Current Trends in PFAS Source Differentiation

"The Science of PFAS Conference"

April 6, 2022

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Agenda

1. Introduction
2. PFAS Source differentiation techniques
3. Visual Presentation Tools
4. Representatives Uses – groundwater, surface water and overburden soils investigations
5. Questions and discussion

Introduction

Why? To identify release sites and address recalcitrant sources

- Water supply impacts are widespread and very costly to mitigate,
- Widespread use : consumer products, industrial applications, hydrocarbon (Class B) fire response,
- Common sources include: stormwater, wastewater, landfills, and fire training and emergency response areas

Strategic Environmental Research Development Program (SERDP) 2020 Statement of Need: *"Forensic Methods for Source Tracking and Allocation of PFAS"*

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Multiple Lines of Evidence Approach Needed

- Changes in manufactured PFAS mixtures over time
  - Limits the ability to use impurities or unique structures
  - Recalcitrance of the primary perfluorocarbon structures
- Filtered analytical data sets due to availability of reference materials
  - Low concentrations also limits the applicability of stable isotope analysis
- Geochemistry – controls PFAS mobility and speciation
  - Environmental transformation leads to common endpoints
- Hydrogeology – groundwater flow paths and aquifer conditions
  - Upgradient concentrations and potential release points?
  - You can't get there from here!

Perfluorinated Chemical (PFC) Manufacturing Processes

1950's through 2001

Electro Chemical Fluorination (ECF) process

- C-8 feedstock produced a complex and variable mixture of compounds
- branched and linear fluorocarbon compounds

Fluorotelomerization process – 1980's to present

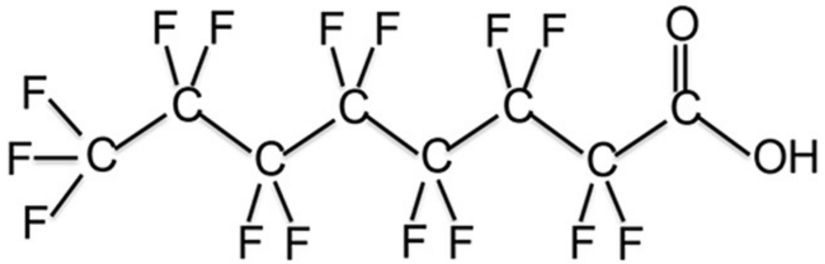
- Produces linear isomers of varying fluorocarbon chain lengths (N+2)
- Specific products utilize odd vs. even numbered perfluorocarbon chains

