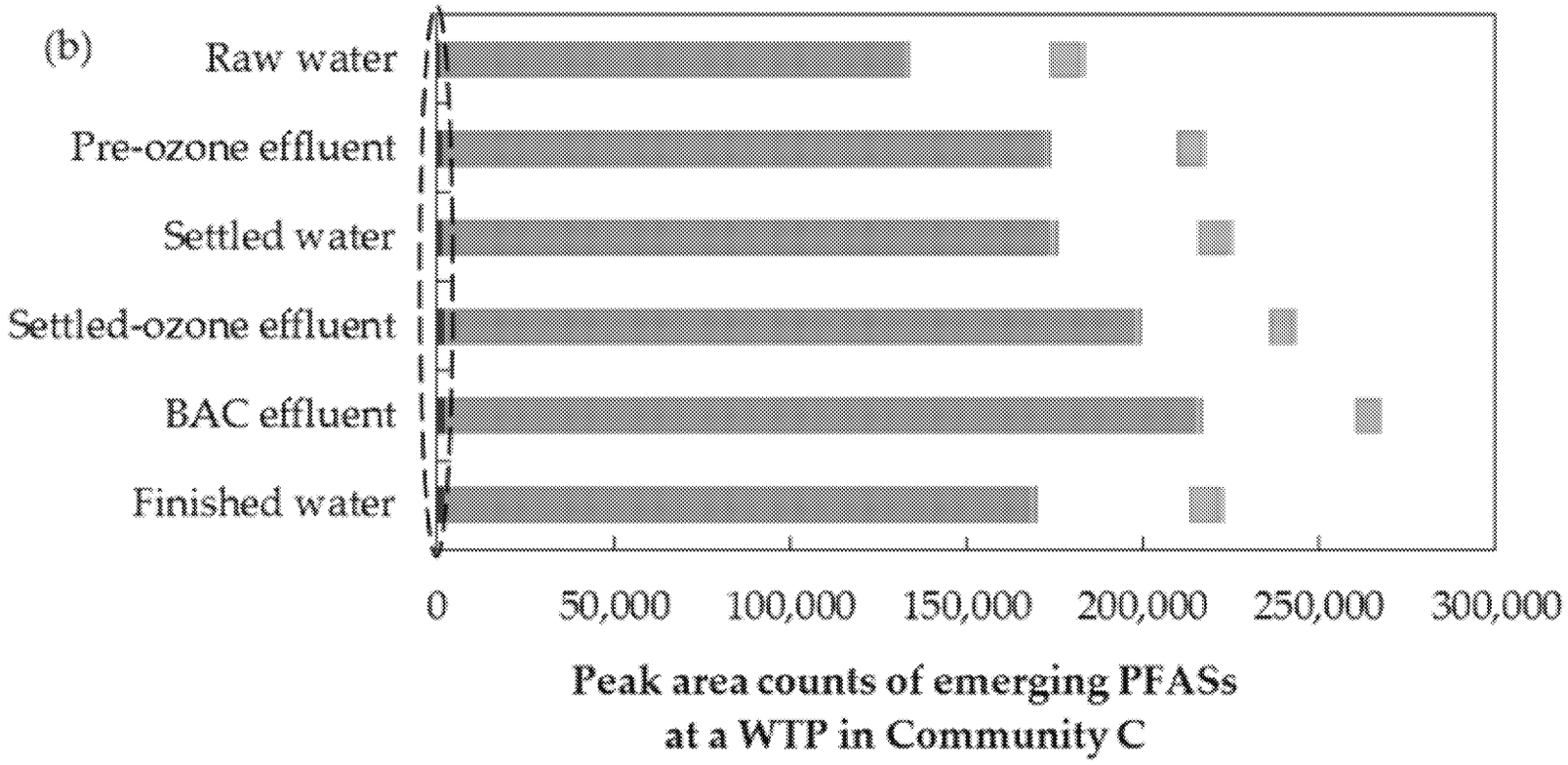
Sun et al., 2017

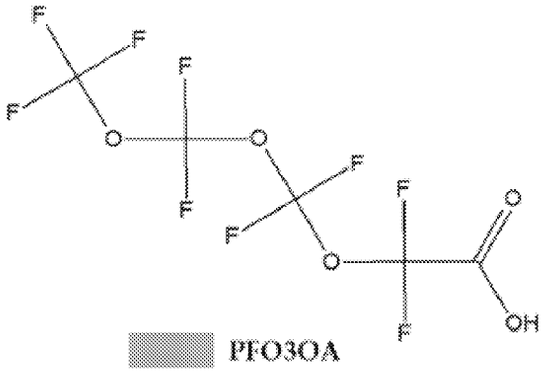
PFAS removal at Sweeney WTP

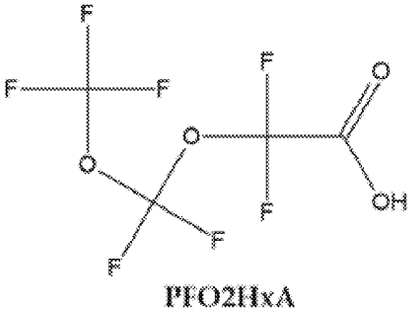


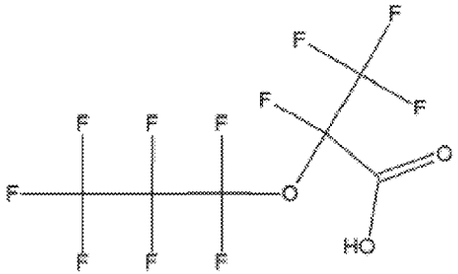
Sun et al., 2017

Other PFECAS Sweeney WTP

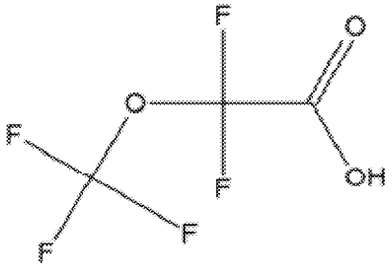








PFPrOPrA (GenX)

