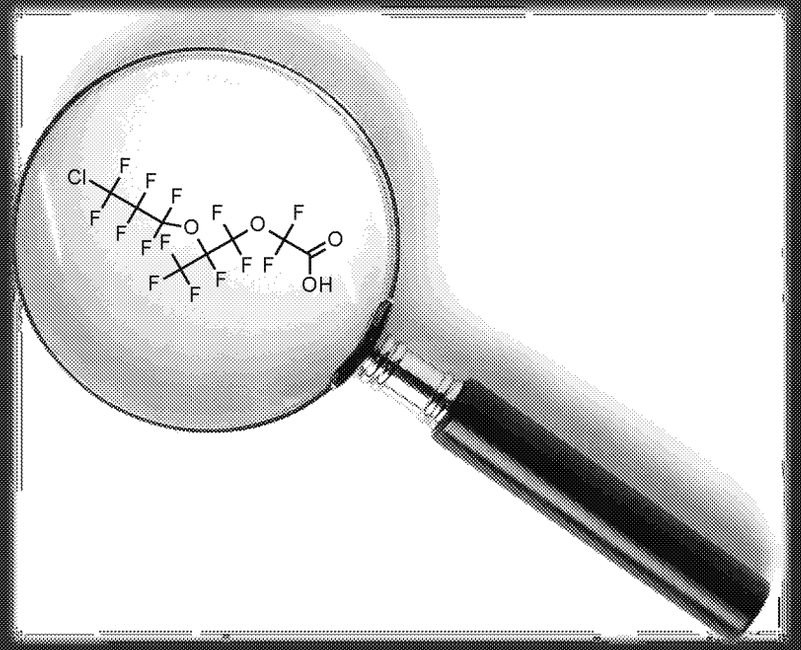
# Identification of PFAS in the Environment

Mark Strynar and James McCord
US EPA
Office of Research and Development (ORD)
National Exposure Research Laboratory (NERL)



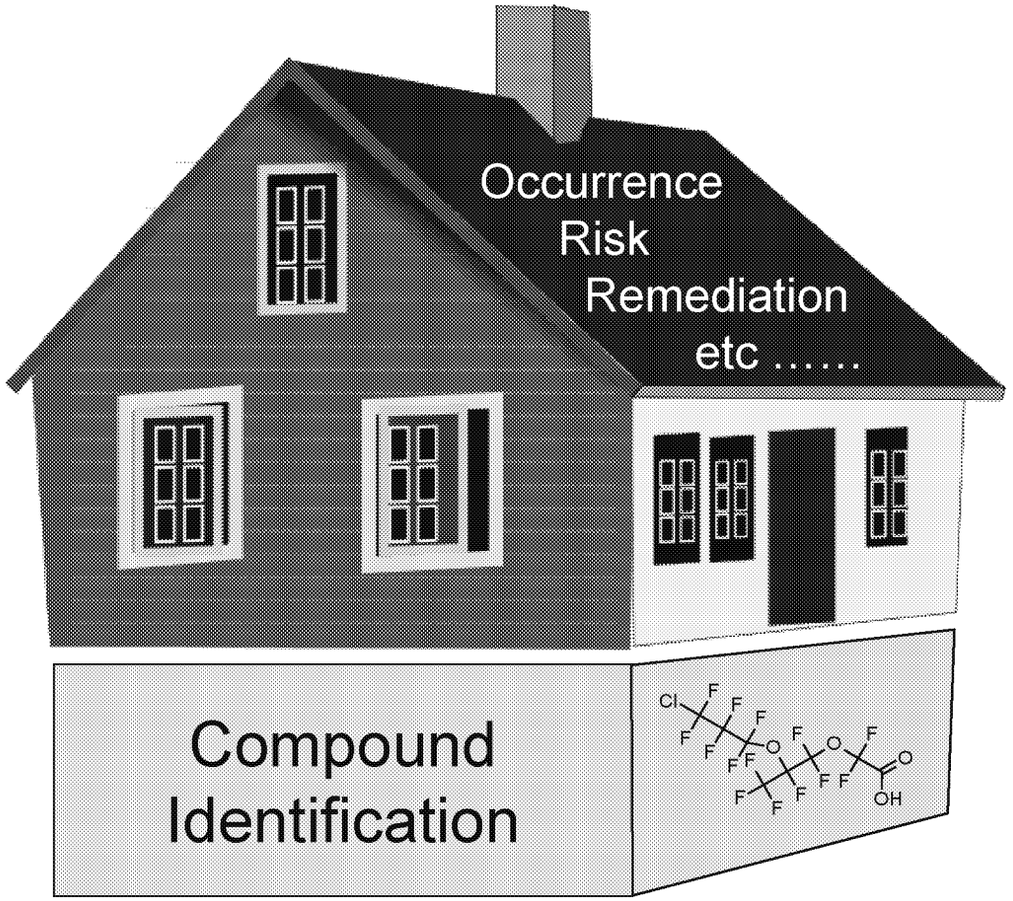

August 12th, 2019
Environmental, Sources, Chemistry, Fate and Transport
PFAS/FTM SETAC



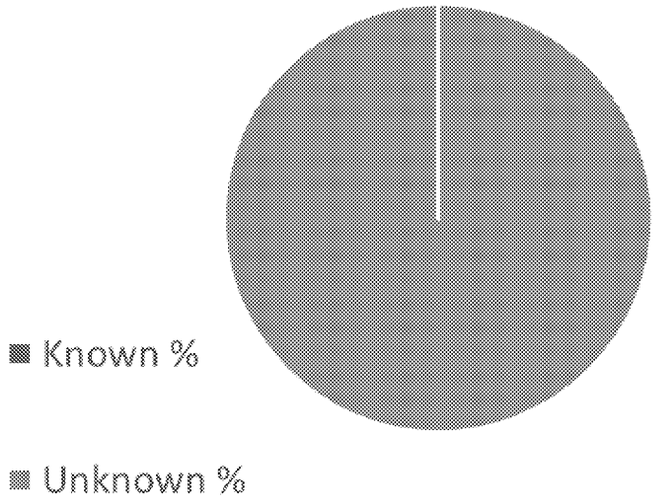
ED_004850_00004154-00001

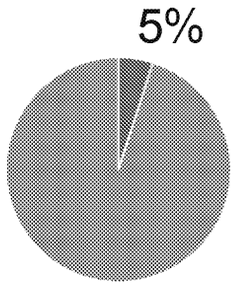
# PFAS identification basis

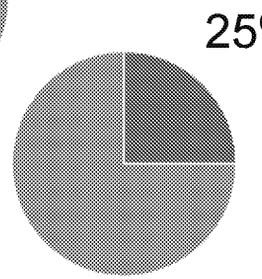
Foundation: First step
Critical for home
Necessary
Everything else is built upon it

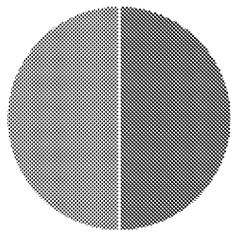


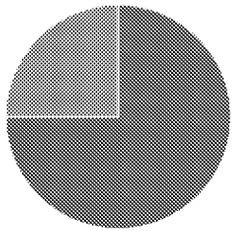
# What is our comfort level?

