Tools for the Characterization of PFAS in Wastewater

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Presentation Topics / Outline

1. Why look beyond the published methods?
2. Analytical methodology
3. Analytical results
4. What Have We Learned?
5. What's Next?

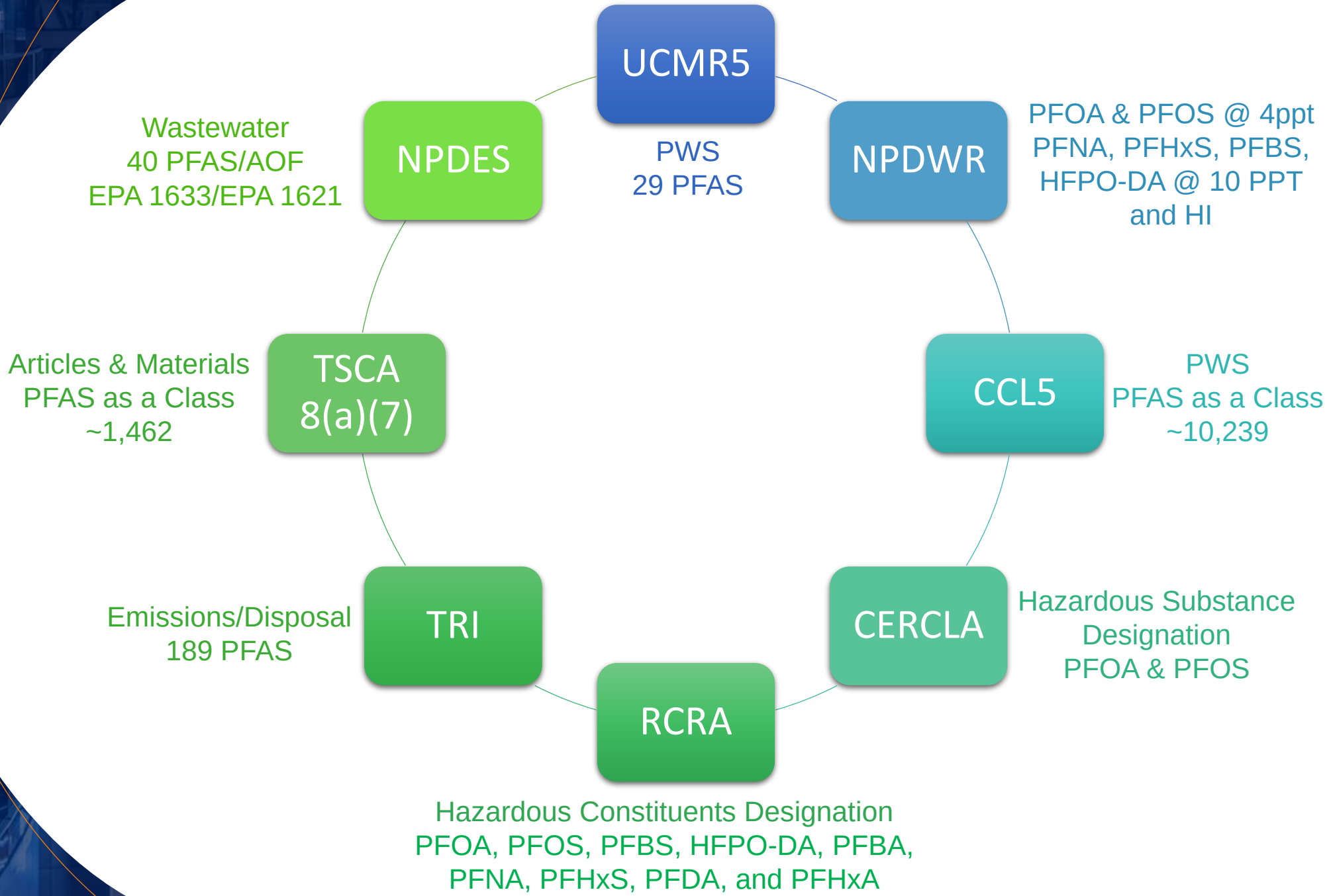
Why look beyond the published methods?

Definitions of PFAS…

How do we define what is a PFAS?