1980's

Linear and Branched Isomers of PFOA

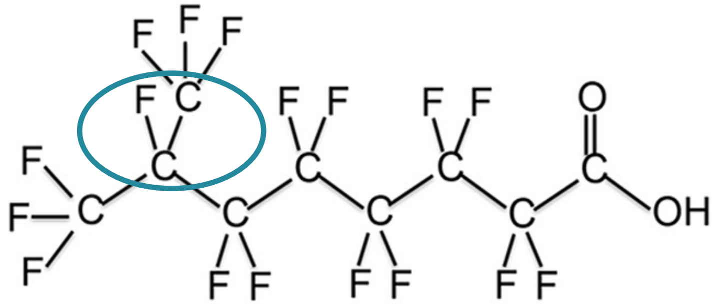
Product of both ECF and FT synthesis

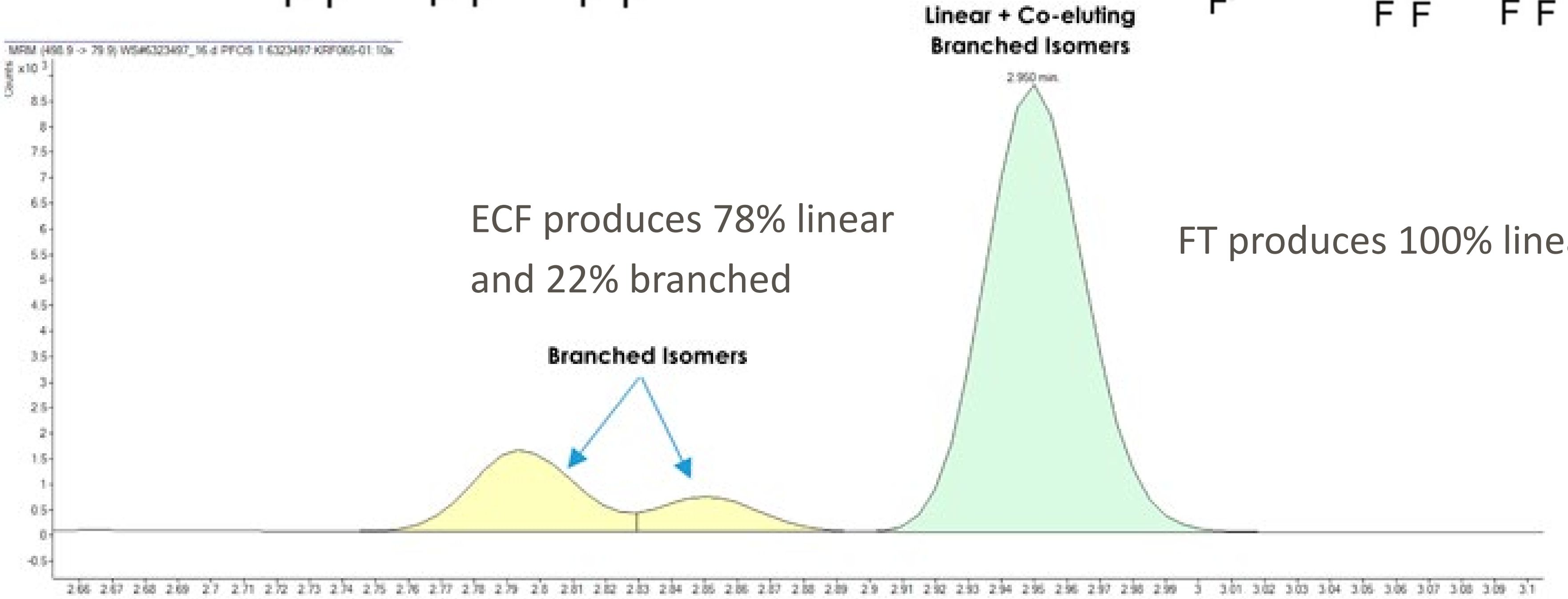
Linear PFOA



Product of ECF Only

Branched PFOA





ECF produces 78% linear and 22% branched

FT produces 100% linear

Targeted PFAS Analysis Procedures (LC MS/MS)

EPA Method 537.1 (March 2020) Version 2.0 – DW Matrices

- 18 Target Analytes including PFCA/PFSAs, PFOSAs, F53-Bs, Gen-X and Adona

EPA Method 533 (December 2019) – DW Matrices

- 25 Target Analytes adding FTS, C2/C3/C4 PFMAs, and
  - Nonafluoro-3,6-dioxheptanoic acid (NFDHA)

DRAFT EPA Method 1633 (Aug. 2021) – Non-DW Matrices

- 40 Target Compounds – All of the above plus, PFOSAAs, PFOSEs, FTCAs
- Multi –lab Validation Study underway

EPA Method 537.1- Modified – Non-DW Matrices

- Laboratory Specific Lists – up to >70 compounds
- Limited by available stable isotope analogs

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Total Oxidizable Precursor (TOP) Assay/Analysis

Commercially available → Aggressive oxidation of environmental sample matrix → Conducted in concert with Target Analysis Procedures → Enables the quantification of precursor compounds (amenable to oxidation conditions) → Can be used to differentiate ECF vs. FT precursor mass (using Br/L ratios)

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Non-Target PFAS Analysis Methods

LC/GC High Resolution Mass Spectrometry (HR-MS)

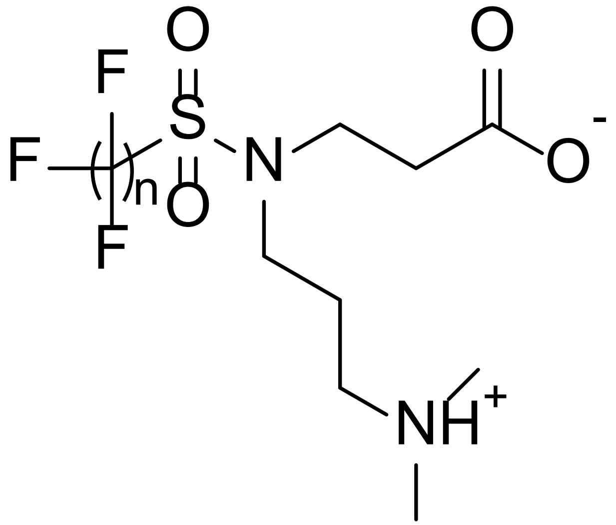
- Can separate and identify a wide range of non-target analytes
- Semi-quantitative analysis with use of known internal standards
- Tentatively Identified Compound structures requires reverse engineering

Fast Atom Bombardment Mass Spectrometry (FAB-MS)

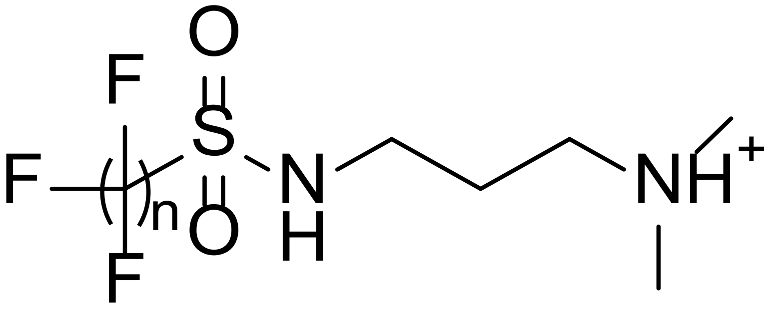
- Product Analysis for PFAS constituents
- Rapid identification of known and unknown structures

