



Identification and Determination of New PFAS in Cape Fear River Water

Ali Haghani¹, Andrew Eaton¹, Yongtao Li², and Joshua S. Whitaker²



A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFAS)?

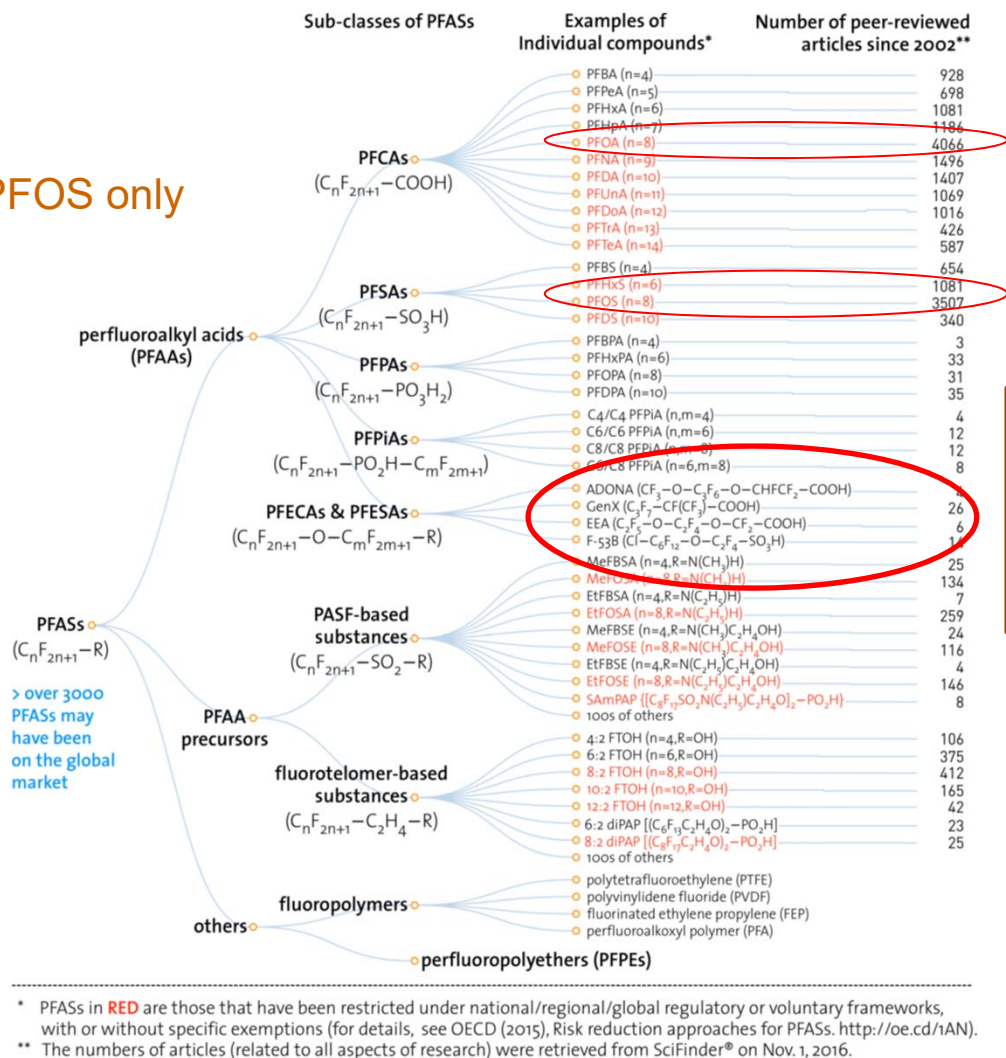


No longer PFOA and PFOS only

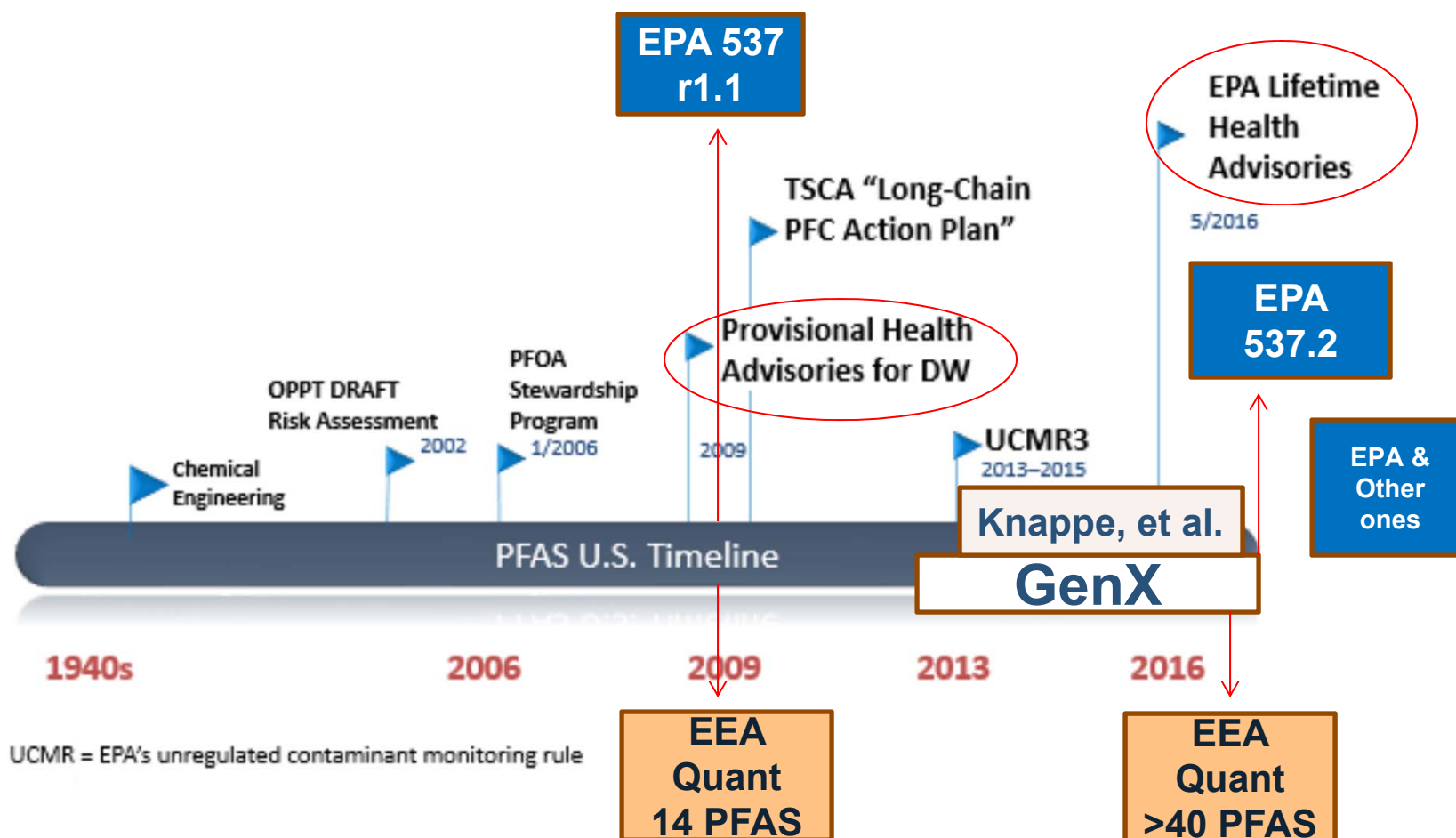
>3000 PFAS

New important class

Wang et al.
2017, ES&T.
PFAS



Which PFAS Will Grow Legs? Regulatory and Methods Impacting Commercial Labs.

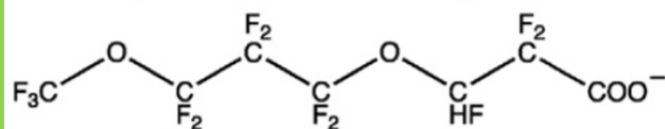


Some of the Fluoropolymers Used by Manufacturers. GenX is to Replace PFOA.

