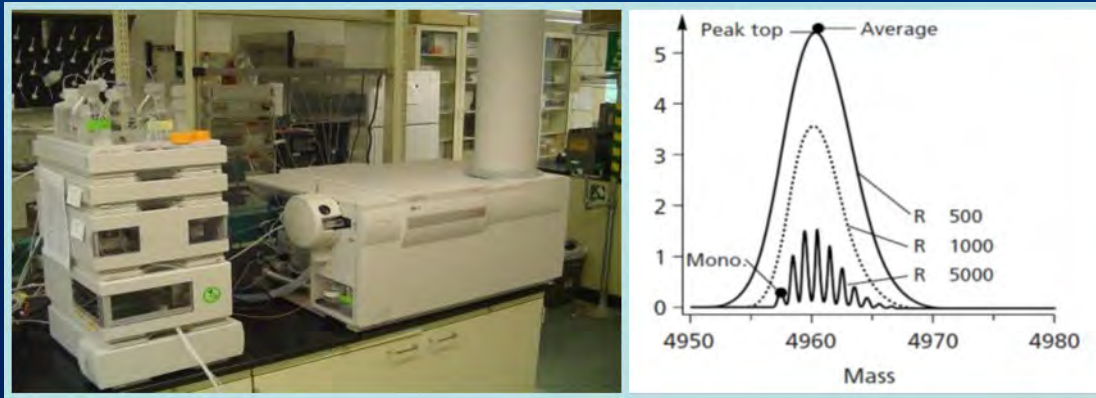




Investigations of Per- and Polyfluorinated Compounds in Environmental Samples

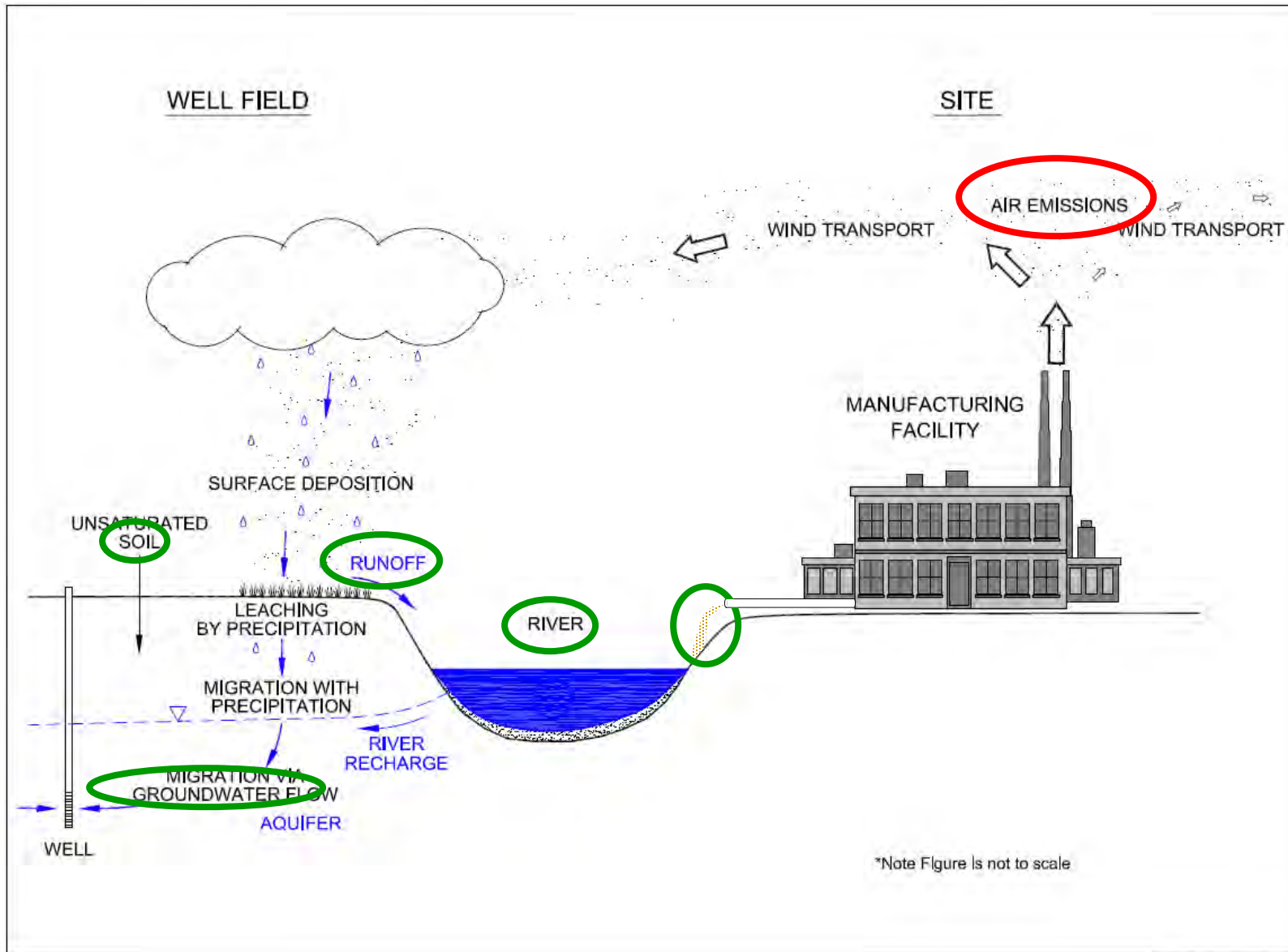
Mark Strynar USEPA/ORD/NERL/EMMD



Friday, September 28, 2018
 Fall 2018 Symposium

“Emerging Contaminants in the Ambient Environment: Perspectives to Guide North Carolina’s Per- and Polyfluoroalkyl Substances (PFAS) Monitoring Network”

Conceptual Model of APFO Emission



Davis et al., 2007 Chemosphere (67) 2011-2019

“Transport of ammonium perfluorooctanoate in environmental media near a fluoropolymer manufacturing facility”

https://comptox.epa.gov/dashboard



United States Environmental Protection Agency

Home Advanced Search Batch Search Lists Predictions Downloads

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762 Thousand Chemicals

Chemicals Product/Use Categories Assay/Gene

Search for chemical by systematic name, synonym, CAS number, DTW/STI or inChIKey

Identifier substring search

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Latest News

Read more news

New publication released: "MS-Ready" structures for non-targeted high-resolution mass spectrometry screening studies

August 31st, 2018 at 12:07:25 PM

"MS-Ready" structures are the basis of many of the searches to support mass spectrometry that are supported on the dashboard. Our recent publication "MS-Ready" structures for non-targeted high-resolution mass spectrometry screening studies" explains the concept and production of MS-Ready structures in detail. Read the paper here.

Discover.

Connect.

Ask.

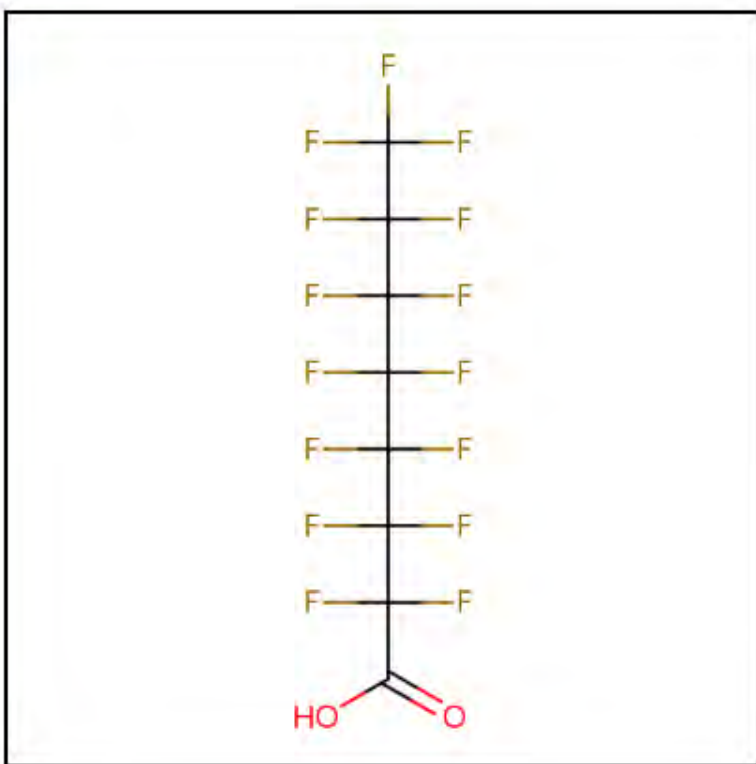


Perfluorooctanoic acid

335-67-1 | DTXSID8031865




Searched by DSSTox Substance Id.

- DETAILS**
- EXECUTIVE SUMMARY
- PROPERTIES
- ENV. FATE/TRANSPORT
- HAZARD
- ADME
- ▶ EXPOSURE
- ▶ BIOACTIVITY
- SIMILAR COMPOUNDS
- GENRA (BETA)
- RELATED SUBSTANCES
- SYNONYMS







Wikipedia

Intrinsic Properties

- 
Molecular Formula: C₈HF₁₅O₂
[Mol File](#)
[Find All Chemicals](#)
- 
Average Mass: 414.07 g/mol
 [Isotope Mass Distribution](#)
- 
Monoisotopic Mass: 413.973702 g/mol

Structural Identifiers

- 
IUPAC Name: Pentadecafluorooctanoic acid
- 
SMILES: OC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
- 
InChI String: InChI=1S/C8HF15O2/c9-2(10,1(24)25)3(11,12)4(13,14)5(15,16)6(17,18)7(19,20)8(21,22)23/h(H,24,25)
- 
InChIKey: SNGREZUHAYWORS-UHFFFAOYSA-N

Usual Suspects for Elevated Scrutiny



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

(Kendrick Plots)

- Diagnostic fragments (CF_3 -69, CF_3CF_2 -119, CF_3O -85, $\text{CF}_3\text{CF}_2\text{O}$ -135)

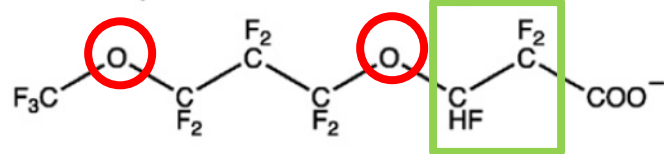


Post PFOA Stewardship Agreement

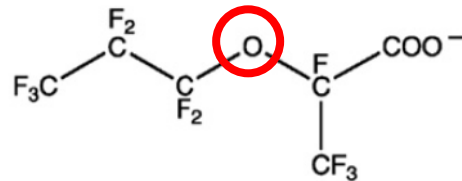


Fluoropolymer manufacture

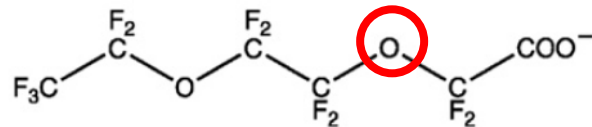
ADONA (CAS No. 958445-44-8)



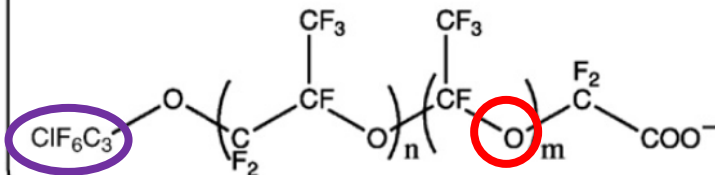
GenX (CAS No. 62037-80-3)