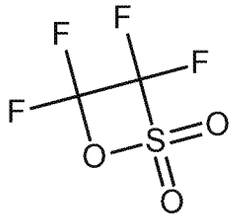


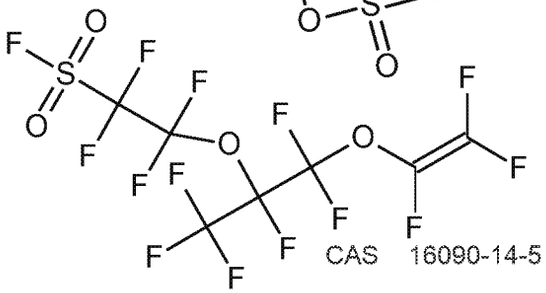
PFMOAA

Chemours Site TSCA Inventory

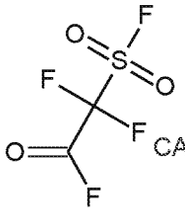
Sulfonyl Fluorides

CAS 697-18-7



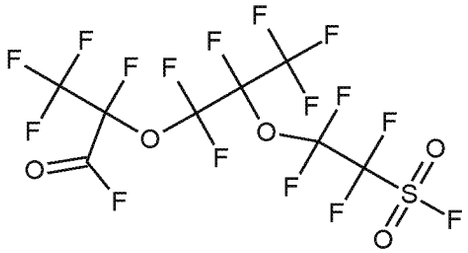


CAS 16090-14-5



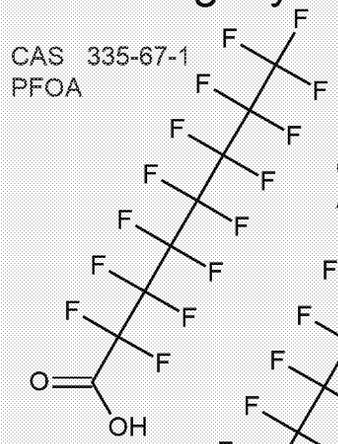
CAS 677-67-8

CAS 4089-58-1

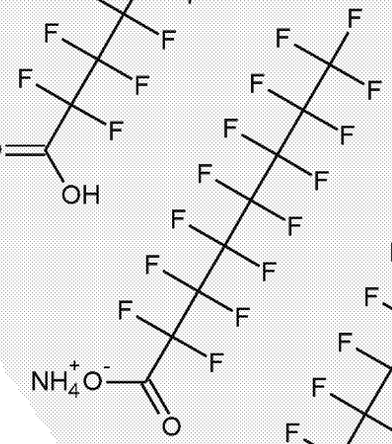


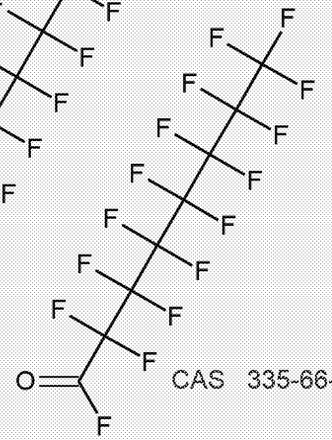
Legacy

CAS 335-67-1
PFOA



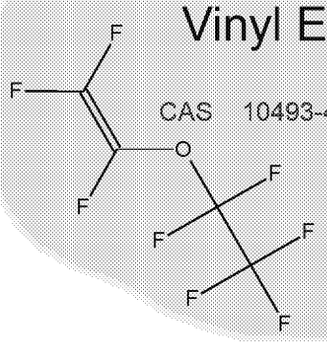
CAS 3825-26-1
APFO





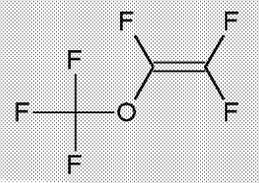
CAS 335-66-0

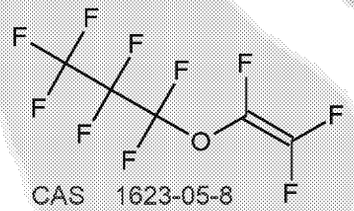
Vinyl Ethers



CAS 10493-43-3

CAS 1187-93-5

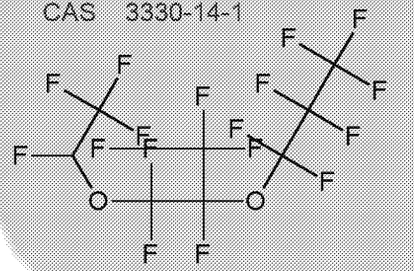




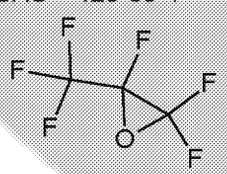
CAS 1623-05-8

Other

CAS 3330-14-1

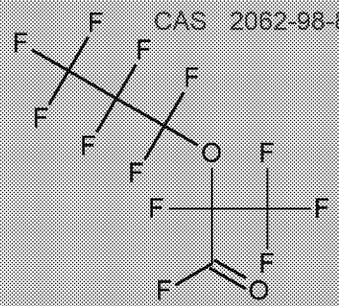


CAS 428-59-1

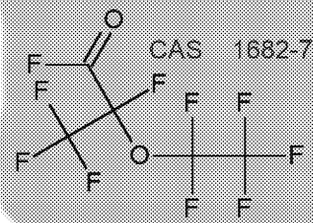


Acid Fluorides

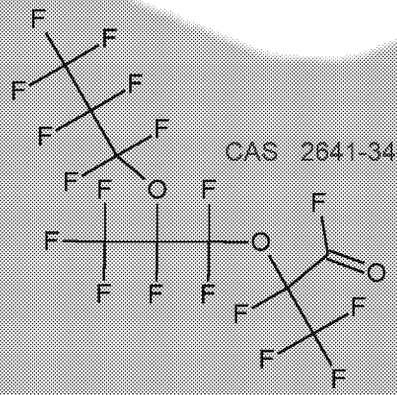
CAS 2062-98-8



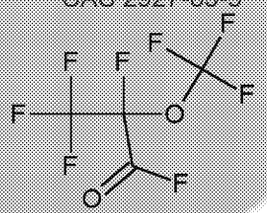
CAS 1682-78-6



CAS 2641-34-1



CAS 2927-83-5

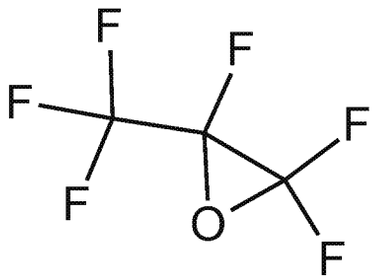


DUPONT FAYETTEVILLE PLANT
22828 NC HIGHWAY 87 WEST
FAYETTEVILLE, NC 28306-7332

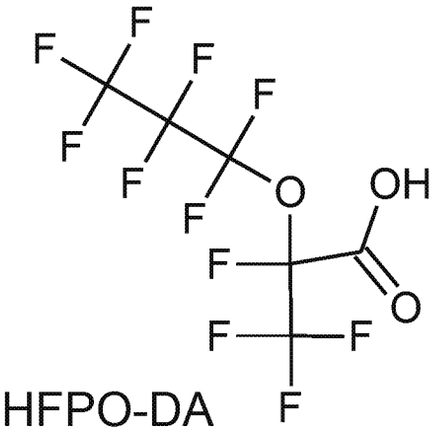
http://iaspub.epa.gov/enviro/tsca.get_chem_info?v_registry_id=110000559609

Hexafluoropropylene Oxide (HFPO)

HFPO
CAS 428-59-1



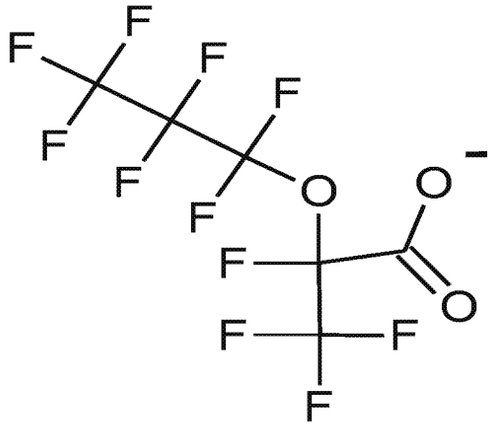
- an intermediate used in industrial organofluorine chemistry
- a monomer for fluoropolymers.
- colourless gas is the epoxide of hexafluoropropylene
- produced by DuPont and 3M and as a precursor to the lubricant Krytox and related materials
- generated by oxidation of perfluoropropylene, e.g. with oxygen as well as other oxidants