Example Non-Target Analysis Indicator Compounds

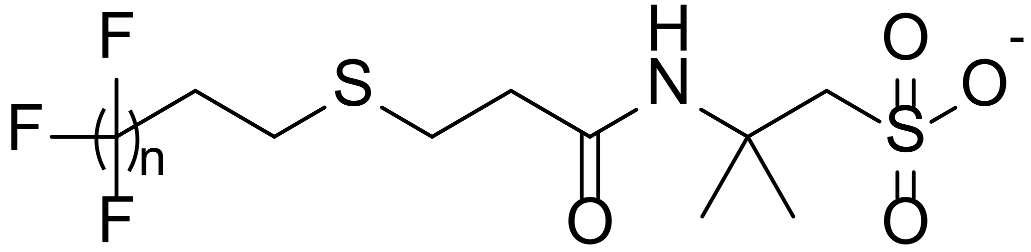
- Perfluoroalkyl sulfonamido amino carboxylic acid (PFASAC)



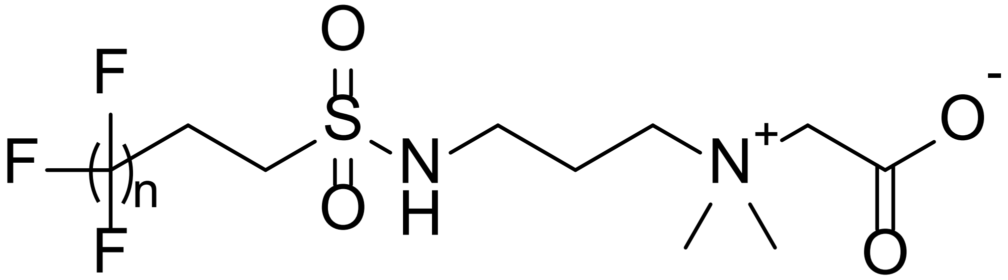
- Perfluoroalkyl sulfonamido amine (PFASA)



- Fluorotelomer thioamido sulfonic acid (FTSAS)



- Fluorotelomer sulfonamide alkyl betaine (FTAB)



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Potential Product Source Indicator Compounds

Perfluoro octane sulfonamido acetic acids (methyl or ethyl- FOSAA)

- Used in textile coating products manufactured by ECF process
- Preserves branched perfluorocarbon isomers

Polyfluoroalkyl phosphate esters (6:2 or 8:2 diPAP)

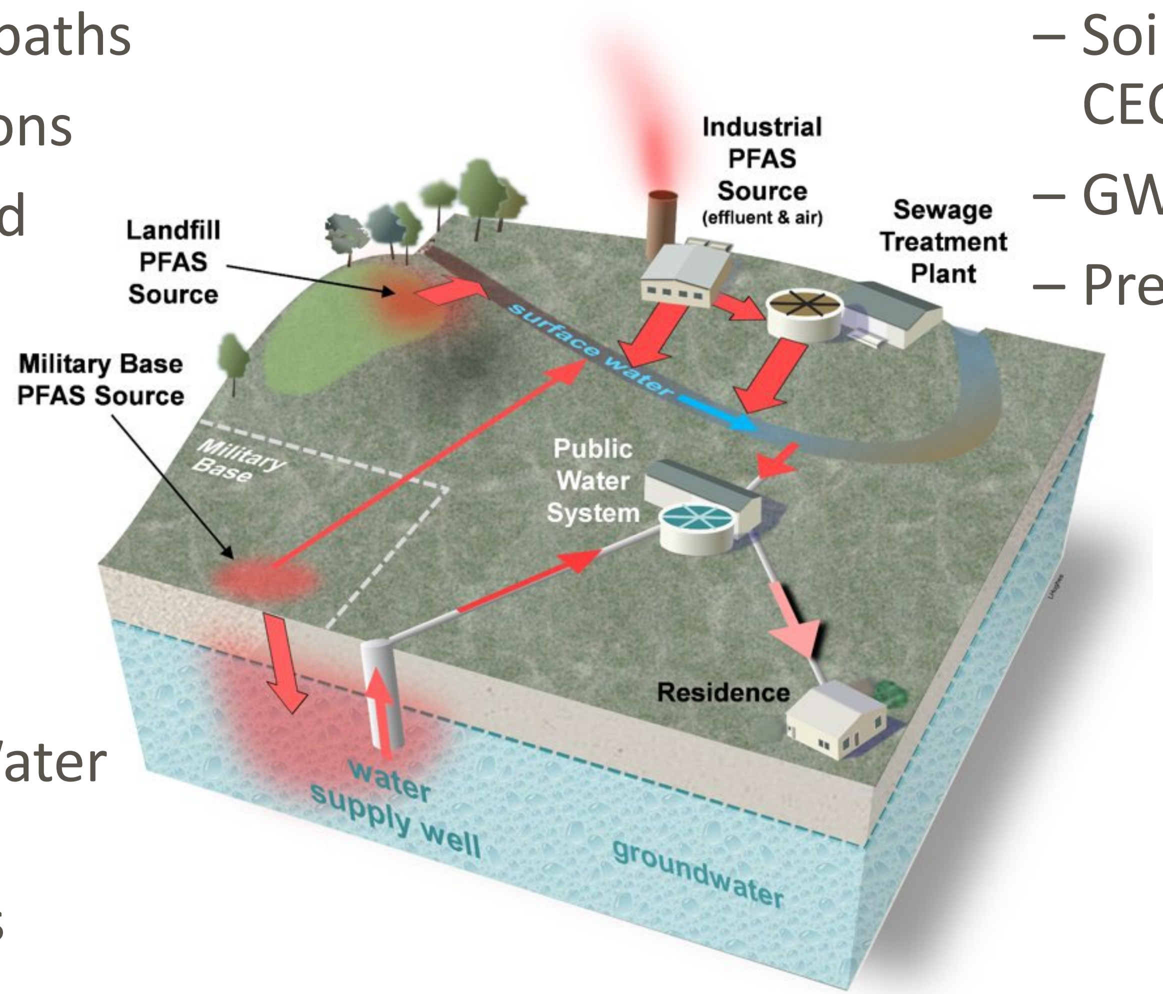
- Used in paper coating products
- Biotransforms to perfluoro and fluorotelomer carboxylic acids
  - (e.g. PFHxA, PFOA, 5:3 FTCA)