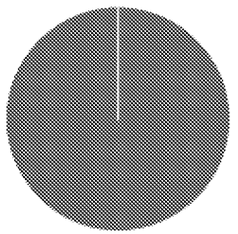


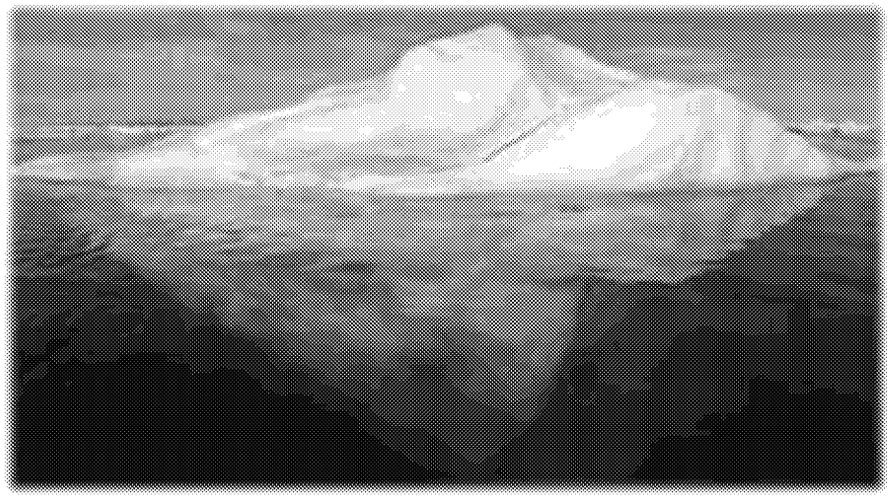



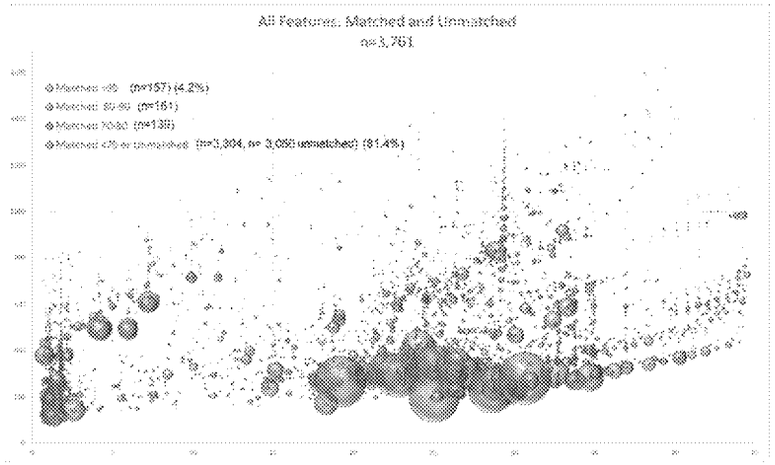



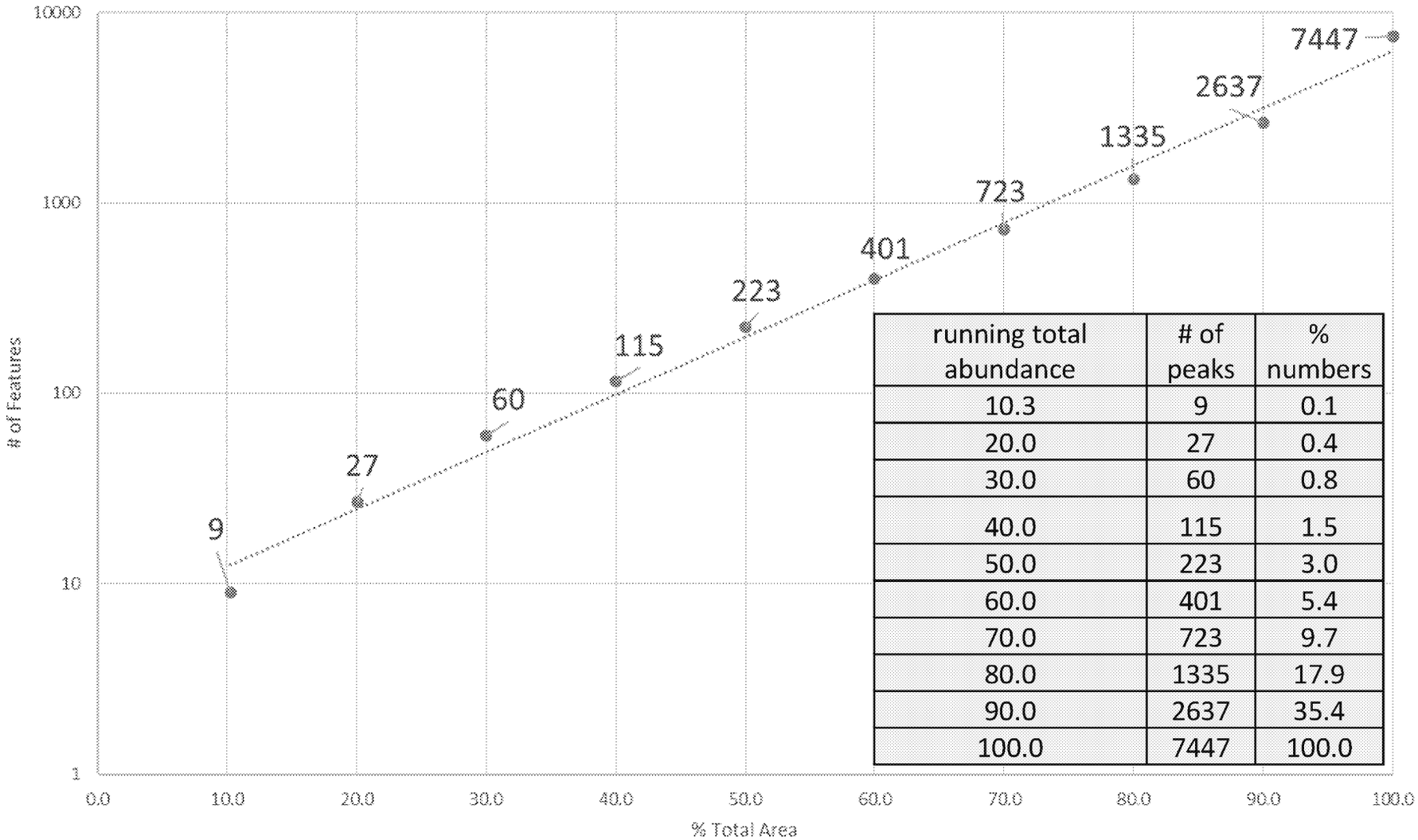





# Visualization of Data: number vs abundance




| running total abundance | # of peaks | % numbers |
|---|---|---|
| 10.3 | 9 | 0.1 |
| 20.0 | 27 | 0.4 |
| 30.0 | 60 | 0.8 |
| 40.0 | 115 | 1.5 |
| 50.0 | 223 | 3.0 |
| 60.0 | 401 | 5.4 |
| 70.0 | 723 | 9.7 |
| 80.0 | 1335 | 17.9 |
| 90.0 | 2637 | 35.4 |
| 100.0 | 7447 | 100.0 |

House Dust Example sorted by Abundance

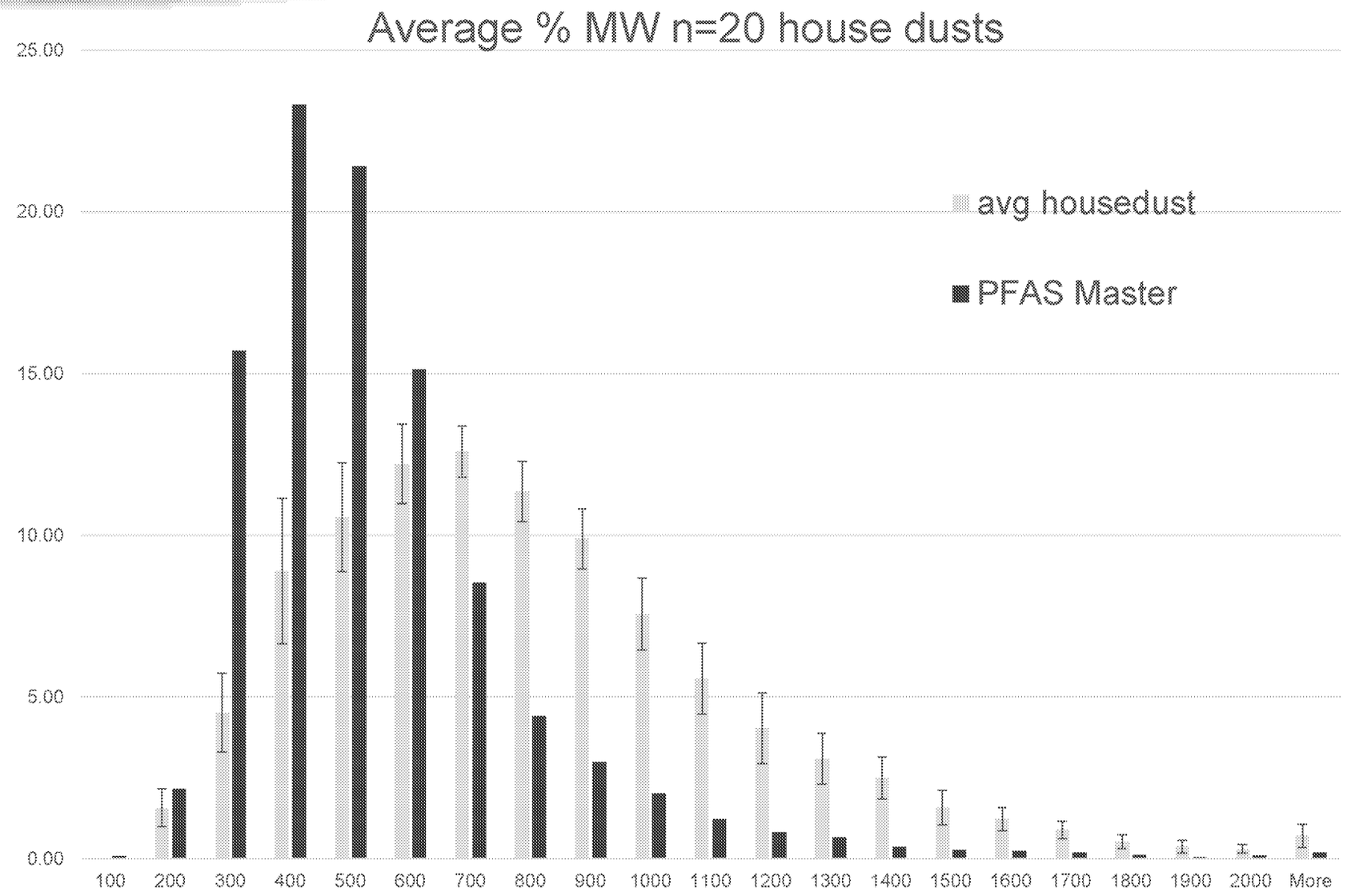
Feature =
- RT
- Abundance
- m/z

# Suspect Screening Molecular Weight Distribution

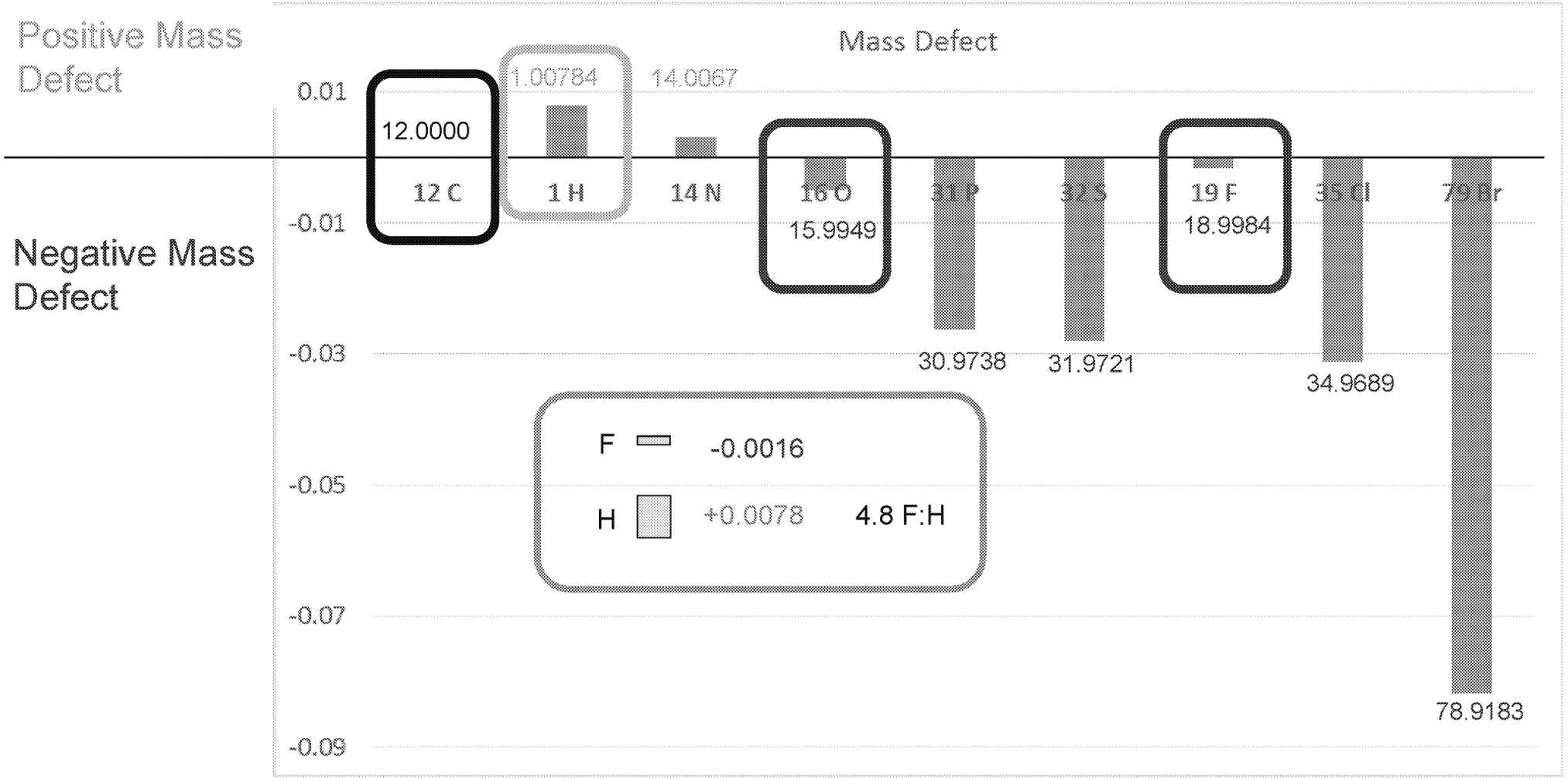
https://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER