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

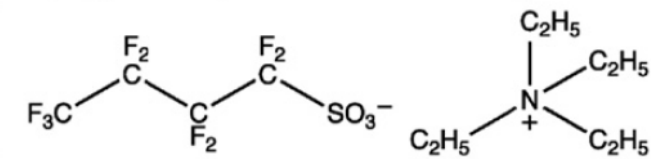


Solvay's product (CAS No. 329238-24-6)

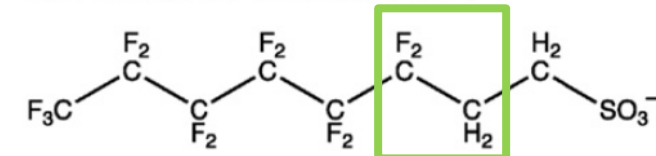


Metal plating

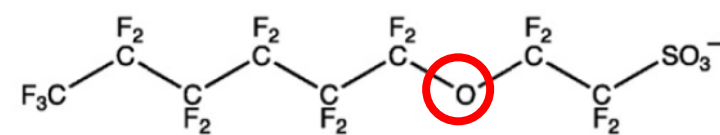
N(Et)₄-PFBS (CAS No. 25628-08-4)



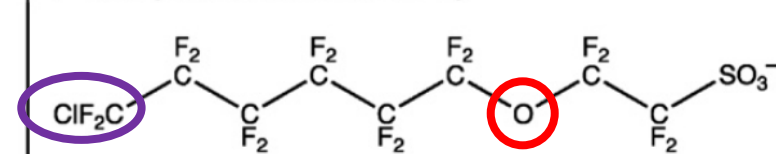
6:2 FTSA (CAS No. 27619-97-2)



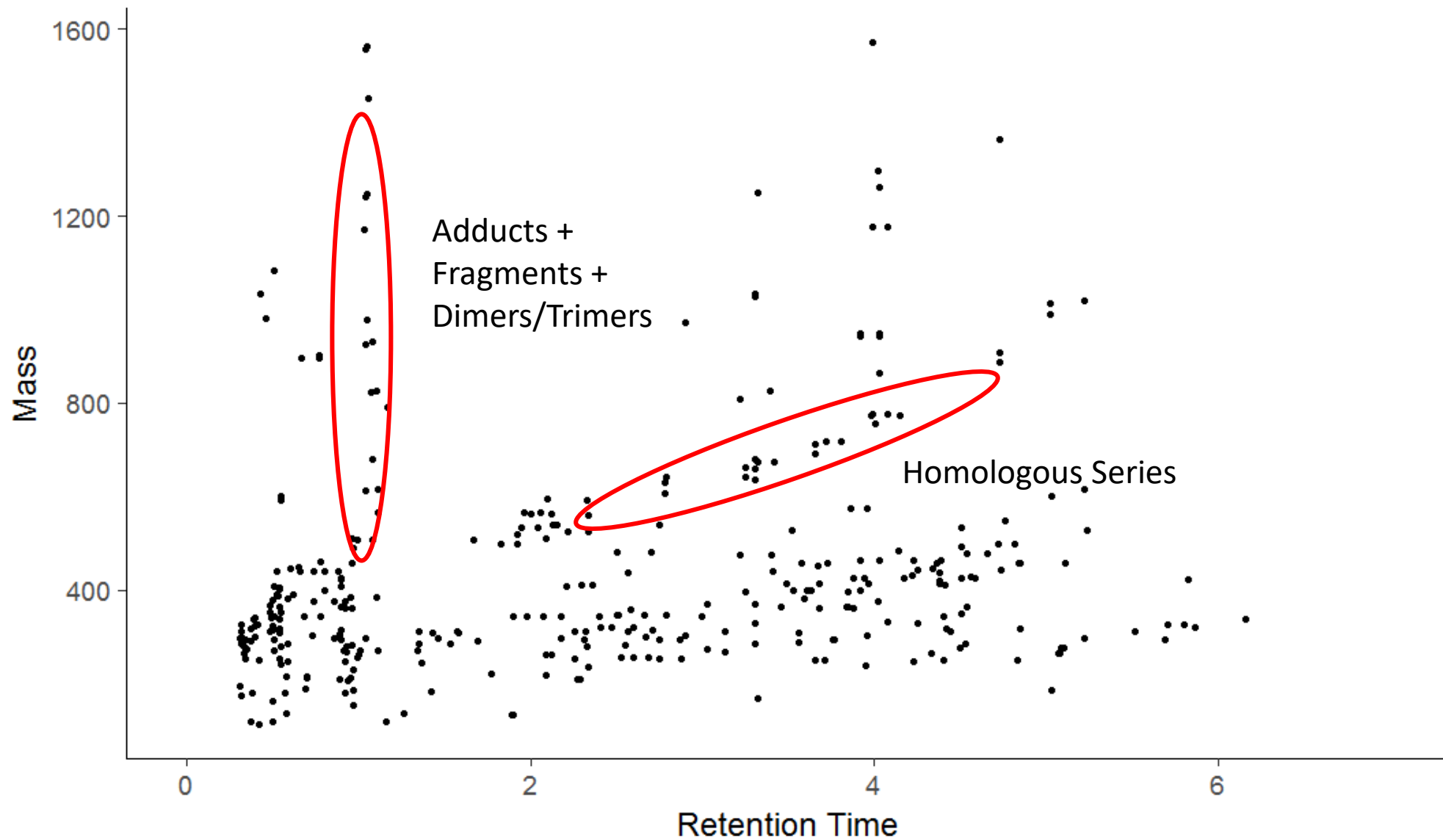
F-53 (CAS No. 754925-54-7)



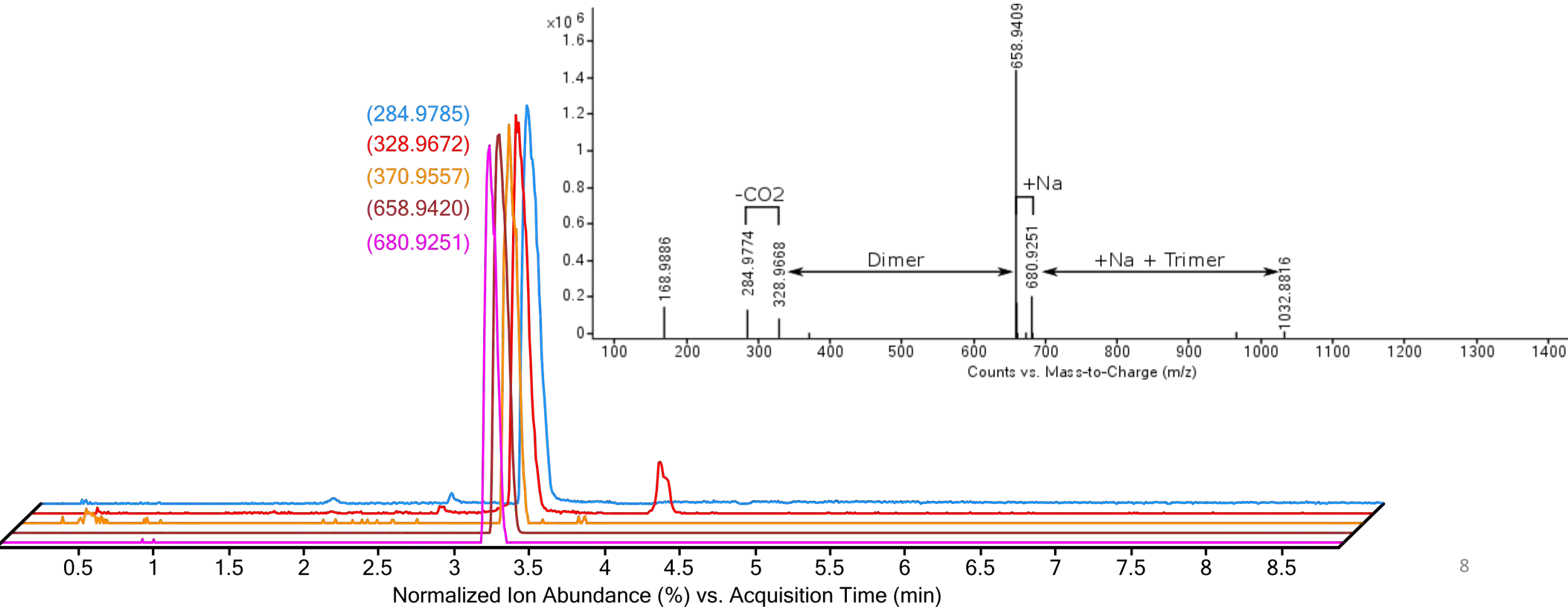
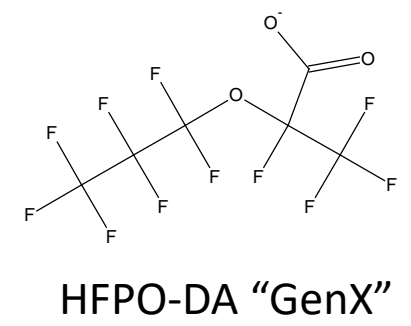
F-53B (CAS No. 73606-19-6)



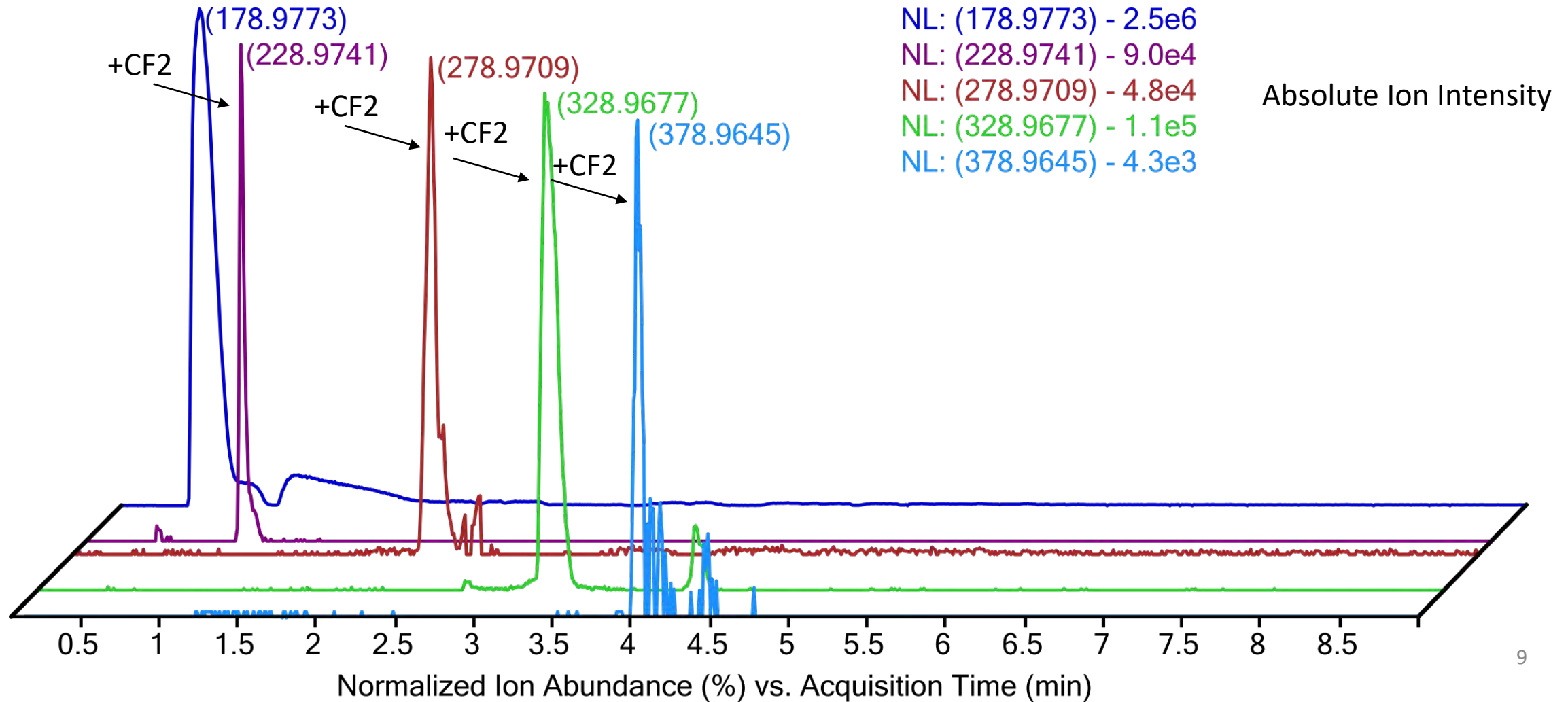
Relationships Reveal Underlying Chemistry