Perfluorohexane sulfonamides (FHxSA)

- AFFF impacted groundwater (ECF and/or FT based products)

Conceptual Site Model Development

- Understand Hydrogeology
  - Preferential flow paths
  - GW/SW Interactions
  - Aquifer matrix and dimensions



- Geochemistry
  - Soil Organic Carbon Content, CEC
  - GW pH, Redox Conditions
  - Precipitation Rates

- Receptors
  - Private / Public Water Supplies
  - Ecological Vectors

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Effects of Site Hydrogeologic conditions

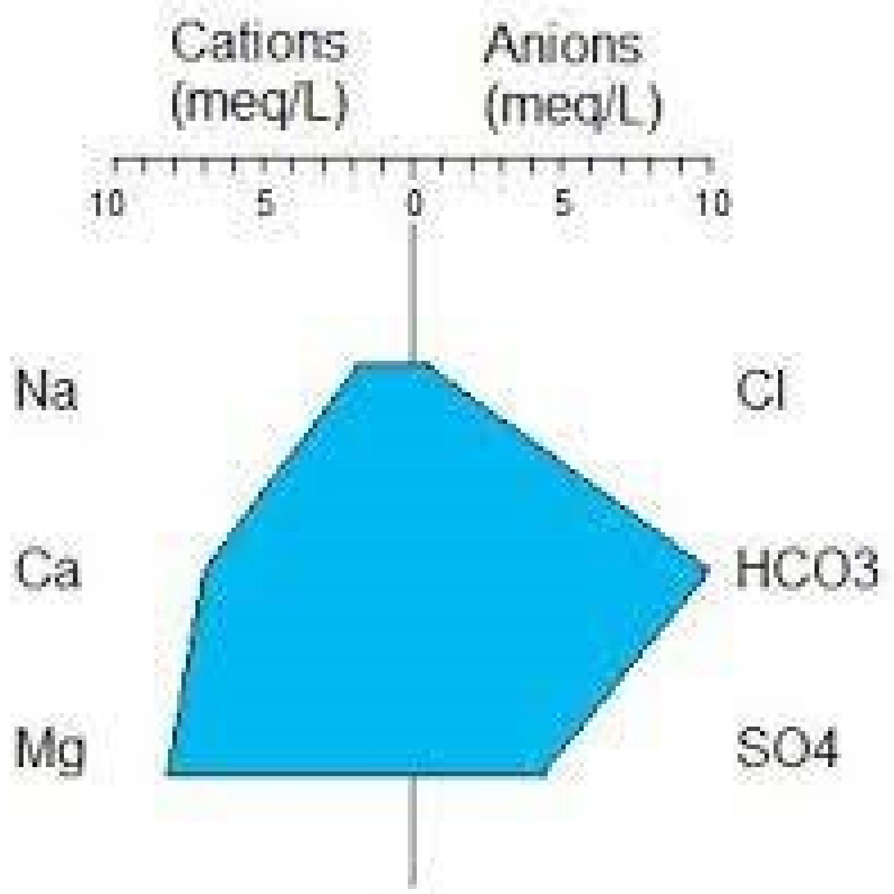
- Longer-chain PFAS exhibit greater sorption characteristics
- Soil organic matter adsorption is predominant mechanism
- Lower pH, higher CEC (Al^{3+}, Ca^{2+}) increase sorption in low SOM soils
- Aerobic GW enhances biotransformation of precursors

	Organic carbon sorption affinity	Reduction in groundwater migration rate due to sorption
	K_{oc}	Retardation
benzene	66	5.1
PFOA	78	5.8
TCE	126	8.8
PFOS	631	40.1

Retardation values predicted for sandy soil with organic carbon content of 1% by weight