n= 6,330 entries
n=5,258 MW

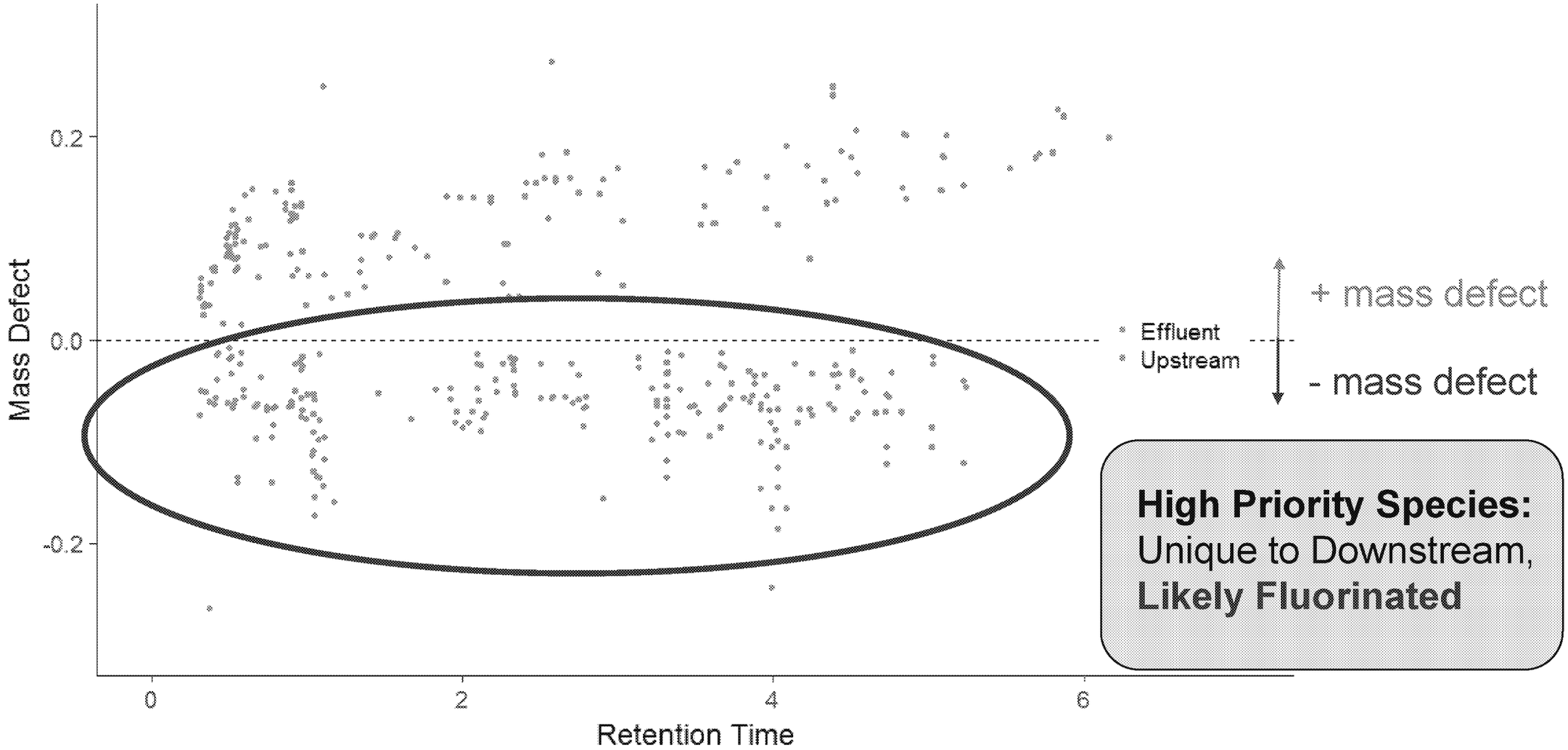
Includes:
OECD (4,729)
KEMI (2,416)
NORMAN (597)
Markush (64)
DSS-TOX (4,354)



# Isotope Signatures: Negative Mass Defect

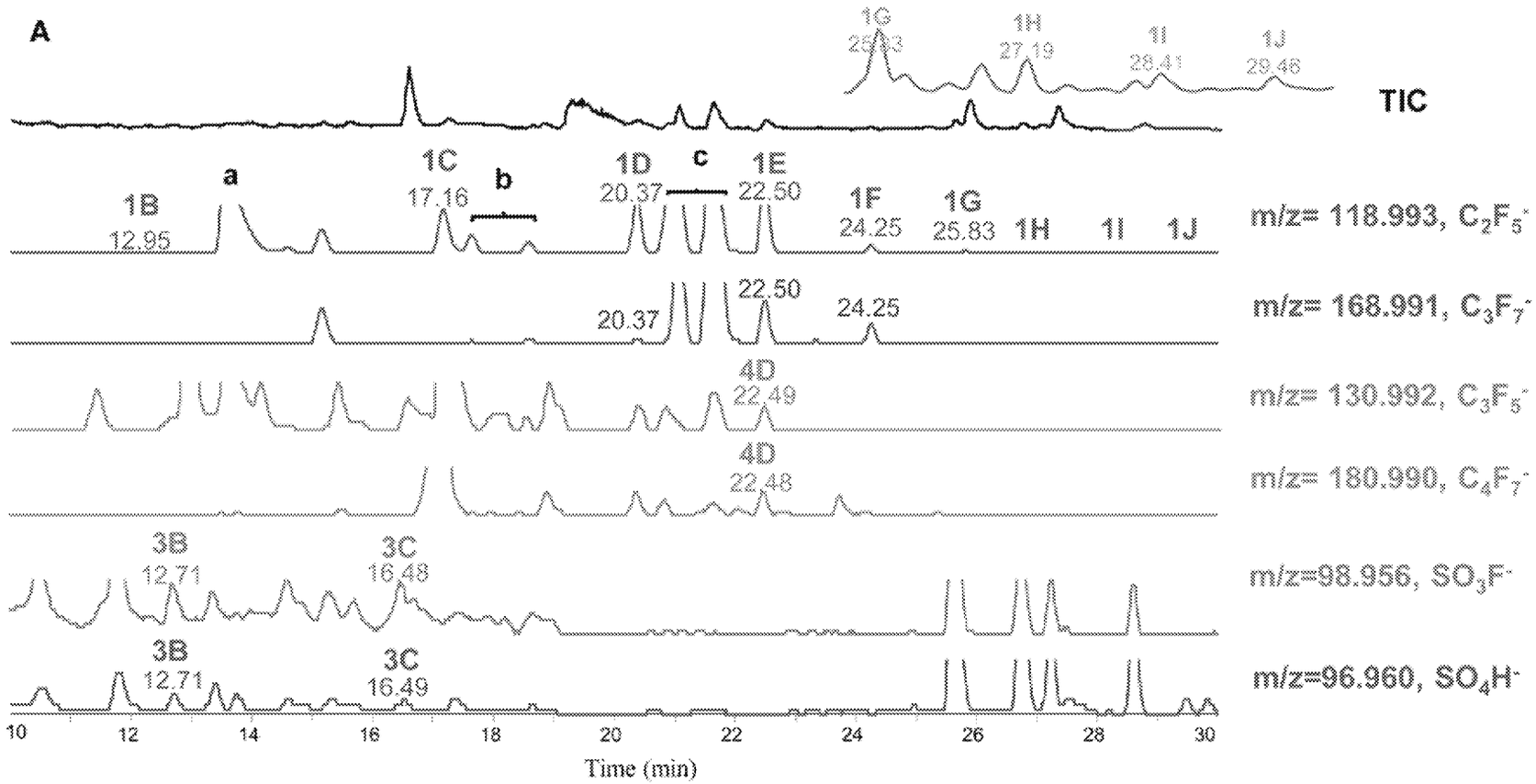


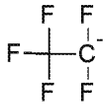
# Mass Defect of Outfall and Cape Fear River Upstream Features

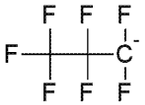



**High Priority Species:**
Unique to Downstream,
**Likely Fluorinated**

# Diagnostic Fragment Ions





PFBS, PFHxS, PFOS

**Liu et al., Analytical Chemistry 2017** Discovery of C5−C17 Poly- and Perfluoroalkyl Substances in Water by In-Line SPE-HPLC-Orbitrap with In-Source Fragmentation Flagging