- Varying definitions of PFAS in literature
- Definitions of PFAS vary by country, at the Federal level, and at the state level
- Definitions change over time

VARIED APPROACH



Analytical Methodology

Published Methodology

EPA 1633 – Targeted PFAS by LC/MS/MS

- Multi-lab validated method
- Weak Anion Exchange (WAX) Solid Phase Extraction (SPE)
- LC/MS/MS Analysis
- Isotope Dilution Quantitation
- 40 analytes
- Reporting limits – low ppt

EPA 1621 – AOF by CIC

- Multi-lab validated method
- Adsorbable Organic Fluorine
- Two separate carbon cartridges
- Reporting limits ~ 1ppb

Published Methodology

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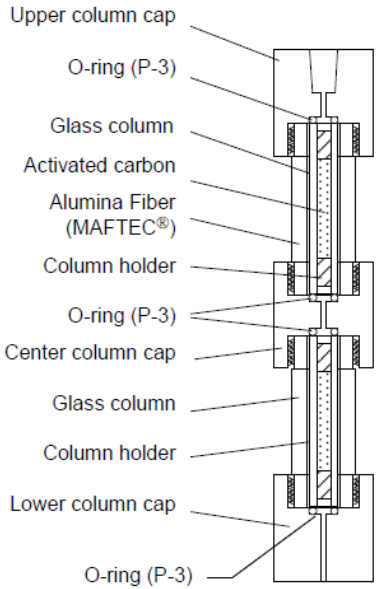
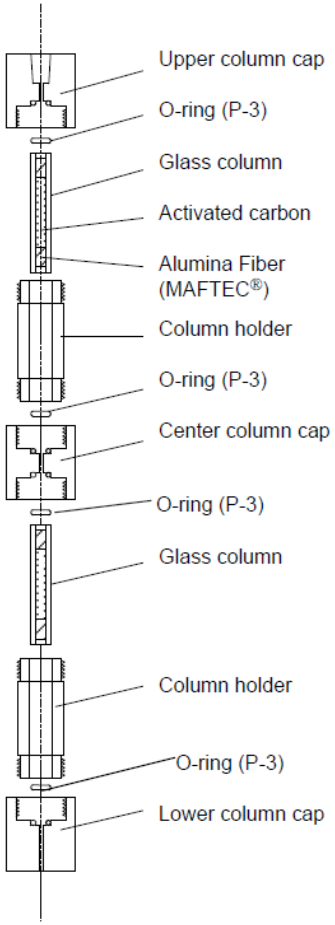




Published Methodology

Laboratory Methodology

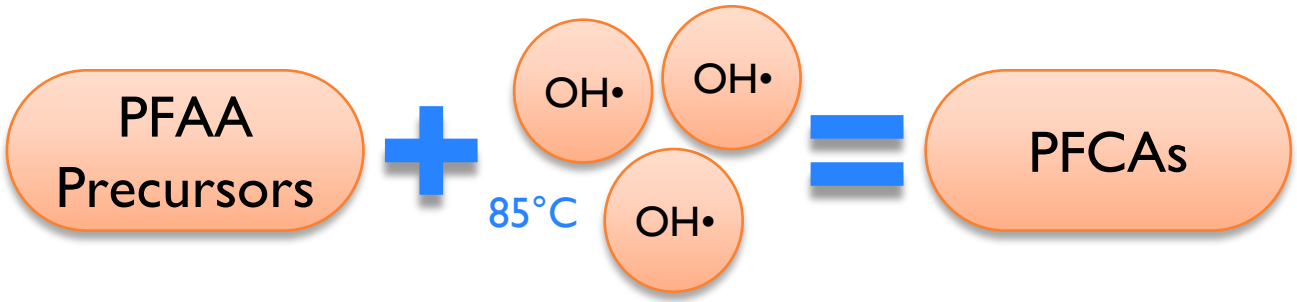
Modified 537 (laboratory SOP)

- Weak Anion Exchange (WAX) Solid Phase Extraction (SPE)
- LC/MS/MS Analysis
- Isotope Dilution Quantitation
- ~75 analytes
- Reporting Limits – single digit ppt levels