In-Source Related Species



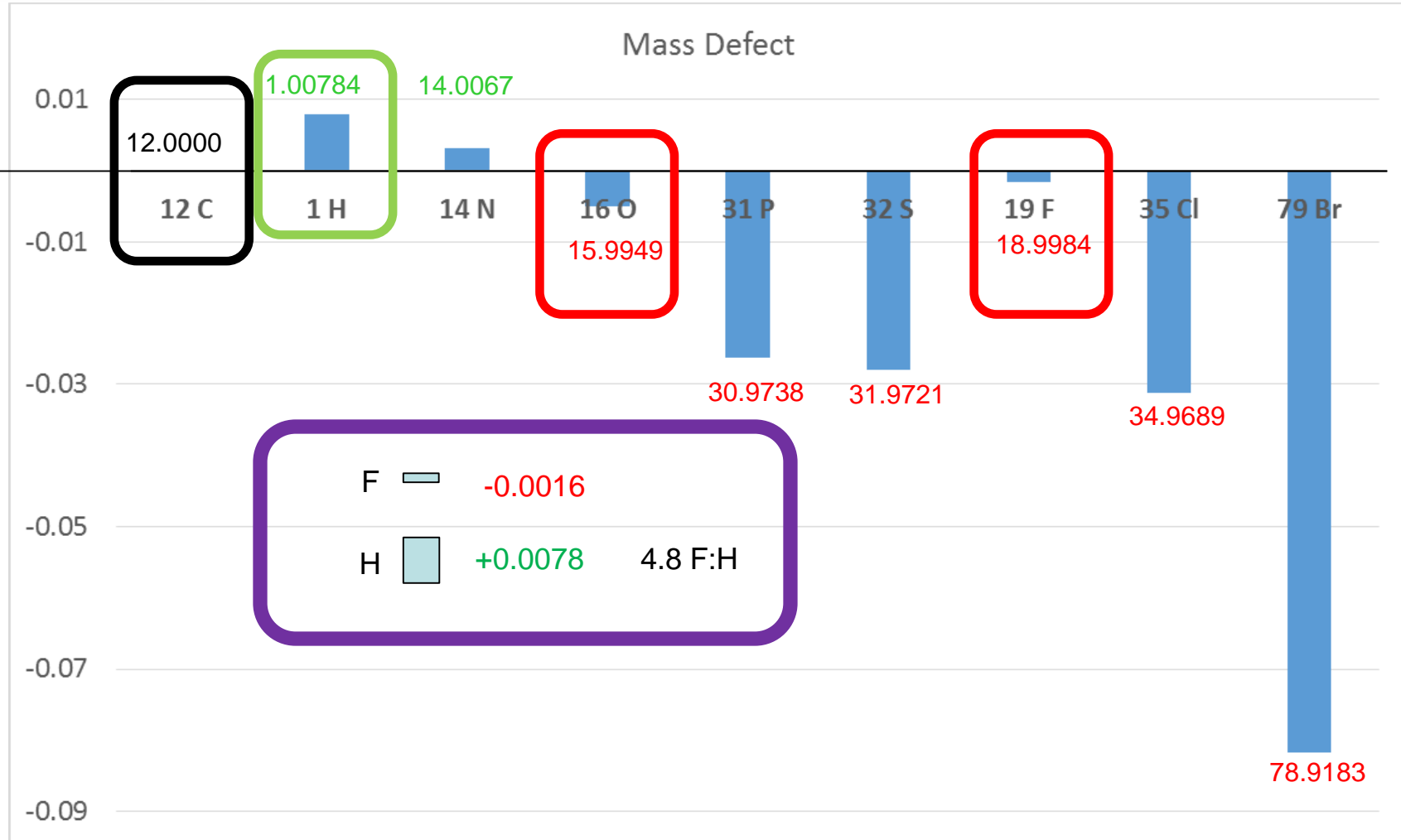
Homologous Series



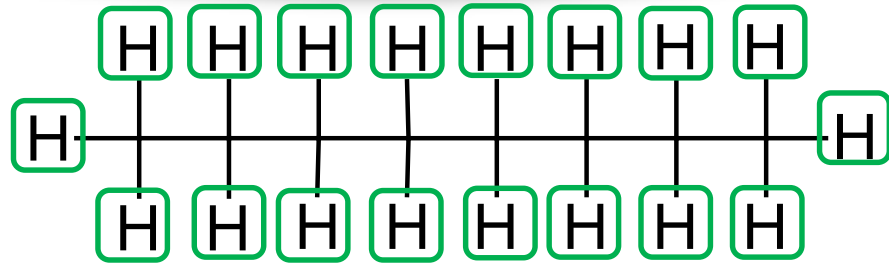
Isotope Signatures: Negative Mass Defect