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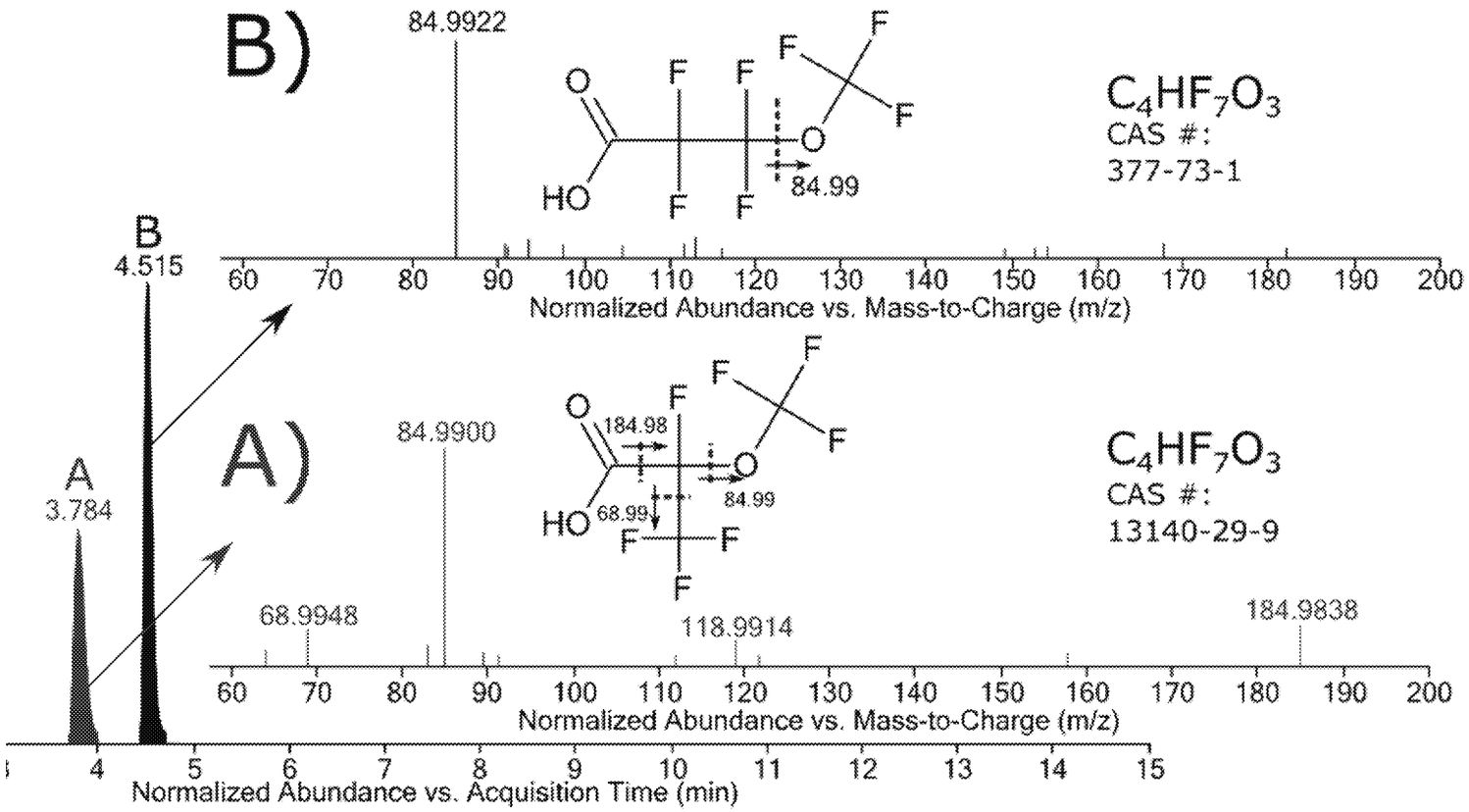
# Diagnostic Fragment Ions contd.

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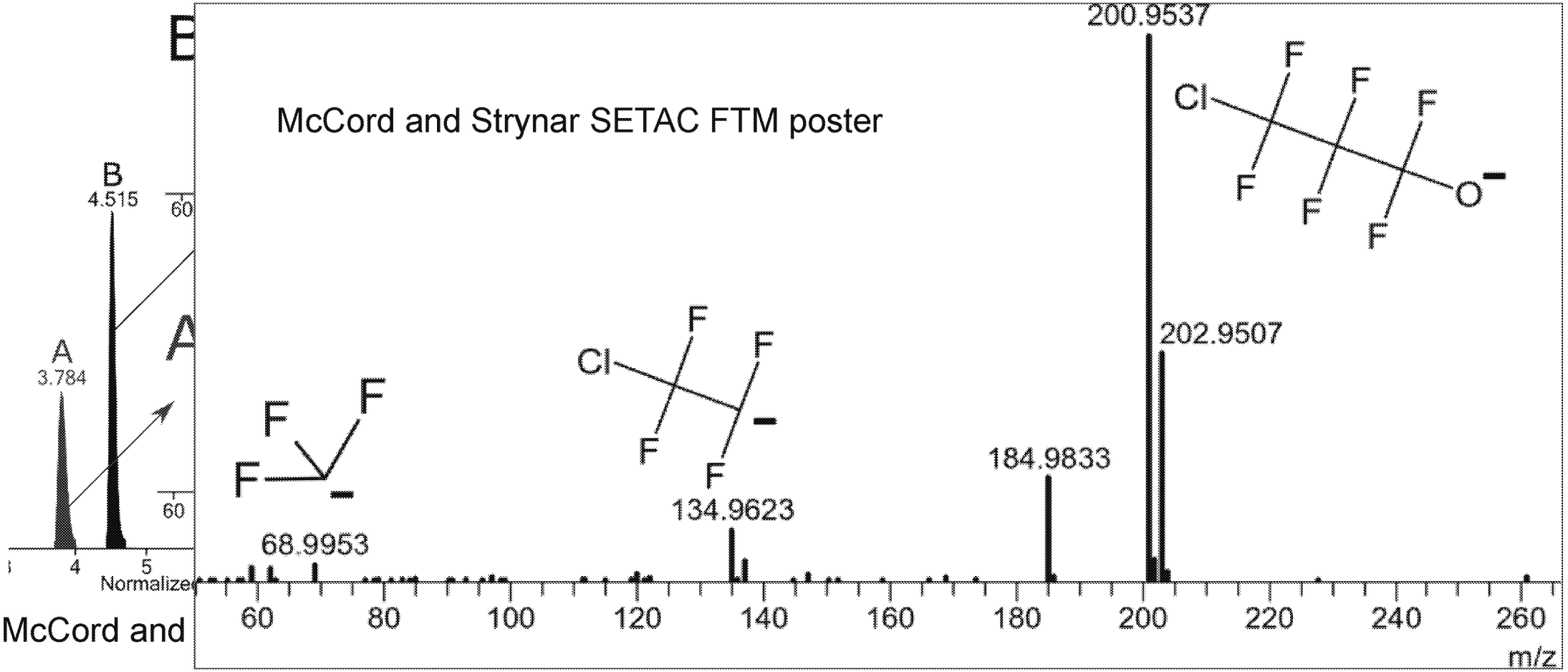
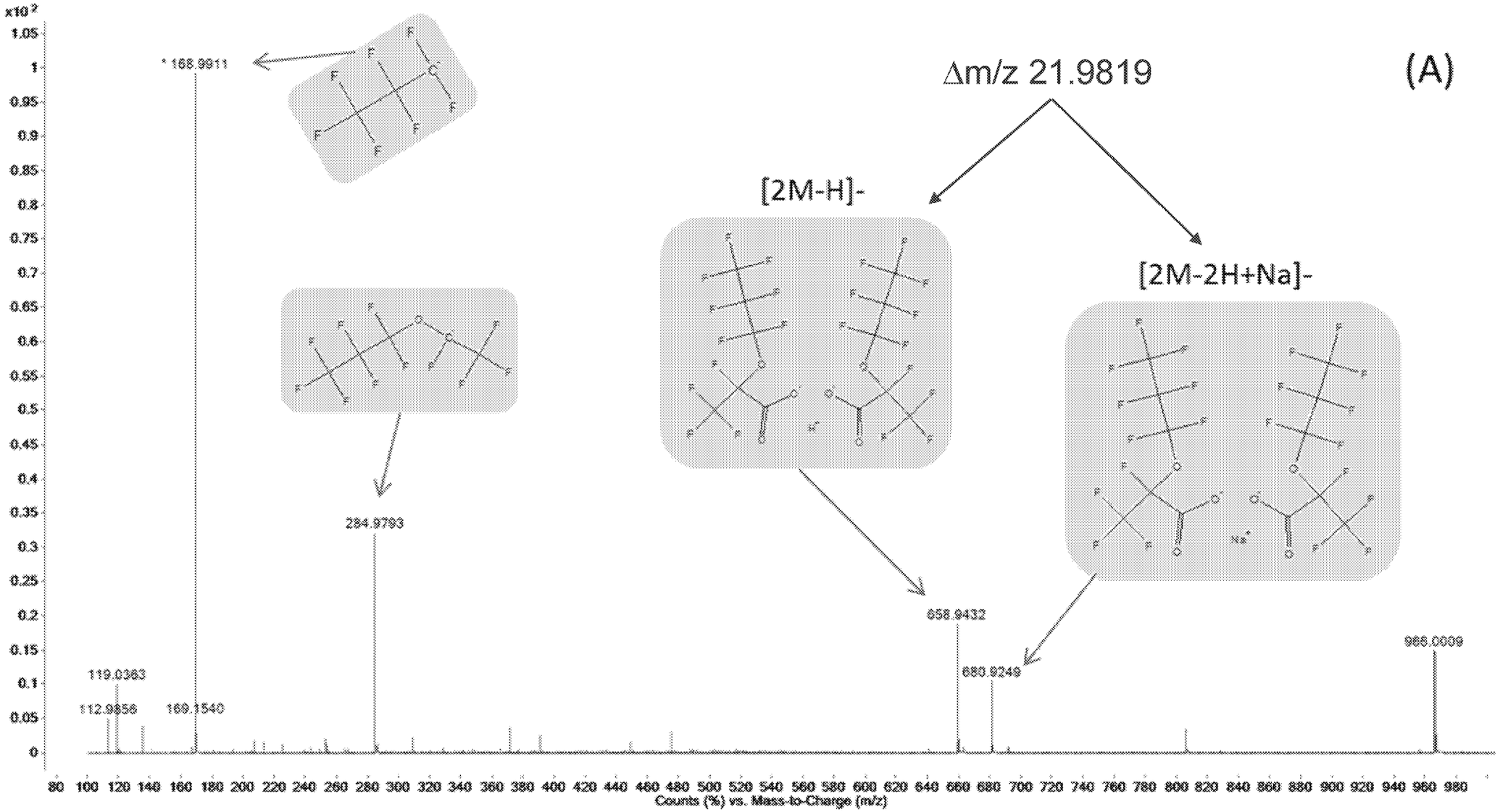
# Diagnostic Fragment Ions contd.