Laboratory Methodology

Total Oxidizable Precursor (TOP) Assay

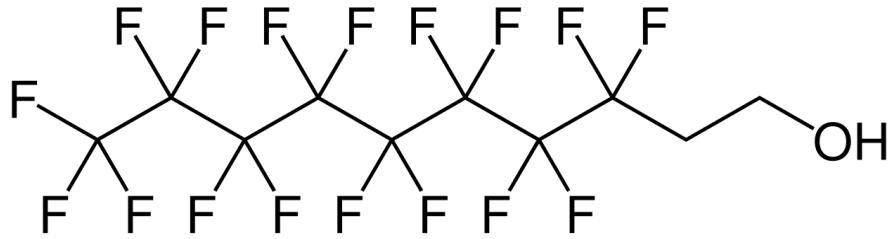
- Pre-oxidation and Post-oxidation analysis required
- Oxidation of unknown precursors
- Oxidized samples processed by EPA 1633 or 537 Mod
- Detection limits – low level ppt



Laboratory Methodology

FTOH by GC/MS/MS (laboratory SOP)

- Liquid-liquid solvent extraction
- Analysis of select fluorotelomer alcohols
- GC/MS/MS analysis
- Internal Standard quantification
- Detection limits ~ 1ppb



Laboratory Methodology

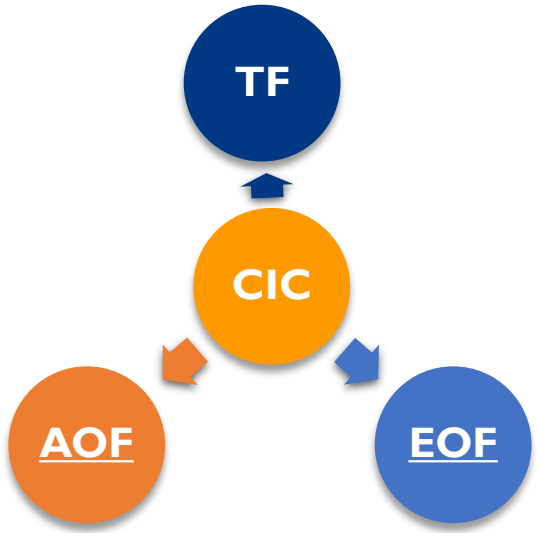
Total Fluorine, Adsorbable Organic Fluorine, and Inorganic Fluorine

Combustion Ion Chromatography

- Total Fluorine (TF)
  - Detection Limits ~ 100ppb
- Adsorbable Organic Fluorine (AOF)
  - Detection Limits ~ 1ppb

Ion Chromatography

- Inorganic Fluorine (IF) – EPA Method 300
  - Detection Limits ~ 0.5 to 1ppm



Analytical Results

Standard Analytical Results

Targeted LC/MS/MS Analysis

- 36 analytes under modified 537
- Most common:
- C6 to C9 PFCAs
- C4 to C8 PFSAs
- Select detections of HFPO-DA
- Some detections for FTSs

	Total PFAS (ng/L)
Influent_1	185.4
Influent_2	122.8
Influent_3	121.7
Influent_4	90.2
Effluent_1	45.0
Effluent_2	51.6

Total Oxidizable Precursor

PFCA Comparison Pre/Post Oxidation

PFCA Influent_1 (ng/L)