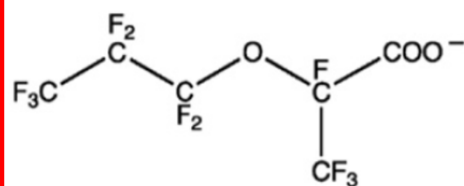


Fluoropolymer manufacture

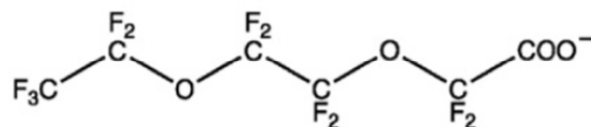
ADONA (CAS No. 958445-44-8)



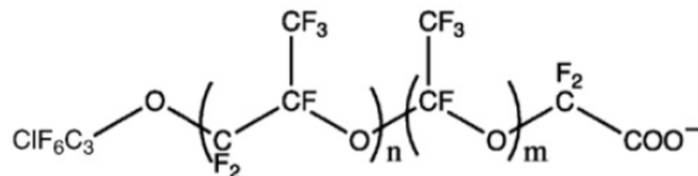
GenX (CAS No. 62037-80-3)



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

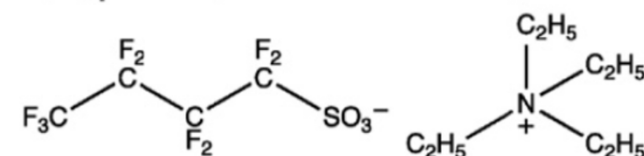


Solvay's product (CAS No. 329238-24-6)

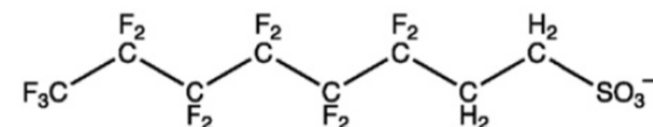


Metal plating

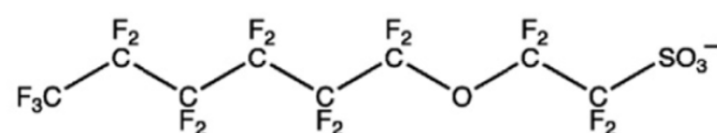
N(Et)₄-PFBS (CAS No. 25628-08-4)



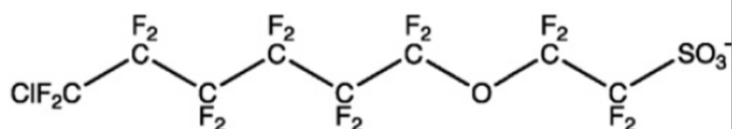
6:2 FTSA (CAS No. 27619-97-2)



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



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



Point & non-point sources

A

B

C

Legacy PFASs

PFPrOPrA ("GenX")

PFAS Concentration (ng/L)

0 200 400 600 800

Fluorochemical Manufacturer

PFPrOPrA ("GenX")



pubs.acs.org/journal/estlcu

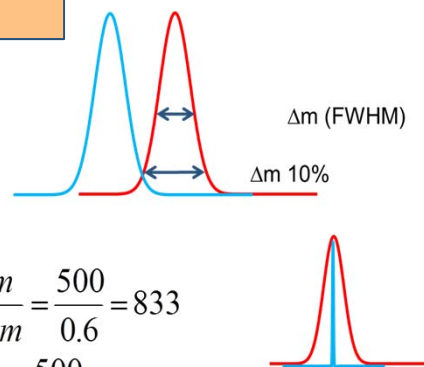
Mei Sun,^{*,†,‡,§} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||}
Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

Two Important Aspects of High Resolution Accurate Mass. (Q Exactive Orbitrap)



Resolution

$$R = \frac{m}{\Delta m}$$



- Quadrupole MS $R = \frac{m}{\Delta m} = \frac{500}{0.6} = 833$

- Orbitrap MS $R = \frac{m}{\Delta m} = \frac{500}{0.0035} = 140000$

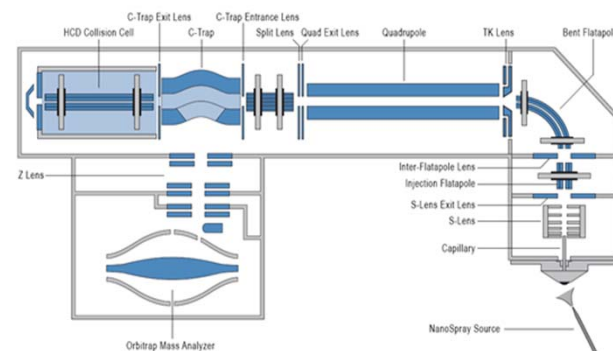
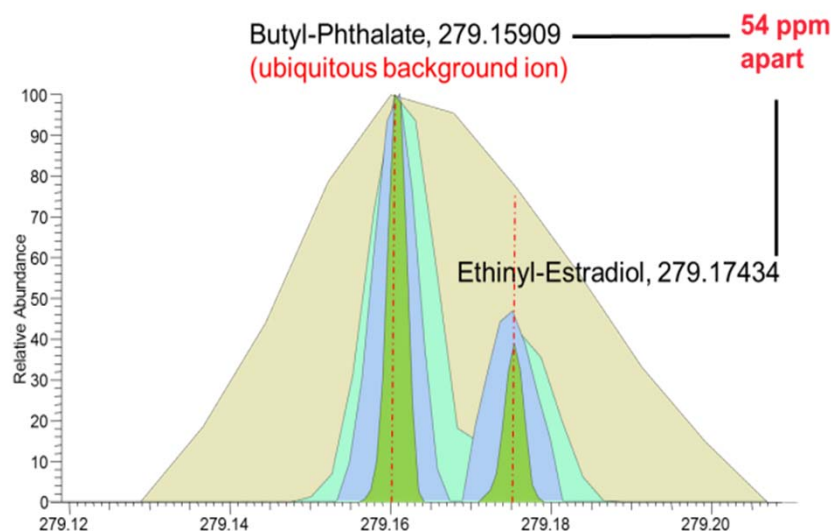
Mass Accuracy

$$\Delta m / z = \frac{m_{meas} - m_{true}}{m_{true}} \cdot 10^6$$

- Quadrupole MS $\Delta m / z = \frac{500.1 - 500.0}{500} \cdot 10^6 = 200 \text{ ppm}$

- Orbitrap MS TOF MS $\Delta m / z = \frac{500.10314 - 500.10214}{500.10314} \cdot 10^6 = 2 \text{ ppm}$

Resolution: 10k, 30k, 50k, 100k



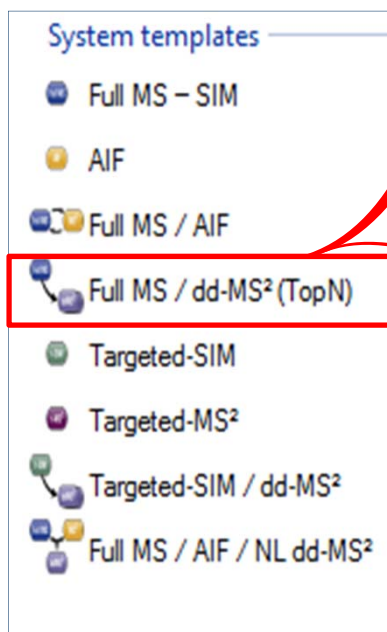
Q Exactive Analysis Set Up



MS conditions:

Spray voltage 3800V, Capillary temperature 295°C, sheath gas 32 au, Aux gas 7 au, S-lens RF level 55

Full MS/data dependent MS²



full MS:resolution **140,000 FWHM**
scan range **100-1500 m/z**

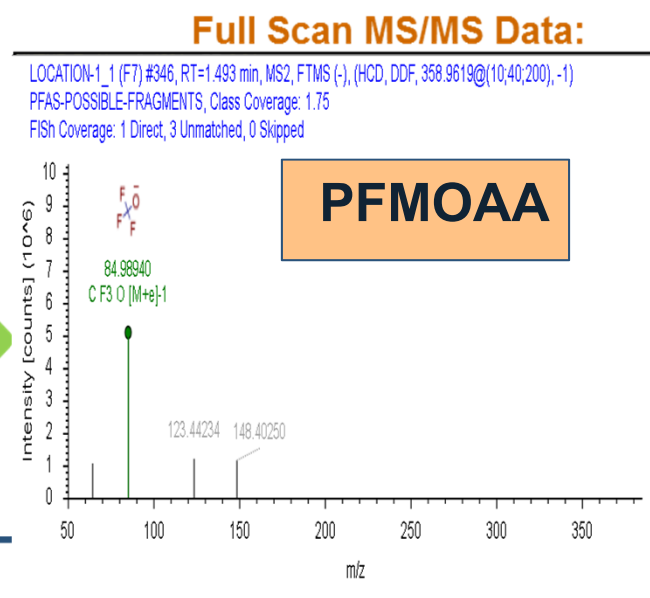
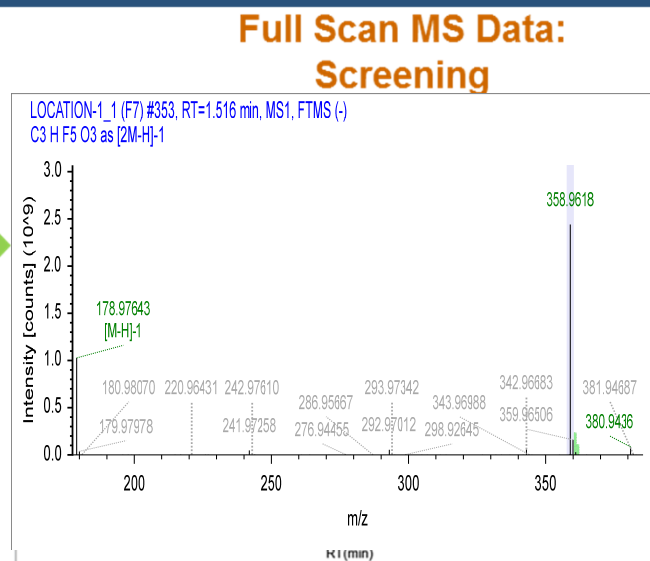
ddMS²:resolution **35,000 FWHM**
Inclusion list **on**
isolation **1 m/z**
exclusion **5 s**
NCE **10,40,200**