McCord and

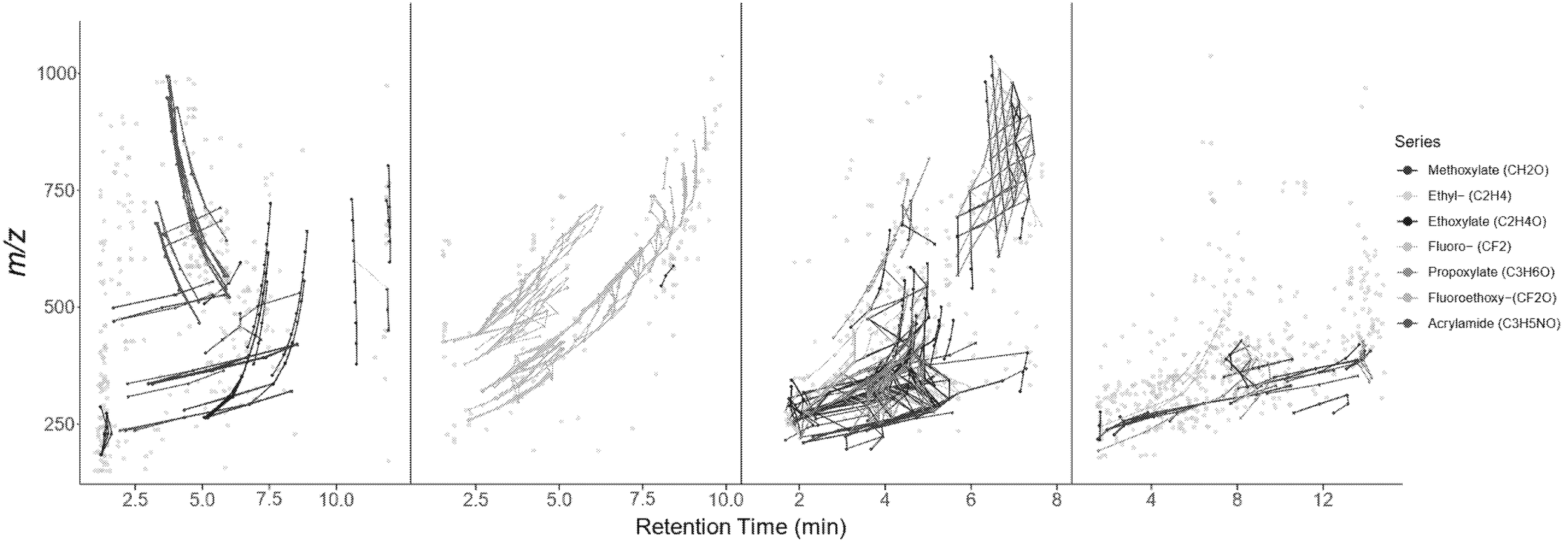
# Gas Phase *n*-mers

Strynar et al., 2015 ES&T




Have also seen:
K+
$NH_4$+
Trimers
tetramers

# Homologous Series/ Repeating units




McCord and Strynar poster

# Some key questions we are all asking:

How good is good enough?

Can we give quantitative values of these chemicals?

How will this data be used?

What are the important analytes?

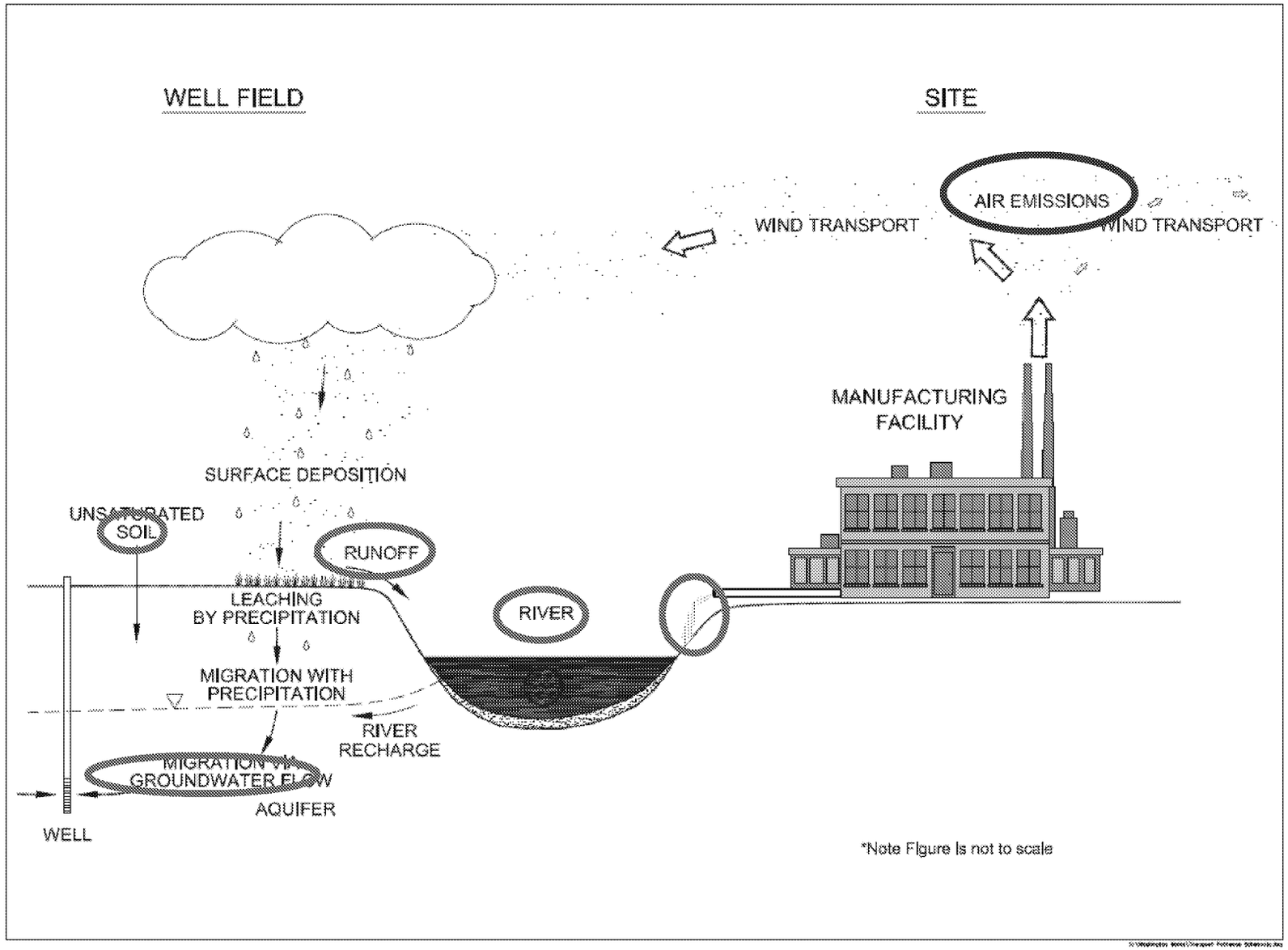
What is my confidence in identification?

What if I miss something?



ED_004850_00004154-00013

# 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"

**NTA Samples to compare:**

Upstream vs. downstream
Pretreatment vs posttreatment
Close vs distant
Upwind vs downwind
Surface vs deep
Etc.…

# Post PFOA Stewardship Agreement

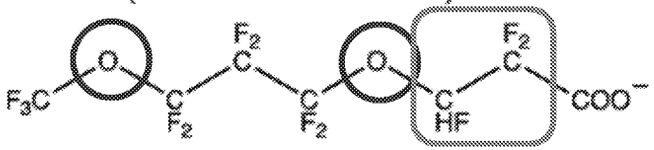
Ethers/Polyethers

Polyfluorinated

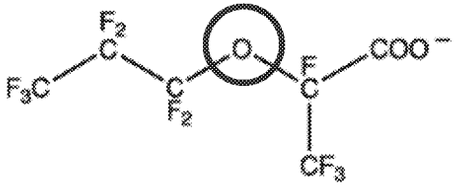
Chlorinated

**Fluoropolymer manufacture**

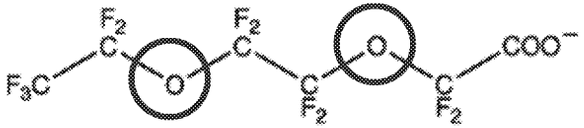
ADONA (CAS No. 958445-44-8)



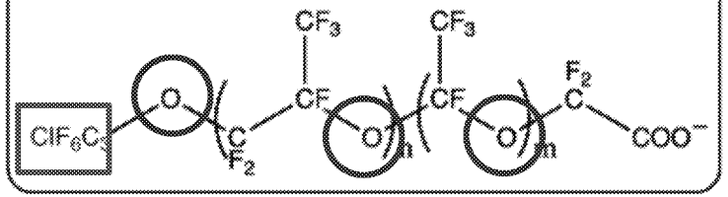
GenX (CAS No. 62037-80-3)



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

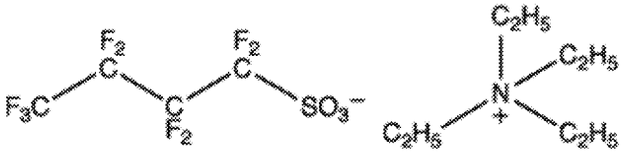


Solvay's product (CAS No. 329238-24-6)

