Forensic Approach for PFAS Source Identification at Contaminated Sites

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Agenda

- Brief Background on PFAS Sources

- Fingerprinting Approach - Study Design

- Results
  - Targeted Analysis
  - Non-targeted Analysis
  - Statistical Analysis

- Conclusions

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PFAS Applications

PFAS are produced by different manufacturers - Many commercial and industrial use applications

Surface Treatments

Food-related
- Non-stick coated pans
- Food wrappers

Apparel, Household & Personal Care
- Stain-resistant fabrics
- Carpet
- Upholstery
- Leather protector
- Hair care products
- Floor polishes
- Air fresheners

Performance Chemicals

Industrial
- Mist suppressant in chrome plating
- Cabling materials
- Molds
- Photolithography
- Semiconductor
- Electronics
- Building
- Construction
- Roofing

Automobile, AFFF
- Car paint
- Wiper blades
- Oil filters, lubricants, etc.
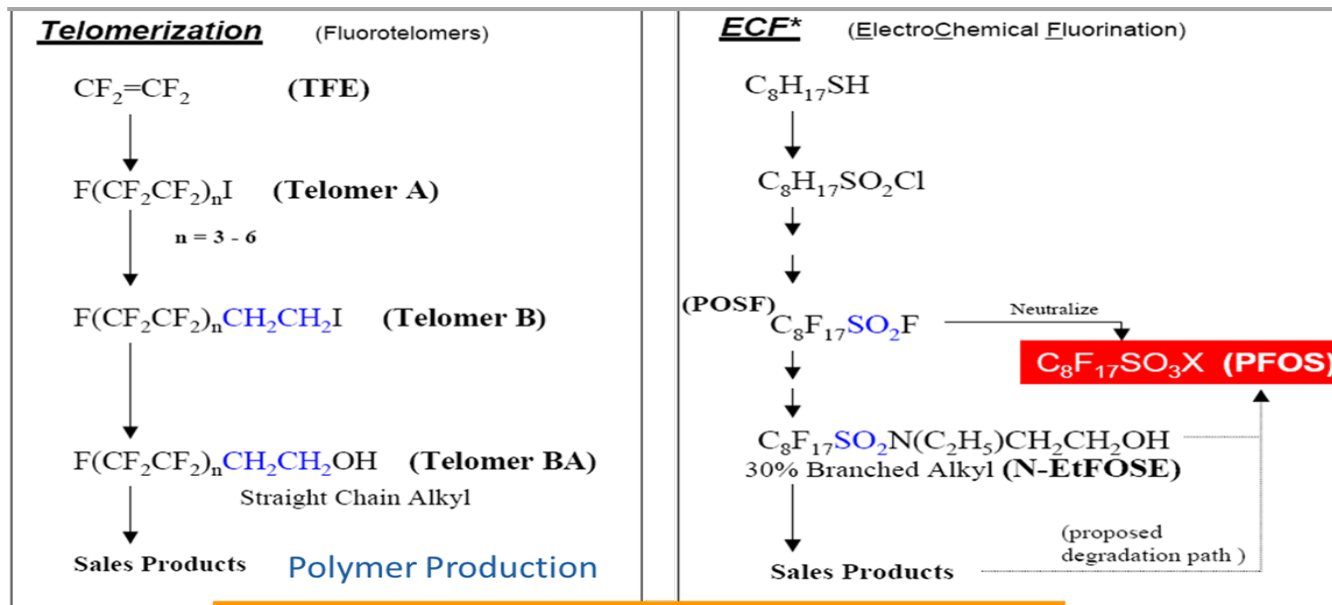- Aqueous film forming foams

Prevedorous et al 2006, Buck et al 2011

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Manufacturing Processes

Telomerization

Electrochemical Fluorination (ECF)

Telomerization (Fluorotelomers)

$CF_2=CF_2$ (TFE)

$F(CF_2CF_2)_nI$ (Telomer A)

n = 3 - 6

$F(CF_2CF_2)_nCH_2CH_2I$ (Telomer B)

$F(CF_2CF_2)_nCH_2CH_2OH$ (Telomer BA)
Straight Chain Alkyl

Sales Products — Polymer Production

ECF* (ElectroChemical Fluorination)

$C_8H_{17}SH$

$C_8H_{17}SO_2Cl$

(POSF) $C_8F_{17}SO_2F$ — Neutralize →

$C_8F_{17}SO_3X$ (PFOS)

$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$
30% Branched Alkyl (N-EtFOSE)

(proposed degradation path)

Sales Products

these chemicals have been used since the 1950s …

Telomerization	ECF
▪ Polymer production ▪ Only even chain length polyfluorinated chemicals, mainly linear isomers	▪ Mixtures of even and odd chains ▪ 30 – 40 % branched isomers

- In 2002, phase out of production of PFOS and related chemicals

- 2010/2015 PFOA Stewardship Program – Most companies stopped manufacturing and import of long-chain PFAS –Shift to shorter chains and alternatives

Prevedouros et al. 2006

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Sources of PFAS

- **Industrial**
  - Manufacturing plants
  - Plastic, paper and textile coatings
  - Metal plating
- **AFFF Usage**
  - Fire training areas
  - Airports
  - Emergency response
  - Oil refineries

Direct Sources

- **Landfills**
- **Wastewater treatment plants**
  - Effluents
  - Land application of biosolids
- **FT based AFFF**

Indirect Sources

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PFAS Fingerprinting Approach

- **What is Fingerprinting ?**

  - Environmental forensic technique

- **Why Fingerprint?**

  - Assist with understanding of PFAS fate and transport

  - Determine concentration and composition trends of PFAS from different contamination source scenarios

  - Identify sources of contamination based on their chemical signature, manufacturing, fate and transport and degradation pathways information

Some Signature Chemistries

- Paper and Food Packaging - Side chain fluorinated polymers and polyfluoroalkyl phosphonic acids (PAPs/diPAPs)

- Metal Plating - PFOS, F-53B, F-53, PFASi

- Surfactant and a plant protection agent - PFOS-related substance EtFOSA

- Textile and Leather - polymers and polymer raw materials

    - Polyfluorinated/perfluorinated (meth)acryl polymers, fluorinated urethanes, alkyl sulfonamide derivatives, etc.