List of 146 PFAS target analytes

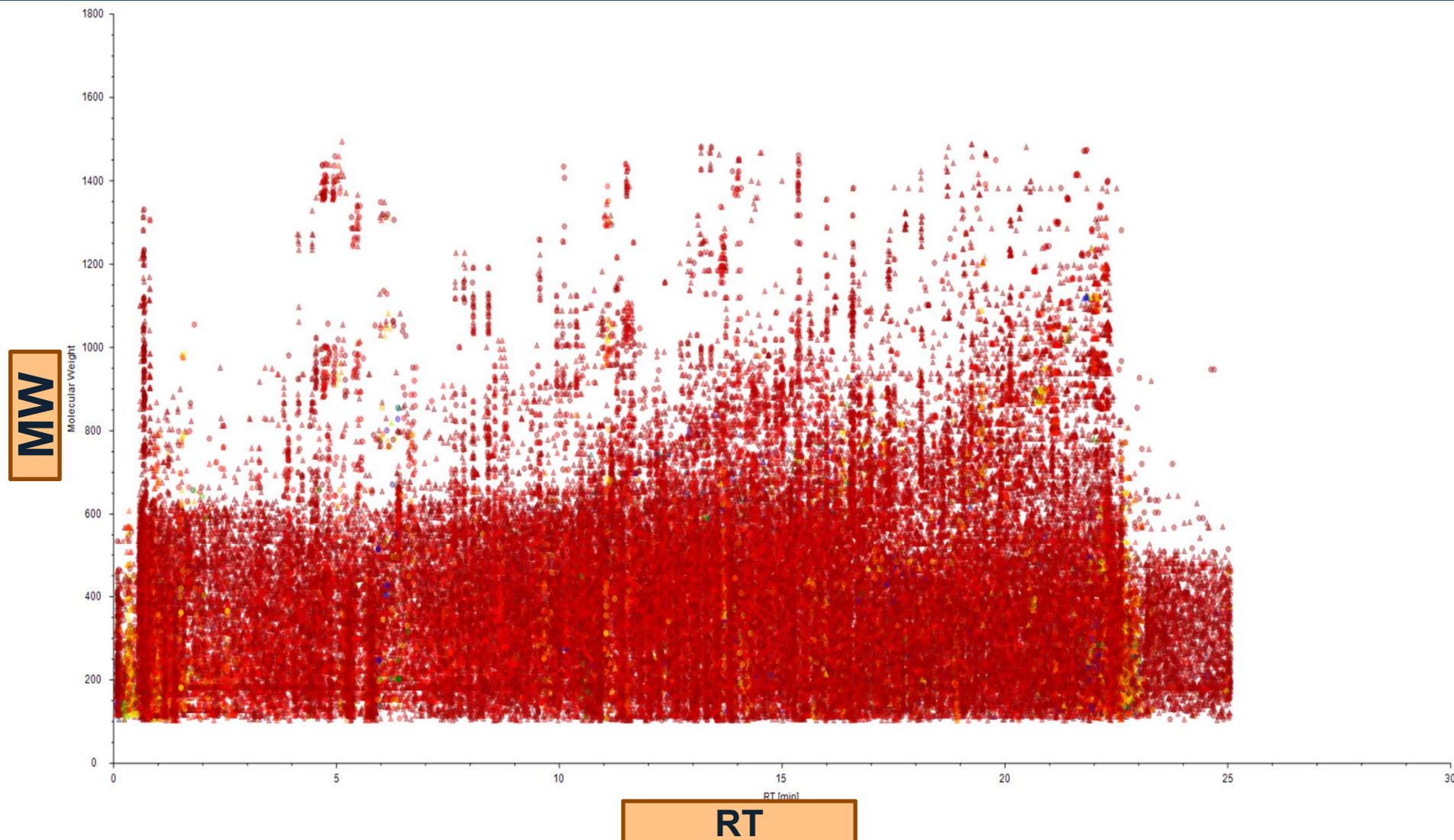
	Mass [m/z]	Formula [M]	Formula type	Species	CS [z]	Polarity
1	178.97731	C3HF5O3	Chemical formula	M-H	1	Negative
2	112.9857	C2HF3O2	Chemical formula	M-H	1	Negative
3	148.9526	CF3SO3H	Chemical formula	M-H	1	Negative
4	162.9823	C3F5O2H	Chemical formula	M-H	1	Negative
5	178.9773	C3HF5O3	Chemical formula	M-H	1	Negative
6	197.9654	C2HF5SO2NH	Chemical formula	M-H	1	Negative
7	198.9494	C2HF5SO3	Chemical formula	M-H	1	Negative
8	212.9792	C4HF7O2	Chemical formula	M-H	1	Negative
9	228.97411	C4HF7O3	Chemical formula	M-H	1	Negative
10	241.9916	C4H5F5N SO3H	Chemical formula	M-H	1	Negative
11	242.01723	C6H5F7O2	Chemical formula		1	Negative
12	244.96903	C4HF7O4	Chemical formula	M-H	1	Negative
13	247.9616	C3HF7NSO2H	Chemical formula	M-H	1	Negative
14	247.9622	C3HF7SO2NH	Chemical formula	M-H	1	Negative
15	248.9461	C3HF7SO3	Chemical formula	M-H	1	Negative
16	252.97601	C5HF9O2	Chemical formula	M-H	1	Negative
17	264.02022	C6H5F9O	Chemical formula		1	Negative
18	276.9411	C4F7SO4H	Chemical formula	M-H	1	Negative
19	278.97092	C5HF9O3	Chemical formula	M-H	1	Negative
20	282.9481	C4HF9SO2	Chemical formula	M-H	1	Negative
21	291.9884	C5H5F7N SO3H	Chemical formula	M-H	1	Negative
22	297.9584	C4HF11NSO2H	Chemical formula	M-H	1	Negative
23	298.94299	C4F9SO3	Chemical formula		1	Negative
24	310.9607	C5HF9O5	Chemical formula	M-H	1	Negative
25	310.96075	C5HF9O5	Chemical formula	M-H	1	Negative
26	312.97281	C6HF11O2	Chemical formula	M-H	1	Negative
27	325.96647	C6H4F9SO3	Chemical formula	M-H	1	Negative



146



Large Data Files Showing > 83000 Data Points To Mine Through.



Some Pre Knowledge is Required to Sieve Through the Large Data Points



- Per and poly fluorinated compounds have negative mass defects .
CH₂(14MW, 14.**01565**MW), CF₂(50MW, 49.**99681**MW).
- Identification and looking for homologues for different class/sub class of PFAS. CF₂ (49.9968m/z), CF₂O (65.9917m/z), etc.
- Retention time shifts to the right as the homologues CF₂ chain increases.
- Using simplified compound prediction composition based on expected compounds compositions can reduce data to be Sieved through .

i.e. C₂₀**H**F₅₀ N₅ O₁₀ P₂ S₂

- Having knowledge of recurring Fragments i.e [CF₃O]-, 84.989m/z

Using Class Coverage: Capturing MS1 Precursors from Designated MS2 Fragments - Compound Discover Software.