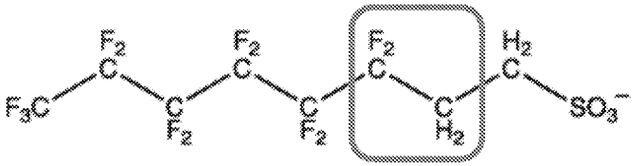


**Metal plating**

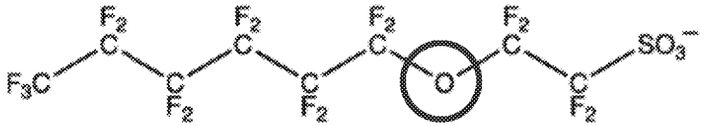
$N(Et)_4$-PFBS (CAS No. 25628-08-4)



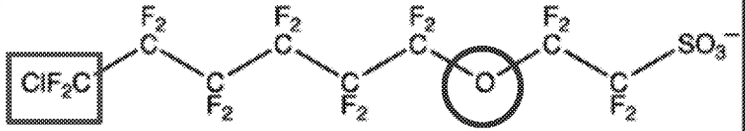
6:2 FTSA (CAS No. 27619-97-2)



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



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





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

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)

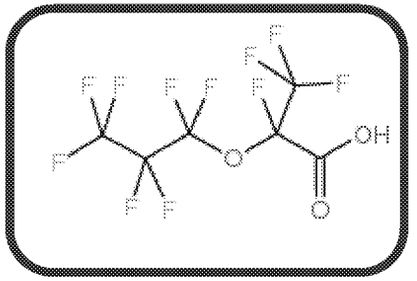
Mark Strynar,*[,†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Liang,[†,‡] Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[∥] Imma Ferrer,[∥] and Carol Ball[⊥]

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

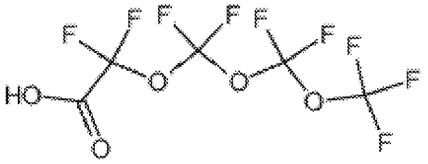
| number | formula | CAS no. | name | $[M]^{\alpha}$ | $[M - H]^-$ $m/z$ | $[2M - 2H + Na]^-$ $m/z$ | $[2M - H]^-$ $m/z$ |
|---|---|---|---|---|---|---|---|
| **Monoether PFECAs** | | | | | | | |
| 1 | $C_3HF_5O_3$ | | | 179.9846 | 178.9773 | 380.9438 | 358.9619 |
| 2 | $C_4HF_7O_3$ | | | 229.9813 | 228.9740 | 480.9372 | 458.9553 |
| 3 | $C_5HF_9O_4$ | 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 | $C_7HF_{15}O_4S$ | 66796-30-3[b] | | 443.9337 | 442.9264 | | |
| 12 | $C_7H_2F_{14}O_5S$ | | | 463.9399 | 462.9326 | | |

3 Found in human serum Wilmington, NC 2019 (NCSU Kotlarz/Hoppin)

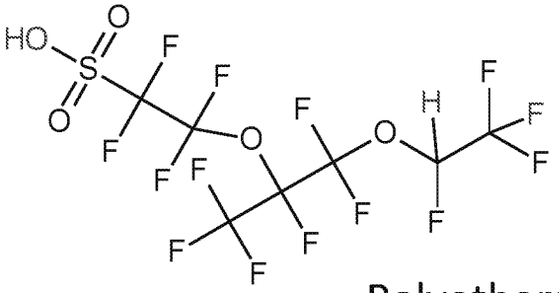
Example Structures



Monoether (6): GenX

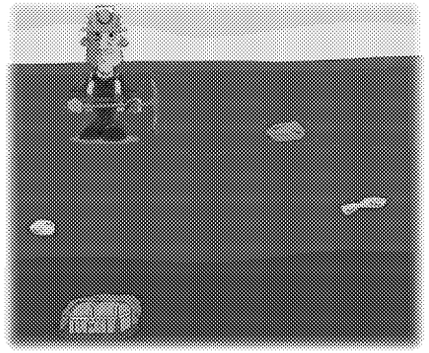


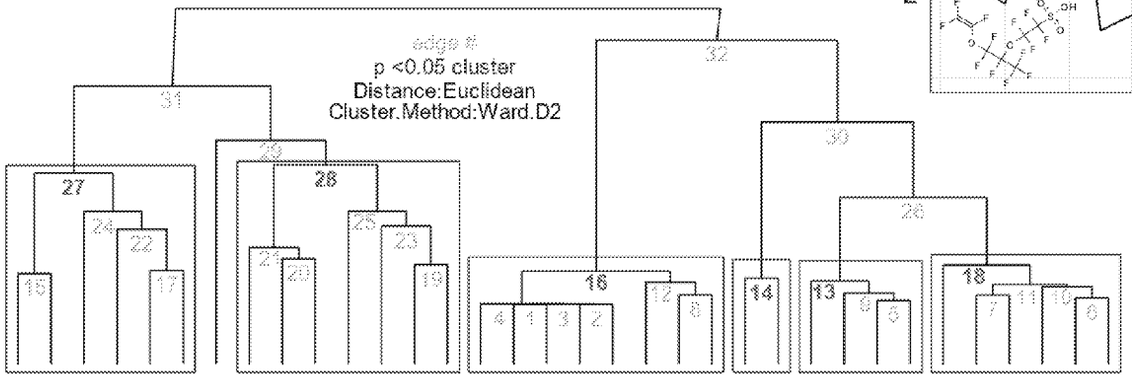
Polyethers (4):

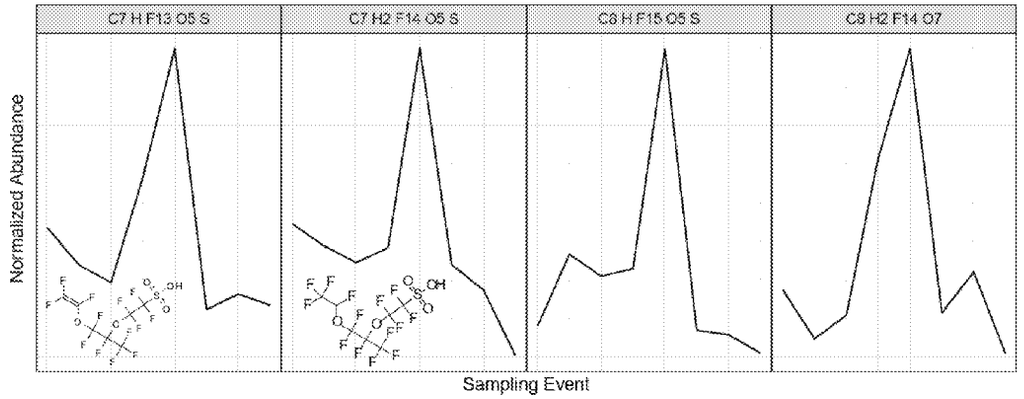


Polyethers sulfonates (2):

# Data Mining





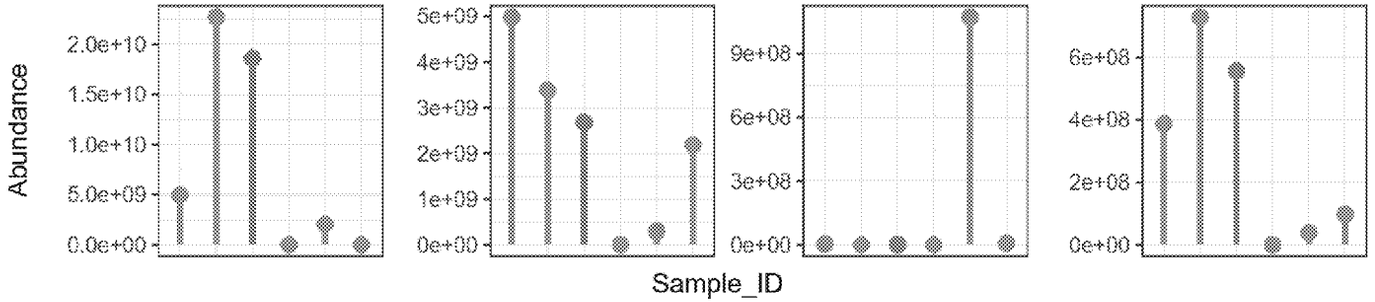




Trends

Clustering

Fingerprinting

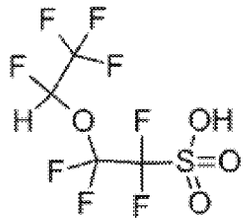
Previously Undiscovered




McCord and Strynar poster

# Retrospective Analysis (McCord 2019)

| 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 | ✓ | ✓ | ✓ | ✓ | ✓ | × | × | × |

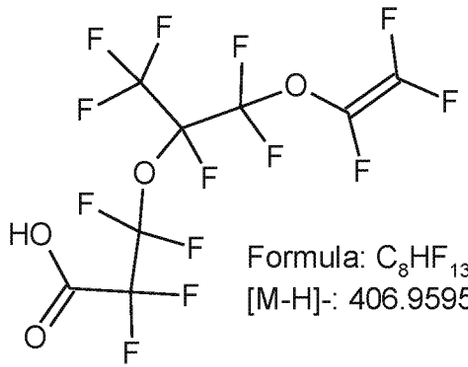


Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

NVHOS

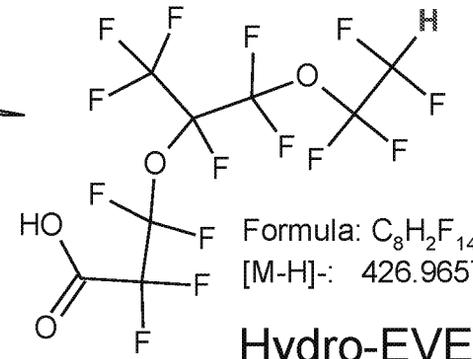
# Retrospective Analysis (McCord 2019)

| 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

Also found in Wilmington, NC serum (NCSU Kotlarz/Hoppin)