Wang et al. 2013; KEMI 2015

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Signature Chemistries (cont'd)

- **AFFF related** – Anions, cations, zwitterions and neutrals
  - Perfluoroalkyl sulfonates (PFOS related),
  - 6/8:2 FTS (fluorotelomer sulfonates),
  - 6/8:2 FTAB (fluorotelomer betaines and amine oxides)

- **WWTP and Landfill Leachates** - FT based biodegradation products
  - n:2 FTUCA, n:3 FTCA

- **Isomer profiles** - provides information about their manufacturing sources
  - Branched and Linear
  - Odd and even chain lengths

- **Fate and Transport** - Environmental fractionation

Barzen et al 2017; Lang et al 2017; KEMI 2015

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PFAS Fingerprinting Approach - Current Study

Goal

- Determine concentration and composition trends of PFAS from different contamination source scenarios

- Identify sources of contamination based on

  - Chemical signature

  - Manufacturing

  - Timeline (Age) of release

  - Fate and transport

  - Degradation products

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Study Design Workflow

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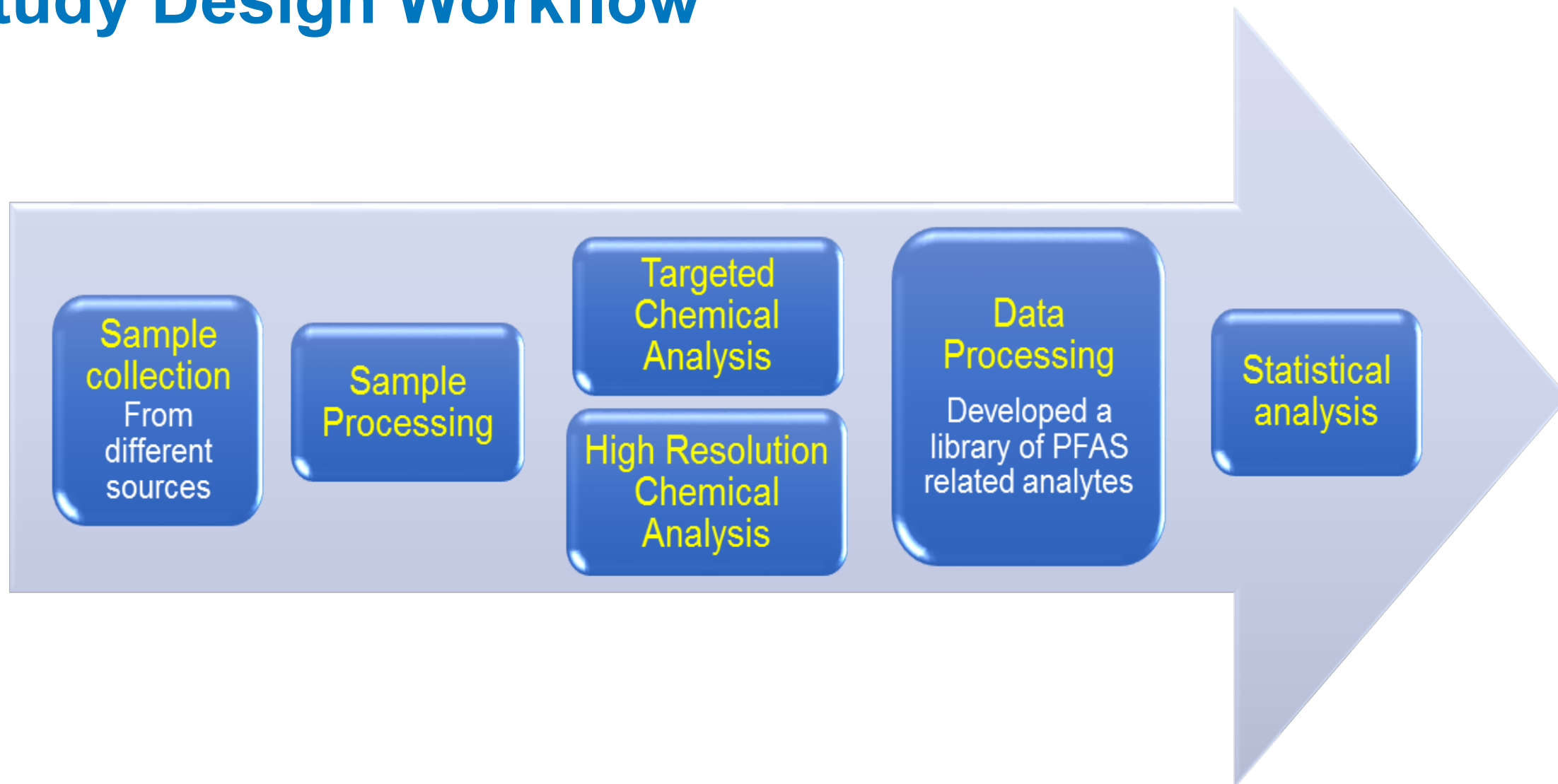
Sample Collection from Different Sources