Positive Mass Defect

Negative Mass Defect

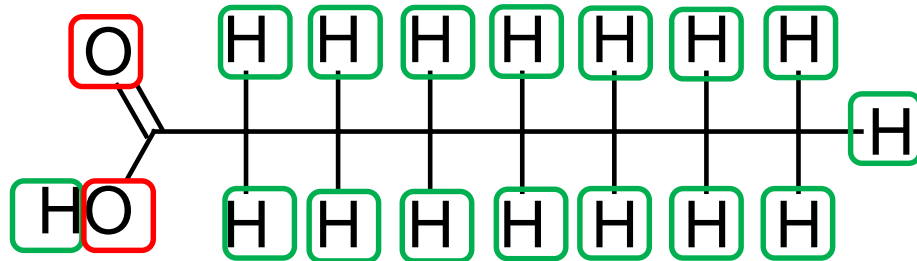


Example of Mass Defect



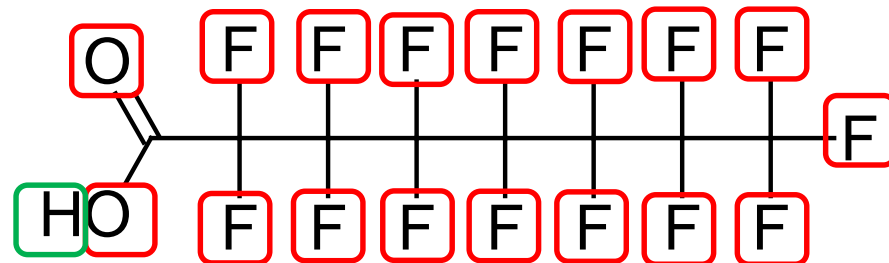
Octane

MI mass 114.**1409**



Octanoic Acid

MI mass 144.**1150**

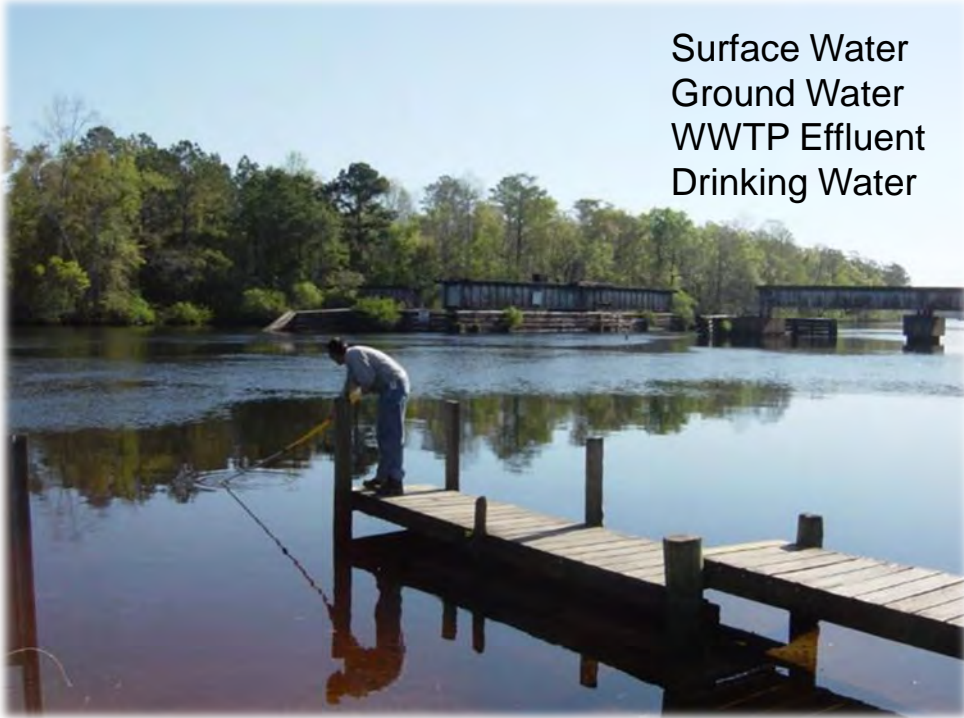


Perfluorooctanoic Acid

MI mass 413.**9737**

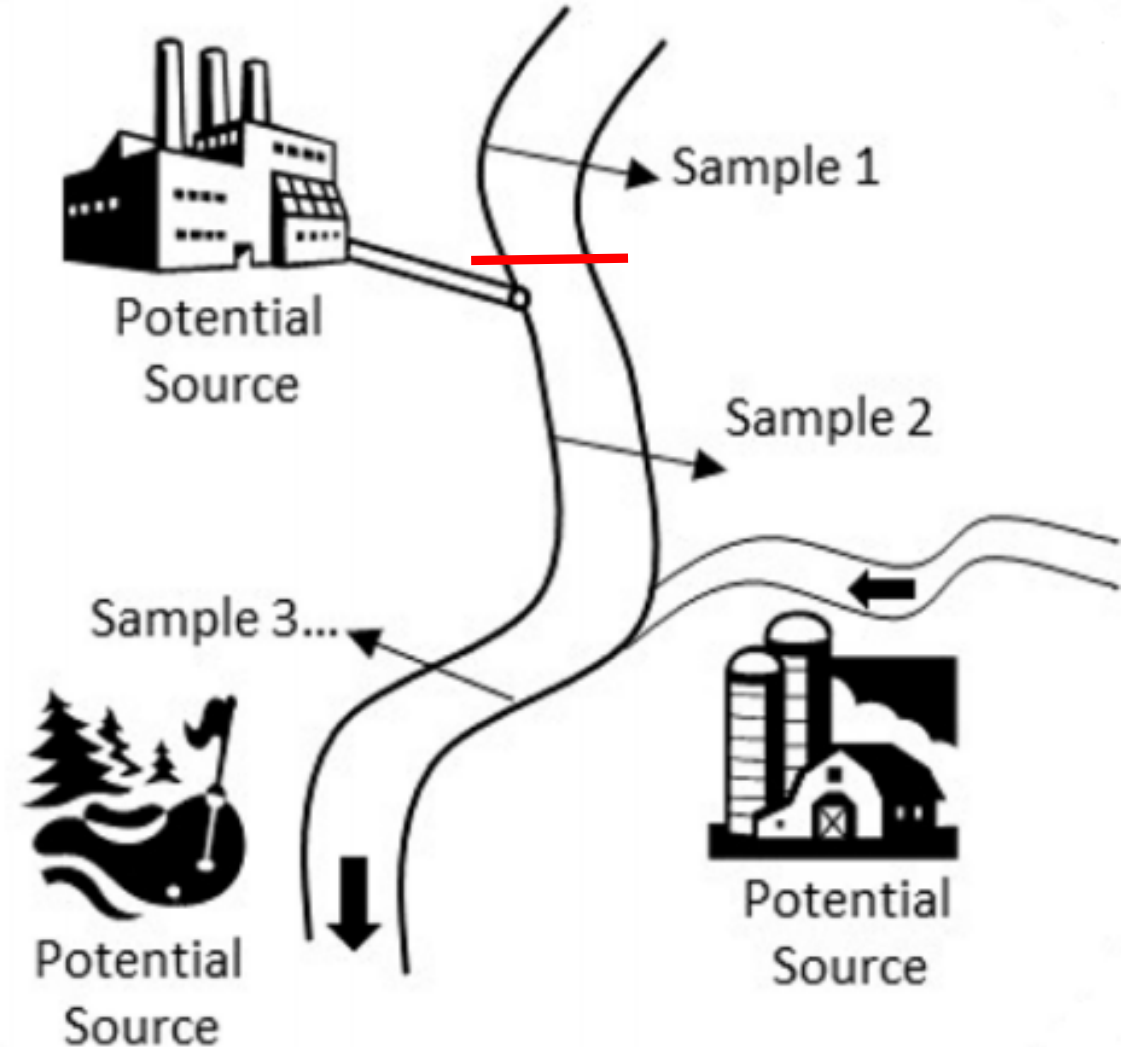
AFFF

Data Generation: Source Determination by NTA



Surface Water
Ground Water
WWTP Effluent
Drinking Water

Sampling from geographically or temporally displaced locations allows triangulation of sourcing



Legacy PFAS found in Cape Fear Water circa 2012

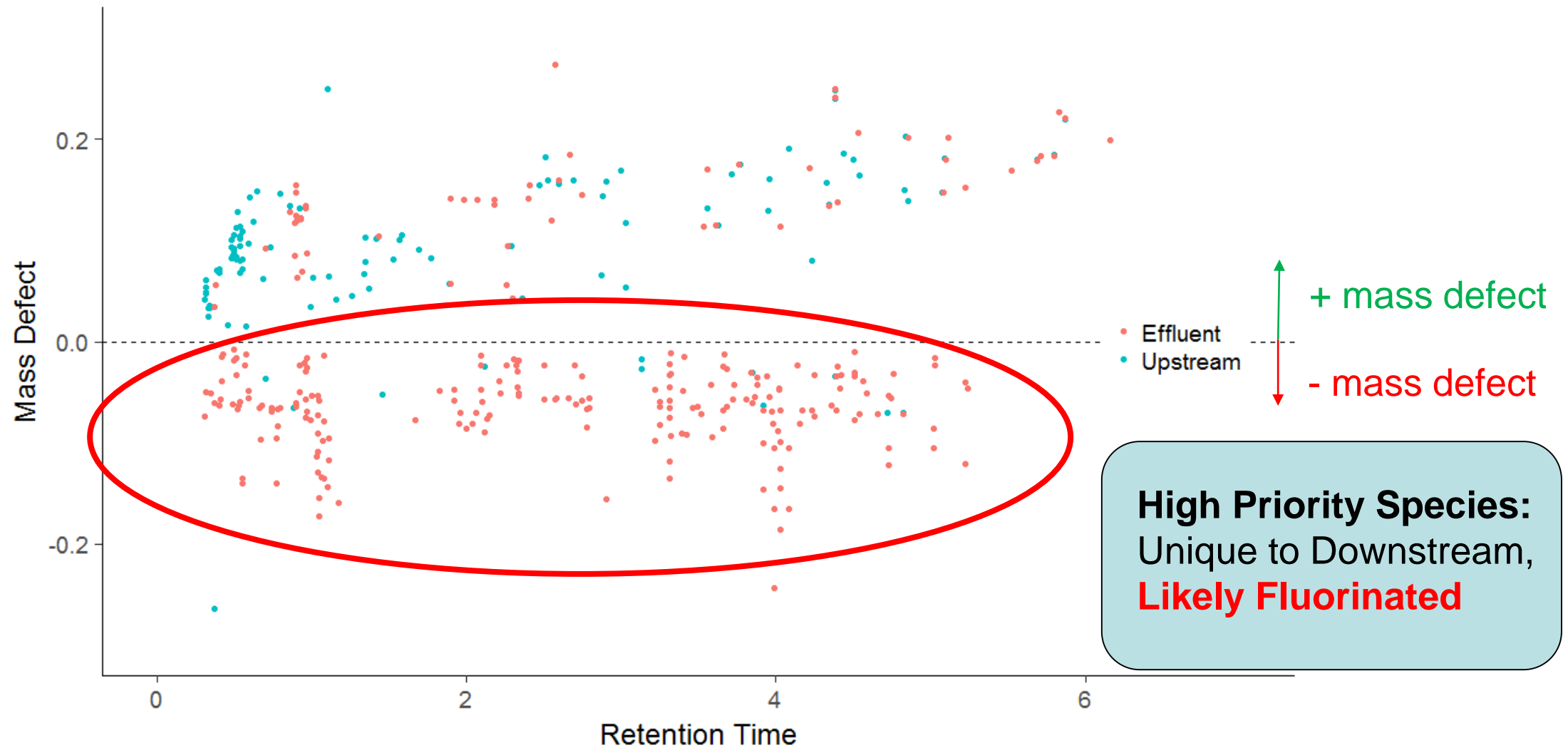


Analyte	001	002	003	004	005	006	007	008	008	009
C4	23	502	3761	6	4	0	8	7	5	3
C5	441	5607	43590*	17	9	1	32	46	12	9
PFBS	4	5	3	4	5	2	9	5	6	4
C6	17	90	434	18	12	2	27	16	18	14
C7	37	599	3873	14	17	0	11	20	21	9
PFHS	7	12	10	9	7	4	9	10	9	22
C8	32	39	71	33	25	2	38	36	41	18
C9	13	34	127	7	11	1	6	8	11	5
PFOS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

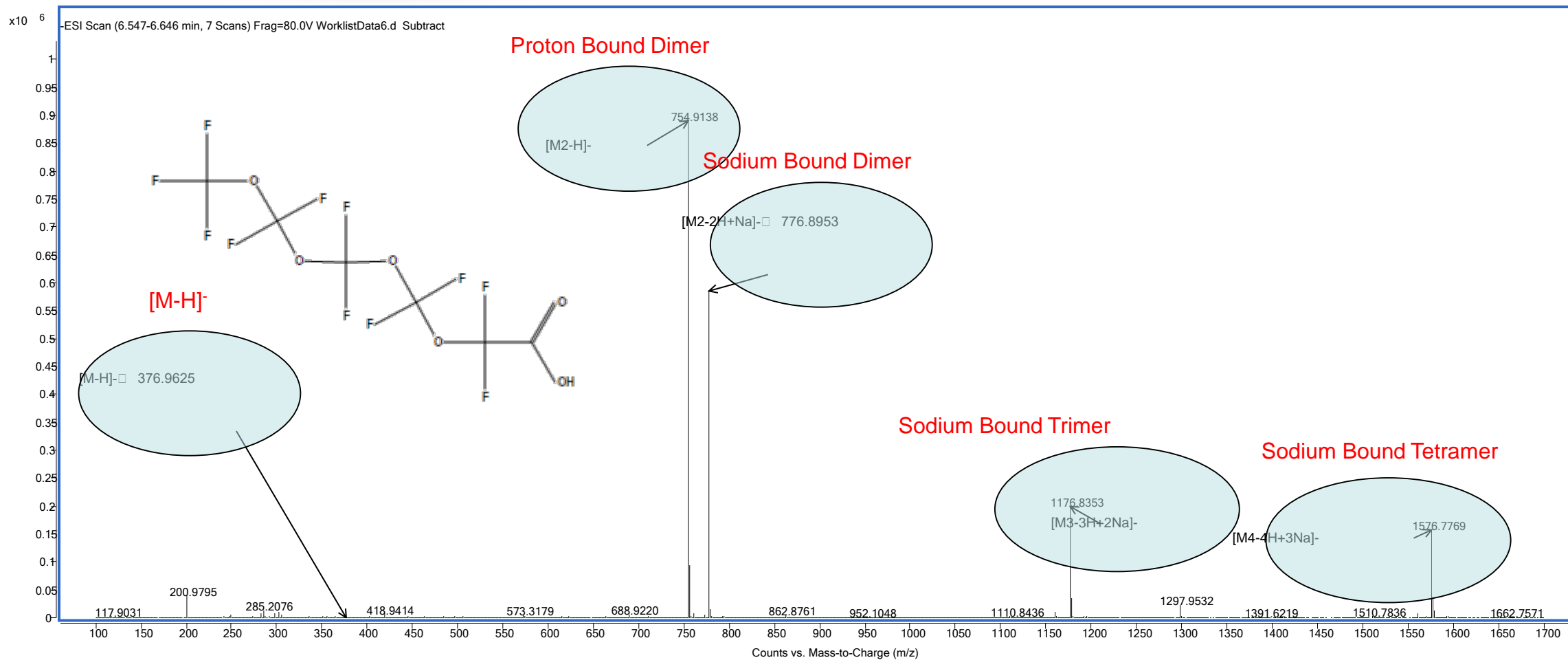
Increase in PFAS below site 003

Legacy PFAS in Cape Fear River

Mass Defect of Outfall and Upstream Features



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.