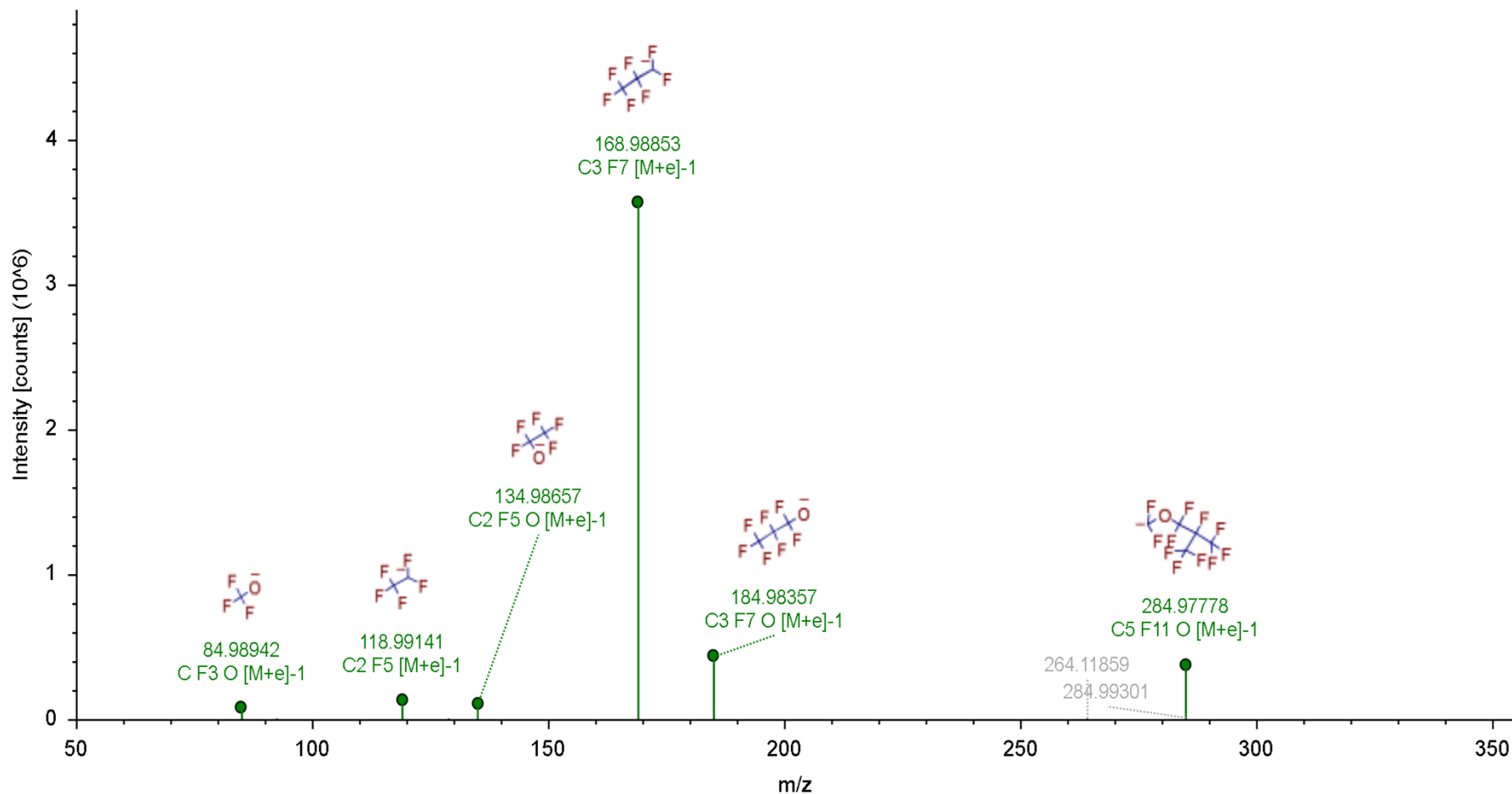


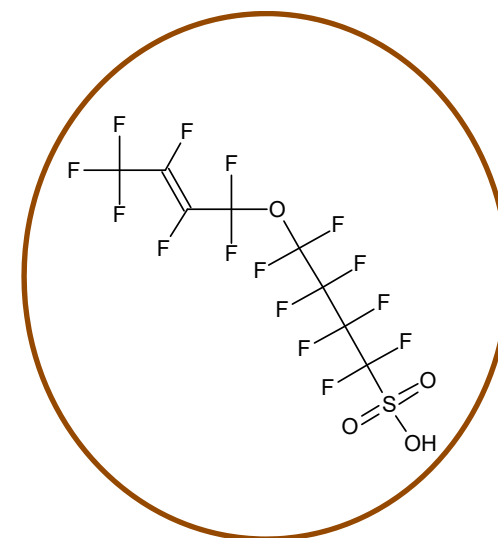
Molecular Weight	RT [min]	Area (Max.)	Class Coverage ☐					Mass List Matches ☐
			PFAS-ETHER-II*	PFAS-85	PFAS-151	PFAS-135	PFAS-167	
201.98601	10.416	122729	50.00	100.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
201.98588	6.316	1242694	50.00	100.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
201.81210	22.377	3816	50.00	100.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
202.04717	22.445	55003	50.00	100.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
201.92006	22.348	9966	50.00	100.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
377.97624	13.077	112909	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐
135.90080	20.586	1450395	25.00	0.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
507.92985	7.888	317687	25.00	0.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
246.03737	22.724	81349	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐
135.90080	20.006	595973	25.00	0.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
201.95194	22.425	36738	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐
247.06489	0.772	132695	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐
307.97679	6.318	328940	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐
246.14657	4.867	14563	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐
311.96811	11.080	1777297	25.00	100.00	0.00	0.00	0.00	☒ ☐ ☐ ☐
135.90080	21.360	1852567	25.00	0.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
427.97270	13.166	225357	25.00	0.00	0.00	100.00	0.00	☐ ☐ ☐ ☐
242.97999	1.608	1914329	25.00	100.00	0.00	0.00	0.00	☐ ☐ ☐ ☐

GenX Continued: Fragments From a Std are Shown



LOCATION-1B_1 (F6) #2894, RT=11.639 min, MS2, FTMS (-), (HCD, DDF, 328.9677@15, -1)
PFAS-POSSIBLE-FRAGMENTS, Class Coverage: 10.53
FISH Coverage: 6 Direct, 4 Unmatched, 0 Skipped



