A Comparison of the Results Generated From the Use of Two New EPA Draft Methods

NEMC Polyfluoroalkyl Substances in the Environment

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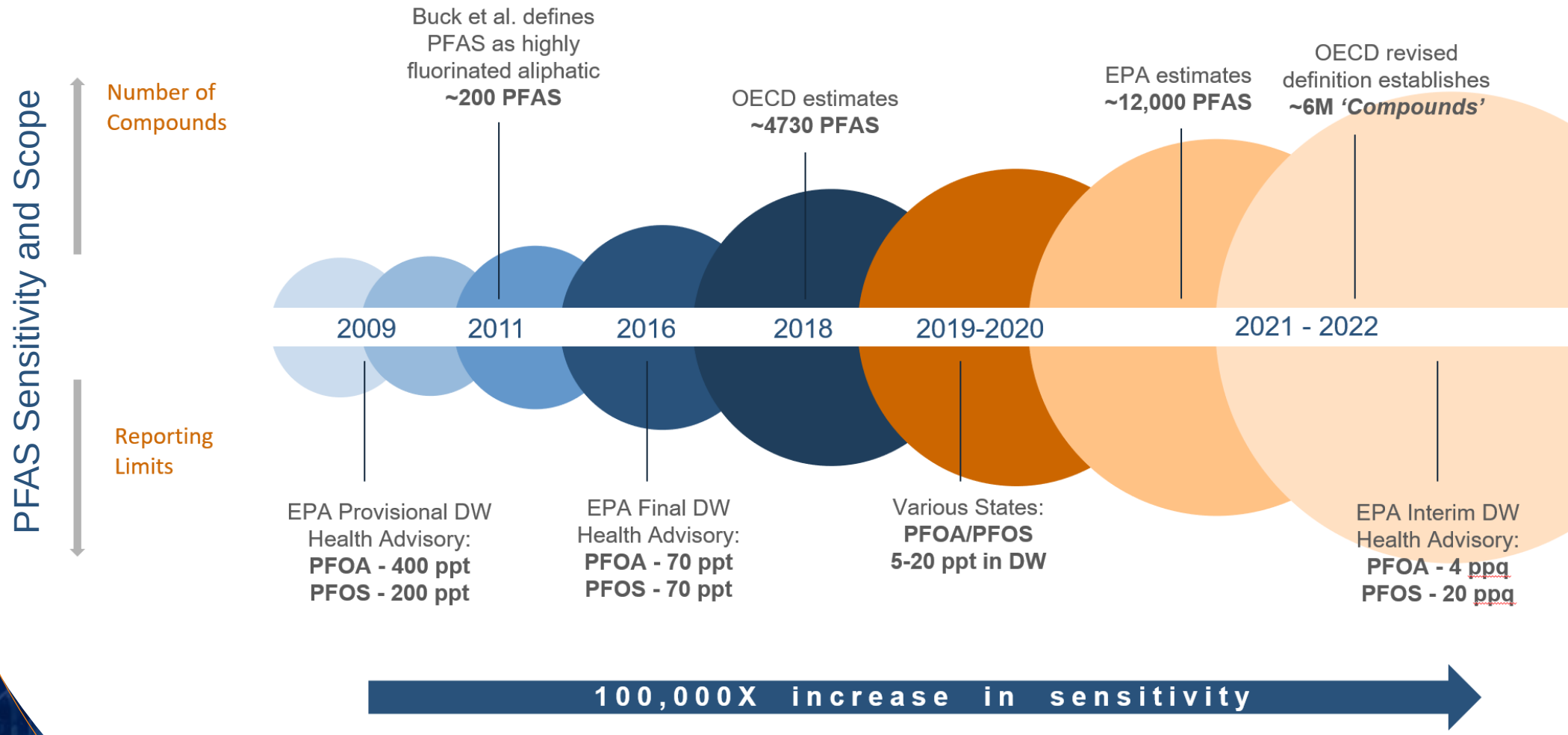
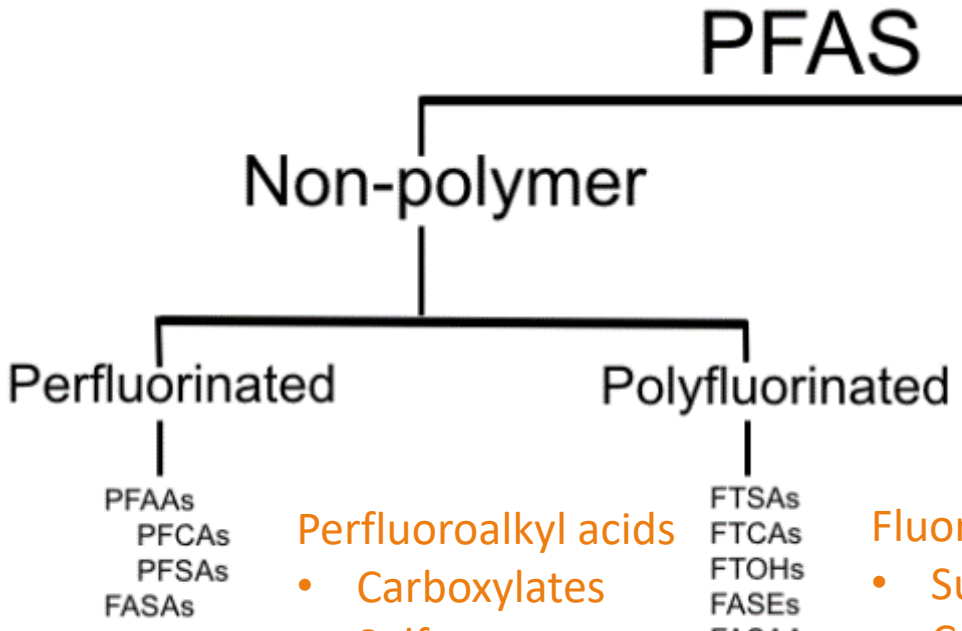
Evolution of the Science



Source – PubChem Classification Browser (nih.gov)

The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)