- Environmental Samples - Surface water collected from nearby

  - Airport

  - Metal plating facility

  - Textile mill (Fluorotelomer coatings)

  - Wastewater treatment plant

  - Landfill

- Landfill leachate (LFL)

- Carpet (Pre-2002 phase out)

- AFFF formulations - known and unknown manufacturing sources

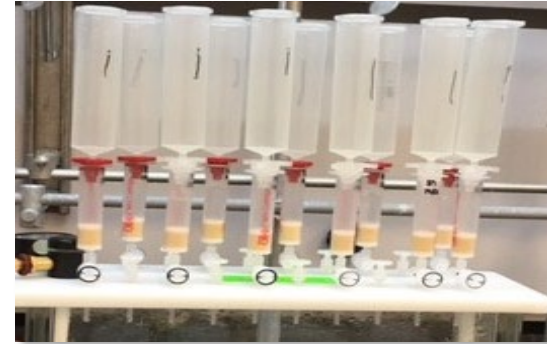 - FT chemistry

  - Electrochemical and

  - Two unknown sources

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Extraction of PFAS – Targeted Chemical Analysis

Method compliant with DoD QSM 5.1 Table B-15 requirements

Samples collected

Surrogates and Targets spiked

Extraction using pre-conditioned SPE cartridges

Elution of SPE cartridges using solvent mixture

Sample concentration followed by reconstitution and addition of internal standards

Analysis on LC-MS/MS

Branched Isomers

Branched isomer standards were run to look for the presence of branched isomers in the samples

Catalog Number	Description
br-PFHxSK	L-PFHxS with branched isomers
br-PFOSK	L-PFOSK with branched isomers
T-PFOS	PFOS (Technical grade)
NaP3MHpS	Sodium perfluoro-3-methylheptanesulfonate
NaP6MHpS	Sodium perfluoro-6-methylheptanesulfonate
ipPFNS	Sodium perfluoro-7-methyloctanesulfonate
T-PFOA	PFOA (technical grade)
P3MHpA	Perfluoro-3-methylheptanoic acid
P4MOA	Perfluoro-4-methyloctanoic acid
ipPFNA	Perfluoro-7-methyloctanoic acid (90%)
P355TMHxA	Perfluoro-3,5,5-trimethylhexanoic acid
P37DMOA	Perfluoro-3,7-dimethyloctanoic acid

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Fingerprint of Environmental Samples - Targeted Analysis

## Based on Targeted analysis – Compounds with known standards
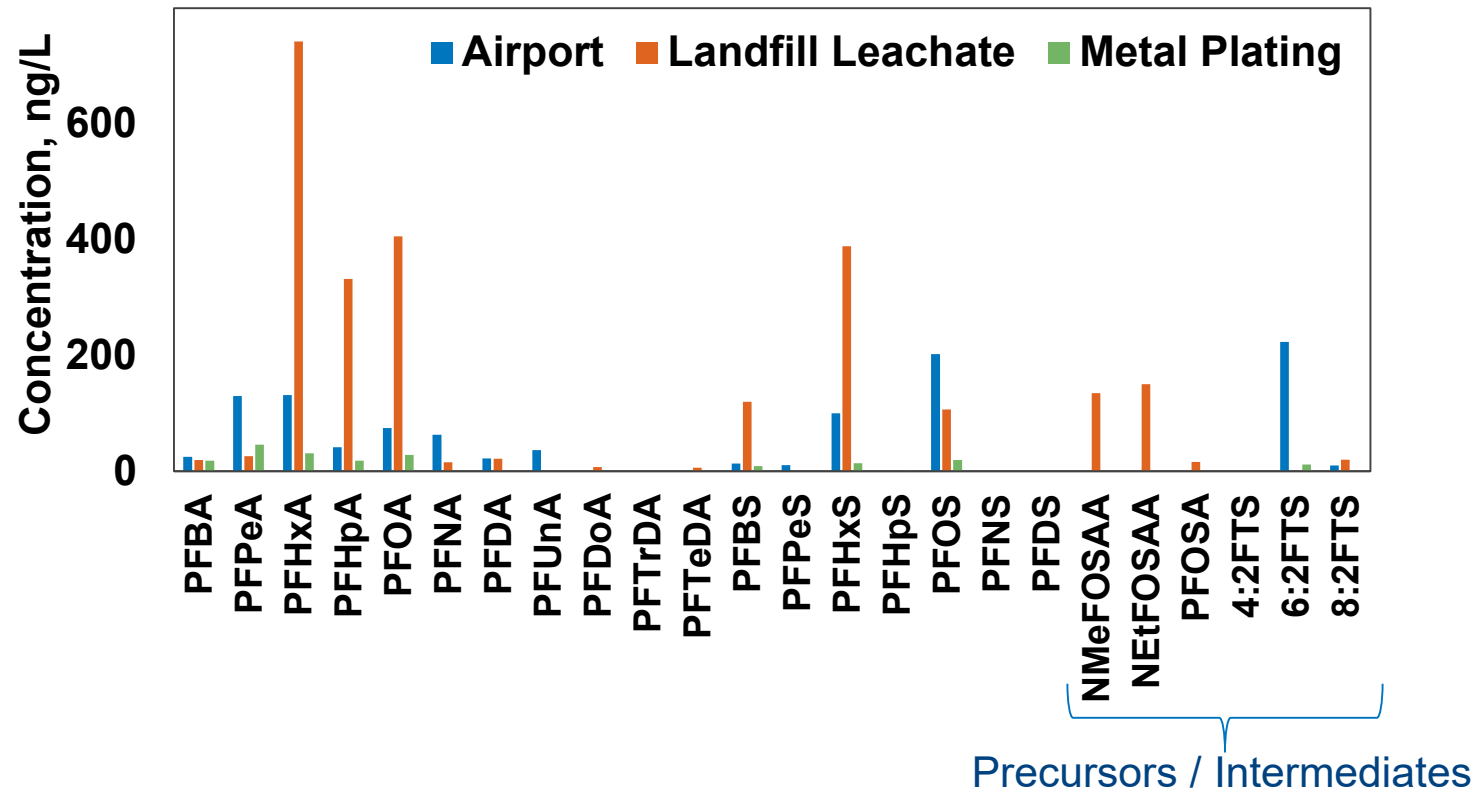
- Surface water samples collected near by Airport, Metal plating facility and landfill leachates
- Presence of precursors or intermediates provides information on biodegradation processes