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 McMahan,^{†,‡} Shuang Liang,^{†,‡} Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,^{||} Imma Ferrer,^{||} and Carol Ball[⊥]

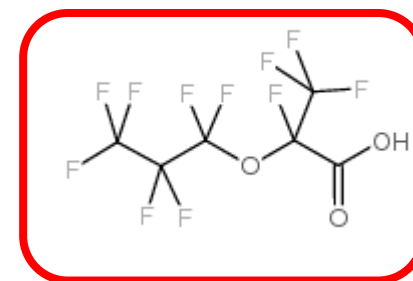
Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

number	formula	CAS no.	name	$[M]^{a}$	$[M - H]^{-}$ m/z	$[2M - 2H + Na]^{-}$ m/z	$[2M - H]^{-}$ m/z
Monoether PFECAs							
1	C ₃ HF ₅ O ₃			179.9846	178.9773	380.9438	358.9619
2	C ₄ HF ₇ O ₃			229.9813	228.9740	480.9372	458.9553
3	C ₅ HF ₉ O ₃	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	C ₆ HF ₁₁ O ₃	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427

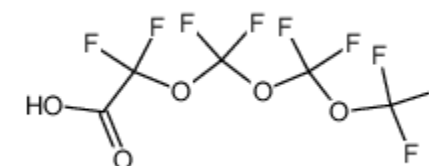
Undecafluoro-2-methyl-3-oxahexanoic acid

8	C ₆ HF ₁₁ O ₆	39492-90-5	perfluoro-3,5,7,9-butaoxadecanoic acid	377.9598	376.9525	776.8942	754.9123
9	C ₅ HF ₉ O ₅	39492-89-2	perfluoro-3,5,7-propaoxaocetanoic acid	311.9681	310.9608	644.9108	622.9289
10	C ₄ HF ₇ O ₄	39492-88-1	perfluoro-3,5-dioxahehexanoic acid	245.9764	244.9691	512.9274	490.9455
PFESAs							
11	C ₇ HF ₁₃ O ₅ S	66796-30-3 ^b		443.9337	442.9264		
12	C ₇ H ₂ F ₁₄ O ₅ S			463.9399	462.9326		

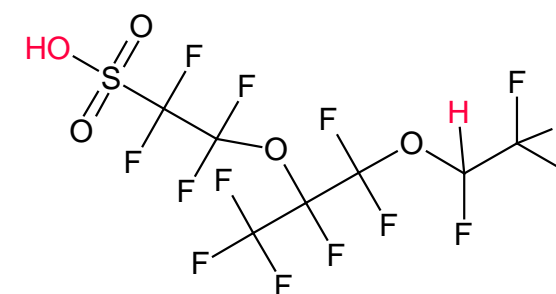
Example Structures



Monoether (6):
HFPO-DA;GenX



Polyethers (4):

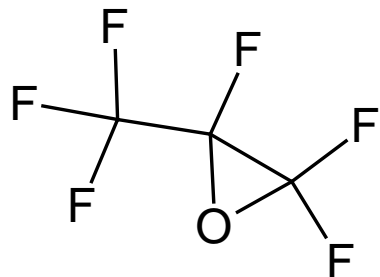


Polyethers
sulfonates (2):

Hexafluoropropylene Oxide (HFPO) Based Chemistry

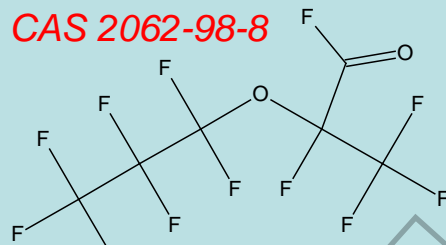
HFPO

CAS 428-59-1



Dimerized to
HFPO-DAF

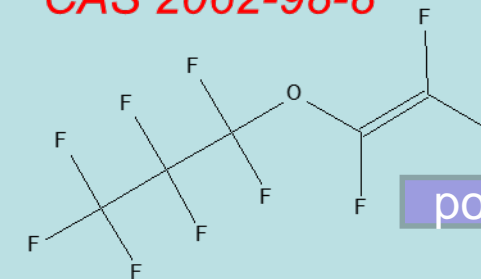
HFPO-DAF
CAS 2062-98-8



Acid Fluorides

Vinyl Ether Production

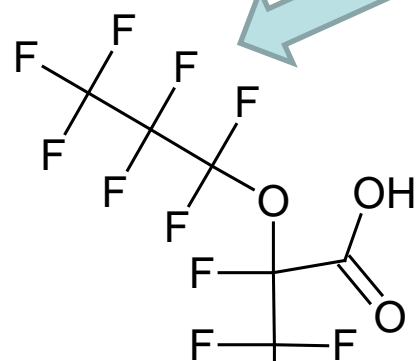
CAS 2062-98-8



Polyvinyl Ether
Intermediates

polymers

In Water

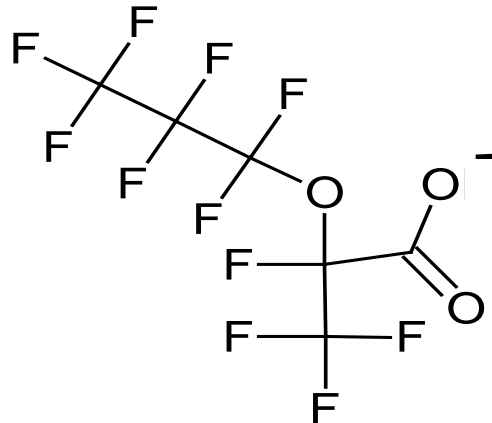


HFPO-DA

CAS 13252-13-6

In Water

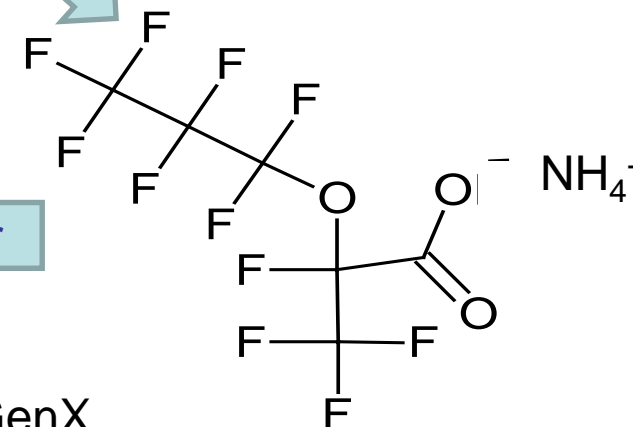
Common Analyte



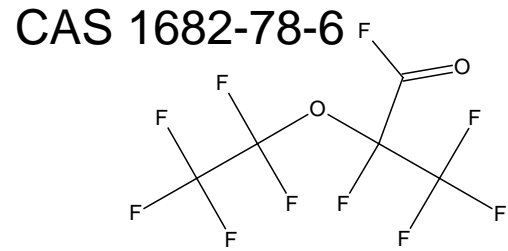
In water

GenX

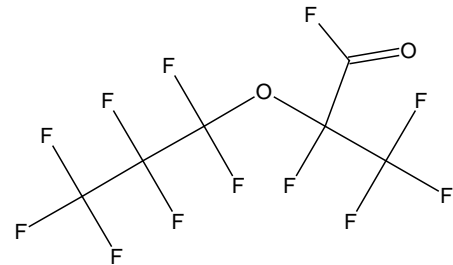
CAS 62037-80-3



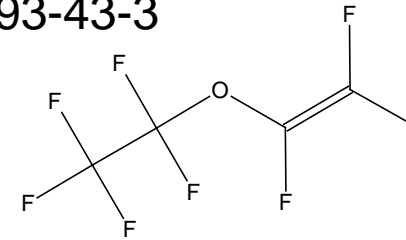
Polyvinyl Ether Production



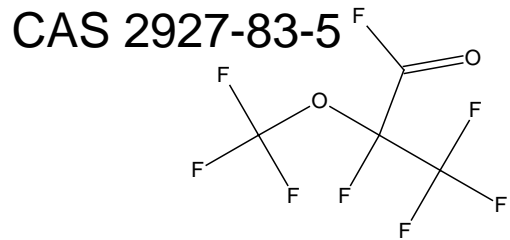
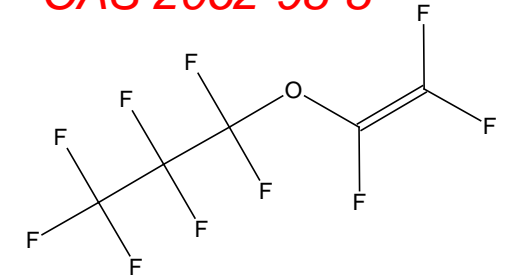
CAS 2062-98-8



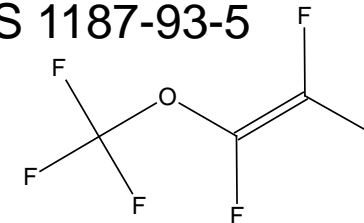
CAS 10493-43-3



CAS 2062-98-8



CAS 1187-93-5



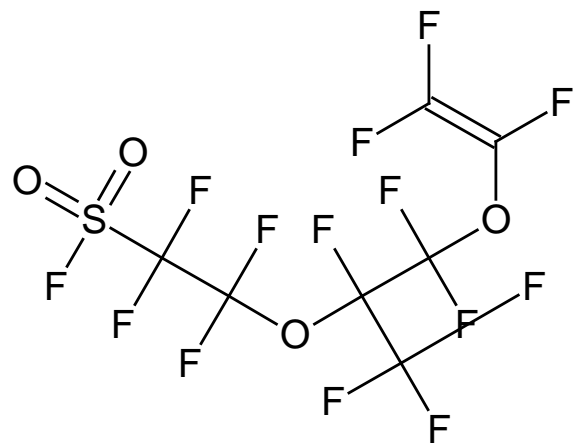
Acid Fluorides

Polyvinyl Ether
Intermediates

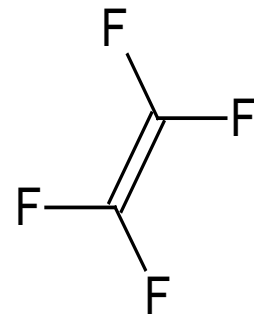
Head-(CF₂)_n(CF₂O)_m-Head
Polyvinyl Ether

Nafion Polymer

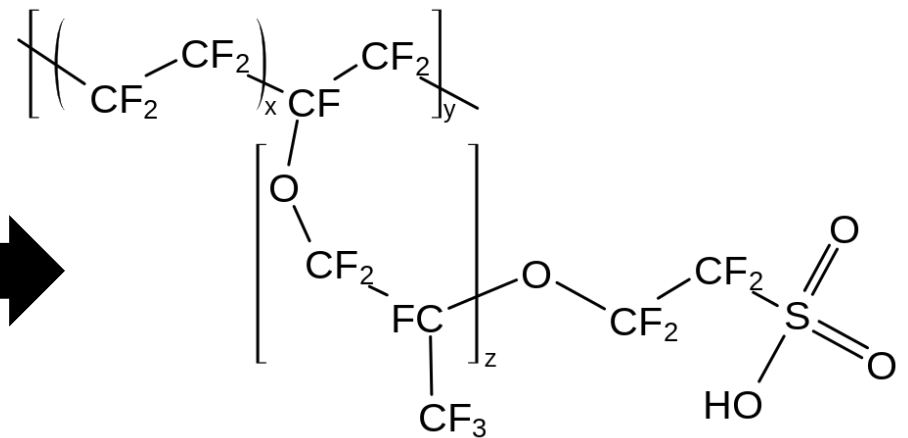
- Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer
- Proton conductor for proton exchange membrane (PEM) fuel cells



CAS 16090-14-5



CAS 116-14-3



CAS 66796-30-3

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[‡]