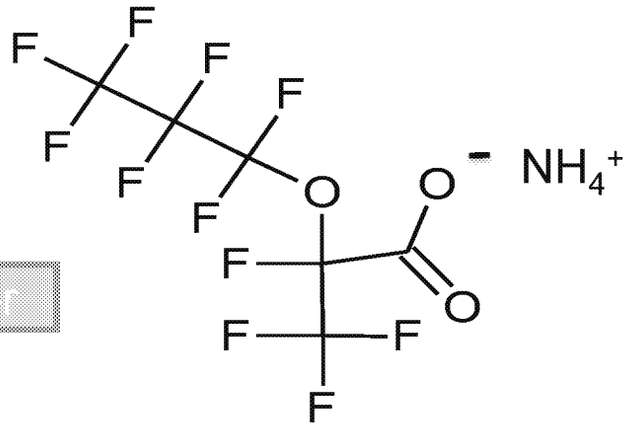
HFPO-DA
CAS 13252-13-6

In Water

Common Analyte



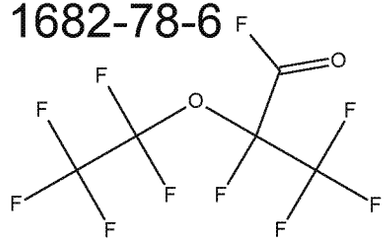
In water



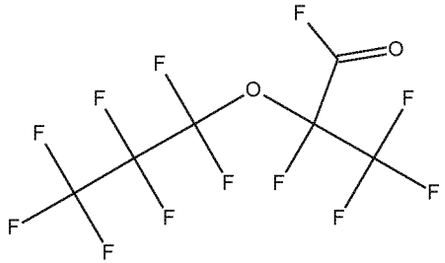
GenX
CAS 62037-80-3

Polyvinyl Ether Production

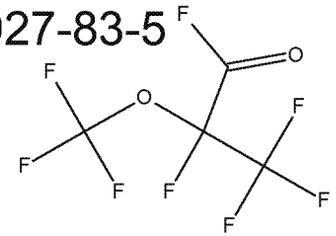
CAS 1682-78-6



CAS 2062-98-8

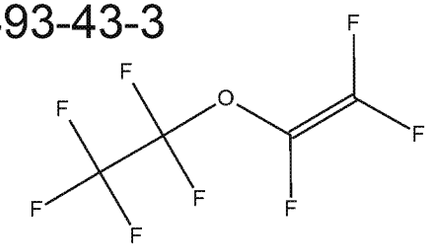


CAS 2927-83-5

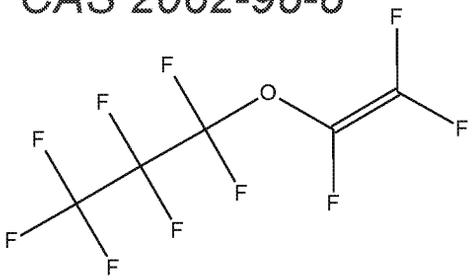


Acid Fluorides

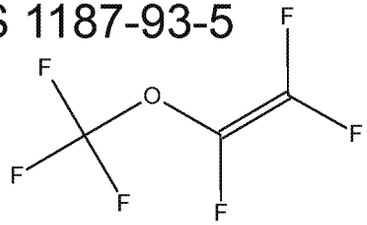
CAS 10493-43-3



CAS 2062-98-8



CAS 1187-93-5

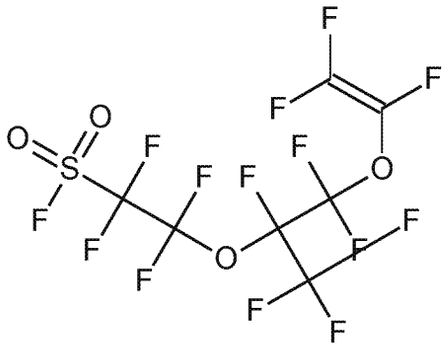


Polyvinyl Ether Intermediates

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



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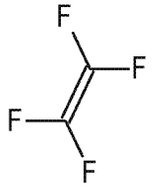
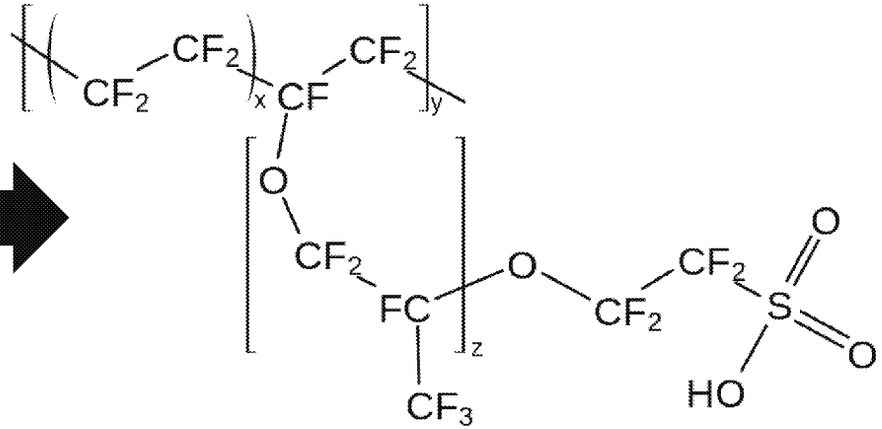