Fingerprint of Environmental Samples – Non-Targeted Analysis

Statistical Analysis: Principal Component Analysis (PCA)
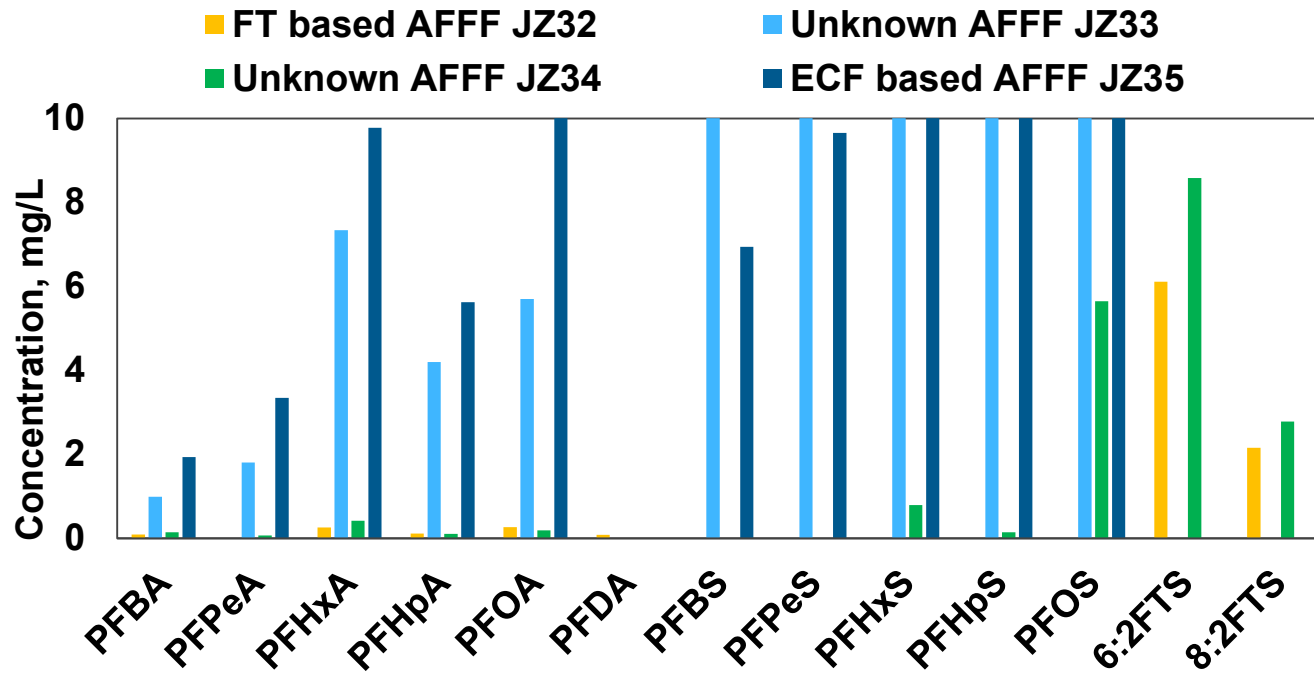
Based on the High resolution MS data – Non-targeted analysis of Environmental samples