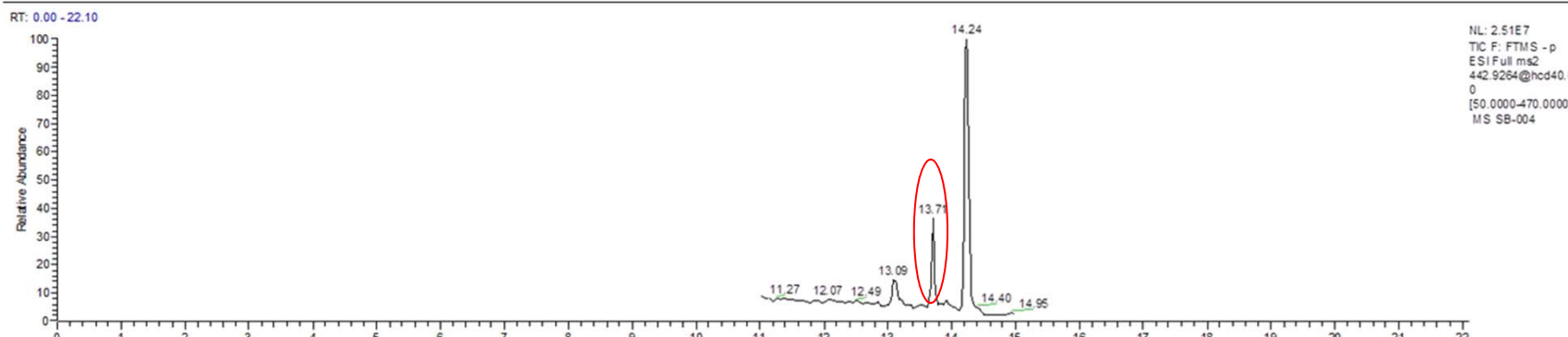


Other Observations: Nafion BP1 Had Multiple Peaks as Candidates



C:\Xcalibur\Data\SB-004

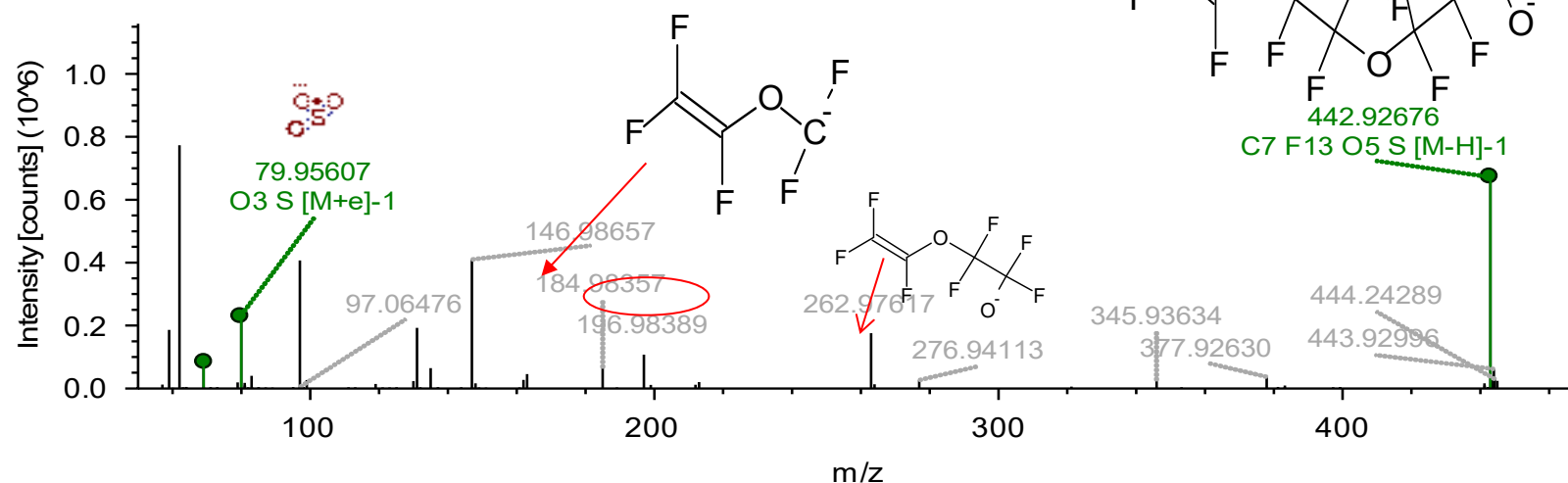
01/06/18 11:49:00



SB-006, #6906, RT=13.688 min, FTMS (-), MS2 (HCD, DDF, 442.93@35.00, z=-1)

n/a, MW: 443.93406, Area: 312819

FISH Coverage: 3 Direct, 39 Unmatched, 40 Skipped



Adjusted Mass Defect Plot: AMD/m/z

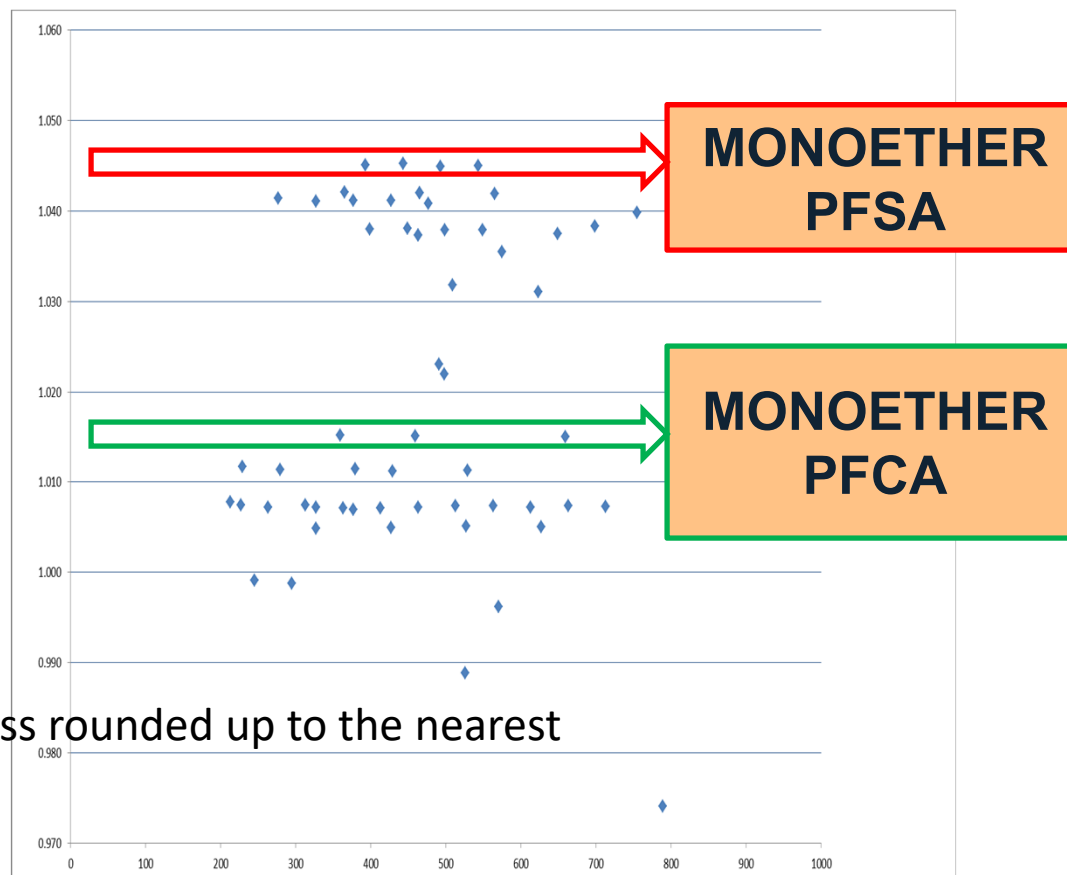


Hill notation: CF_2
Nominal mass: 50
Monoisotopic mass: 49.99681

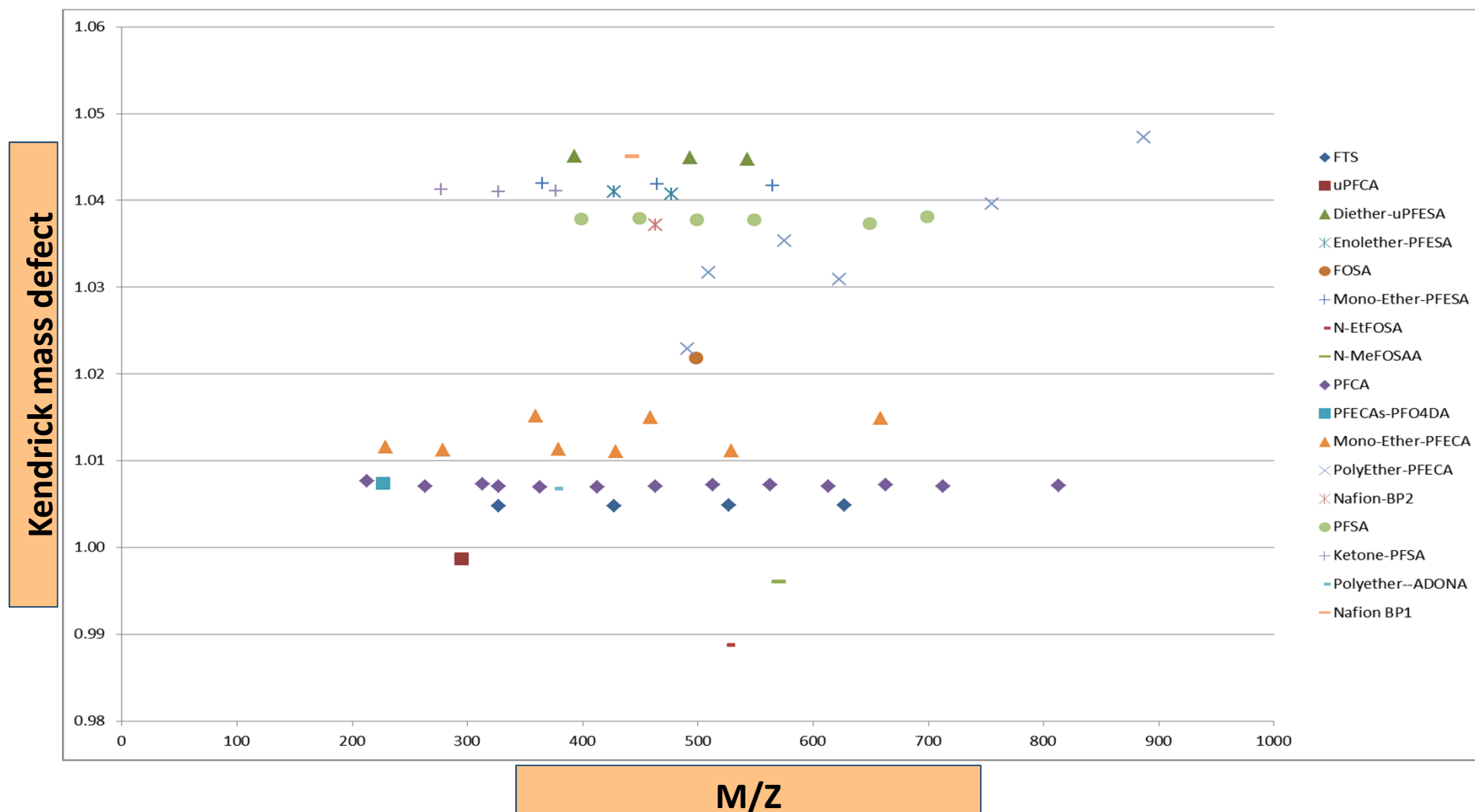
1) Kendrick Mass = $m/z \cdot 50 / 49.99681$