- Fluoropolymers
- Perfluoropolyethers (PFPE)
- Side-chain fluorinated polymers

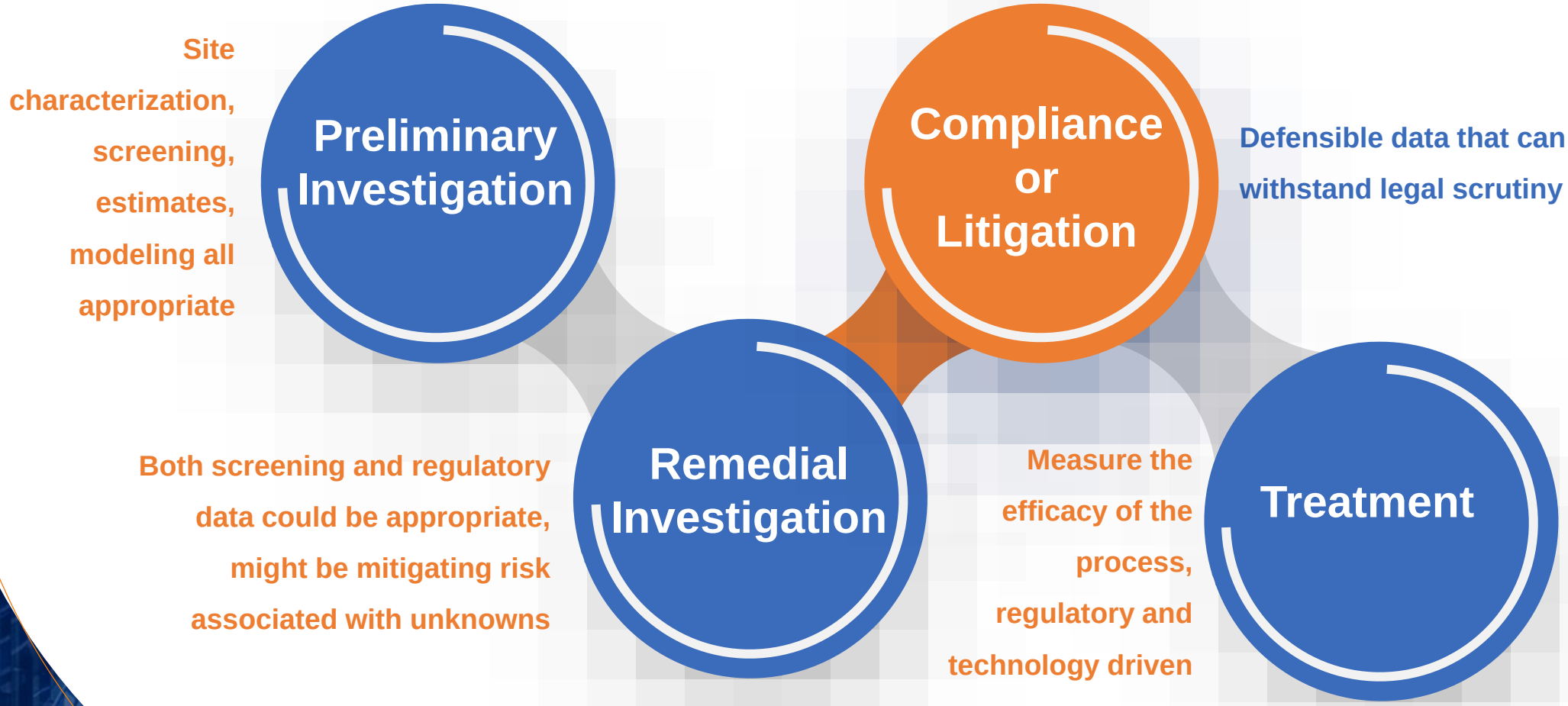
Perfluoroalkyl acids
- Carboxylates
- Sulfonates

Fluorotelomers:
- Sulfonates
- Carboxylates
- Alcohols

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet

What Are The Data Being Used For?

QUALITY DRIVERS



Current Analysis Climate

- Current methods for LCMSMS
  - USEPA 533
  - USEPA 537.1
  - ASTM D7979
  - SW846 method 8327
  - Individual laboratory "537 Mod"/Isotope Dilution
  - 3rd Draft EPA Method 1633
- Largest of these options are method(s) that are limited to only 70+ compounds
- Might add in analysis for fluorotelomer alcohols

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Comprehensive PFAS Testing

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In-line SPE

LEAF

537.1

QSM

ISM

Isotope Dilution

Direct Injection

533

SPLP

User-Defined Methods: PUT TO THE TEST!

Complex Matrices

- Biphasic
- Biosolids
- Tissues
- Dispersions
- Activated Carbon
- Cosmetics
- Concrete

Audits & PTs

- NELAC
- DoD ELAP
- Client/Program Specific Audits
- Semiannual PT
- NMI International Round Robin
- DOW Study

3rd Party Validation

- >85% of all PFAS data includes a validation package
- >300,000 sample data validated

LCMSMS/GCMSMS Analysis

Compounds Included in EPA Draft 1633

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPeA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnA)
- Perfluorododecanoic acid (PFDoA)
- Perfluorotridecanoic acid (PFTriA)
- Perfluorotetradecanoic acid (PFTeA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluoropentanesulfonic acid (PFPeS)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluoroheptanesulfonic Acid (PFHpS)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorononanesulfonic acid (PFNS)
- Perfluorodecanesulfonic acid (PFDS)
- Perfluorododecanesulfonic acid (PFDoS)
- Perfluorooctanesulfonamide (FOSA)
- NEtFOSA
- NMeFOSA
- NMeFOSAA
- NEtFOSAA
- NMeFOSE
- NEtFOSE
- 4:2 FTS
- 6:2 FTS
- 8:2 FTS
- 9Cl-PF3ONS
- 11Cl-PF3OUdS
- DONA
- HFPO-DA (GenX)
- 3:3 FTCA
- 5:3 FTCA
- 7:3 FTCA
- NFDHA
- PFMBA
- PFMPA
- PFEESA

Target Compounds Not Part of EPA Draft 1633

- 10:2 FTS
- 6:2 FTCA
- 8:2 FTCA
- 10:2 FTCA
- 6:2 FTUCA
- 8:2 FTUCA
- 10:2 FTUCA
- PFECHS
- PFPrS
- PFPrA
- PFMOAA
- PFECAG
- PFO4DA
- PFO3OA
- PFO2HxA
- R-EVE
- NVHOS
- Hydro-EVE Acid
- Perfluoro-n-octadecanoic acid (PFODA)
- Perfluoro-n-hexadecanoic acid (PFHxDA)
- EVE Acid
- PFO5DA
- PMPA
- PEPA
- MTP
- PS Acid
- Hydro-PS Acid
- R-PSDA
- Hydrolyzed PSDA
- R-PSDCA
- 6:2 diPAP
- 8:2 diPAP
- 6:2/8:2 diPAP
- 10:2 diPAP
- 10:2 FTOH (RL= 20 ng/L)
- 8:2 FTOH (RL= 20 ng/L)
- 7:2 FTOH (RL= 20 ng/L)
- 6:2 FTOH (RL= 20 ng/L)
- 4:2 FTOH (RL= 20 ng/L)

EPA Draft Method In Progress

EPA Draft 1633

- Targeted Analysis of 40 PFAS
- Non-Potable Water, Soil & Tissue
- LCMSMS, WAX SPE, Isotope Dilution
- Multi-Lab Validation Underway

EPA METHODS

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https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

EPA *Draft* 1633 for Non-Potable Water & Solids

SIMILARITIES

- Applicable to a variety of solids and aqueous matrices
- Solid Phase Extraction using WAX
- Isotope Dilution Quantitation using all available isotopes
- Ion Transitions, monitoring ratios
- *Using non-Extracted Internal Standards (NEIS) for quantitation of extracted internal standards (EIS)
- **Use of carbon cleanup

*QSM 5.3 dropped it, but they are bringing it back with B-24

**User-defined methods use stacked carbon vs. loose carbon

Compared to:
User-Defined Methods
and
DoD QSM Table B-15

DIFFERENCES

- Soil/Tissue Prep: concentration step
- S/N Ratio
- Waters Oasis WAX SPE Cartridge with loose carbon cleanup
- TDCA Check: 60 sec window specification
- Includes frozen storage option
- Complex dilution scheme with 10X dilution limitation
- Mass transitions vary for some

Current Analysis Climate

- Need for screening method – For total Fluoride
  - Better risk assessment tool for true "impact" in the environment
  - Screening method for narrowing focus of target compound approach
- What are the options?
  - TOP Assay
  - PIGE (particle induced gamma-ray emission spectroscopy)
  - XPS (x-ray photoelectron spectroscopy)
  - TOF (total organic fluorine)