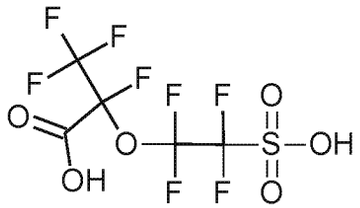


Formula: $C_8H_2F_{14}O_4$
[M-H]-: 426.9657 Da

Hydro-EVE

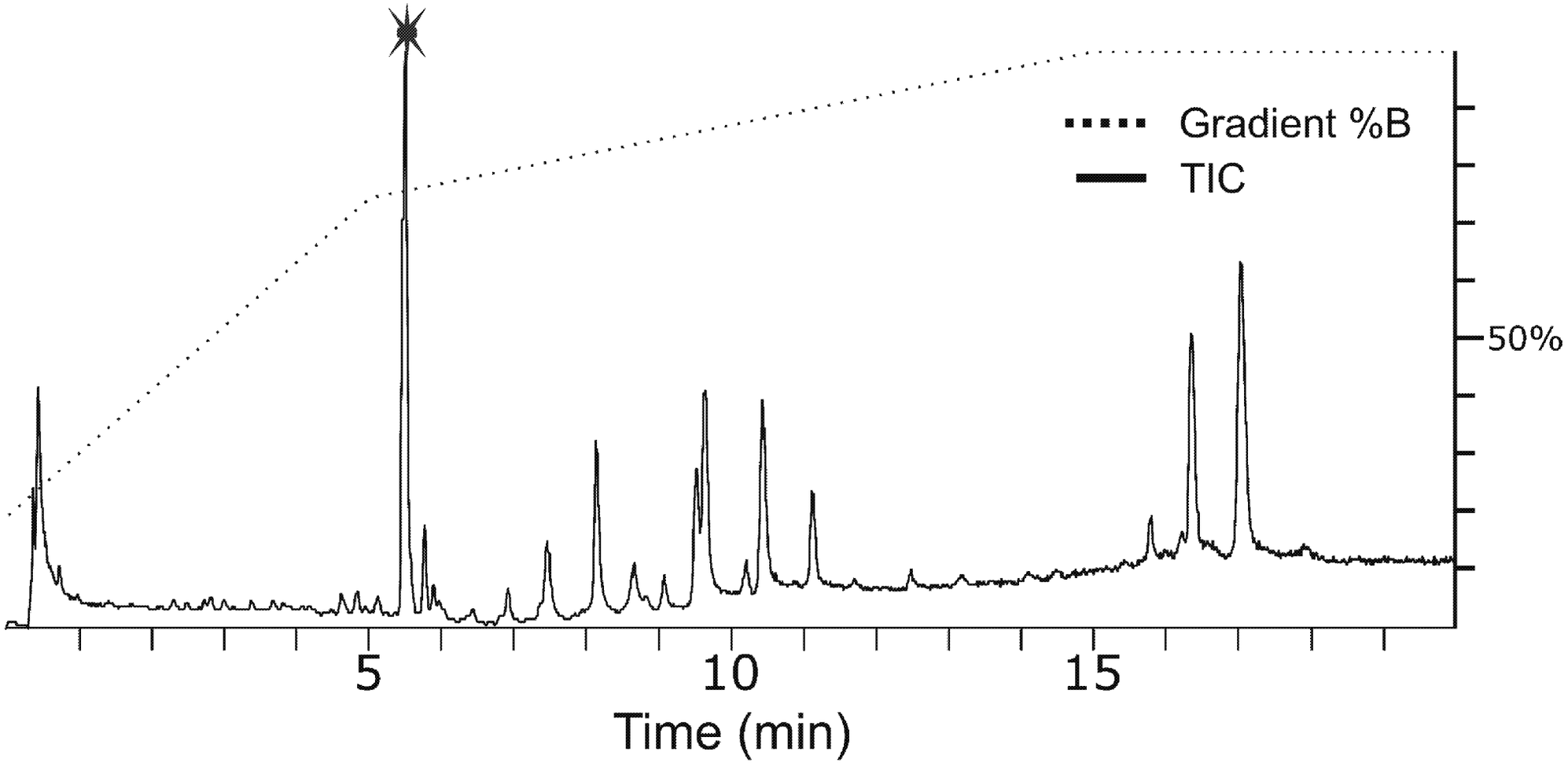
# Retrospective Analysis (McCord 2019 *in review*)

| 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 | ✓ | ✓ | ✓ | ✓ | ✓ | × | × | × |