■ Airport (n=6)
■ Landfill Leachate (n=3)
■ Metal plating (MP)(n=6)
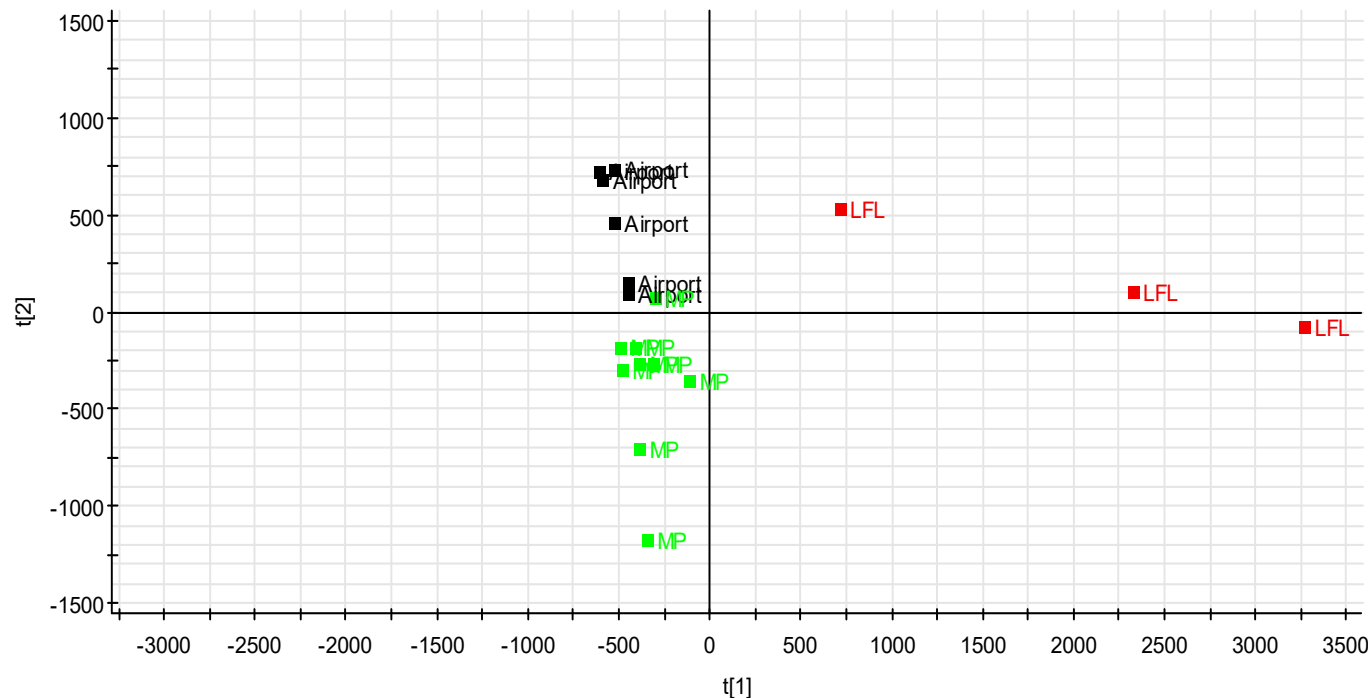
- Landfill leachate sample showing significantly different pattern compared to other source contaminated samples

- Samples collected near airport shows different pattern compared to the samples collected near metal plating facility

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Fingerprint of AFFF Samples – Targeted Analysis

Legend:
- FT based AFFF JZ32 (yellow/gold)
- Unknown AFFF JZ33 (light blue)
- Unknown AFFF JZ34 (green)
- ECF based AFFF JZ35 (dark blue)

Y-axis: Concentration, mg/L (0 to 10)

X-axis categories: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, 6:2FTS, 8:2FTS
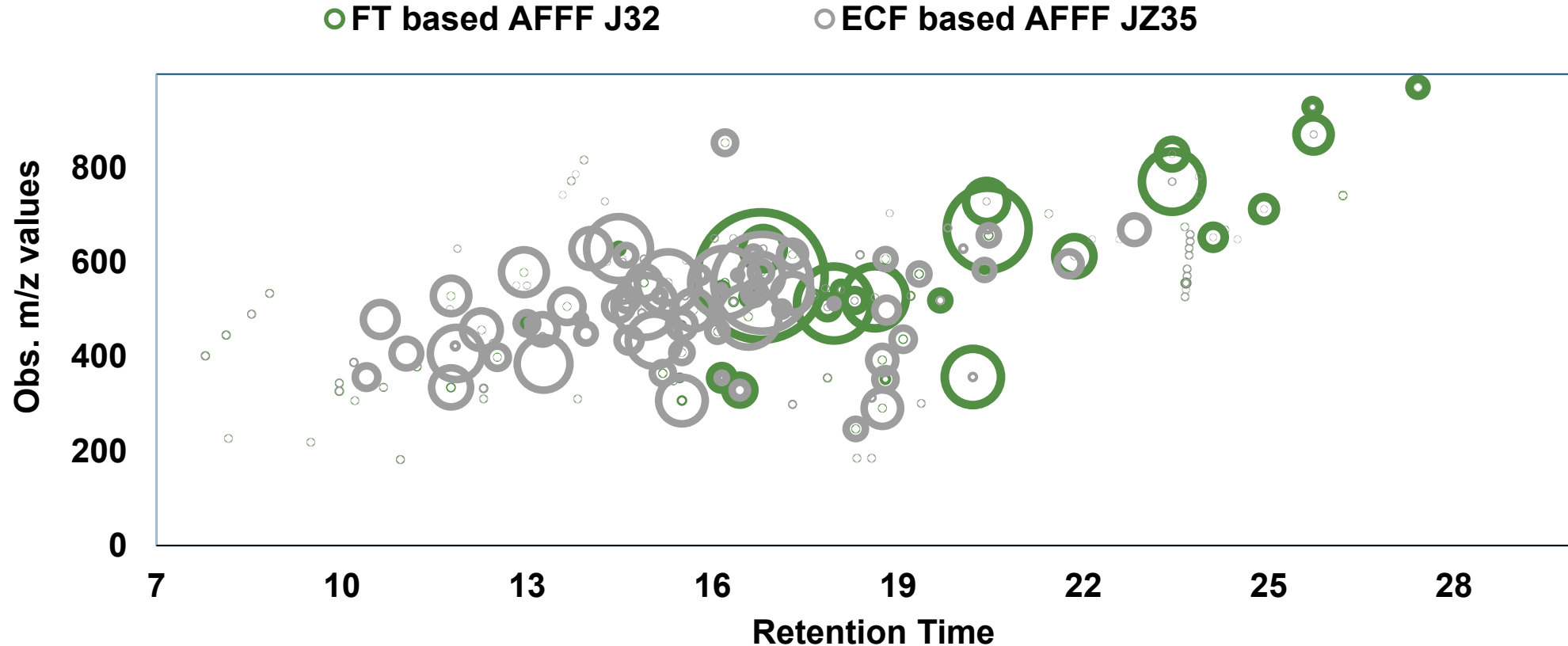
- **ECF based AFFF 35**
  - High concentrations of both even and odd chains of PFAAs,
  - Presence of branched isomers and
  - Absence of FT precursors – typical of ECF based AFFF
  - PFOS concentrations ~1000ppm