Total Organic Fluorine Analysis

Marriage of TOX and IC

Sample (or treated sample) is combusted in a furnace at 900°C – 1100°C

Effluent collected in buffer and injected into ion chromatograph (IC)

Quantify fluorine (as fluoride) content

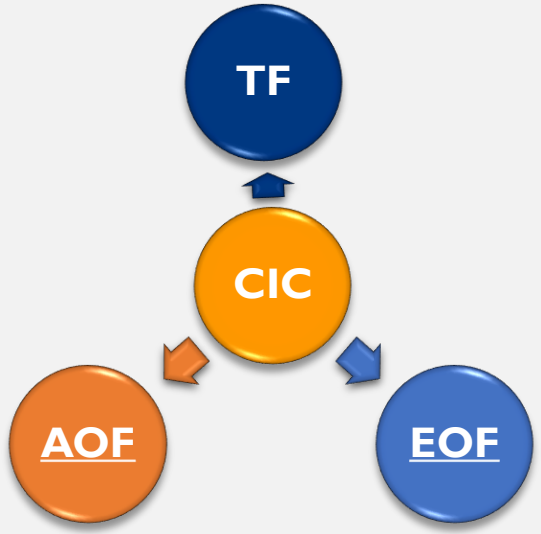
Compare ratio of total (or extractable) fluorine to total PFAS

Oxidative pyrohydrolytic combustion

Handling of the sample prior to fluoride determination determines result evaluated

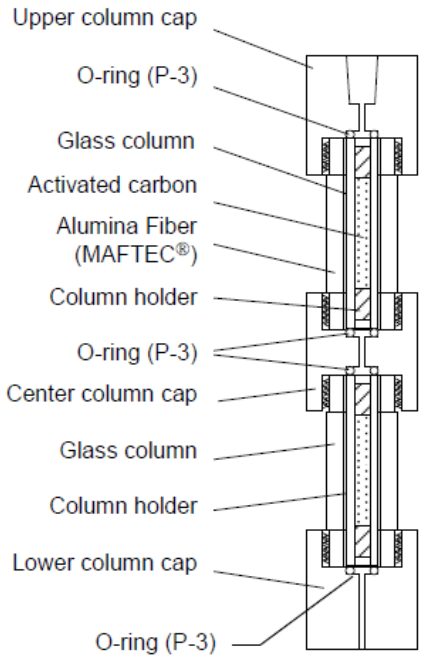
EOF – Extractable Organic Fluorine

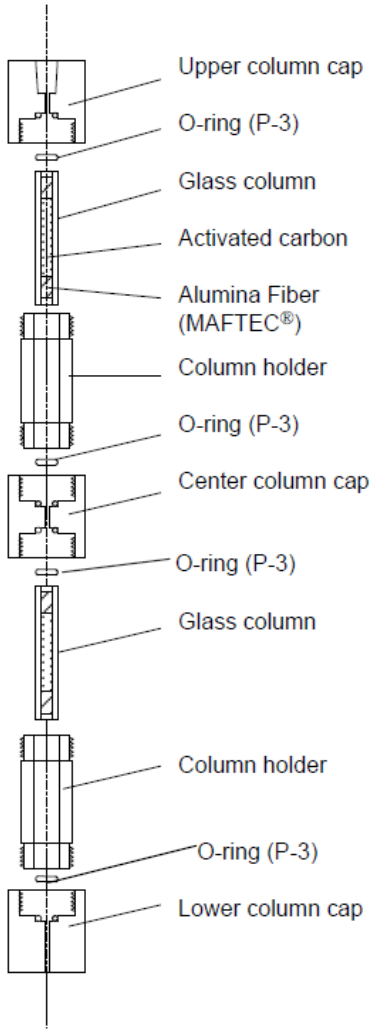
AOF – Absorbable Organic Fluorine



Adsorbable Organic Fluoride (AOF)

- Currently Proposed ASTM Method (WK 68866)
- Currently Proposed DIN committee NA 119-01-03-01-12
- Basics of method
  - 100mls of water sample is passed through two vertically aligned carbon cartridges
  - Organic compounds (PFAS) are adsorbed on carbon bed
  - Final rinsing is performed with Potassium Nitrate to remove inorganic Fluoride (interference)
  - Carbon is then combusted with CIC





Courtesy of Dr. Jayesh Ghandi - Metrohm

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Fluorine Content

Compound	Fluorinated Alkane Carbon Chain Length	Chemical Abstracts Service (CAS) No.	Molecular Weight	Weight of Fluorine	Percent Fluorine
Perfluoroalkylcarboxylic acids (PFCAs)					
PFBA	C4	375-22-4	214.04	132.99	62.13%
PFPeA	C5	2706-90-3	264.05	170.99	64.76%
PFHxA	C6	307-24-4	314.05	208.98	66.54%
PFHpA	C7	375-85-9	364.06	246.98	67.84%
PFOA	C8	335-67-1	414.07	284.98	68.82%
PFNA	C9	375-95-1	464.08	322.97	69.59%
PFDA	C10	335-76-2	514.08	360.97	70.22%
PFUnDA	C11	2058-94-8	564.09	398.97	70.73%
PFDoDA	C12	307-55-1	614.1	436.96	71.16%
PFTrDA	C13	72629-94-8	664.11	474.96	71.52%
PFTeDA	C14	376-06-7	714.11	512.96	71.83%
PFHxDA	C16	67905-19-5	814.13	588.95	72.34%
PFODA	C18	16517-11-6	914.14	664.94	72.74%
Perfluorinated sulfonic acids (PFSAs)					
PFBS	C4	375-73-5	300.1	170.99	56.98%
PFPeS	C5	2706-91-4	350.11	208.98	59.69%
PFHxS	C6	355-46-4	400.11	246.98	61.73%
PFHpS	C7	375-92-8	450.12	284.98	63.31%
PFOS	C8	1763-23-1	500.13	322.97	64.58%
PFNS	C9	474-511-07-4	550.13	360.97	65.62%
PFDS	C10	335-77-3	600.14	398.97	66.48%
PFDoS	C12	79780-39-5	700.16	474.96	67.84%

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Fluorine Content

Compound	Fluorinated Alkane Carbon Chain Length	Chemical Abstracts Service (CAS) No.	Molecular Weight	Weight of Fluorine	Percent Fluorine
Perfluorooctane Sulfonamide and Derivatives					
PFOSA	C8	754-91-6	499.14	322.97	64.71%
NEtPFOSAE	C8	1691-99-2	571.25	322.97	56.54%
NMEPFOSAE	C8	24448-09-7	577.22	322.97	55.95%
NEtPFOSA	C8	4151-50-2	527.2	322.97	61.26%
NMEPFOSA	C8	31506-32-8	513.17	322.97	62.94%
NMeFOSAA	C8	2355-31-9	571.21	322.97	56.54%
NEtFOSAA	C8	2991-50-6	585.23	322.97	55.19%
Fluorotelomer sulfonates (FTS)					
4:2-FTS	C4	757124-72-4	328.15	170.99	52.11%
6:2-FTS	C6	27619-97-2	428.17	246.98	57.68%
8:2-FTS	C8	39108-34-4	528.17	322.97	61.15%
10:2-FTS	C10	120226-60-0	628.2	398.97	63.51%
Perfluoroalkyl ether carboxylic acids (PFECA)					
HFPO-DA	C6	13252-13-6	330.05	208.98	63.32%
ADONA	C9	919005-14-4	378.04	227.98	60.31%
Polyfluoroalkyl Ether Sulfonic Acids (PFESAs)					
9Cl-PF3ONSA	C9	756426-58-1	532.58	303.97	57.08%
11Cl-PF3OUdS	C11	763051-92-9	632.62	379.97	60.06%