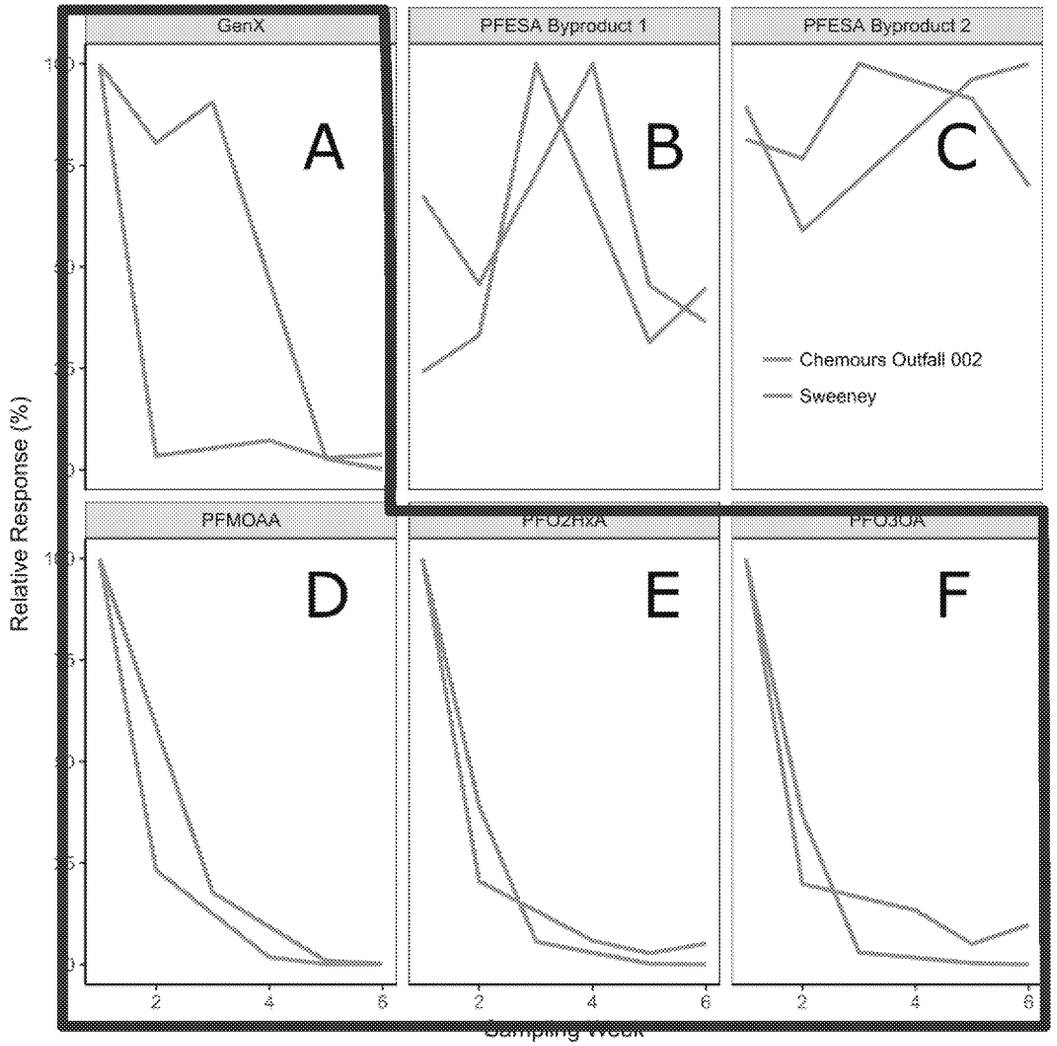
CAS 116-14-3

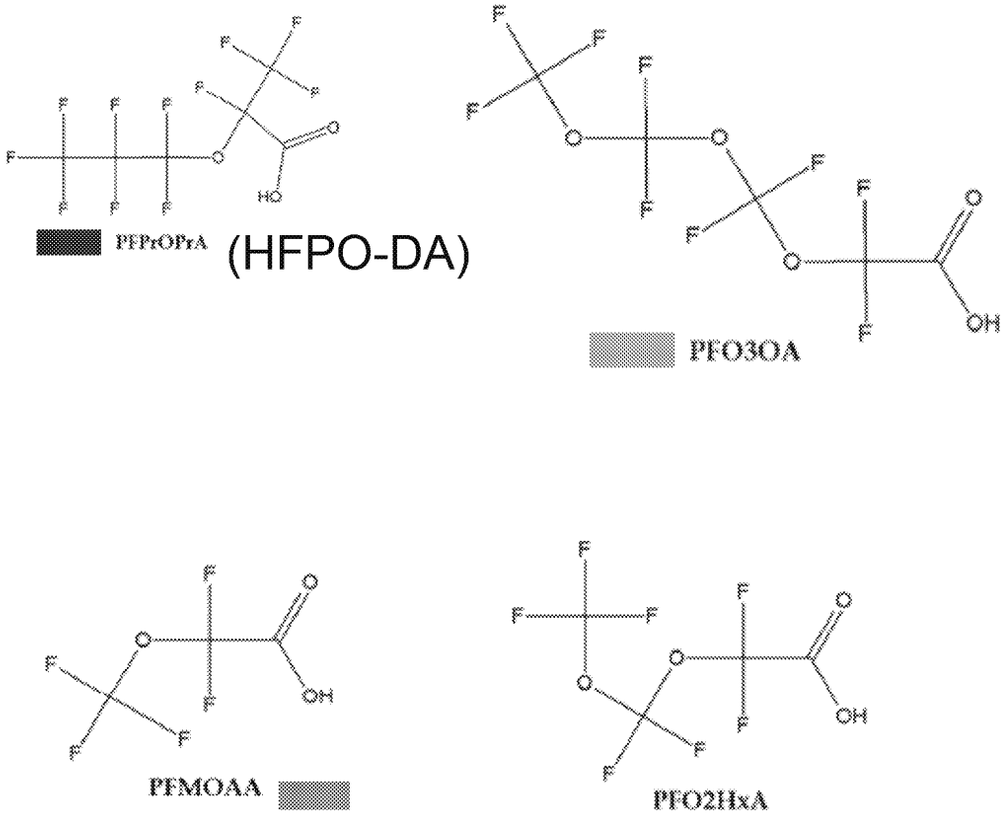


CAS 66796-30-3

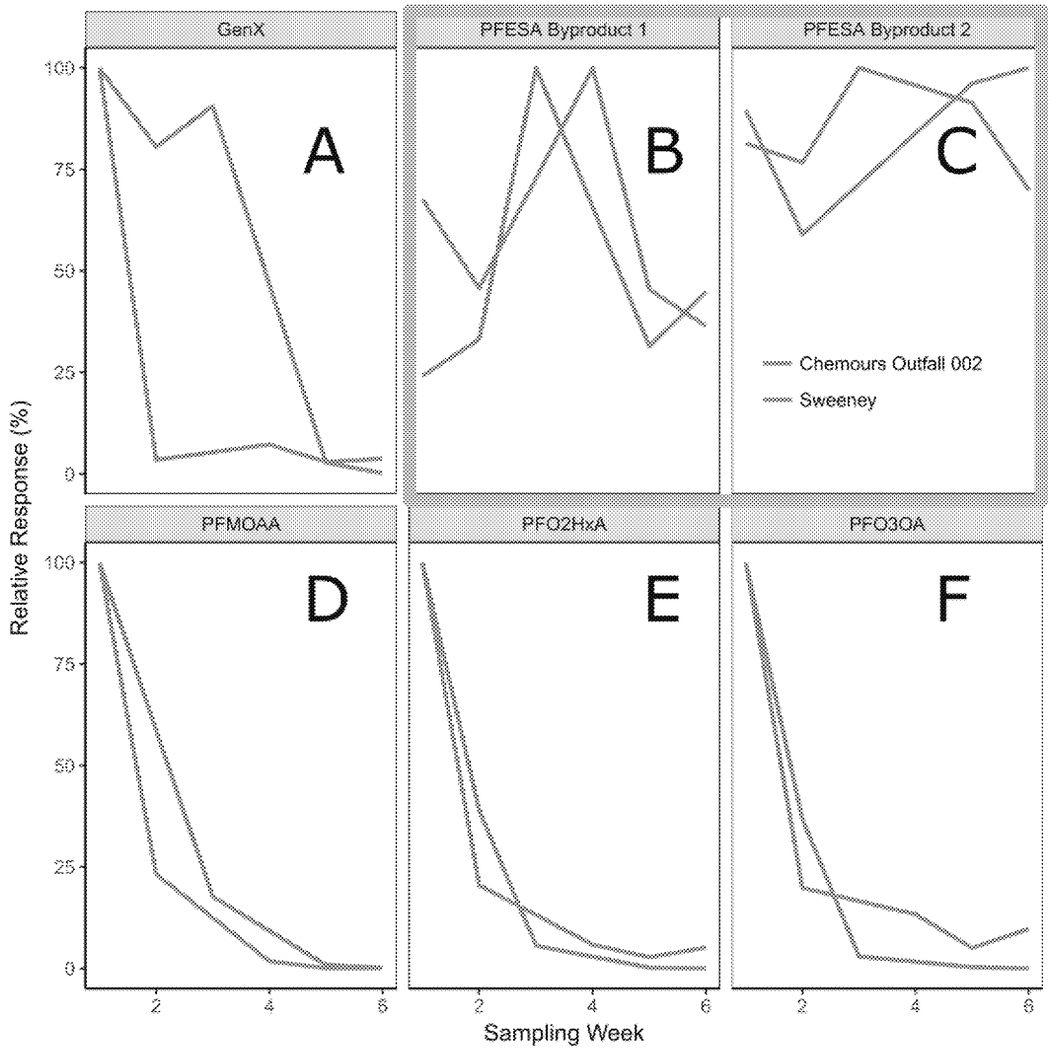
Relative Quantitation Time Trends

6 weeks mid June – early August

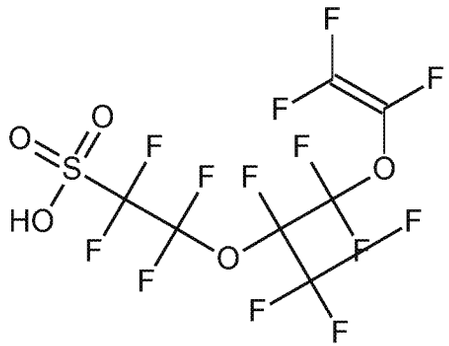




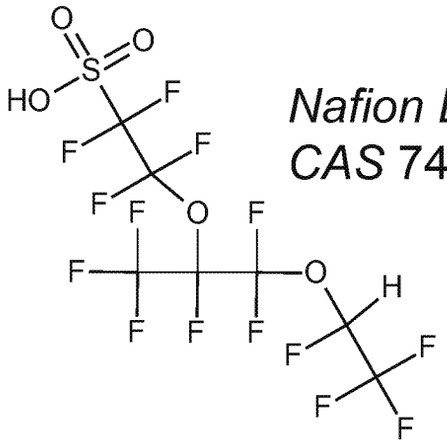
Relative Quantitation Time Trends



6 weeks mid June – early August



Nafion BP1
CAS 29311-67-9