2) Kendrick mass defect = Kendrick mass rounded up to the nearest whole number – Kendrick mass

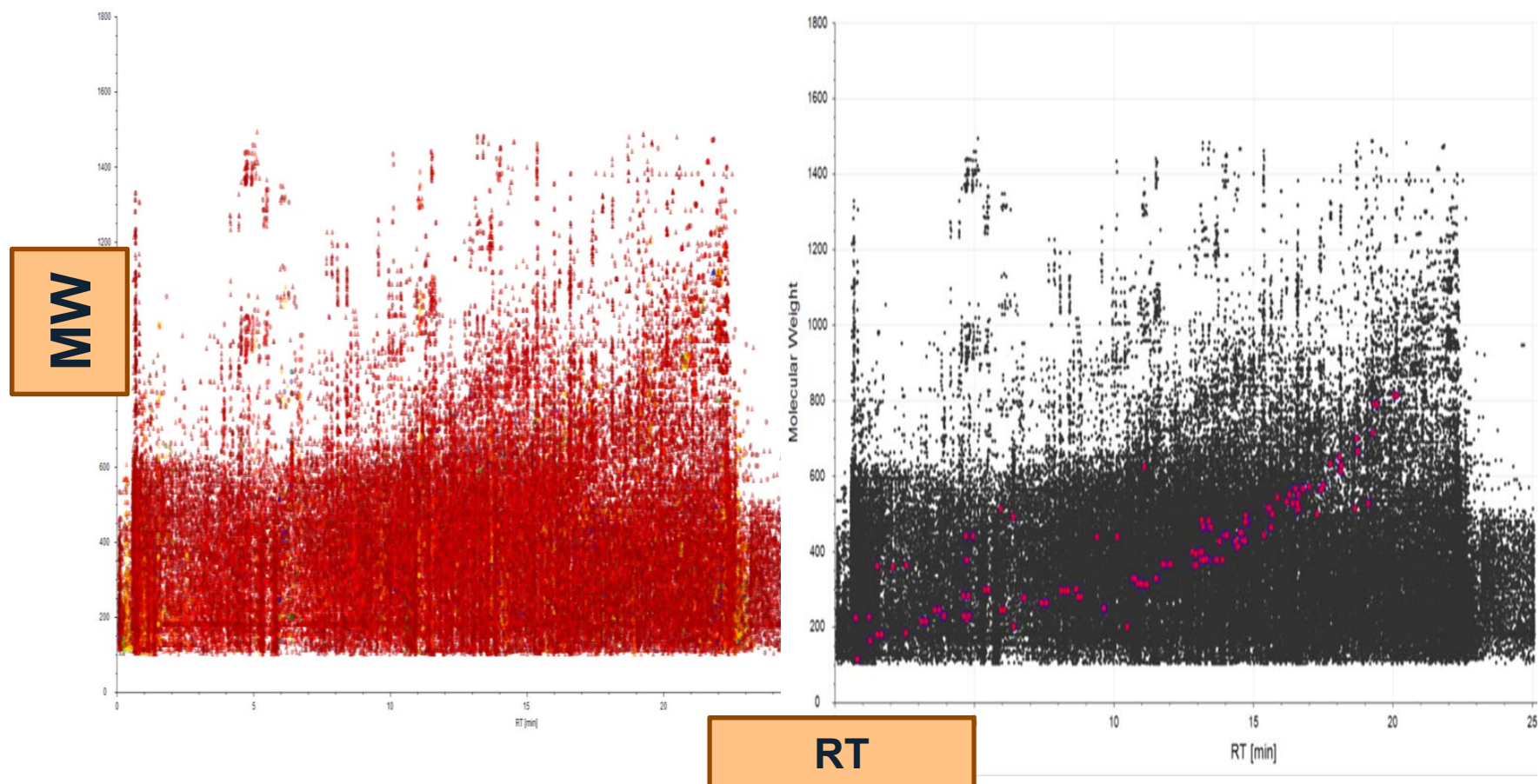
3) Adjusted Mass Defect = Kendrick mass defect