EPA Draft Method In Progress

EPA Draft 1621

- Adsorbable Organic Fluorine (AOF)
- Applicable to waters
- Proxy analysis for 'Total PFAS'
- Single lab validation complete; multi-lab validation in process

EPA METHODS

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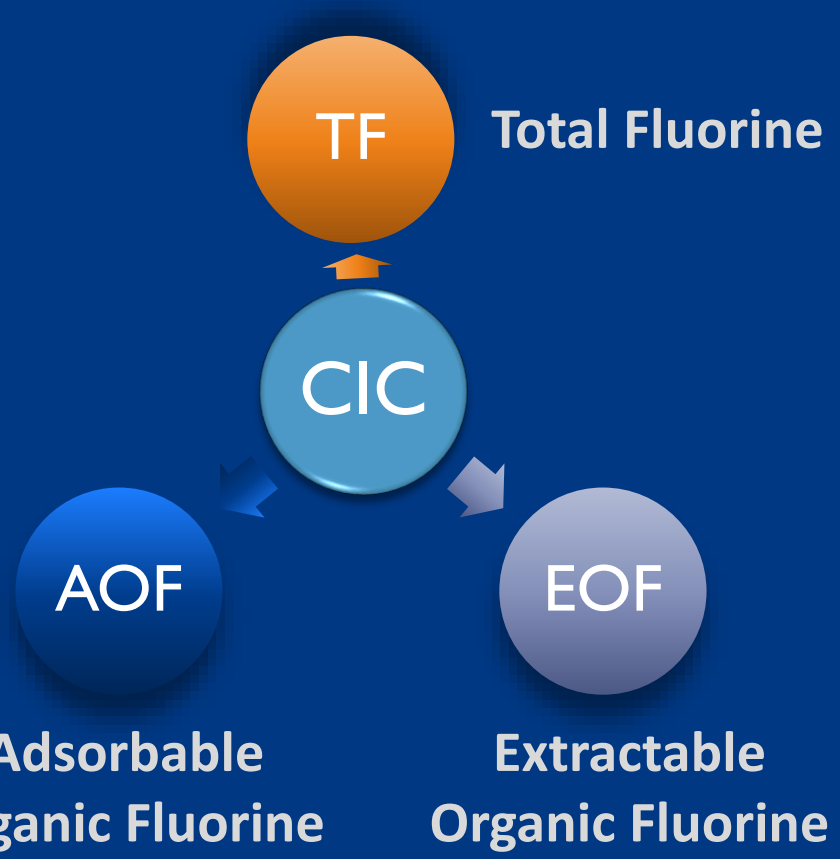
https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

Total Fluorine Analysis by Combustion Ion Chromatography (CIC)



Strengths & Utility

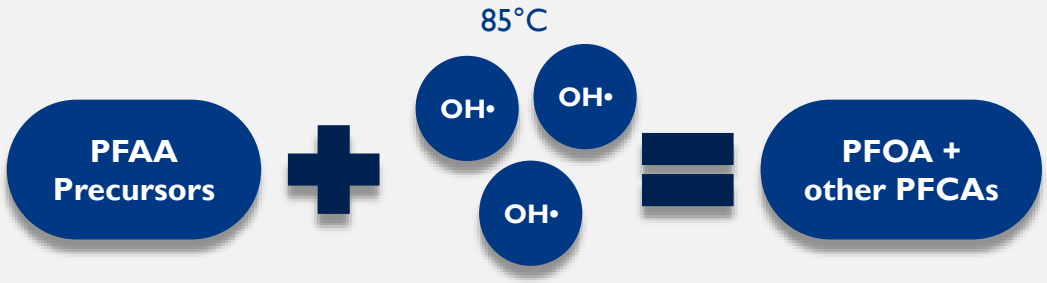
~ Proxy for entire class of PFAS
~300ppb – 1ppm reporting limit