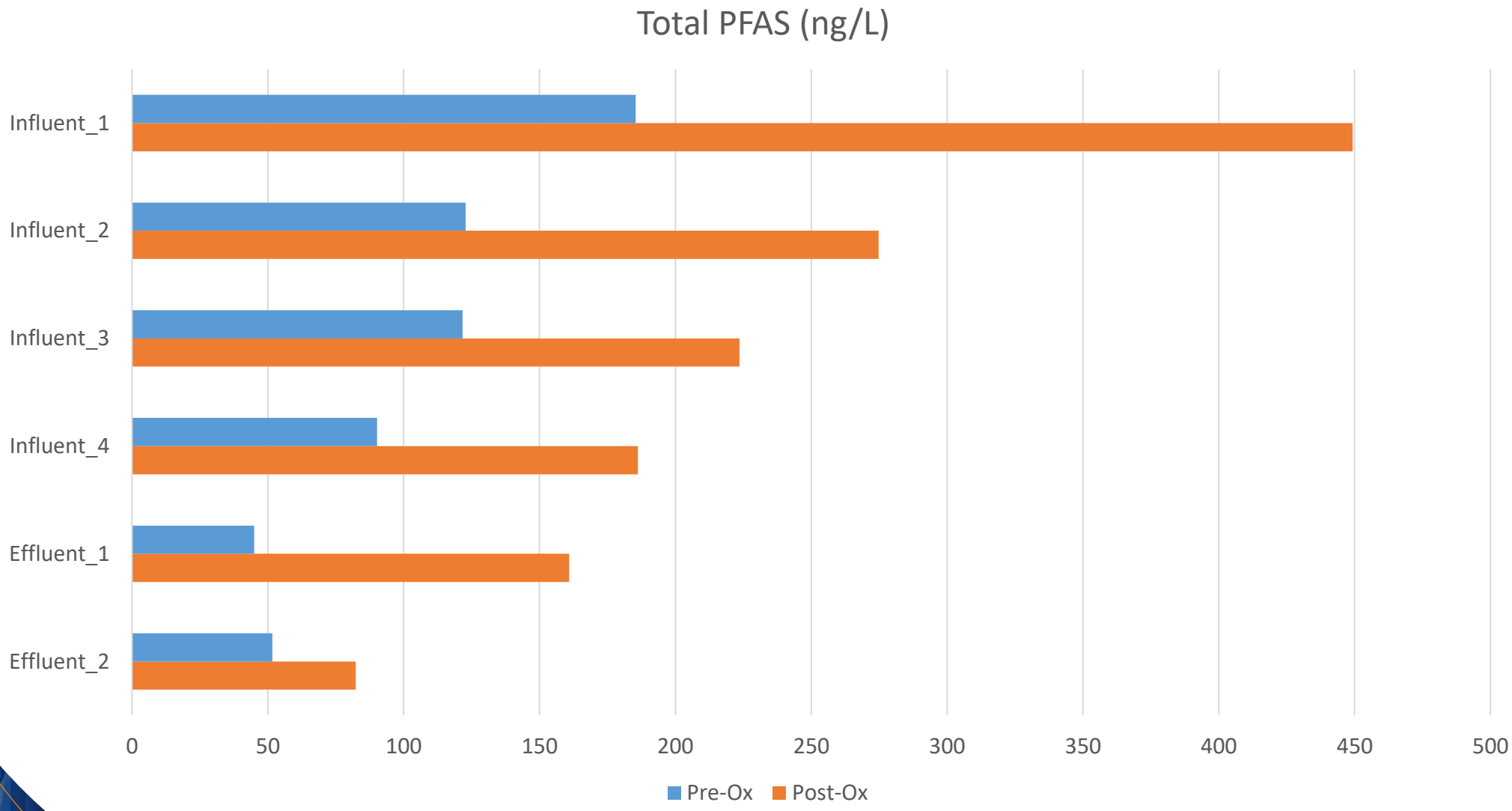
	Pre-Ox	Post-Ox
PFBA	ND	130
PFPeA	ND	140
PFHxA	18	41
PFHpA	4	16
PFOA	42	59
PFNA	8	13
Total	72	400

Total PFCA Concentrations (ng/L)

	Pre-Ox	Post-Ox	Δ
Influent_1	72	400	328
Influent_2	74	220	146
Influent_3	76	160	84
Influent_4	47	120	73
Effluent_1	22	120	98
Effluent_2	32	62	30