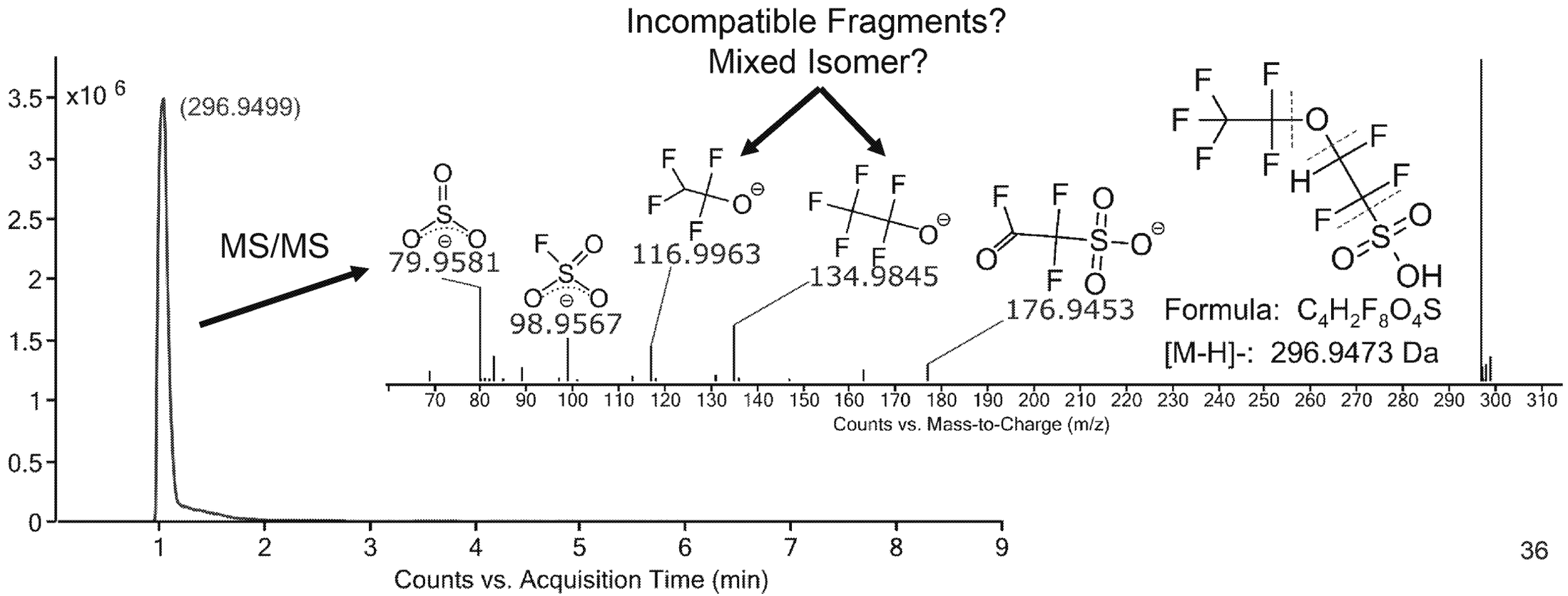


Nafion BP2
CAS 749836-20-2

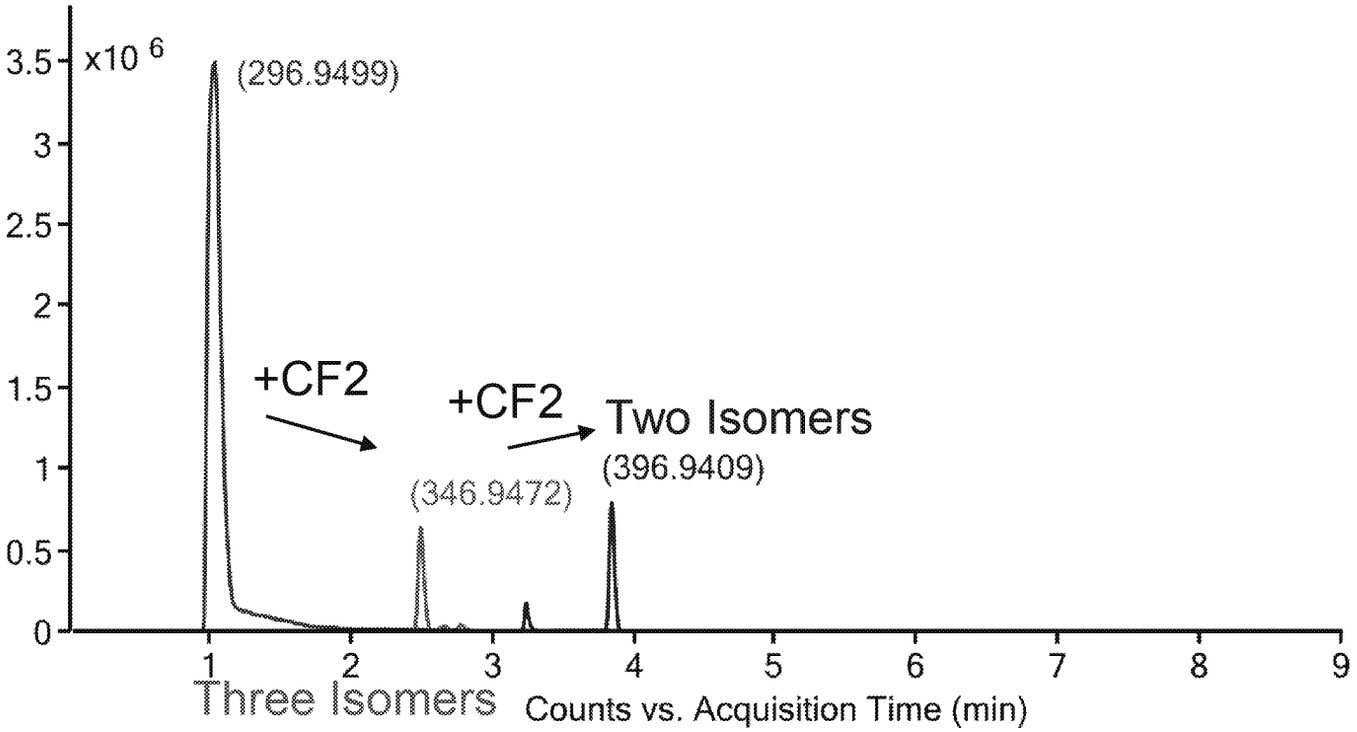
Retrospective HRMS Data Analysis

- Samples analyzed via HRMS (TOF, QTOF, Orbitrap)
- Store data files for reanalysis; like “data specimen banking”
- Data Independent Acquisition when possible (QTOF) for MS/MS
- Possible for presence absence analysis
- Eventual sharing of data files and/or spectra to public location