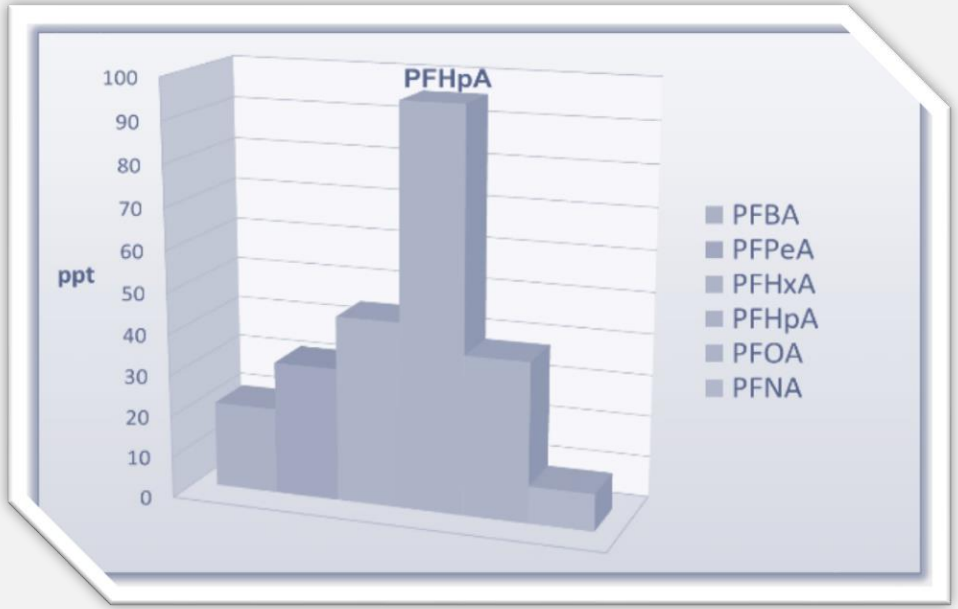
Weaknesses

~ Doesn't quite close the mass balance
~ Subject to certain interferences

Total Oxidizable Precursors

TOP Assay





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Non-Target Analysis

LC-QToF-MS

Liquid Chromatography
Quadrupole Time of Flight
Mass Spectrometry

Targeted Analysis

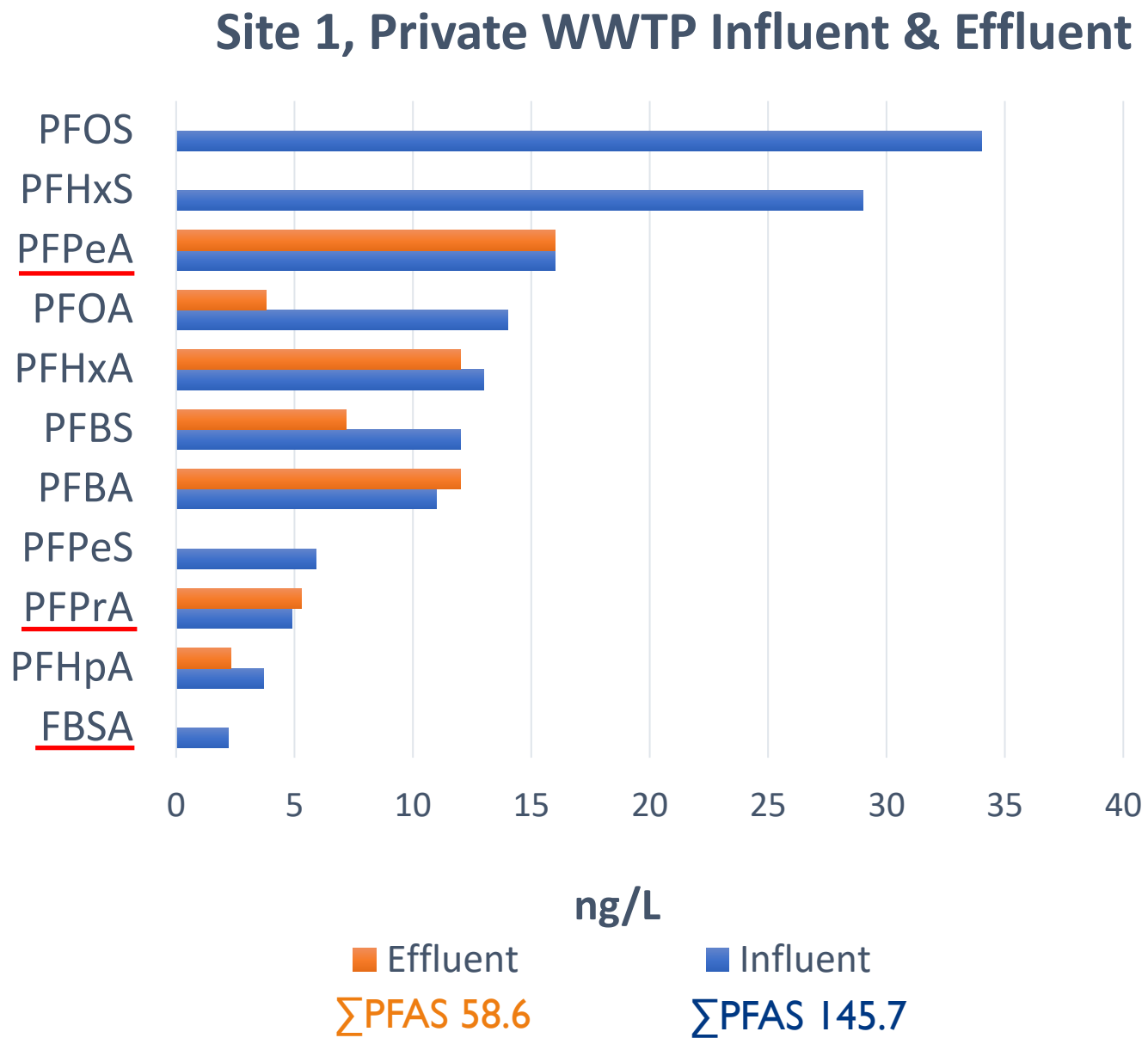
Suspect Screening Analysis

Non-Targeted Analysis

WWTP Study

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	1,300	110
Influent Dup	1,300	120
Effluent	1,500	220
Effluent Dup	1,100	230

FTOHs are all non-detect @ 1,000 ng/L

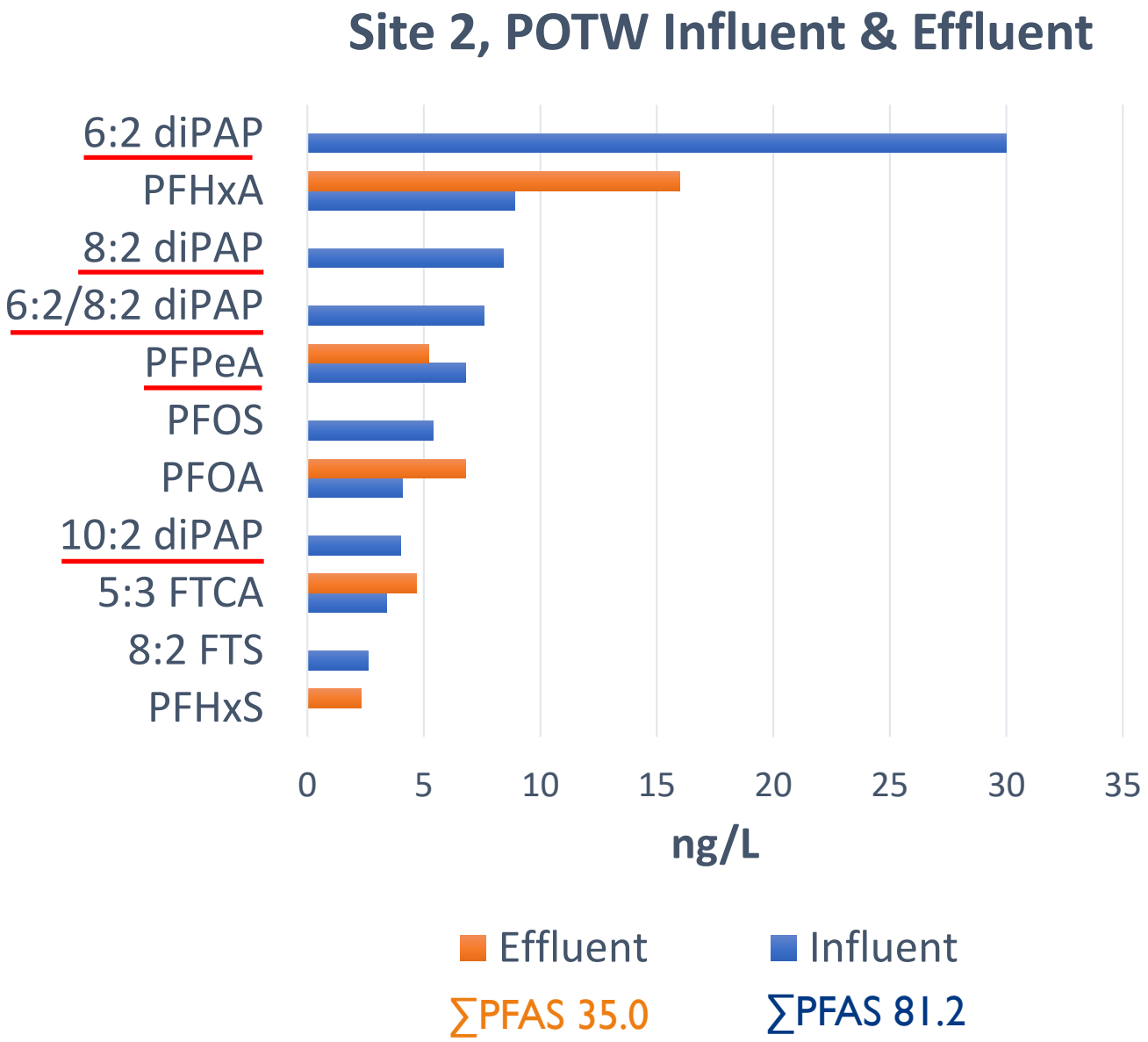


AOF Equivalent for these samples is 63%

Site 2
POTW

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	ND @ 10,000	Not available
Influent Dup	ND @ 10,000	Not available
Effluent	2,400	Not available
Effluent Dup	2,800	Not available