- **Unknown AFFF JZ 33**
  - Absence of FT precursors
  - Shows similar pattern as ECF based AFFF

- **FT based AFFF JZ 32 and 34**
  - Presence of FT precursors – typical of FT based AFFFs

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High Resolution MS Data – FT based AFFF
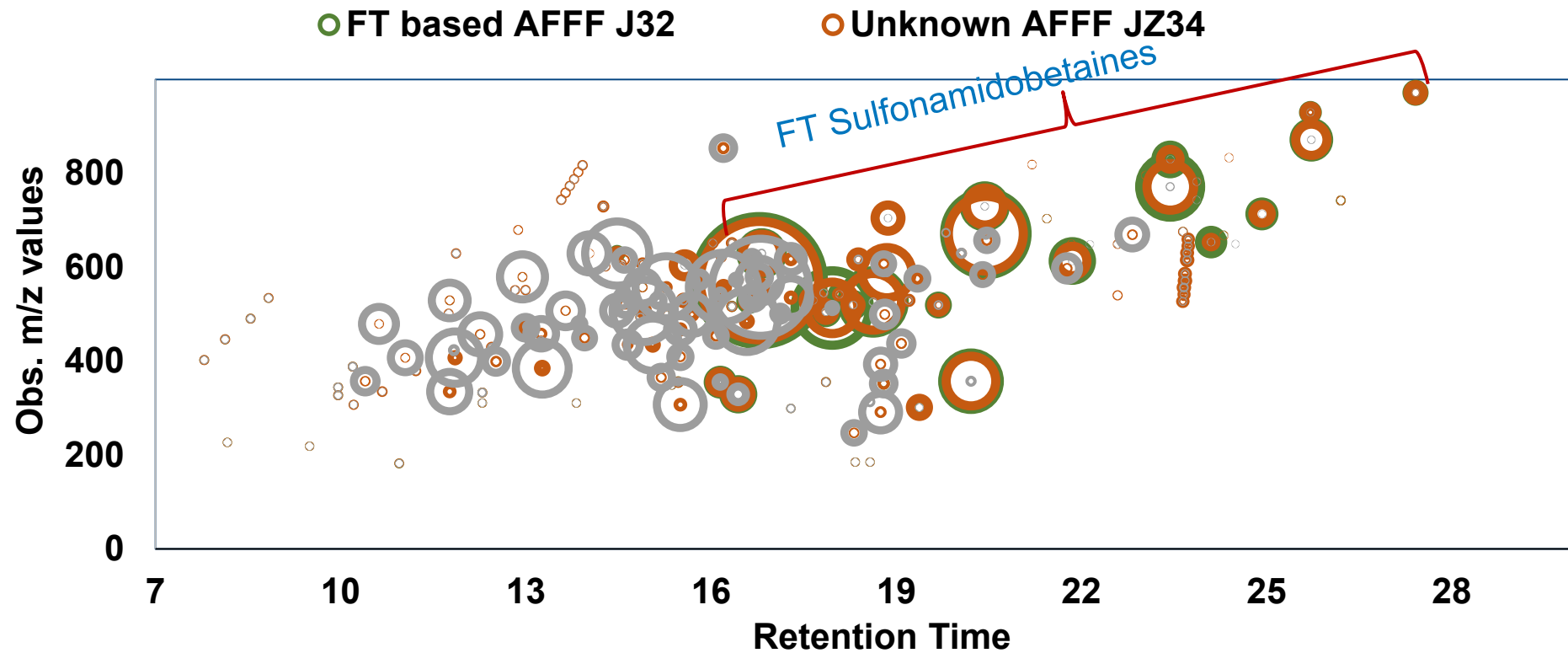