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

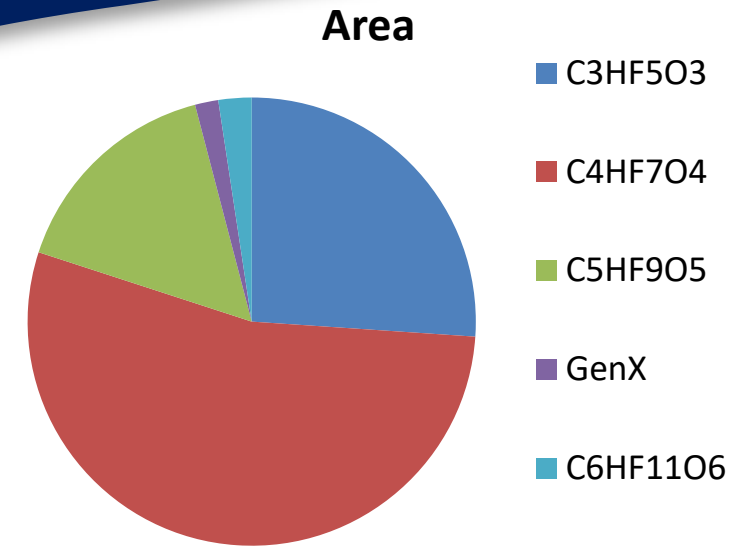
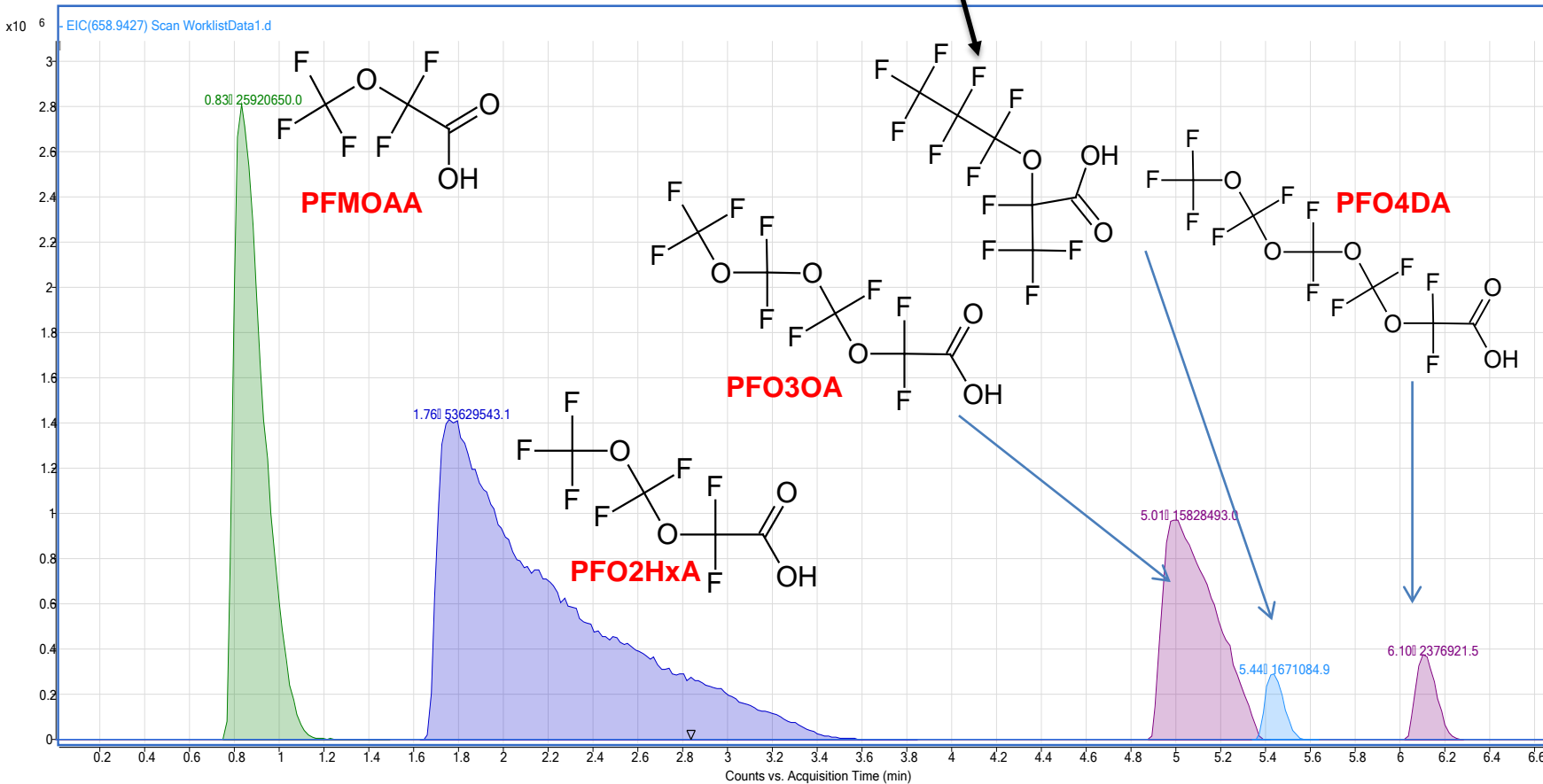


June 7th, 2017

Cape Fear River
Fayetteville to
Wilmington, NC

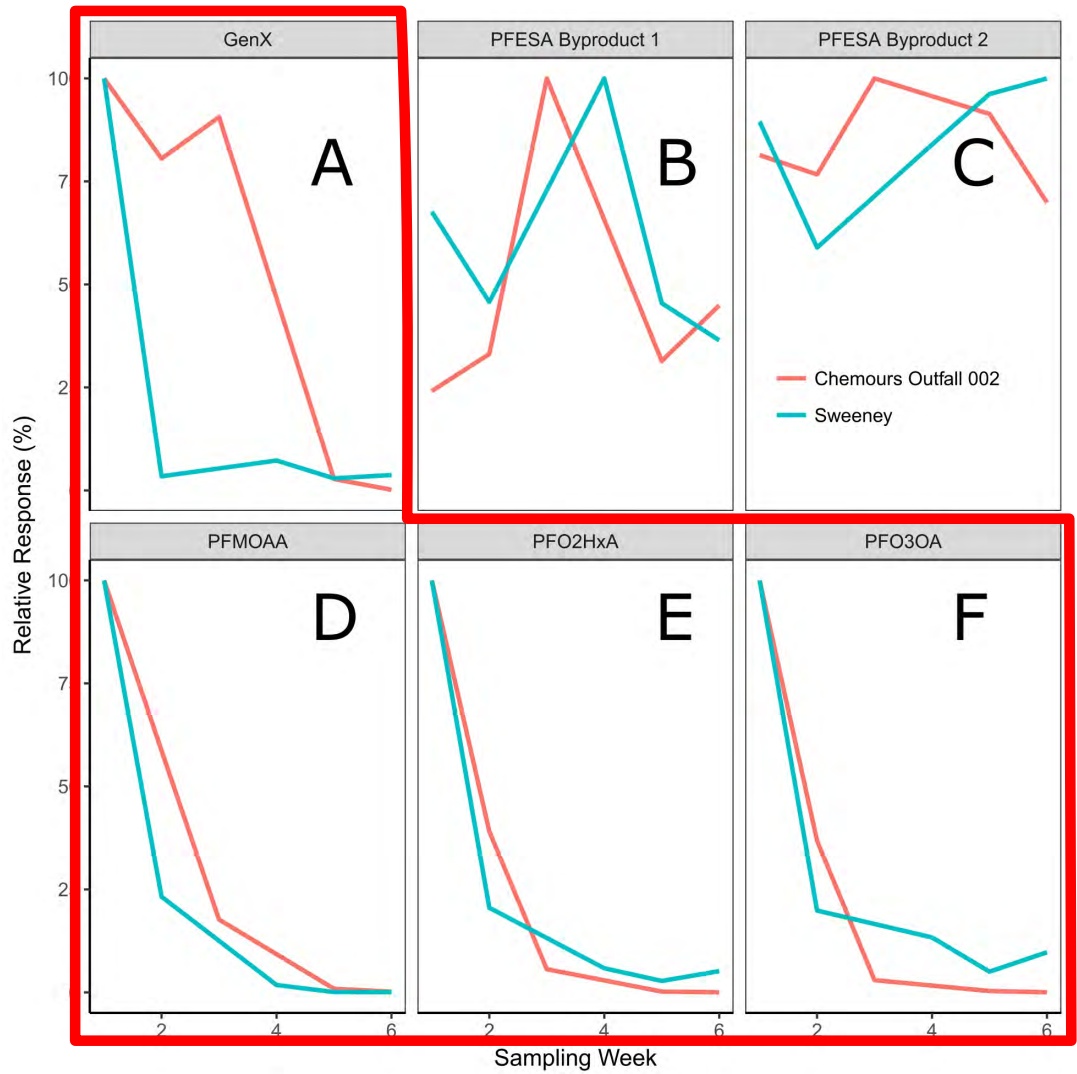
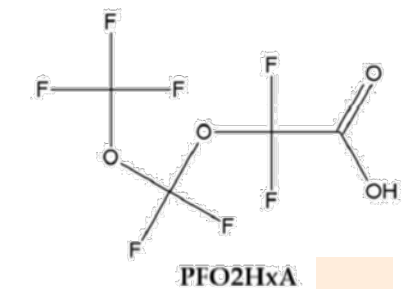
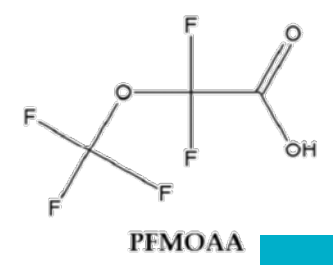
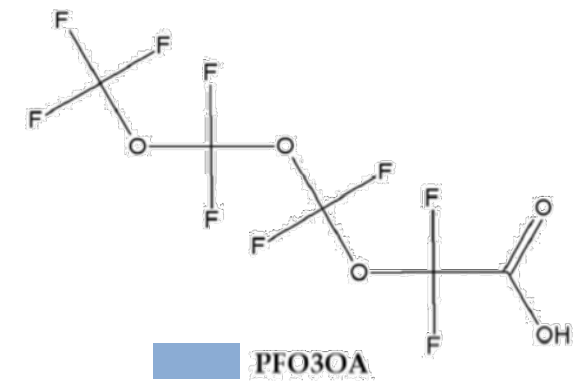
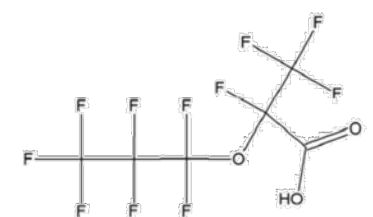
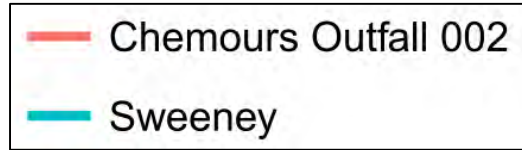
PFECAs in 5-15-17 Cape Fear River Sample