Total Oxidizable Precursor

Total PFAS Pre/Post Oxidation



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%

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%

Total Fluorine Concentrations

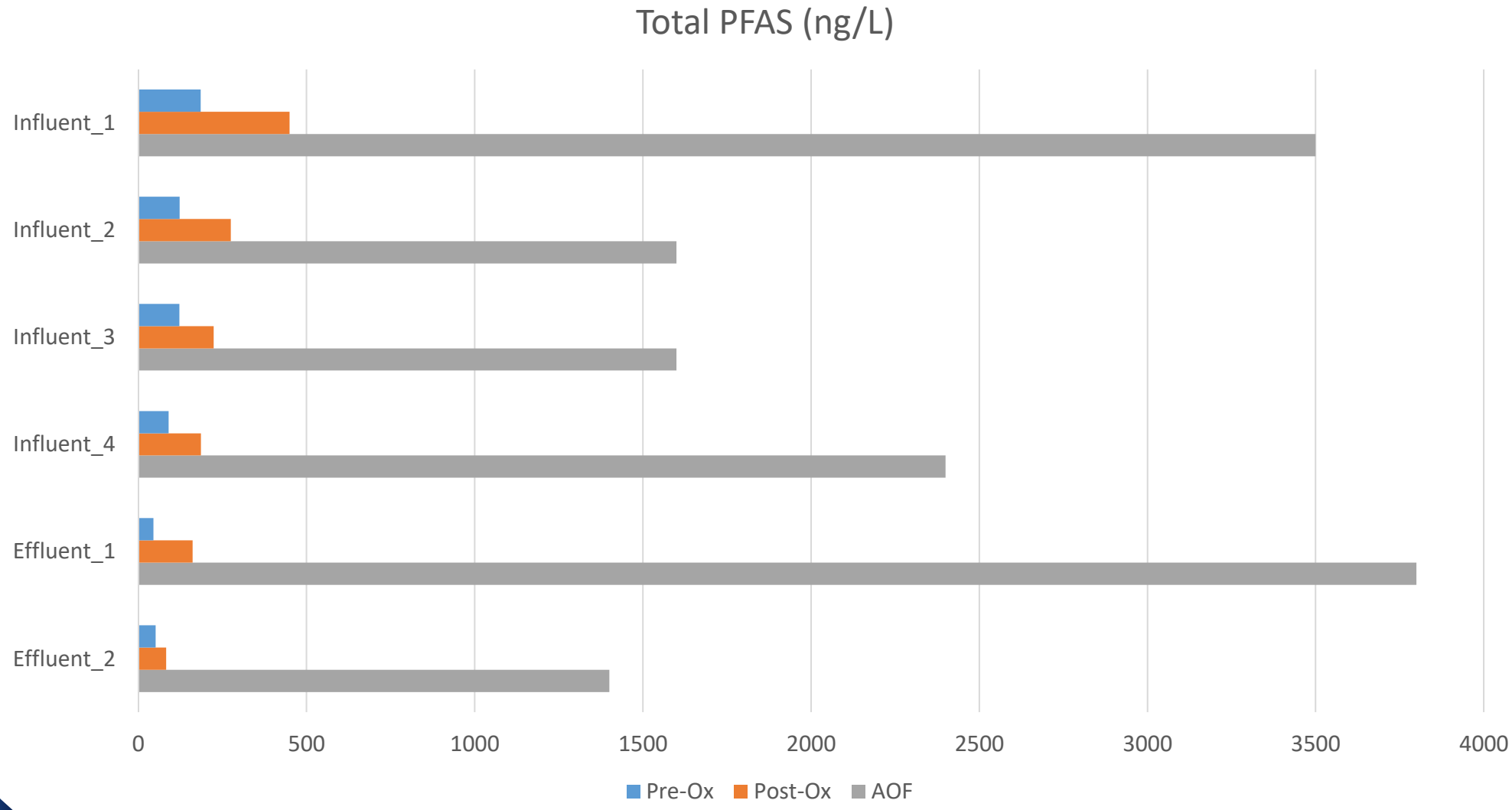
	Inf_1	Inf_2	Inf_3	Inf_4	Eff_1	Eff_2
Total Fluorine	570	560	540	530	570	510
AOF (Lab SOP)	3.5	1.6	1.6	2.4	3.8	1.4
EPA 1621 (Plug 1)	1.7	1.4	1.1	1.9	1.2	ND
EPA 1621 (Plug 2)	1.6	ND	ND	ND	ND	ND
EPA 1621 Total	3.3	1.4	1.1	1.9	1.2	ND
IF (EPA 300)	1,600	650	ND	ND	ND	480

EPA 1621 Total = Sum of Plug 1 and Plug 2

TF / AOF / IF

Potential PFAS Concentrations

Pre/Post-TOP and AOF



What Have We Learned?

What do we do with the data?

- There are still a lot of unknowns regarding PFAS
- Potential high and low bias in AOF concentrations
- Method sensitivity plays a key role in comparing different methods

What's Next?

Targeted Analysis

Expanded Analyte List

- Additional analyte classes
  - PAPs, diPAPs, SAmPAP
  - Additional FTCAs
  - Additional FTSs
  - FTUCAs
  - PFECA
  - PFAPA
  - X:XPFPi
- Ultra-Shorts
  - Pre and Post oxidation

Fluorotelomer PFAS

- Expand GC/MS/MS to include additional precursors
  - FT alcohols
  - FT acetates
  - FT acrylates
  - FT methacrylates
- Lower Detection Limits and Reporting limits
- Isotope Dilution

Targeted Analysis