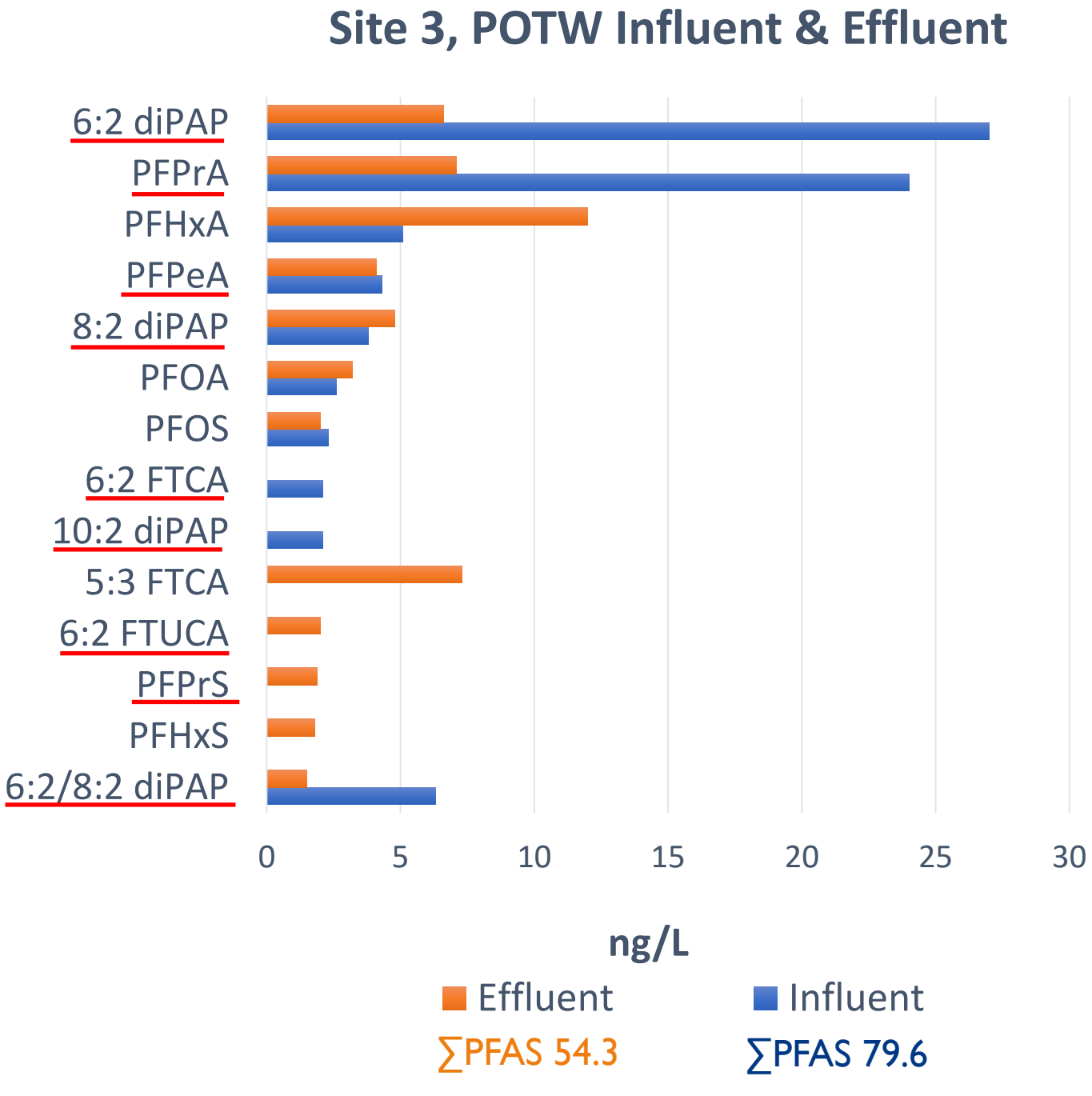
FTOHs are all non-detect @ 1,000 ng/L



Site 3 POTW

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	5,200	170
Influent Dup	4,600	170
Effluent	3,100	94
Effluent Dup	1,800	85