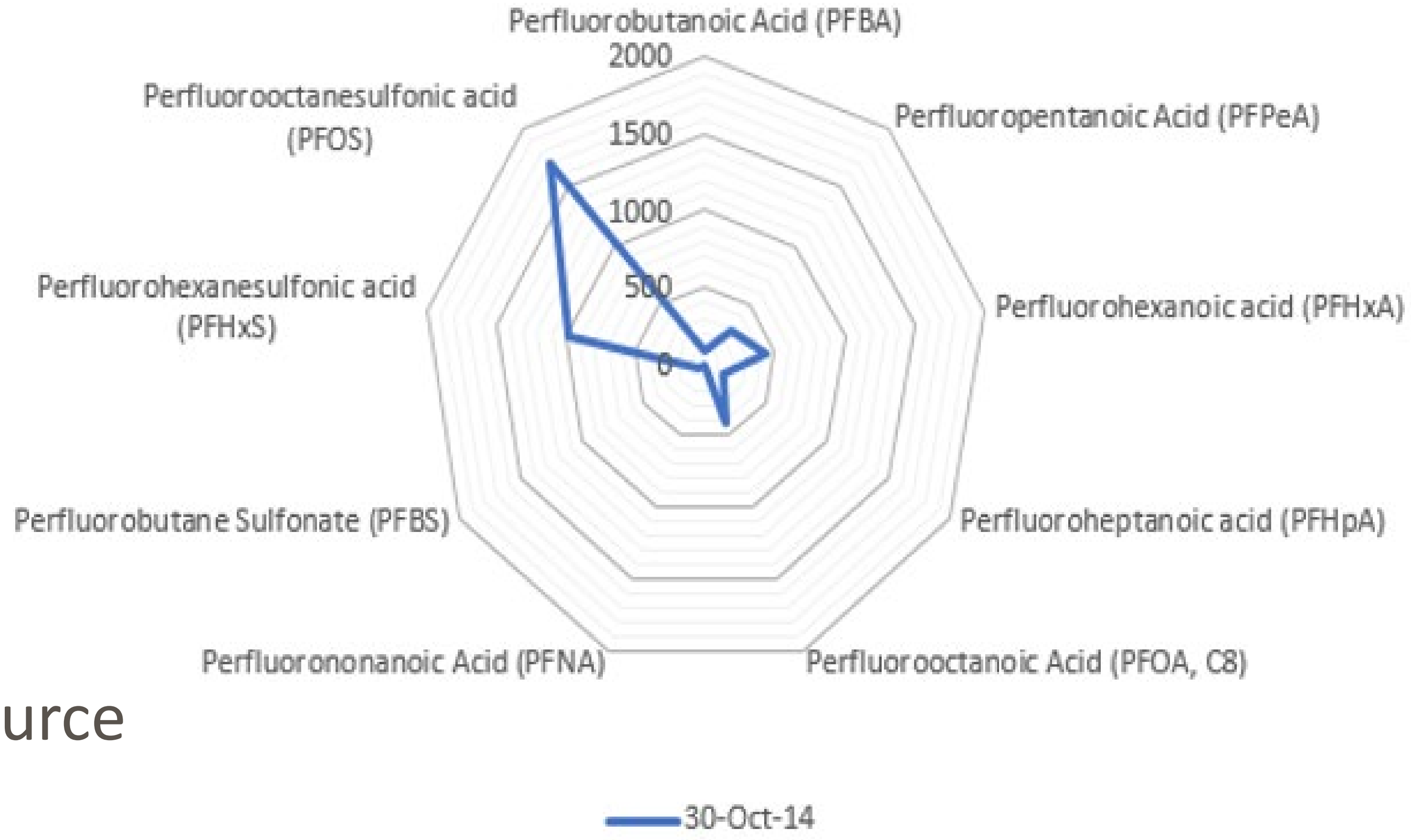
Development of Visual Tools for Source Differentiation

- Stiff Diagrams
  - Used to evaluate water quality
  - Major Cations and Anions
  - Differentiates potential impacts
    - Landfill Leachates
    - Mining wastes
    - Surface waters