FT based AFFF J32

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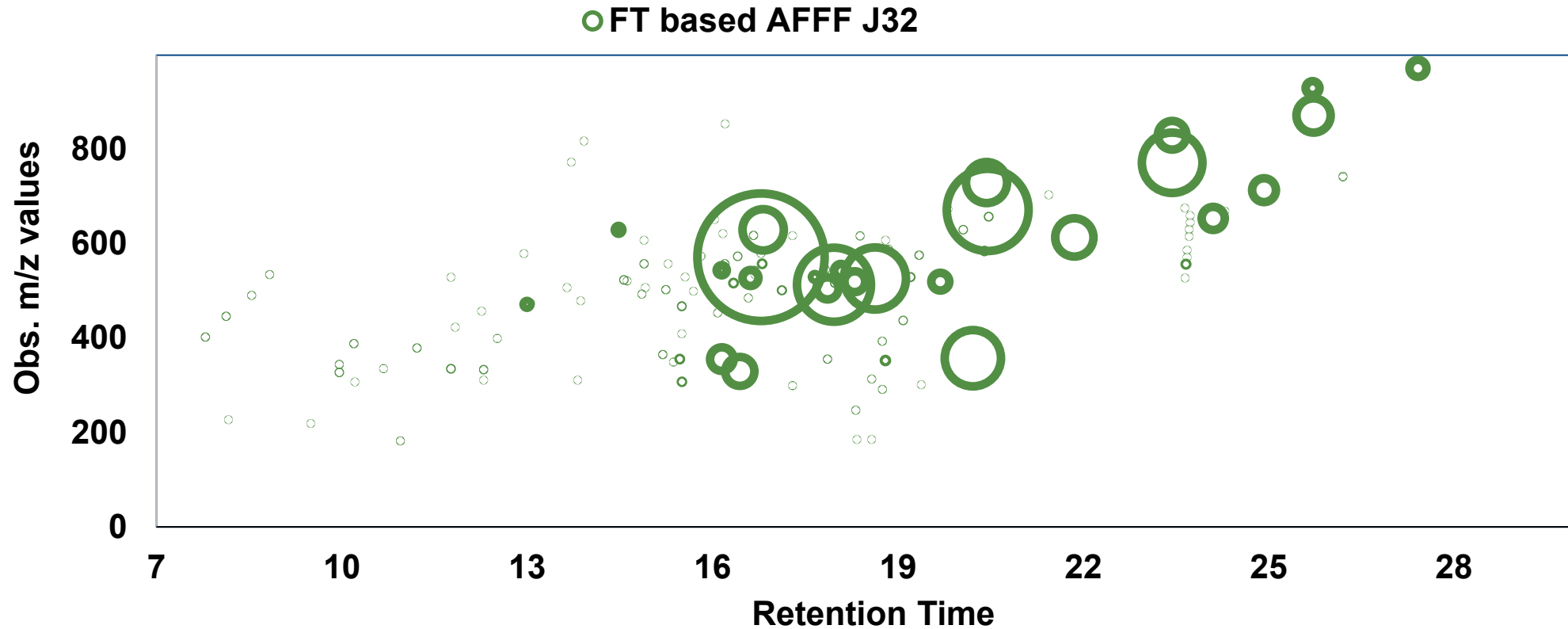
High Resolution MS Data - Comparison of AFFF Sources

- FT based AFFF and ECF based AFFF shows distinct features

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High Resolution MS Data - Comparison of Unknown AFFF Sources

- Source of unknown AFFF was identified by comparing with other known AFFFs from different manufacturers
- Signature of unknown AFFF is similar to FT based AFFF

This data will be important to identify co-occurrence of AFFFs from distinct sources

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Statistical Analysis: PCA of AFFF samples