FTOHs are all non-detect @ 1,000 ng/L

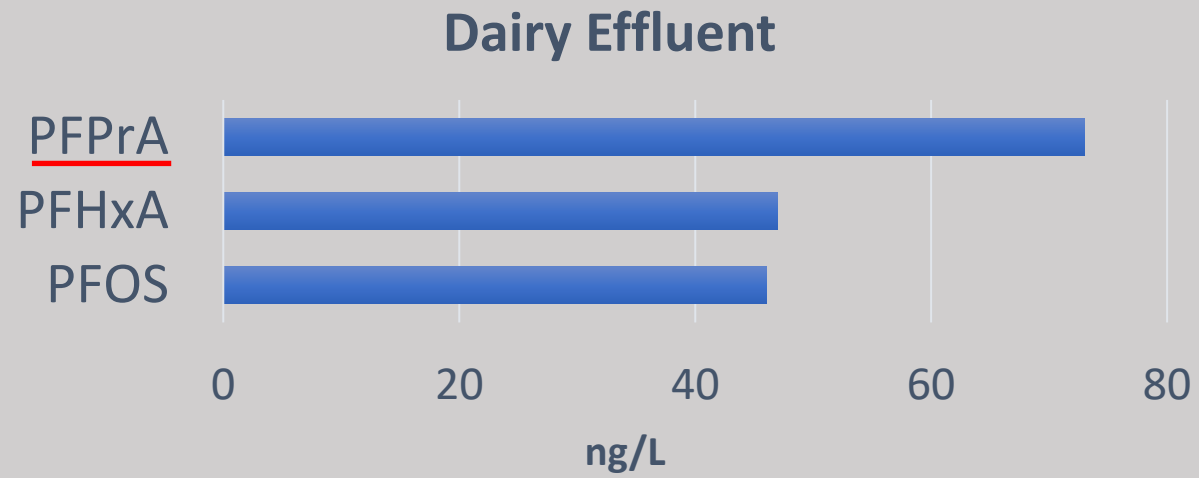


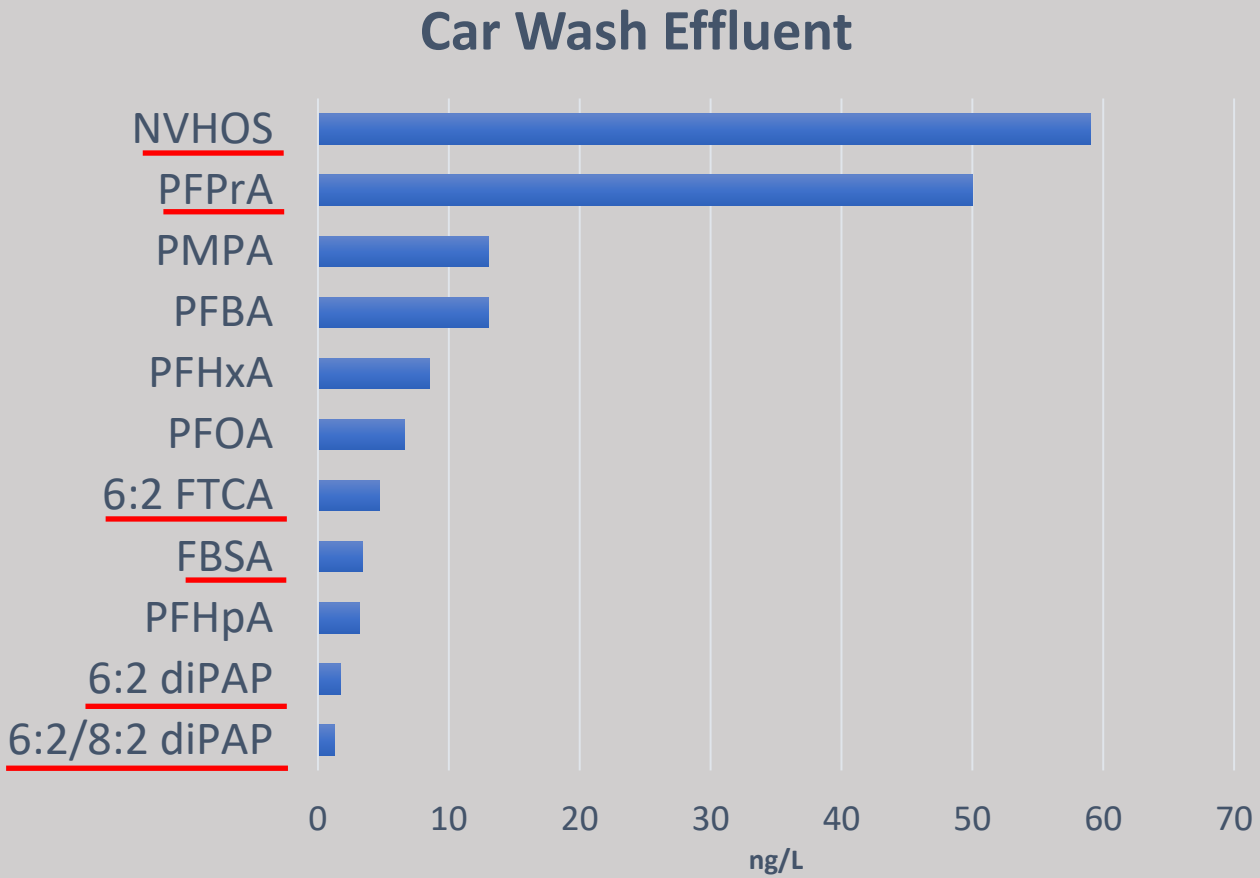
Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Effluent (Circuit Board 1)	2,300	7.1
Effluent (Circuit Board 2)	3,300	140
Effluent (Aerospace)	3,700	43
Effluent (Landfill)	1,400	100

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Effluent (Circuit Board 1)	2,300	7.1
Effluent (Circuit Board 2)	3,300	140
Effluent (Aerospace)	3,700	43
Effluent (Landfill)	1,400	100

Site 4 – Industrial Discharge

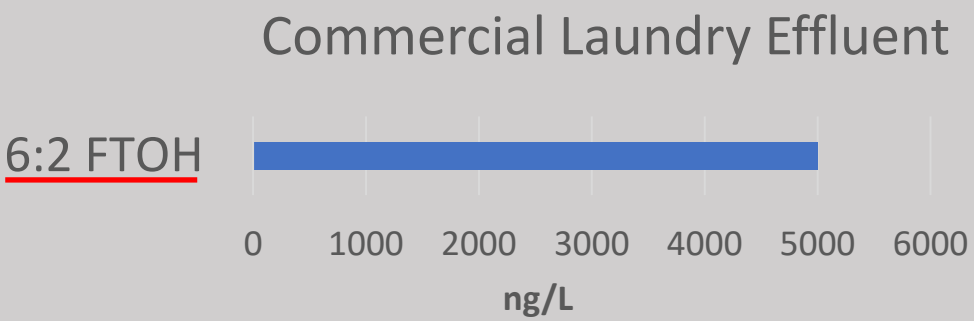
Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Effluent Dairy	33,000	360
Effluent Car Wash	ND @ 1,000	84

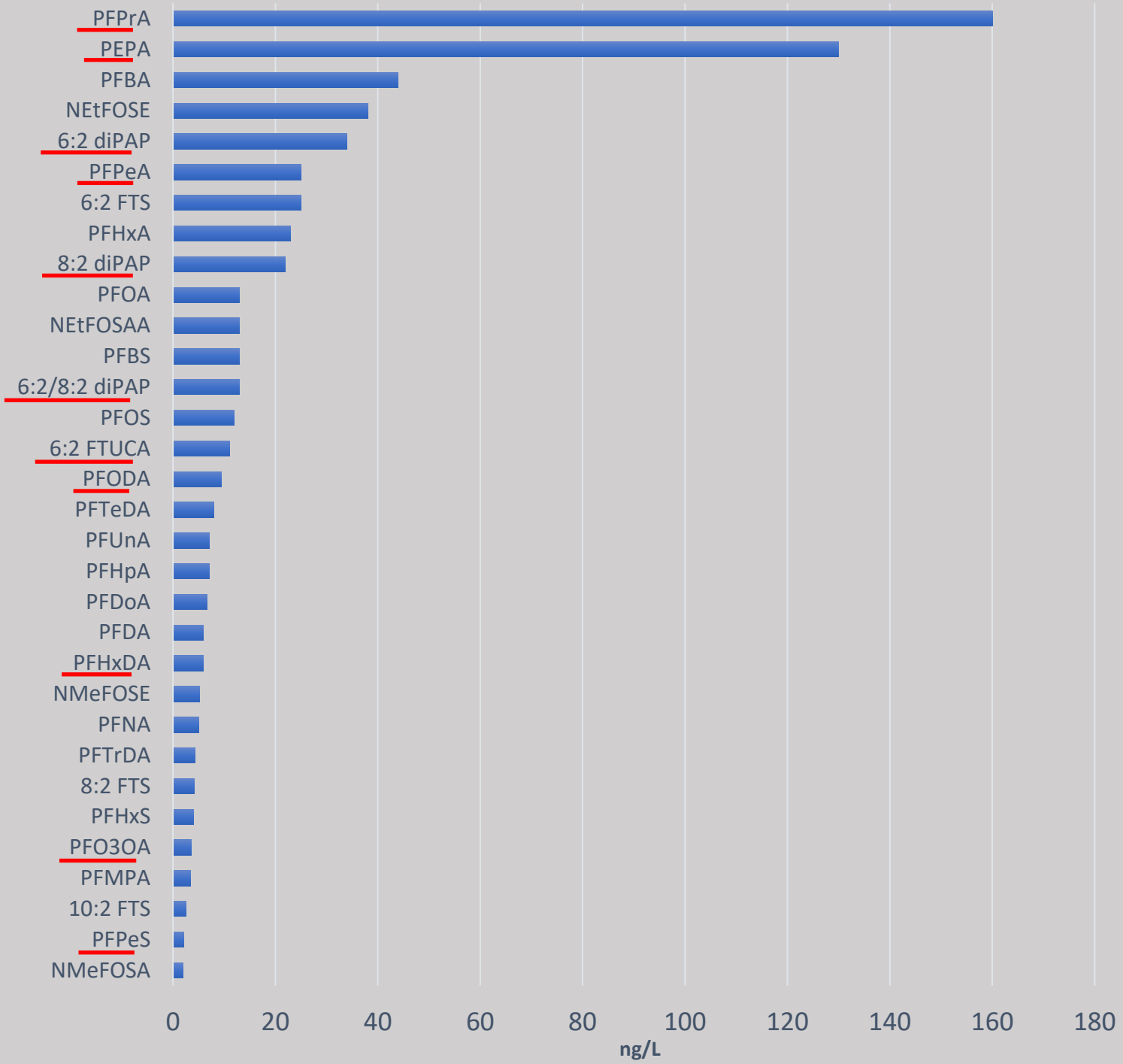




Site 4 – Industrial Discharge

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Effluent Commercial Laundry	39,000	6,100