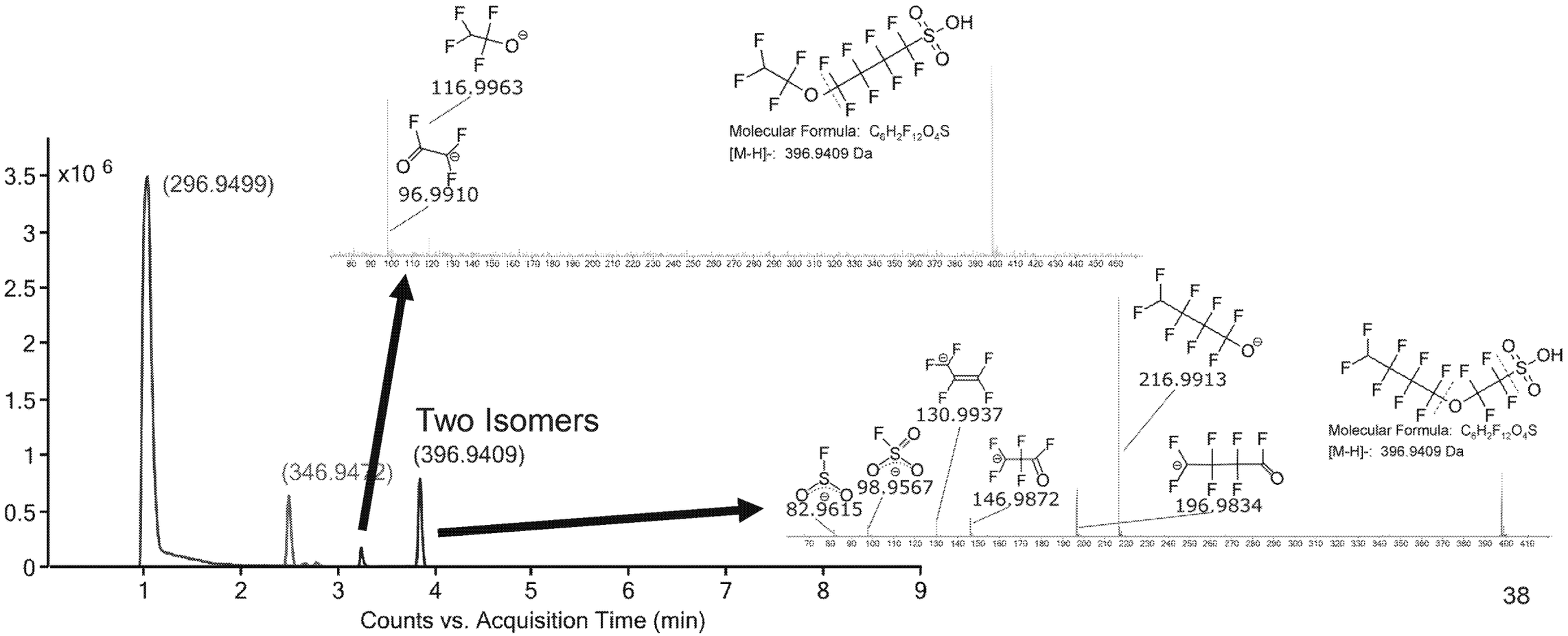
Novel Sulfonated Fluoroethers



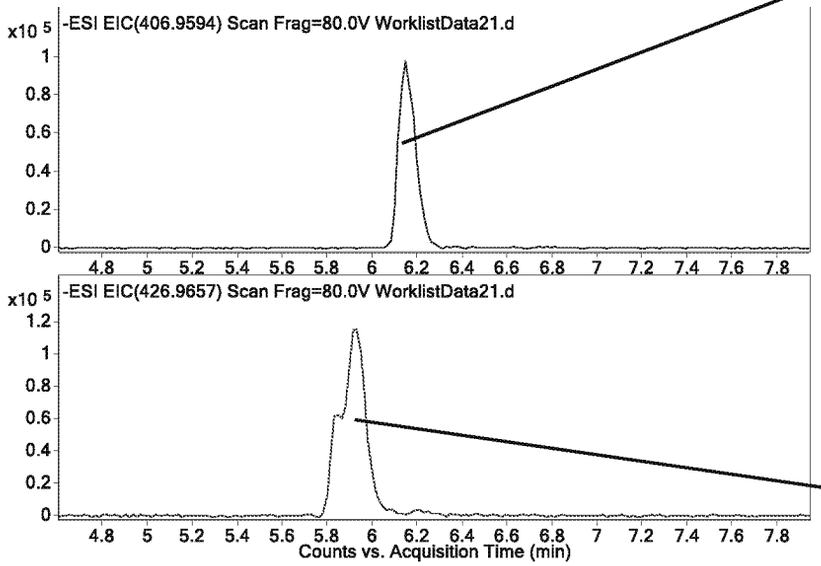
Homologous Series Improves Confirmation

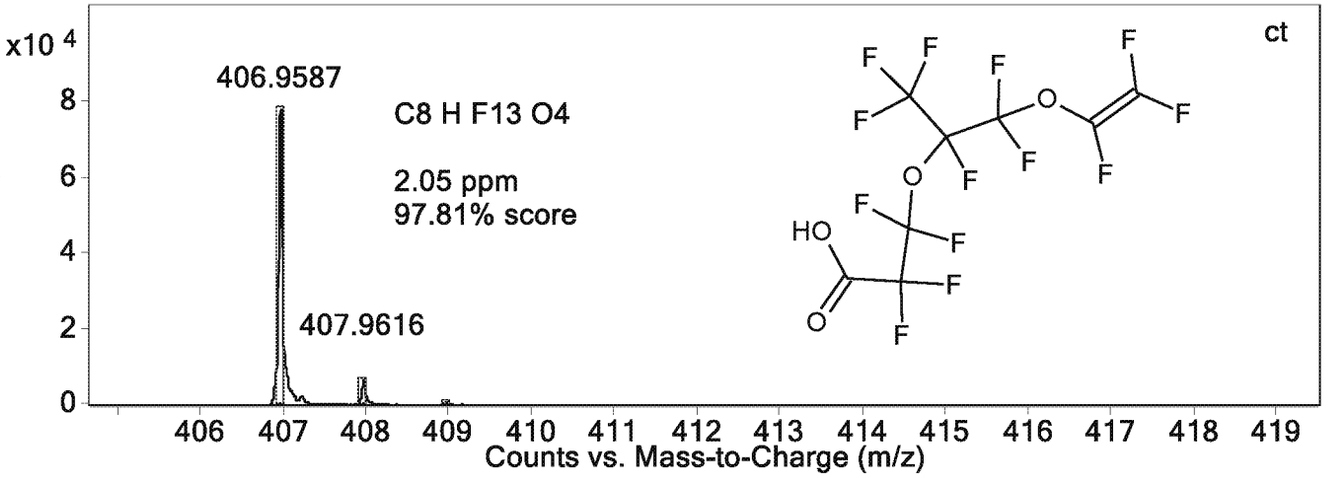