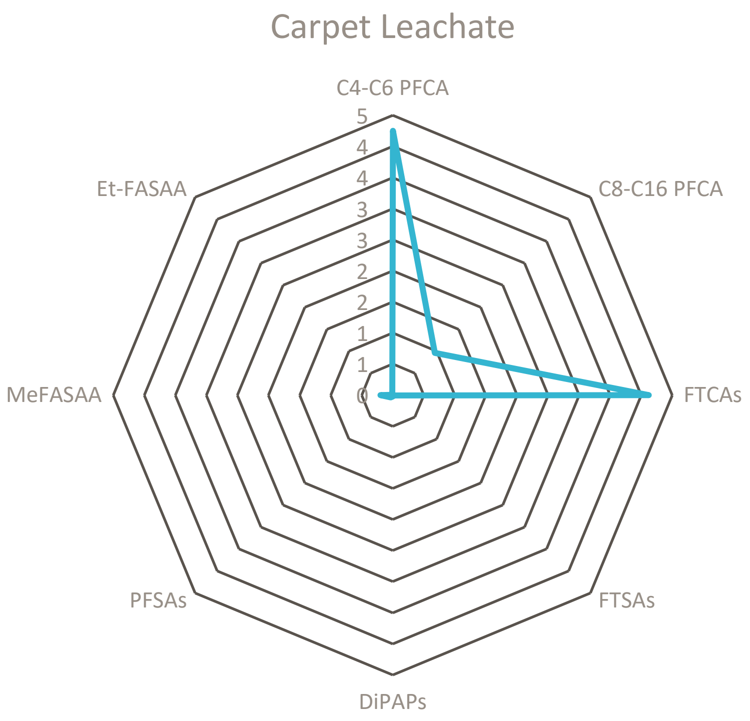


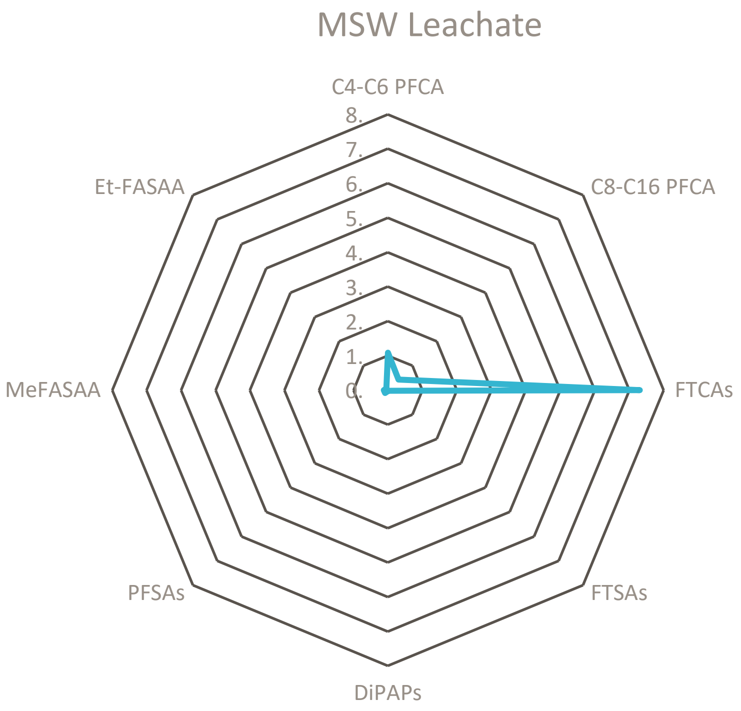
Radar Plot Diagrams

- Groundwater Samples
  - Targeted PFAS Compounds
  - PF Carboxylates and Sulfonates
- Evaluate compositions over time/distance
  - Same location
  - Multiple locations
- Qualitatively Differentiate Source Contributions
  - Mixed plumes



Anaerobic Digester Study – Simulated Landfill Leachates





Data from Lang et.al., ES&T 2016

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Groundwater Investigation – Fate & Transport Studies

Groundwater Samples

- Long-term multi-year monitoring program
- Suspected source and downgradient locations

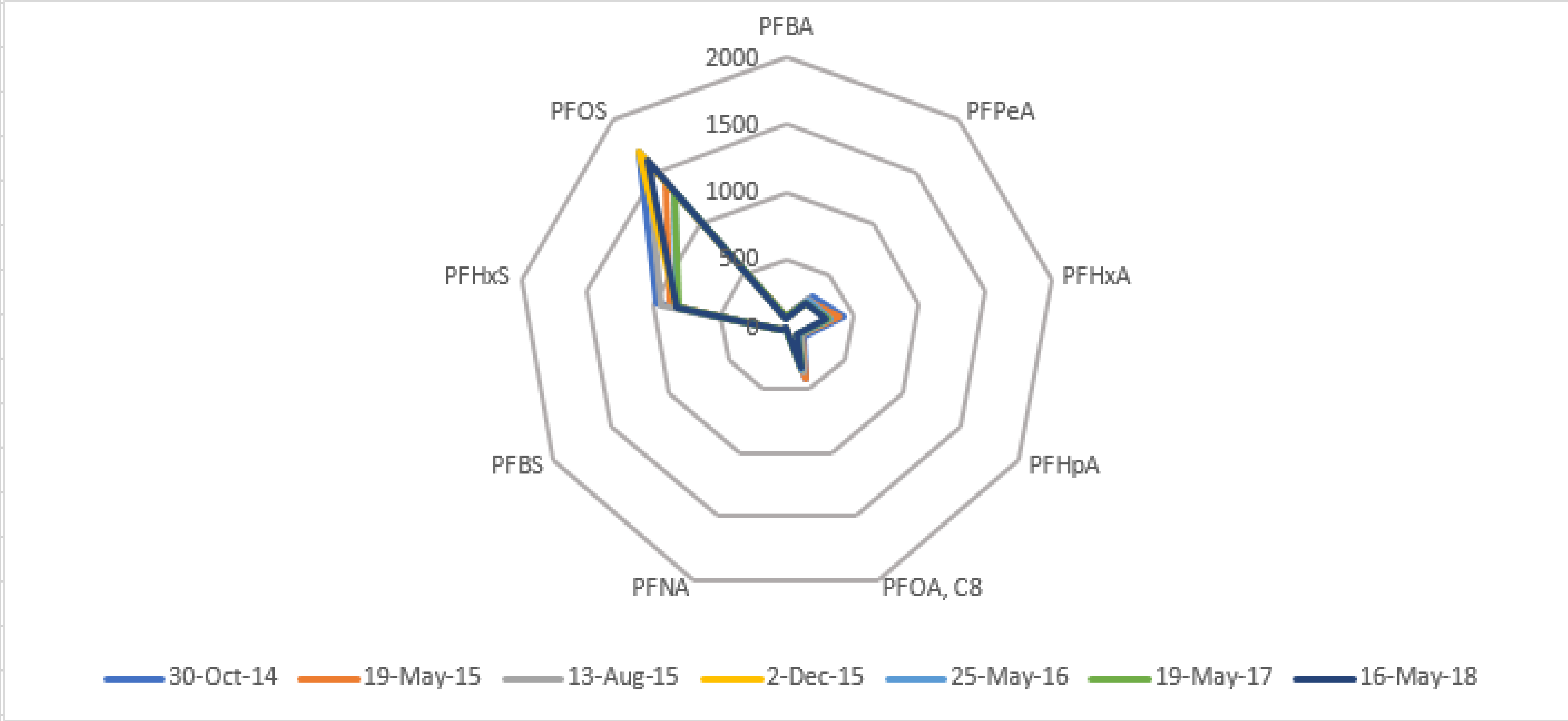
PFAS Targeted Analysis – Project Specific List