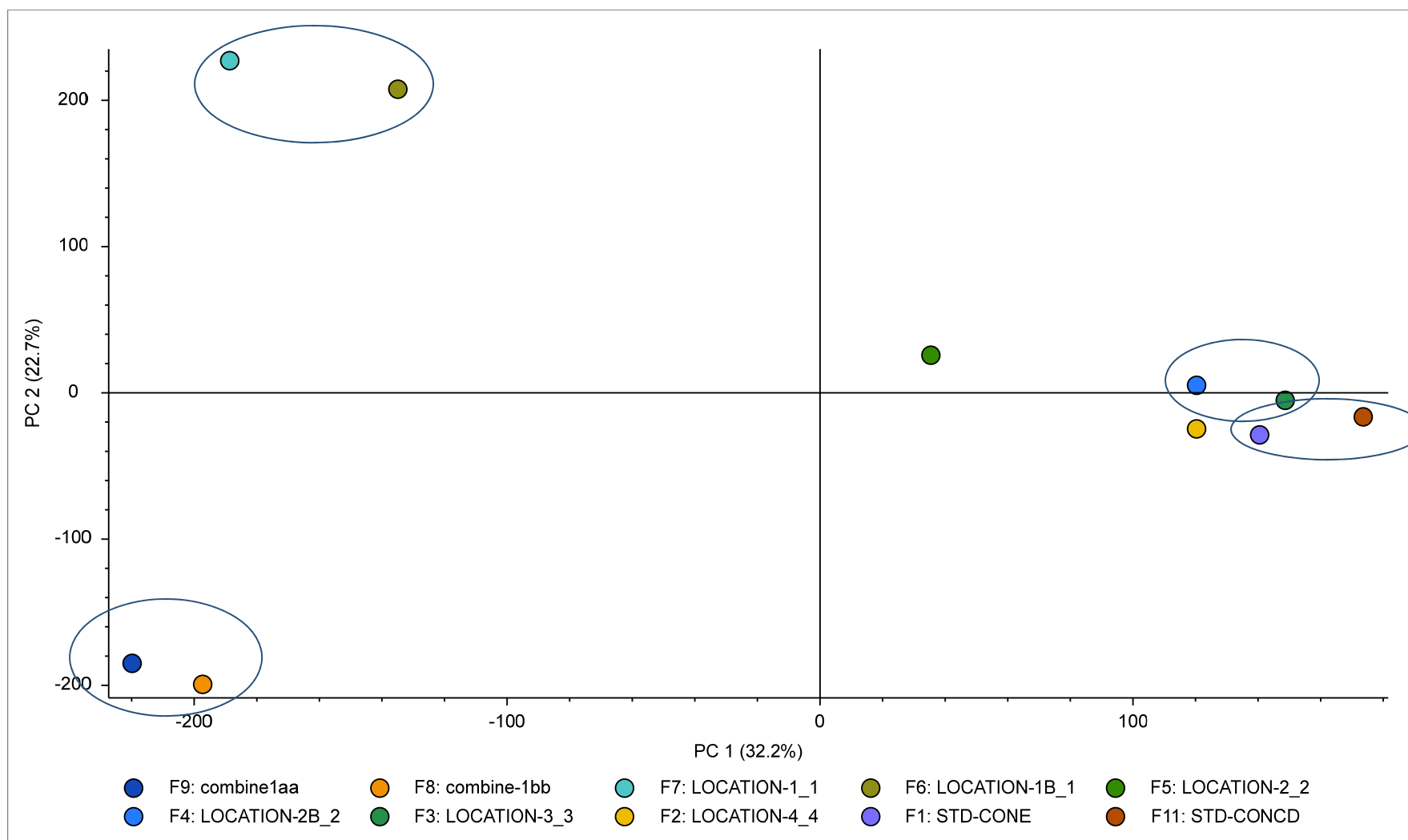
Adjusted Mass Defect Plot



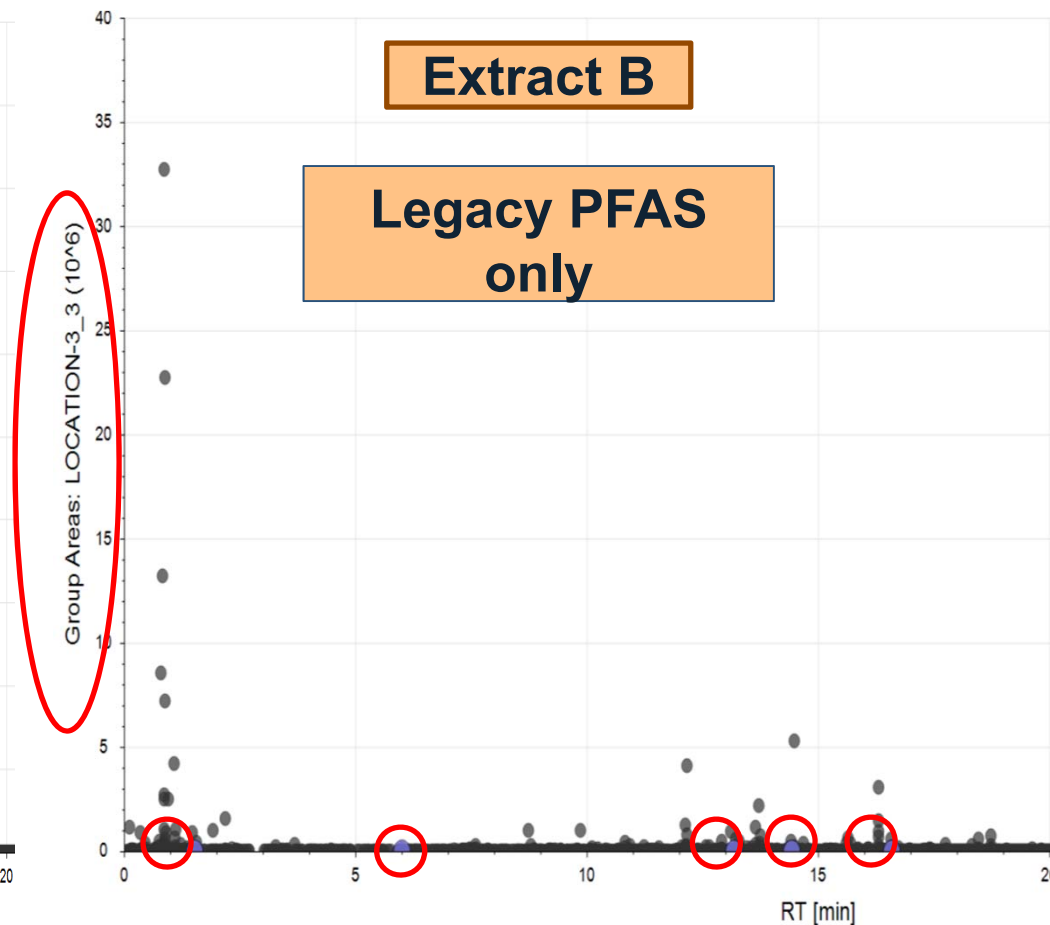
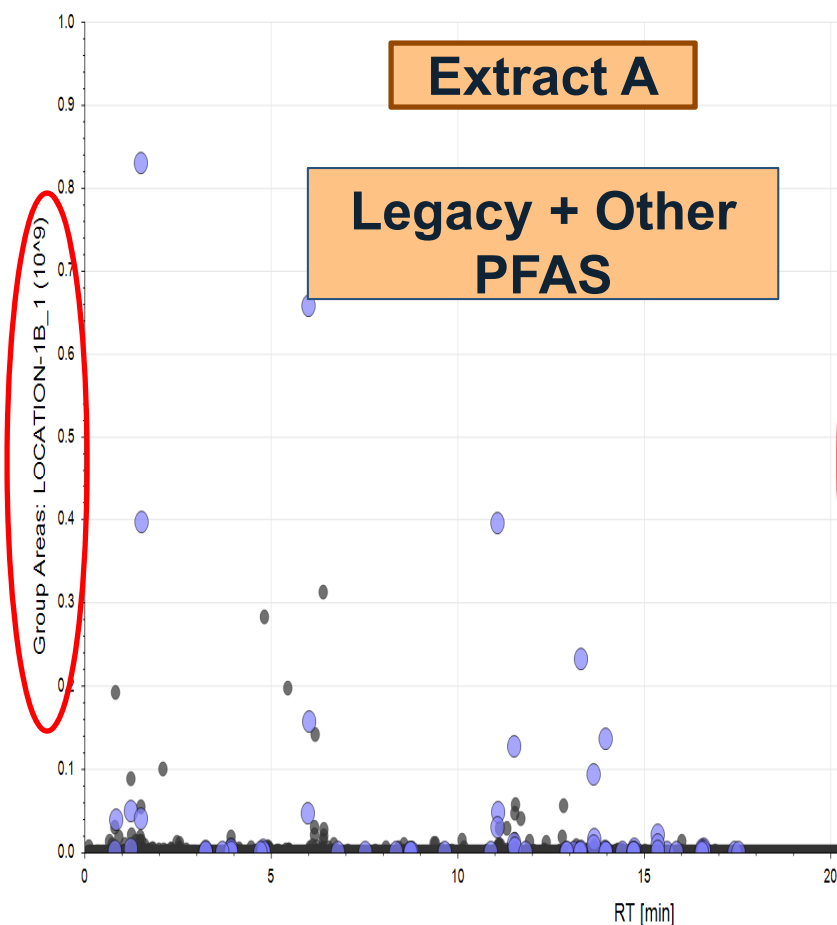
Showing the Non Target Candidates on the Right.



Principal Component Analysis (PCA)



Extract A has Distinguishable Higher Area Counts for PFAS With Additional Ether PFAS.