HFPO-DA; GenX

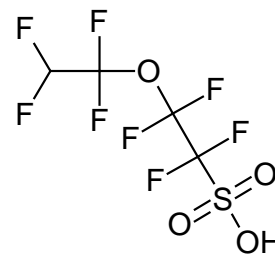


Relative Quantitation Time Trends

6 weeks mid June – early August



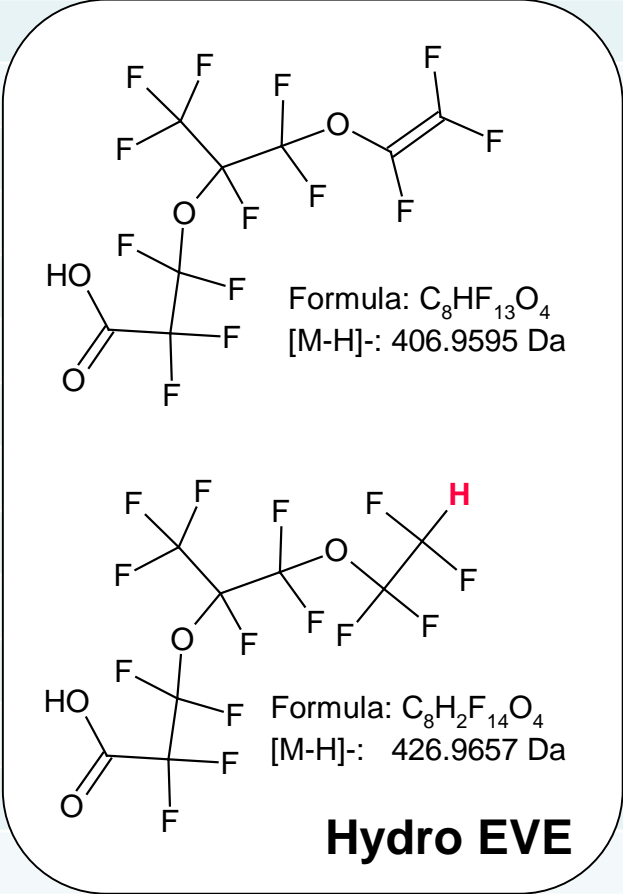
Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	✗	✗	✗
	1-26-12	✓	✗	✗	✓	✓	✗	✗	✗
2012	2-1-12	✓	✗	✗	✓	✓	✗	✓	✗
	2-9-12	✓	✓	✓	✓	✓	✓	✗	✗
	5-4-12	✓	✗	✗	✓	✗	✗	✗	✗
	5-4-12	✓	✗	✗			✗	✗	✗
2014	11-24-14	✓	✗	✗			✗	✗	✗
2015	5-12-15	✓	✓	✓			✓	✓	✓
	5-12-15	✓	✓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



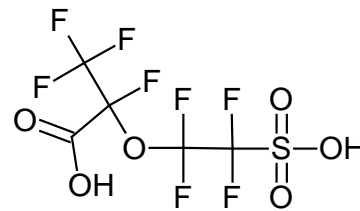
Formula: C₄H₂F₈O₄S
[M-H]⁻: 296.9473 Da

NVHOS

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

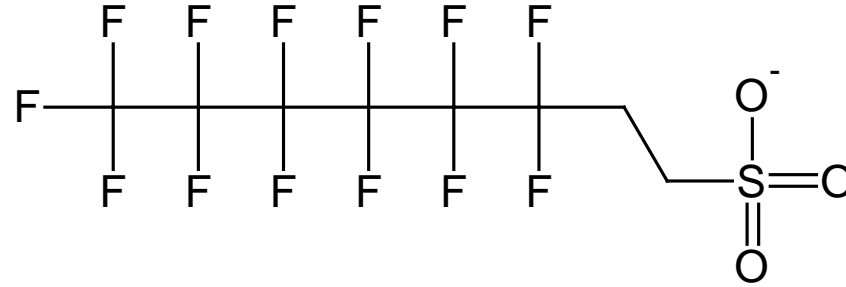


Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	✗	✗	✗
	1-26-12	✓	✗	✗	✓	✓	✗	✗	✗
2012	2-1-12	✓	✗	✗			✗	✓	✗
	2-9-12	✓	✓				✓	✗	✗
	5-4-12	✓	✗				✗	✗	✗
	5-4-12	✓	✗				✗	✗	✗
2014	11-24-14	✓	✗				✗	✗	✗
2015	5-12-15	✓	✓				✓	✓	✓
	5-12-15	✓	✓				✓	✓	✓
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



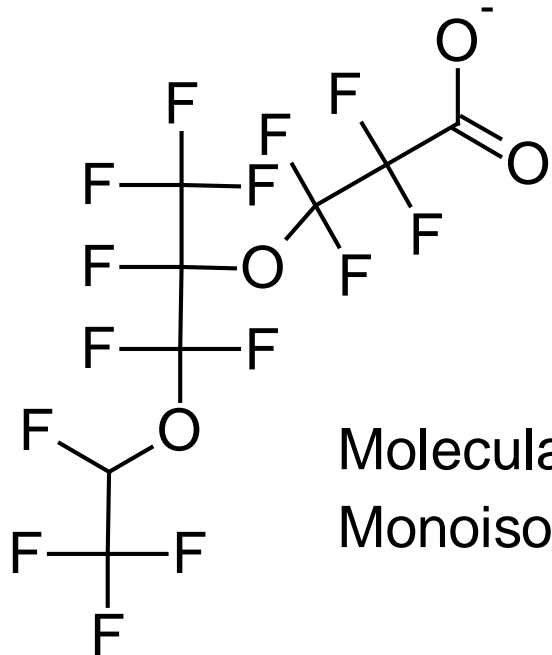
Formula: C₅H₂F₈O₆S
[M-H]⁻: 340.9372 Da

EIC Confusion



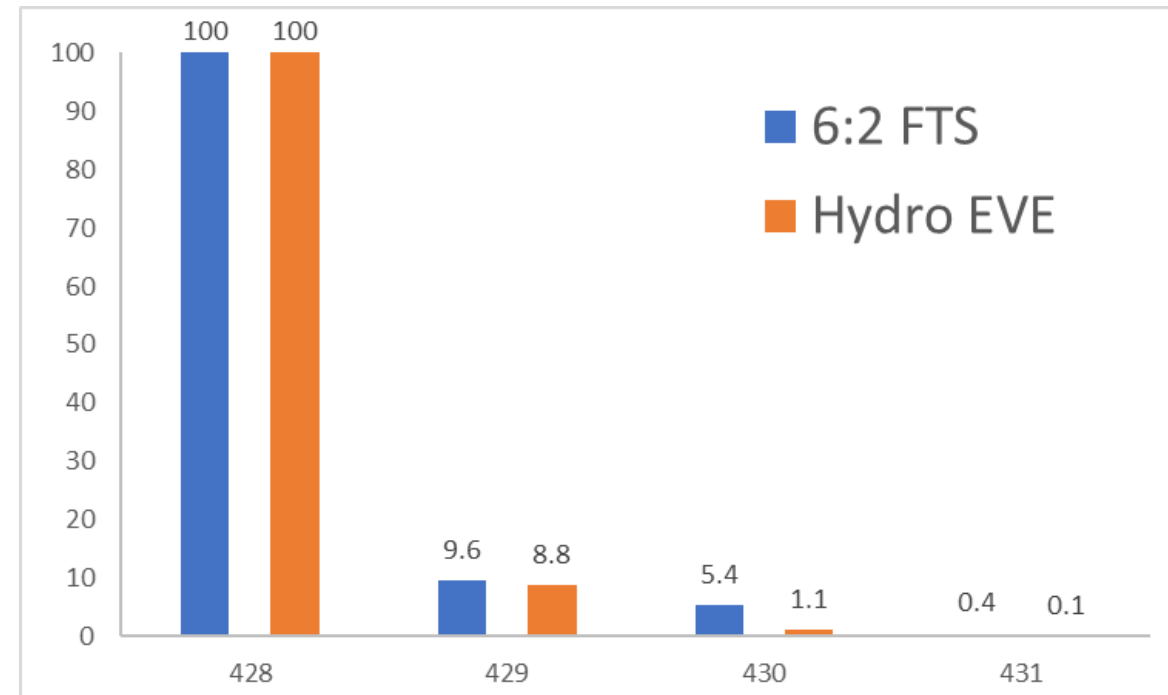
6:2 FTS

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



Novel PFAS Discovery

- CI-PFAS in surface water near fluoropolymer manufacturing facility
- PFAS from XAD trap and control technology water from fluoropolymer use facility
- CI-PFAS in house dust (NIST SRM 2585)