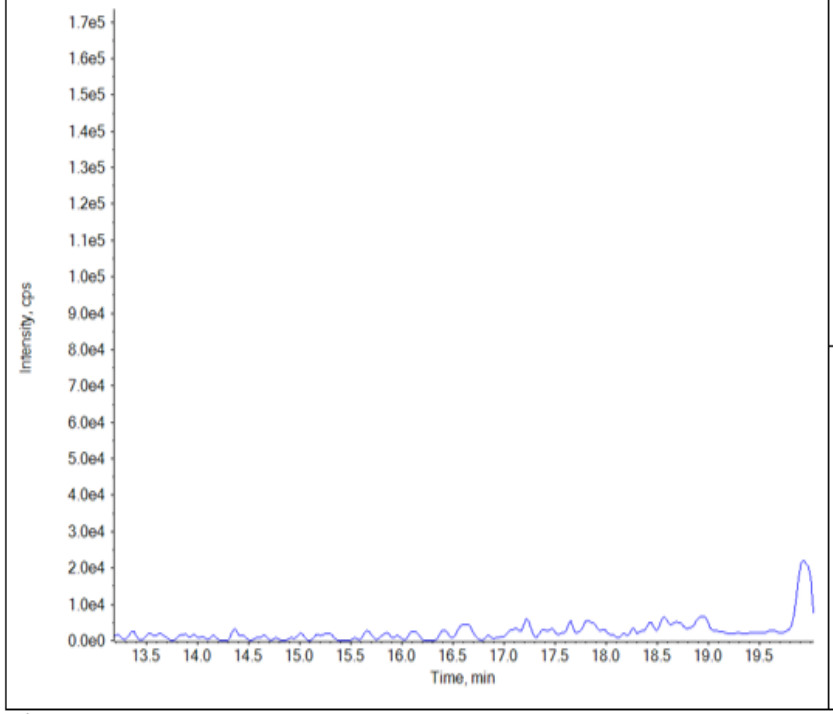
What did the NTA tell us?

Sites	Detections
Sites 1, 2, & 3	1:3 fluorotelomer carboxylic acid – Moderate to High Confidence
Site 1	N-dimethyl ammonio propyl perfluorohexane sulfonamido propanoic acid - Low Confidence / Possible identification of a group

1:3 fluorotelomer carboxylic acid (Mass/FragMass/RT/Isotope/Library/Formula/Ion Ratio)

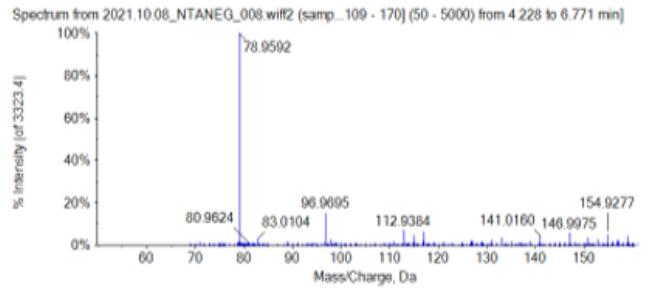
Retention Time: 2.65 minutes
Precursor m/z : 141.0169
Fit (%) N/A **RFit (%)** N/A

Exp RT: 17.02 minutes
Analyte Name:
1:3 fluorotelomer carboxylic acid

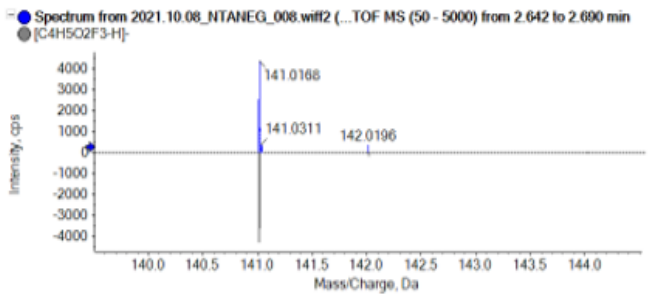


Collision Energy = 35 ± 15 eV

Acquired / Library MSMS



Acquired / Theoretical MS



Targeted PFAS

All Matrices – Up to 80 Compounds

Strengths: Selectivity, Sensitivity at ~1-5ppt

Can be used for risk assessment

Weaknesses: Limited list of compounds

TOP Assay

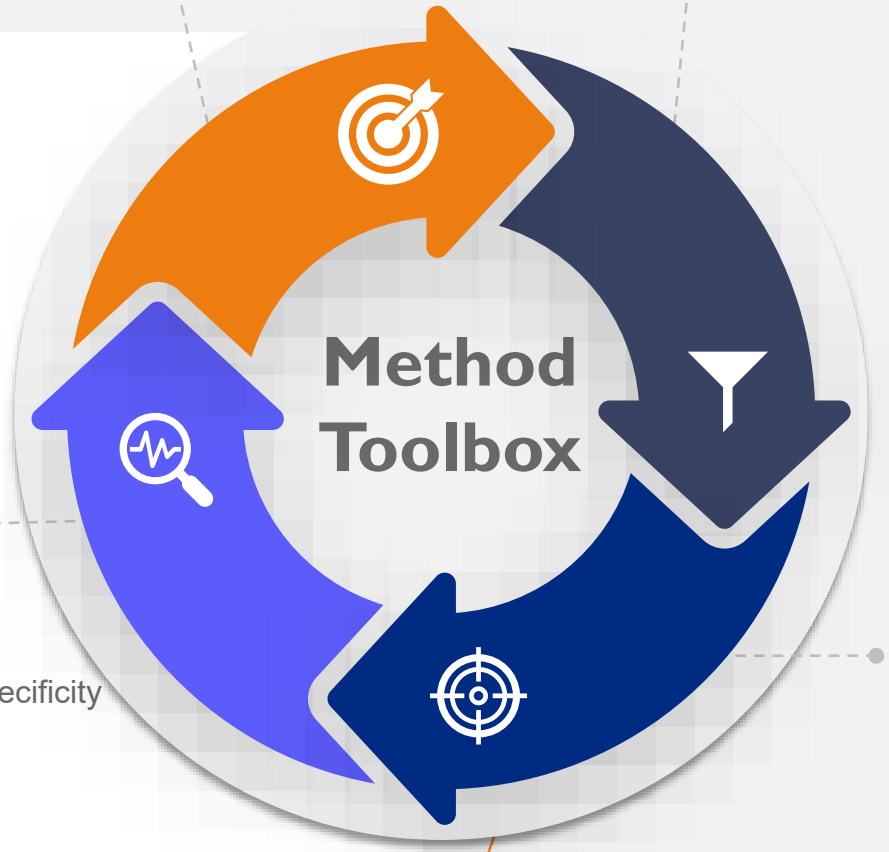
All Matrices – Oxidizable Precursors

Strengths: Sensitivity at ~1-5ppt

Specific to ‘unknowns’ with potential to convert to risk drivers

Weaknesses: Not specific

Does not complete a mass balance



Non-Target Analysis

All Matrices – Unknowns

Strengths: Ability to identify ‘unknowns’ with specificity

Ability to conduct novel compound identification

Weaknesses: Limited to current libraries

Limited quantitation

Total Organic Fluorine

All Matrices – Organic Fluorine

Strengths: Closest to a mass balance

Weaknesses: Sensitivity at ~1ppb

No selectivity

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THANK YOU

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