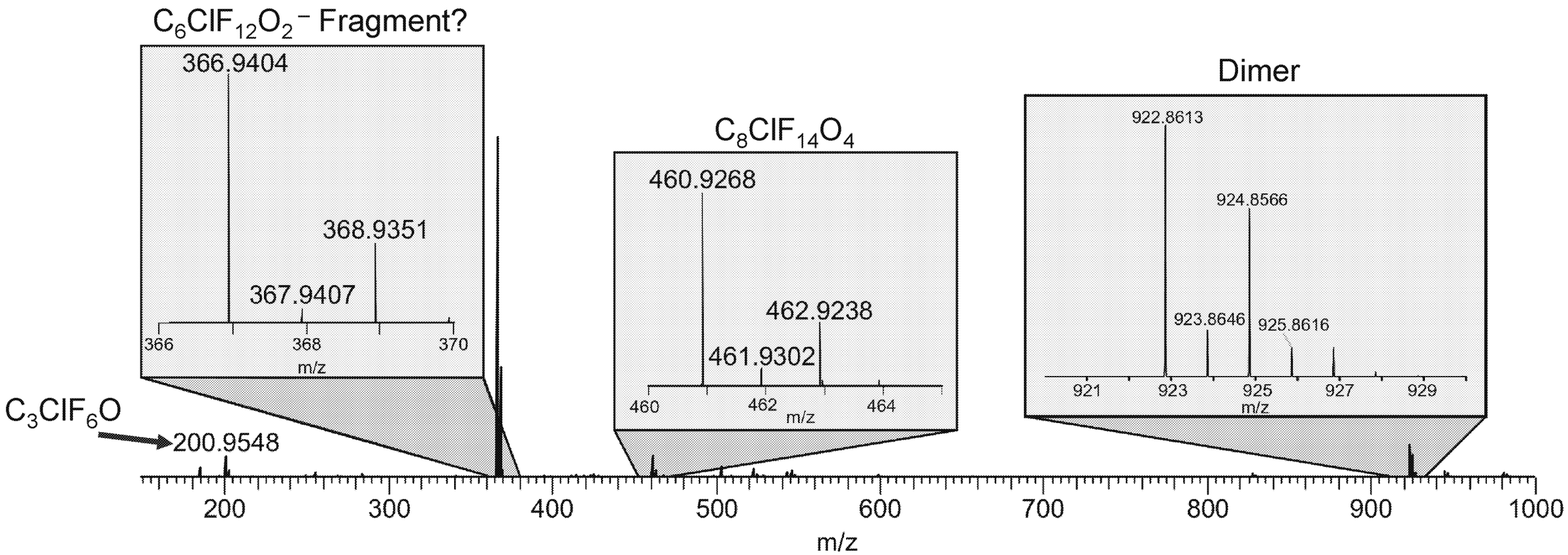


Formula: $C_5H_2F_8O_6S$
[M-H]-: 340.9372 Da

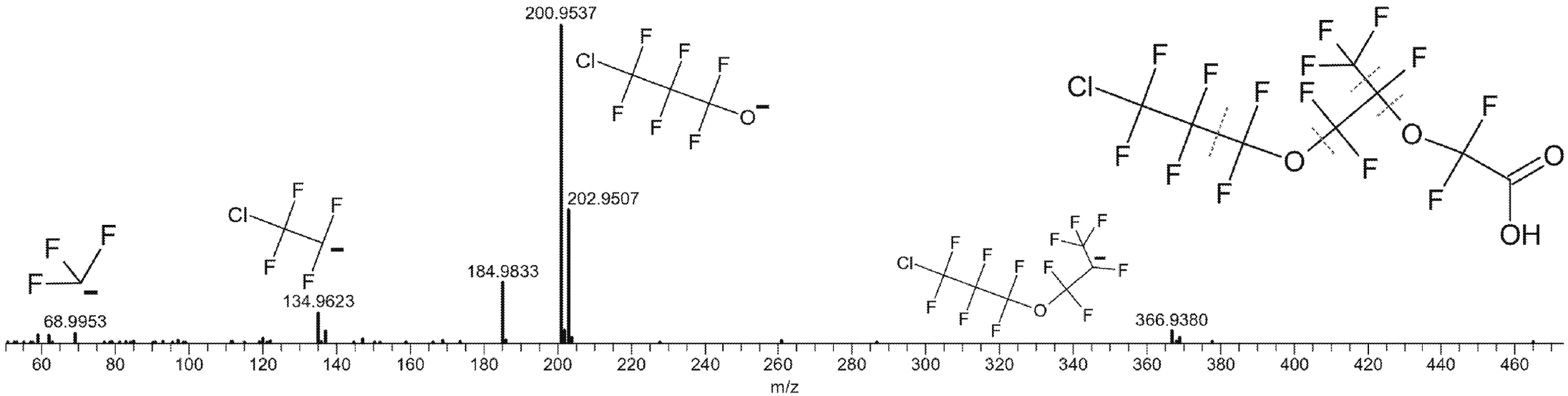
# Representative Chromatography NTA



# Major Peak Constituents Predicted Formula

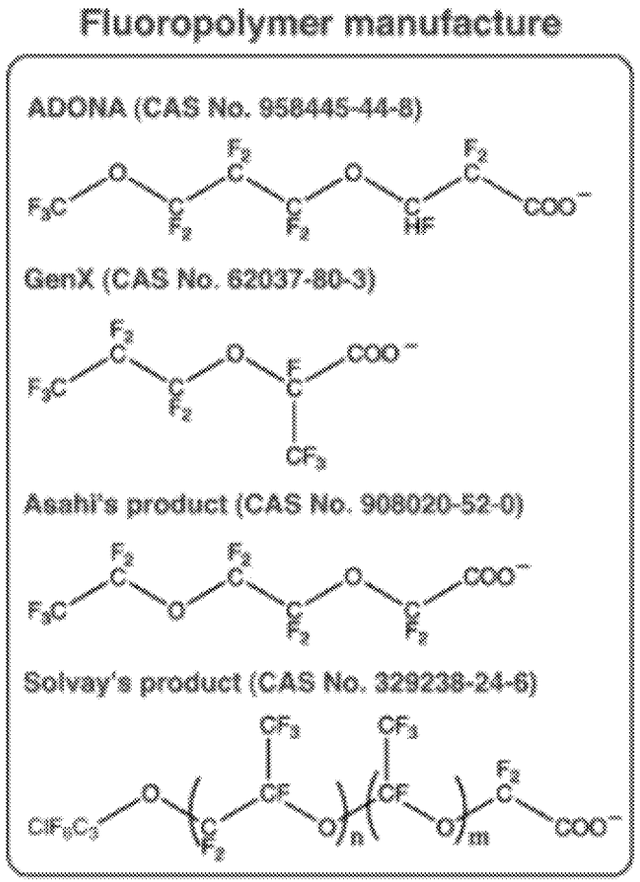


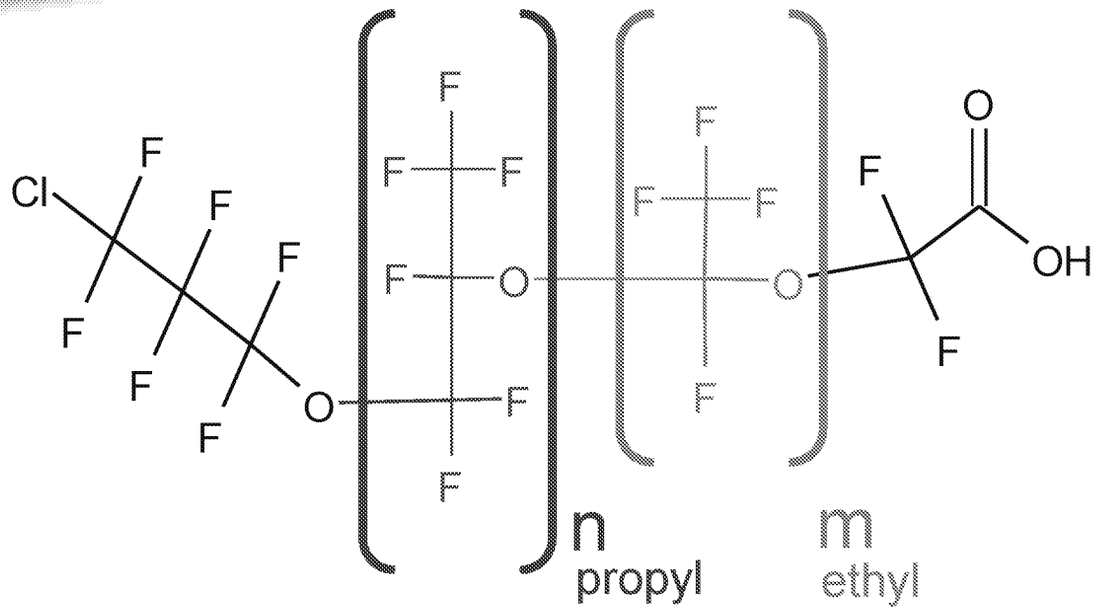
# Structural Elucidation by MS/MS




- Unequivocal assignment of terminal Cl and ether positions based on MS/MS experiments
- Confirmation of Dimers and in-source fragments from prior slide, with additional experiments (not show)

# Literature Support

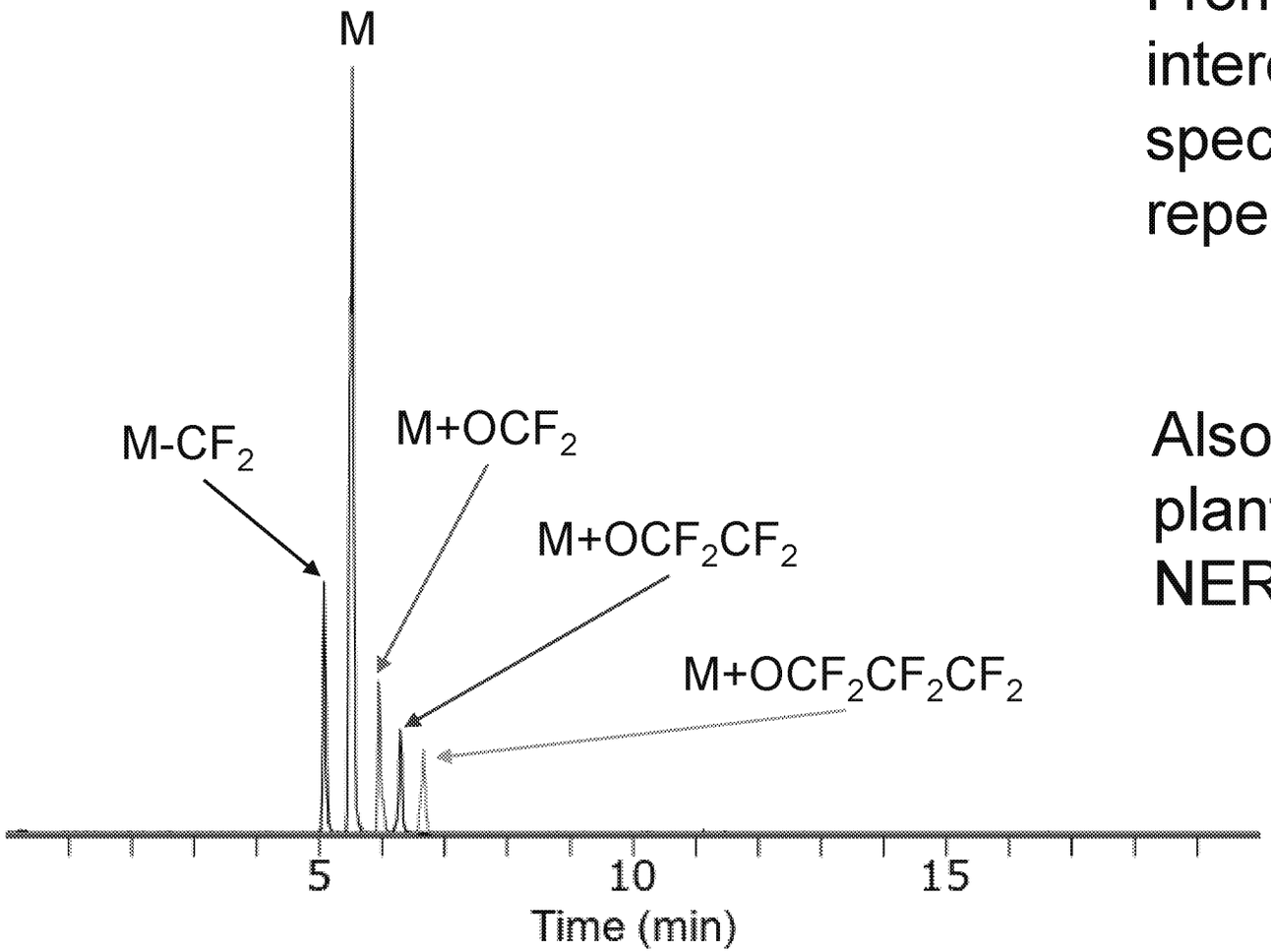



Chloro perfluoro polyether carboxylic acids ClPFPECAs(n,m)

Wang, Z., et al. (2013). Environ. Int. **60: 242.**
EFSA J, 8 (2) (2010), p. 1519, 10.2903/j.efsa.2010.1519

# Homologous Fluoropolymer Series

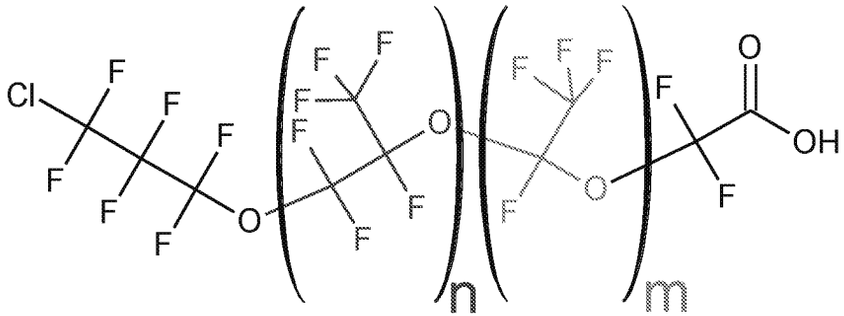



From single identified mass of interest we identified additional species related by $CF_2$ repeating units

Also found in soil, sediment and plant material (John Washington – NERL Athens)

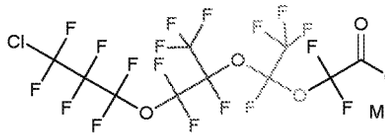
# Structural Homologs

CAS 329238-24-6



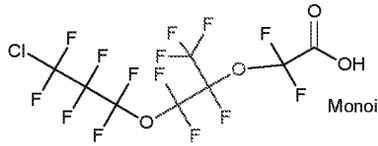
propyl, ethyl

CIPFECA 1,1



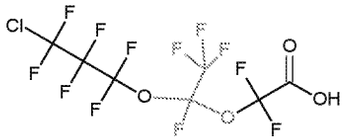
Monoisotopic Mass: 577.922508 Da

CIPFECA 1,0



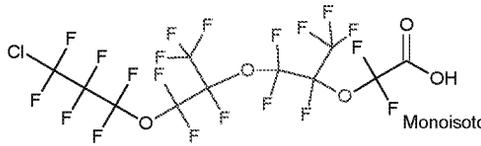
Monoisotopic Mass: 461.933981 Da

CIPFECA 0,1



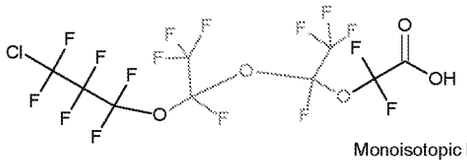
Monoisotopic Mass: 411.937175 Da

CIPFECA 2,0



Monoisotopic Mass: 627.919315 Da

CIPFECA 0,2



Monoisotopic Mass: 527.925702 Da

# 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.*



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