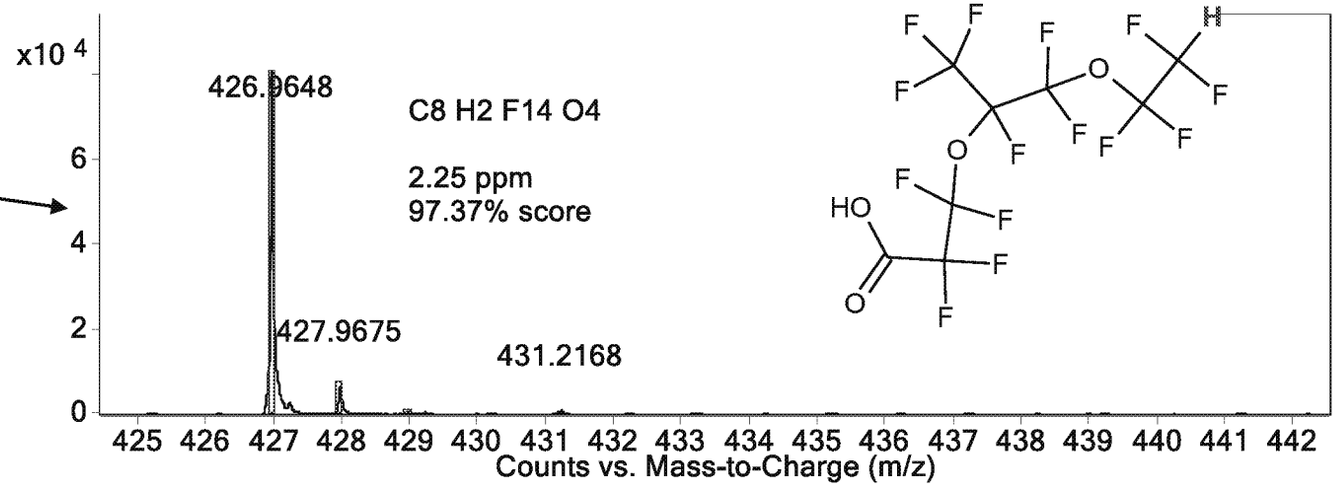
Unique MS/MS Fingerprints



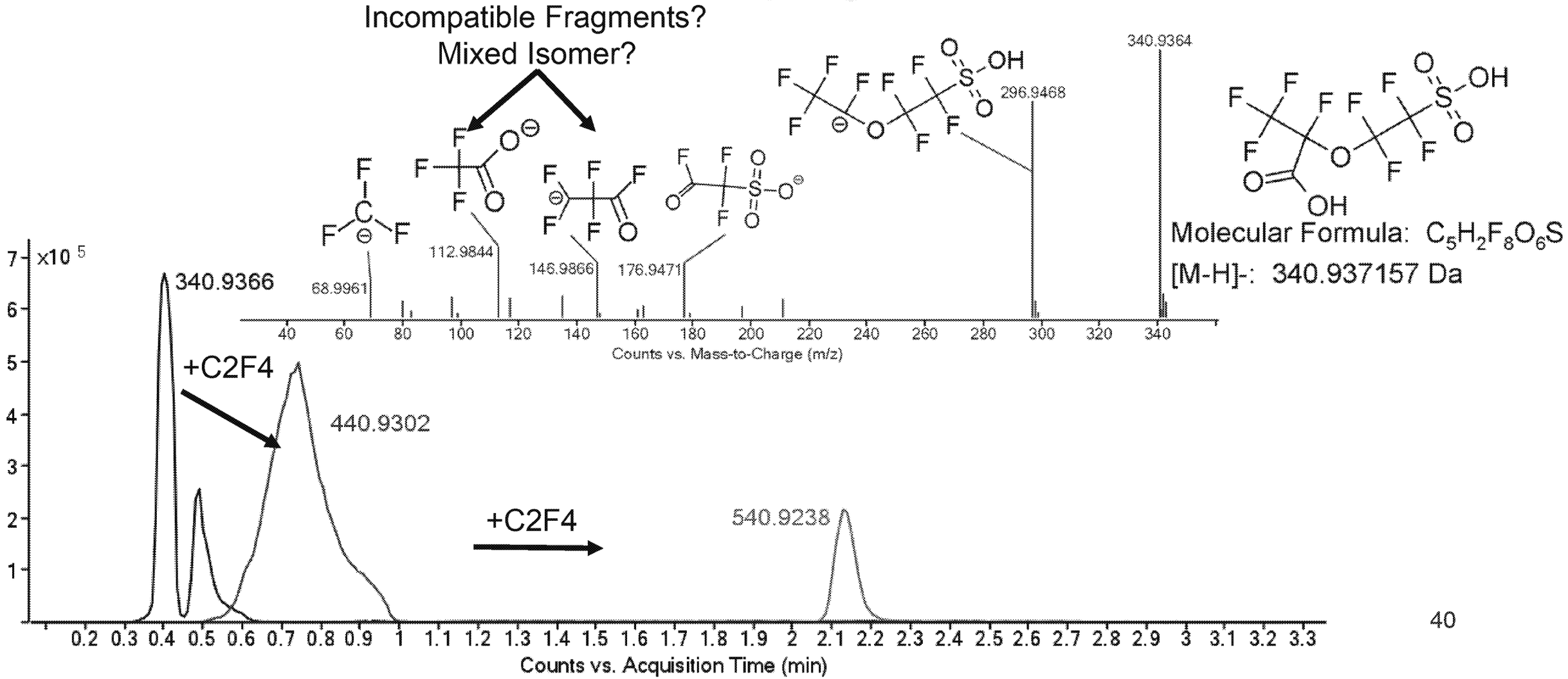
Additional Polyfluoro Ether Carboxylic Acids