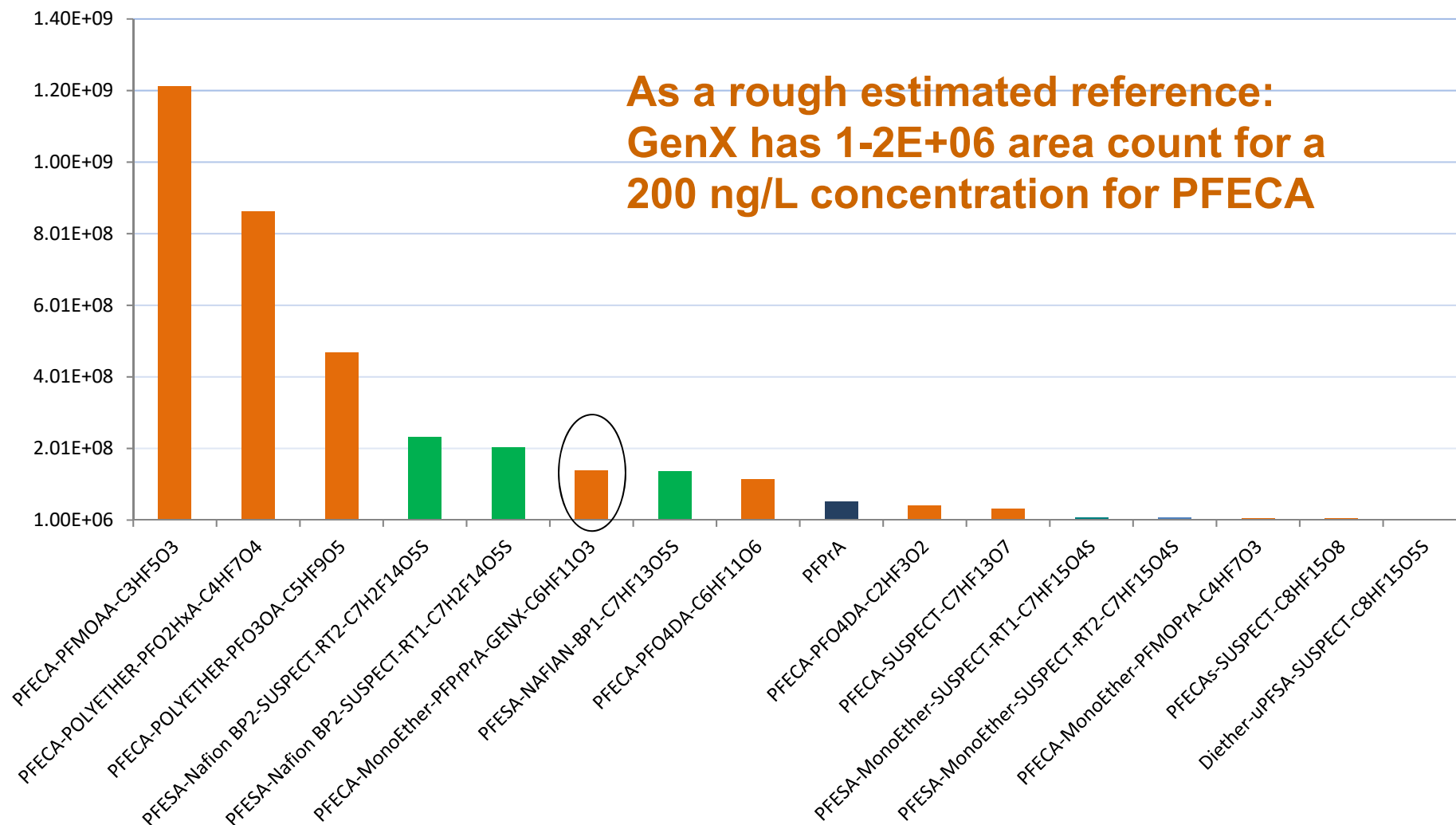


16 PFECA and PFESA Suspects Identified. The Potential New Ones are Marked.

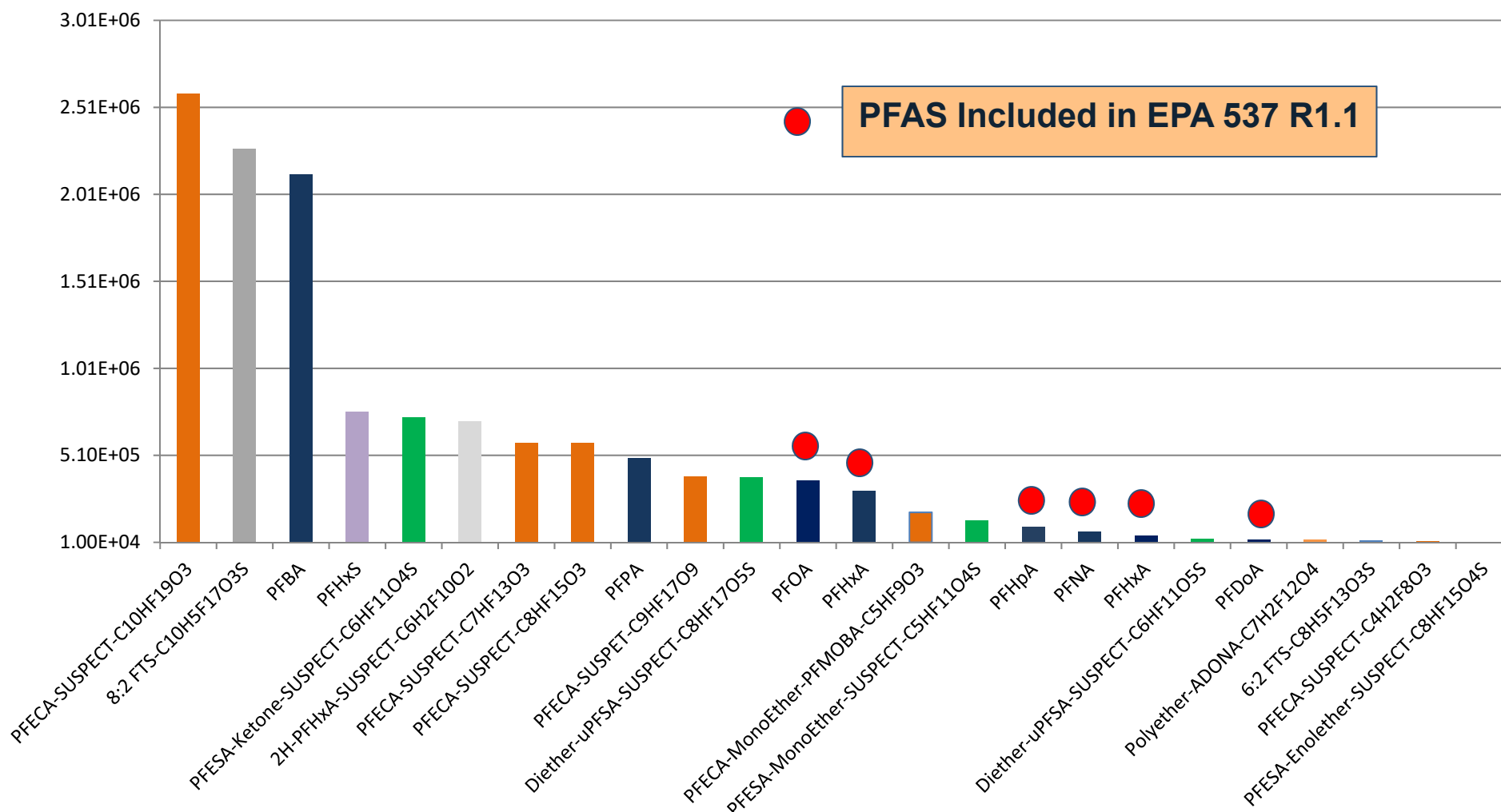


		1A	2A	COMP
Compound Name	Chemical Formula	Area	Area	Area
Diether-uPFSA-suspect ●	C6 H F11 O5 S		1.E+06	
Diether-uPFSA-suspect ●	C8 H F15 O5 S		1.E+06	4.E+04
Diether-uPFSA-suspect ●	C9 H F17 O5 S		3.E+05	
Enoether-PFSA-suspect ●	C8 H F15 O4 S	TRACE	1.E+06	2.E+04
Mono-Ether-PFSA-suspect ●	C4 H F7 O4 S		2.E+07	
Mono Ether-PFSA-suspect ●	C5 H F11 O4 S		3.E+05	2.E+04
Mono-Ether-PFSA-suspect ●	C6 H F11 O4 S		1.E+06	
Mono Ether-PFSA-suspect-RT1 ●	C7 H F15 O4 S			4.E+04
Mono-Ether-PFSA-suspect-RT2 ●	C7 H F15 O4 S			4.E+04
PFECA-DIMER-suspect	C7 H F13 O3		3.E+05	1.E+04
PFECA-DIMER-suspect	C8 H F15 O3		8.E+05	1.E+04
PFECA-DIMER-suspect ●	C10 H F19 O3		3.E+06	1.E+05
PFECAs-Polyether-DIMER-suspect ●	C8 H F15 O8		8.E+06	3.E+04
PFECA-Polyether-DIMER-suspect ●	C9 H F17 O9	TRACE	8.E+05	TRACE
PFECA-Polyether-DIMER-suspect	C7 H F13 O7		3.E+07	2.E+05

Showing PFAS with Area Counts of $>2.6E+06$



Continued: Showing >1E+04<2.6E+06 area Count.



In-house SB Test Results of DW (NC)



39 legacy and GenX were quantitated.

- **13 PFAS were detected.**
- **26 PFAS were not detected.**

Four new PFECA and two Nafion BPs were estimated.

- **5 new PFAS were detected.**
- **1 new PFAS was not detected.**

In-House Results of 147 DW Samples (NC)



Compound	Highest Conc. ng/L	Mean Conc. ng/L	% of Results $\geq$ MRL	% of Results > HA
PFPeA	59	25	95	---
PFHxA	74	25	90	---
PFBA	26	14	86	---
PFHpA	50	13	79	---
PFOA	24	6	77	0
PFBS	12	2	60	---
PFOS	52	4	35	0
PFHxS	43	<2	30	---
PFNA	6	<2	21	---
PFDA	6	< 2	15	---
PFPeS	8	<2	0.7	---
NEtFOSAA	10	< 2	0.1	---

EPA 537 & In-house SB Test Results: Emerging PFAS (NC)



MRL Confirmation Study					
	Mean	sd	HPIR	Lower PIR >50%	Upper PIR <150%
GenX	4.58	0.334	1.322	65	118

Compound	# of Sample	Highest Conc. ng/L	Mean Conc. ng/L	Median Conc. ng/L	% of Results ≥ 5 ng/L
GenX (DW)	288	230	14	< 5	43
GenX (GW)	181	179	16	< 5	48

In-house SB Test: 6 Non-Target PFAS (PFECAs)



Compound	Acronym	Reference	Highest Conc. ng/L	% of Results ≥ 5 ng/L
Perfluoro-2-methoxyacetic acid	PFMOAA	GenX	5560	98
Perfluoro (3,5-dioxahecanoic) acid	PFO2HxA	GenX	180	80
Perfluoro (3,5,7-trioxaoctanoic) acid	PFO3OA	GenX	109	55
Perfluoro (3,5,7,9-tetraoxadecanoic) acid	PFO4DA	GenX	31	33
Nafion Byproduct 1	Nafion BP1	---	< 5	0
Nafion Byproduct 2	Nafion BP2	Nafion BP1	33	35

Conclusions



- **Q Exactive Orbitrap can be used for identification of site specific emerging contaminants.**
- **New suspects were identified with matching Kendricks adjusted mass defect plot and MS2 fragmentation.**
- **PFAS quantitation and estimated concentrations from Cape Fear samples were presented.**
- **New standards are required for confirmation of the potentially new found suspects.**

Any Questions?



Ali Haghani: alihaghani@eurofinsus.com

Andy Eaton: andyeaton@eurofinsus.com

Yongtao Li: yongtaoli@eurofinsus.com

Joshua S. Whitaker: joshuawhitaker@eurofinsus.com

Eurofins Eaton Analytical, LLC

www.eurofinsus.com/eaton