Modified Method 5: Stack emission sampling

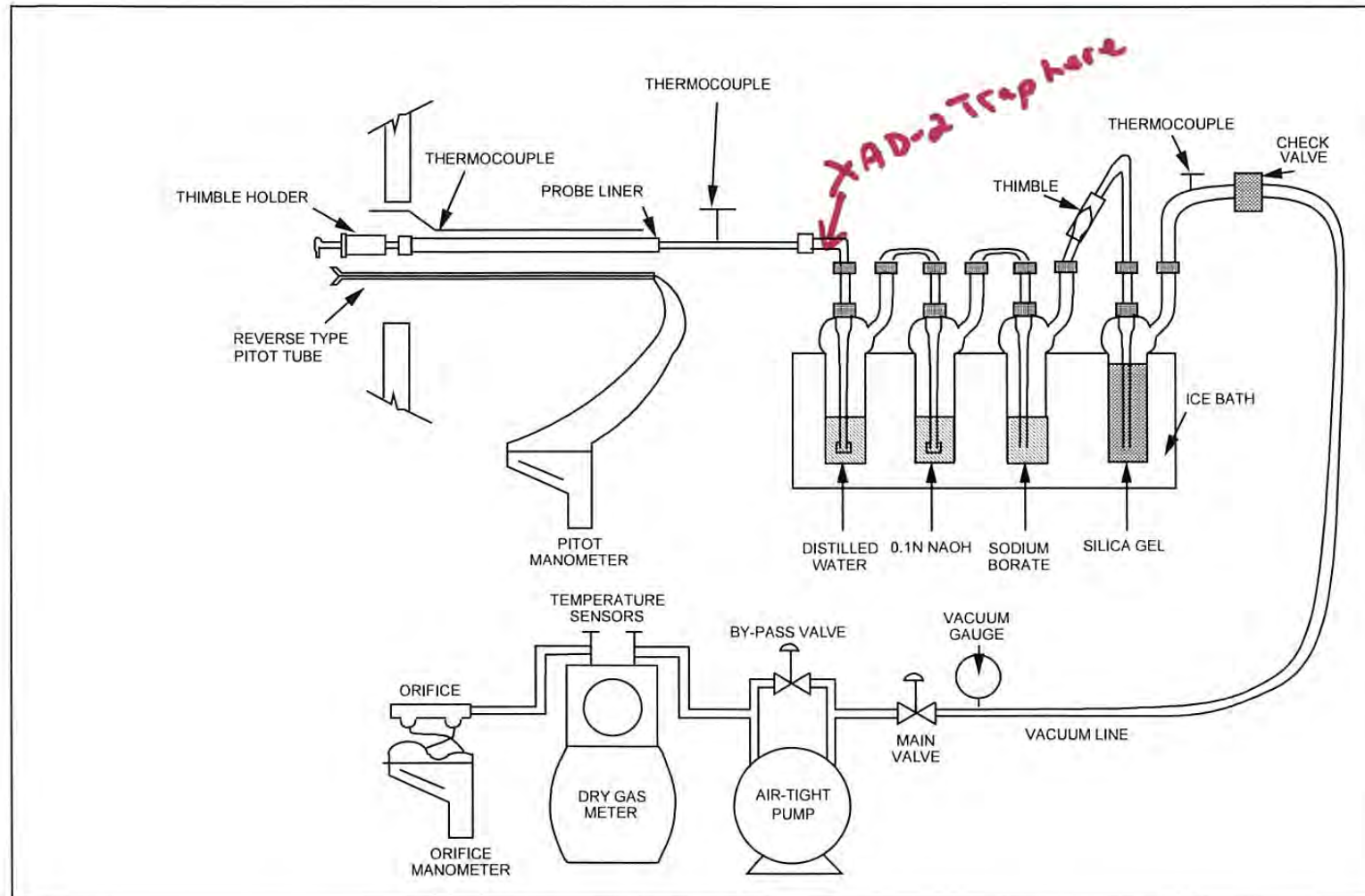
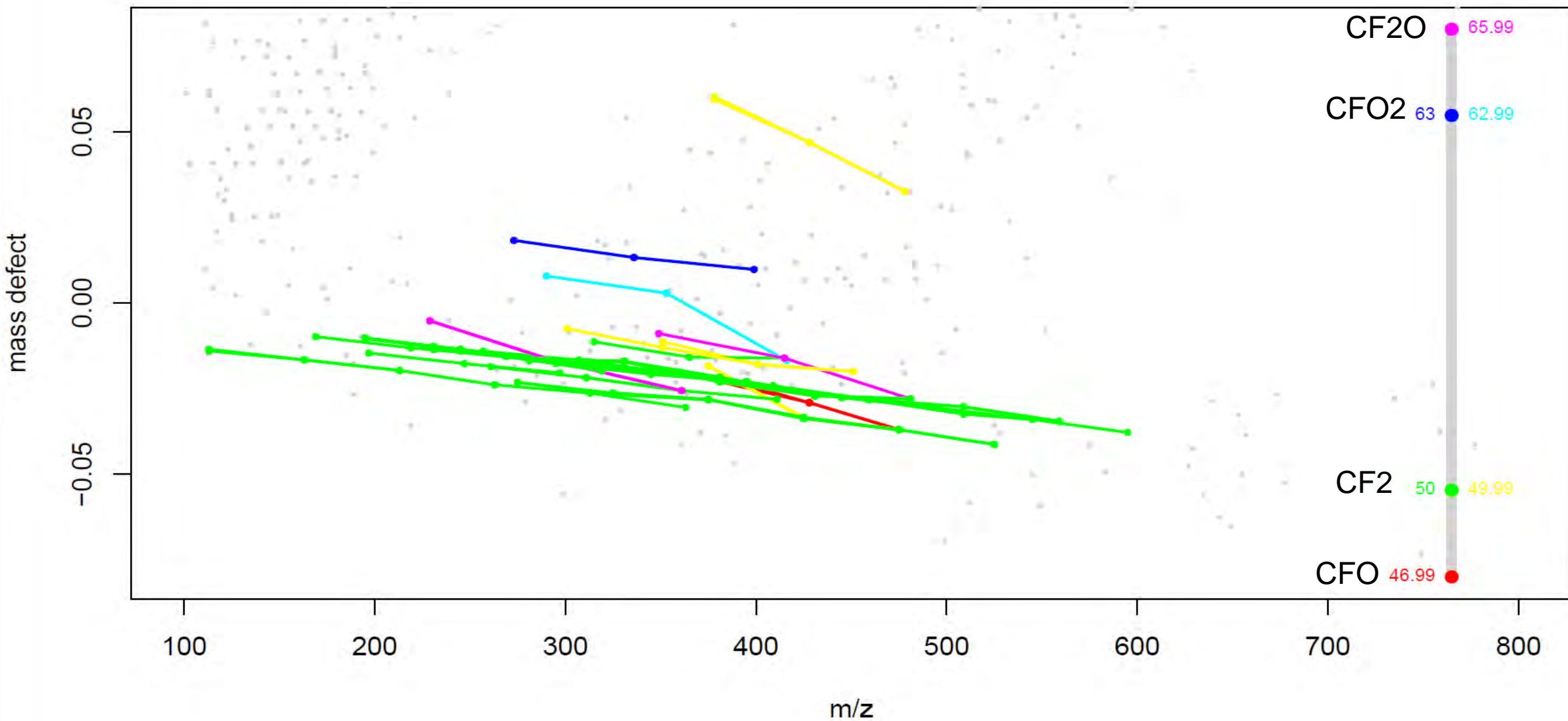
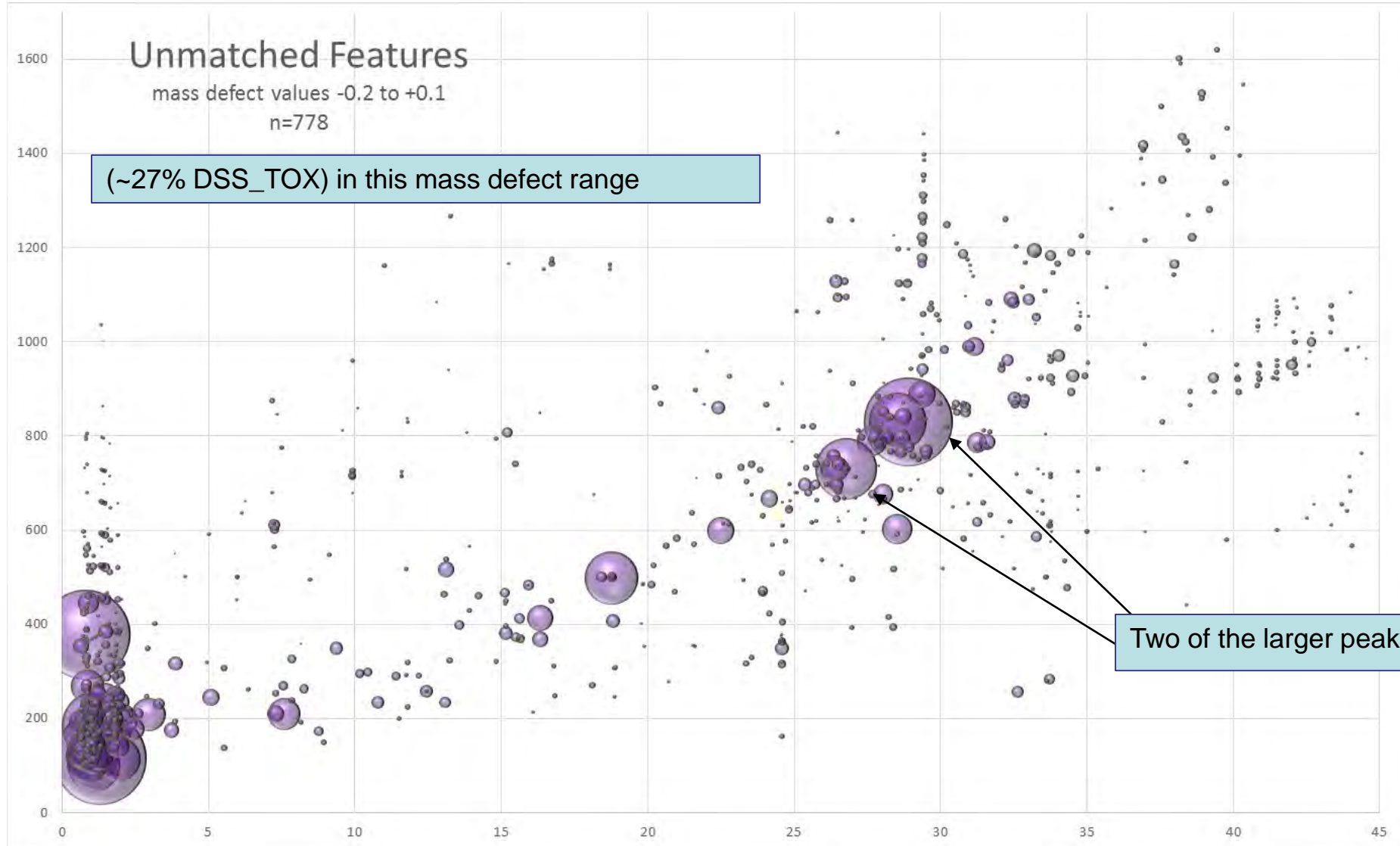


FIGURE 3-1
MODIFIED EPA METHOD 5
PFOA SAMPLING TRAIN

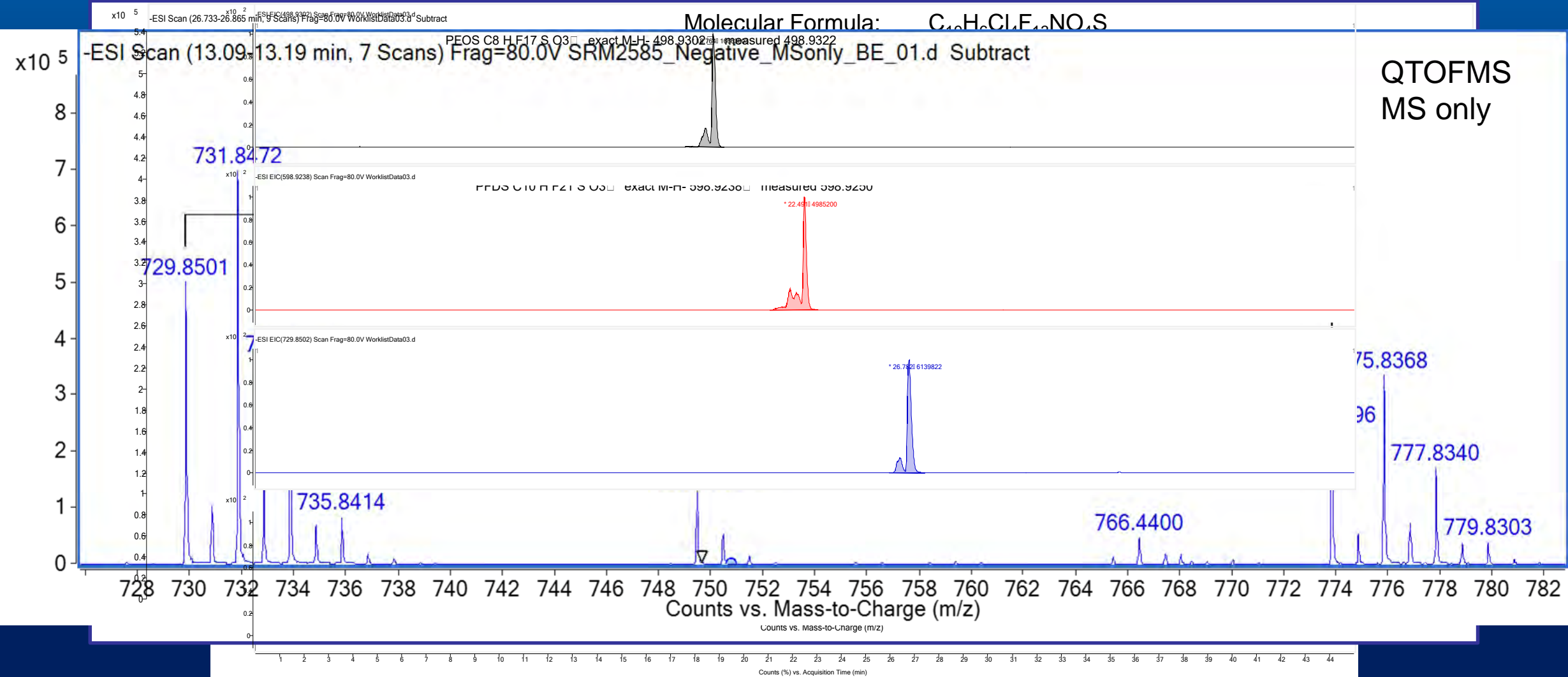
Mass Defect Plots C, F, H, O



NIST SRM 2585 Organic Compounds in Hose Dust



Chromatogram and Spectral Evidence





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.