■ FT based AFFF JZ32 & Unknown AFFF JZ34
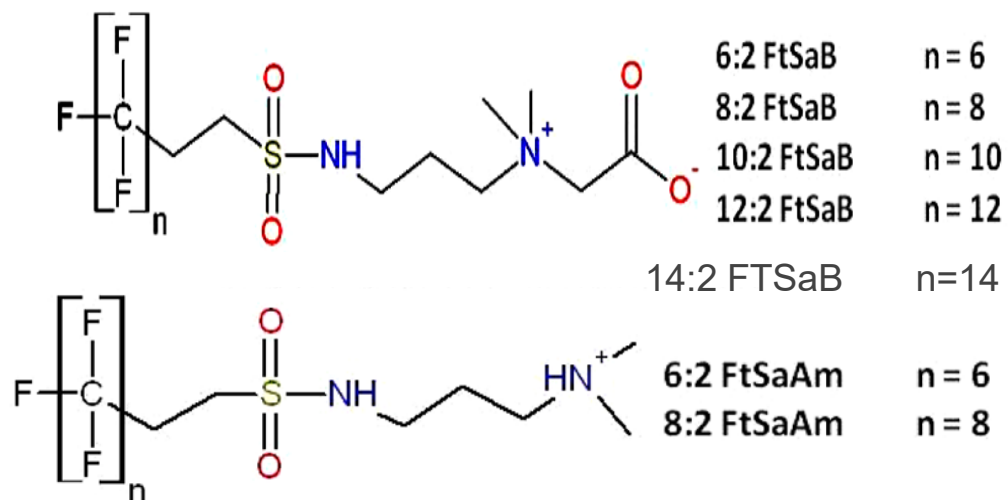■ ECF based AFFF JZ35 & Unknown AFFF JZ33
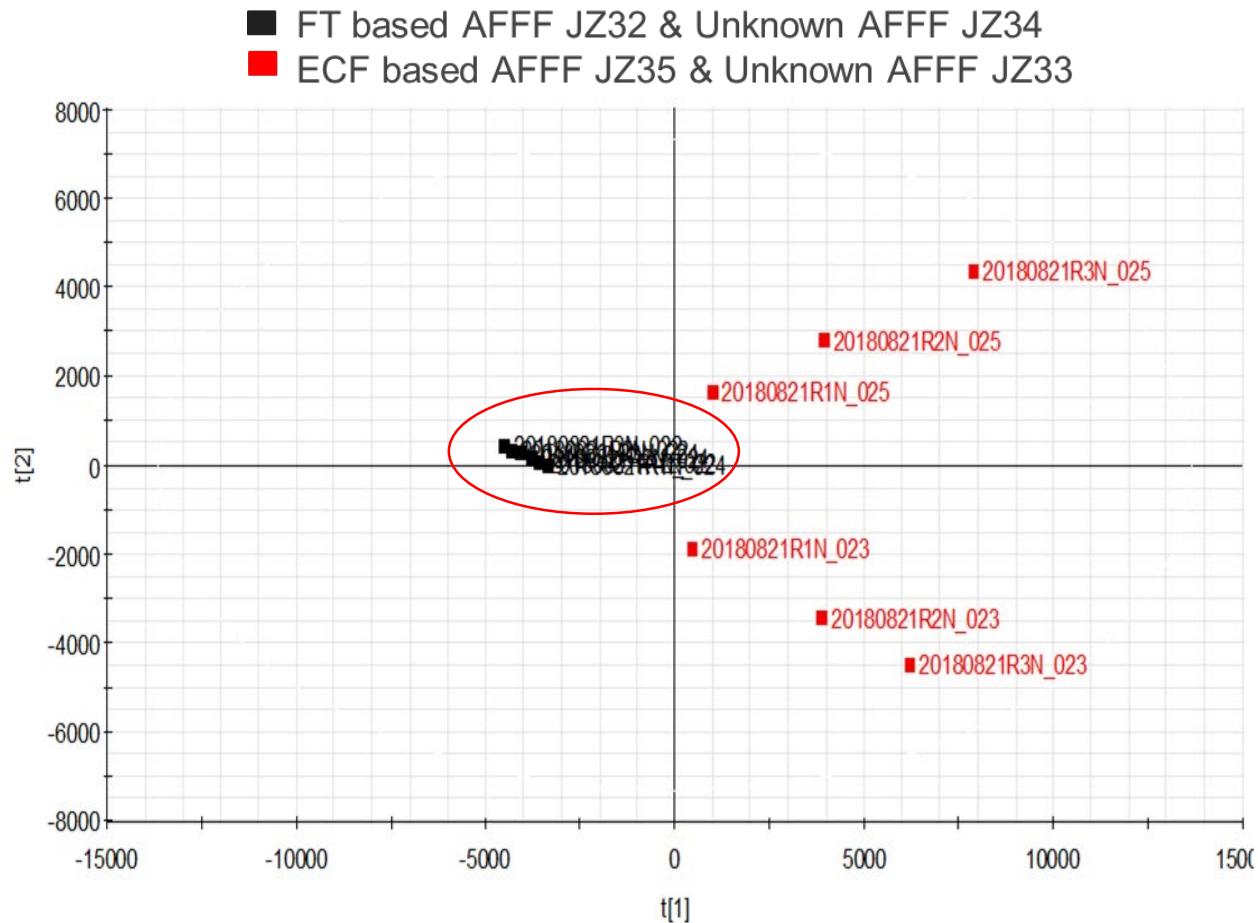
- Cluster of FT based AFFF JZ 32 & Unknown AFFF JZ 34 - potentially from same source

- FT based AFFF JZ 32 & Unknown AFFF JZ 34 samples are significantly different compared to other AFFF's

- ECF based AFFF JZ35 & Unknown AFFF JZ 33 are from different sources or from different formulations

This data will be important to identify co-occurrence of AFFFs from distinct sources

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Further Detailed Analysis of AFFF Samples

FT based AFFF

		Precursor ion (m/z)	
6:2 FtSaB	n = 6	571	
8:2 FtSaB	n = 8	671	Fluorotelomer Sulfonamido Betaines (FT based AFFF and JZ 34)
10:2 FtSaB	n = 10	771	
12:2 FtSaB	n = 12	871	
14:2 FTSaB	n = 14	971 (current study)	
6:2 FtSaAm	n = 6	513	Fluorotelomer Sulfonamido Amines (FT based AFFF and JZ 34)
8:2 FtSaAm	n = 8	613	

ECF based AFFF

Mix of Perfluorinated alkyl acids –PFOS and PFHxS found in higher concentrations with both linear and branched isomers were found

Backe et al 2013, Houtz et al. 2013

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Conclusions

- Collected PFAS fingerprint from various environmental samples and AFFF sources using
  - Targeted analysis (using available standards)
  - Non-targeted analysis (compounds that don't have standards)

- PFAS fingerprints added to the spectral library

- Some of the key factors to consider when comparing the distinct source signatures:
  - manufacturing source
  - timeline of release (age)
  - fate and transport
  - degradation products

- Further identification/confirmation of the analytes and the statistical analysis of the data in progress

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Request for Samples to Further Augment Battelle's Library of PFAS Source Fingerprints

- Ground water/surface water/soil samples (Water - 250 ml; Soil – 25 g) from contamination sources such as

  - Metal plating facility, landfill leachates, WWTP influents and effluents, AFFF impacted and other commercial industry sites where PFAS were/are manufactured or used as performance coatings (textile, paper mills, plastics) etc.

- The exact location or source does not need to be disclosed or known.

- It will be helpful if any existing data on these samples (e.g., PFAS concentrations, soil characteristics, timeline of release) can also be shared.

- To meet with the on-going research timeline, Battelle would appreciate receiving the samples no later than May 31st 2019.

- All the participating states/organizations will be acknowledged (if desired) in the publication resulting from this research; or can remain completely anonymous.

For additional details contact: dasu@battelle.org, 614-424-3144

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Thank You

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For more information visit our website: www.battelle.org/PFAS

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