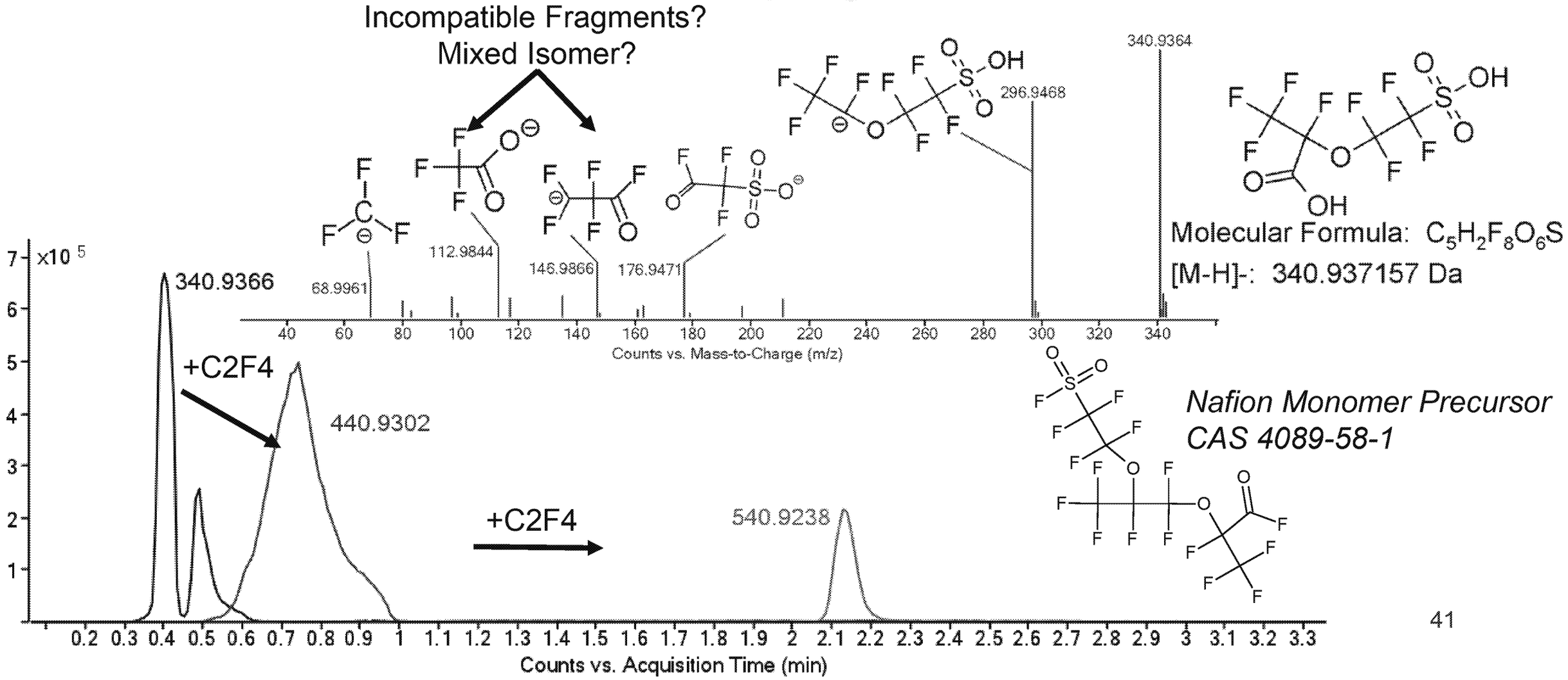




Double Headed Fluoropolymer Intermediates

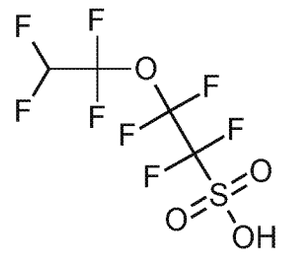


Double Headed Fluoropolymer Intermediates



Retrospective Analysis

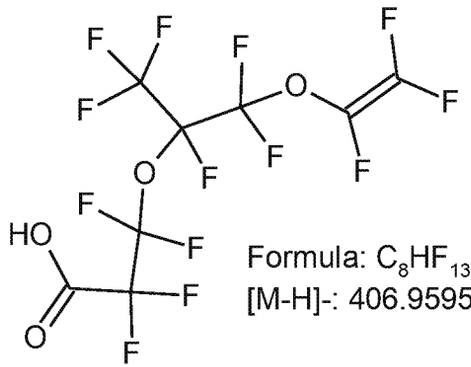
Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	×	×	×
	1-26-12	✓	×	×	✓	✓	×	×	×
2012	2-1-12	✓	×	×	✓	✓	×	✓	×
	2-9-12	✓	✓	✓	✓	✓	✓	×	×
	5-4-12	✓	×	×	✓	×	×	×	×
	5-4-12	✓	×	×			×	×	×
2014	11-24-14	✓	×	×			×	×	×
2015	5-12-15	✓	✓	✓			✓	✓	✓
	5-12-15	✓	✓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



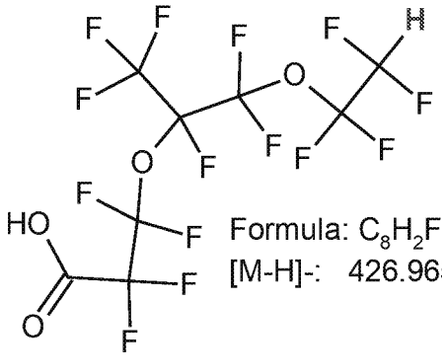
Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

Retrospective Analysis

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	✓	✓	✓	✓	✓	×	×	×



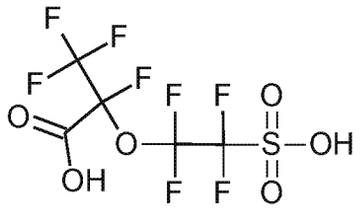
Formula: $C_8HF_{13}O_4$
[M-H]-: 406.9595 Da



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

Retrospective Analysis

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

Questions?

Contact Information

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