- EPA Method 537.1 Modified

Study Results

- Recalcitrance of source
- Transformation / attenuation observed

PFSA Composition shift over time



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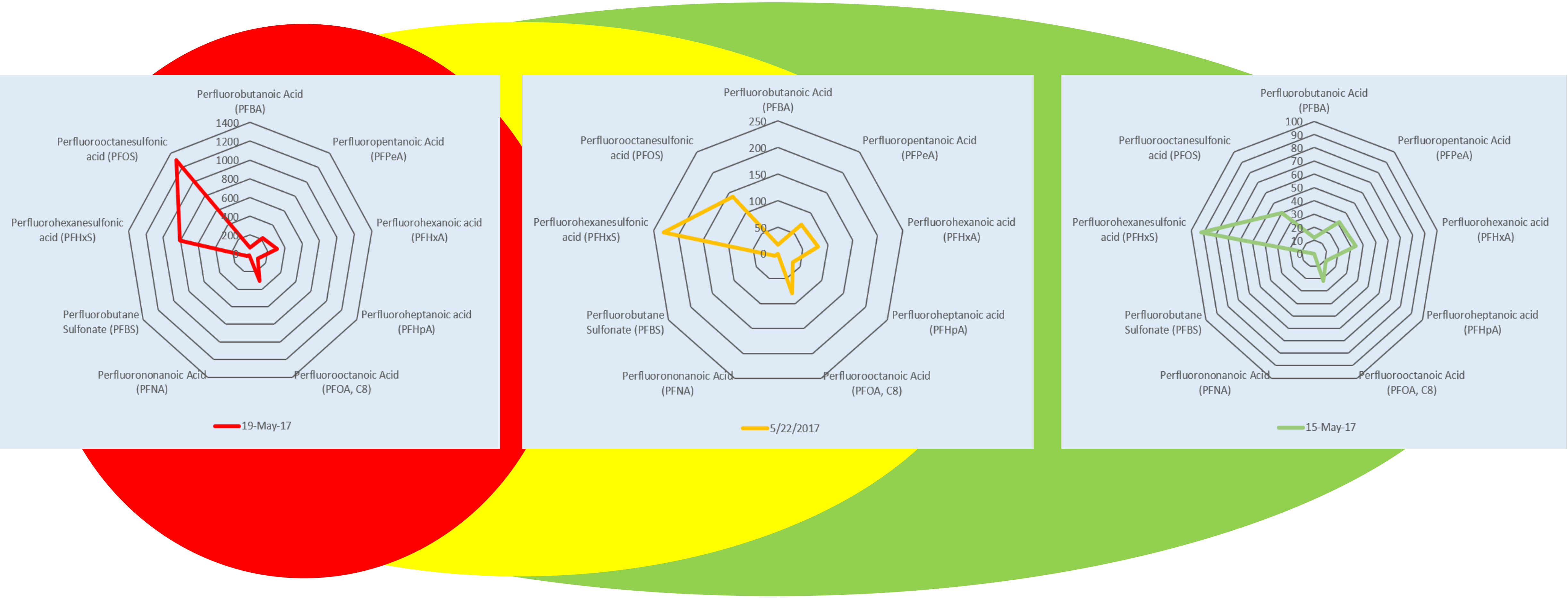
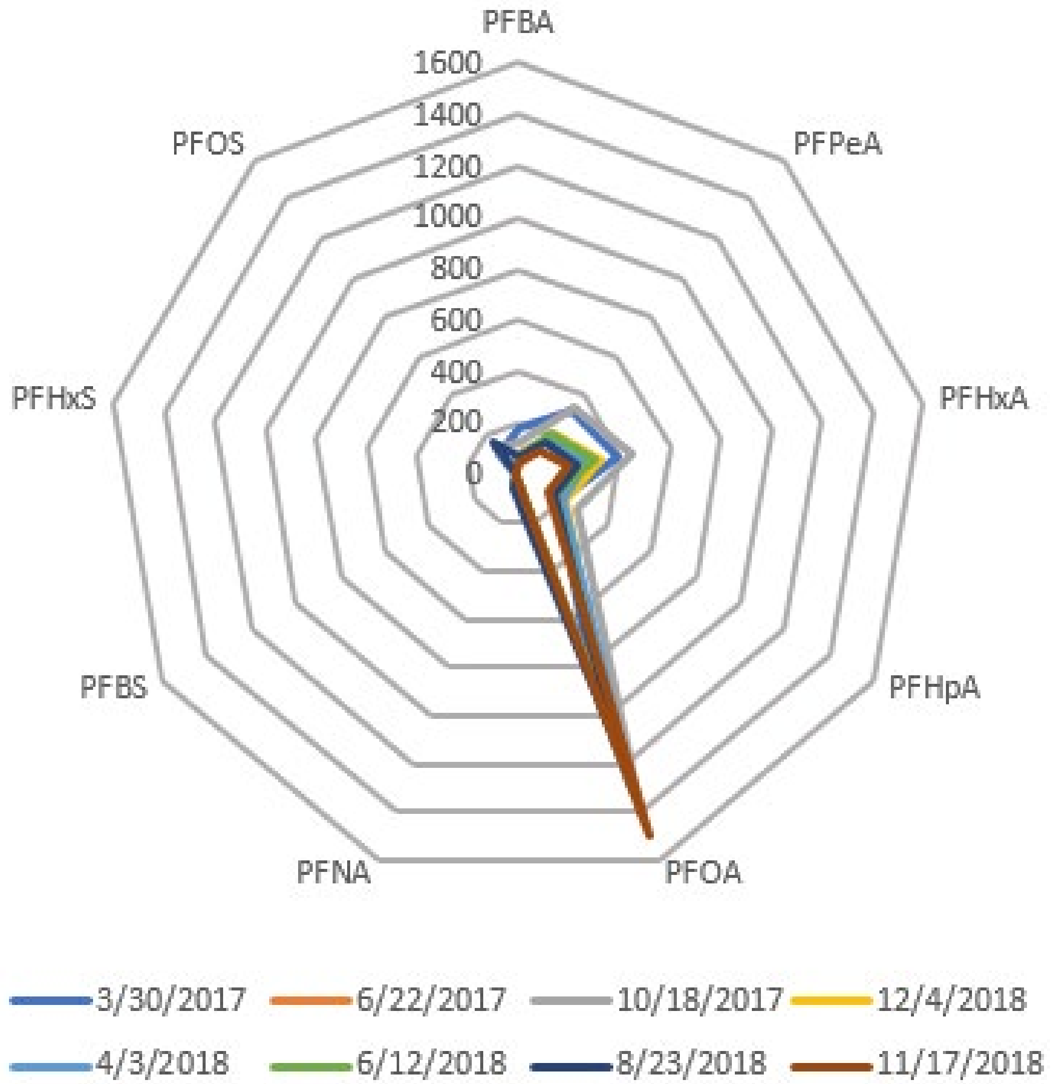
PFSA Composition changes with distance

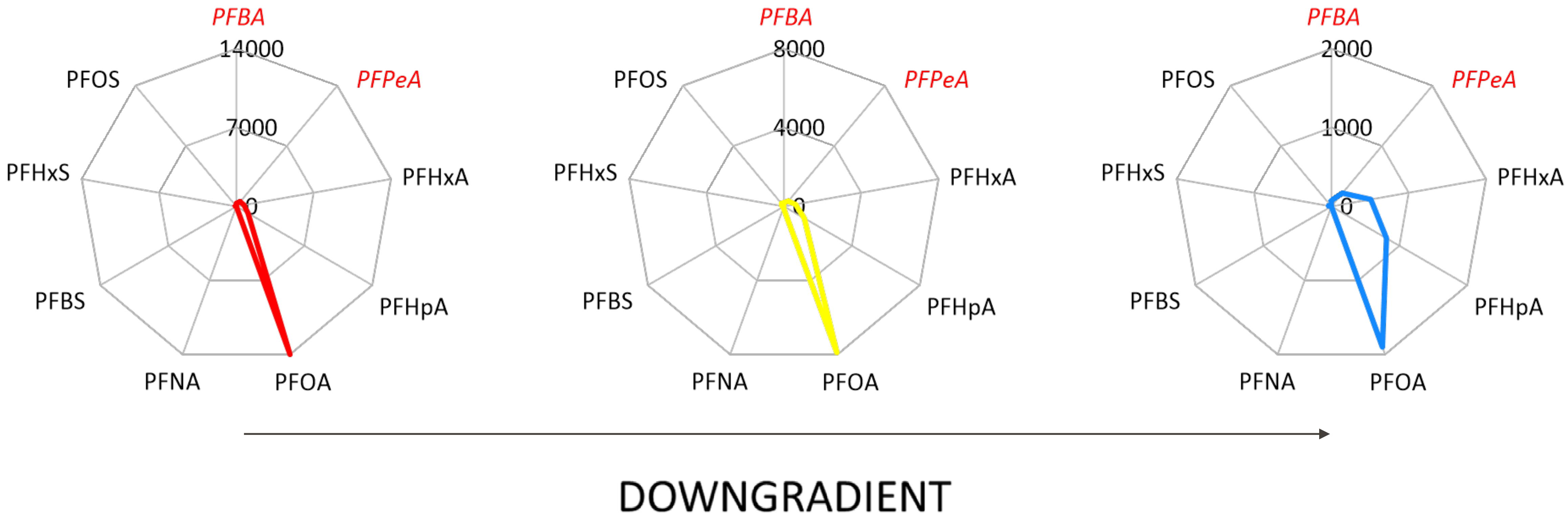


DOWNGRADIENT

PFCA Composition shifts over time



PFCA Composition changes with distance



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Surface water Background Study – NE River Systems

Grab Surface water Samples

- Direct bottle collection w dipper cup

PFAS Targeted Analysis – Project Specific List

- EPA Method 537.1 Modified

Study Results

- Unique composition by river system
- Point source contribution identified
- Positive correlation with population density

Selected rivers

- Androscoggin
- Merrimack
- Connecticut

Map of the Androscoggin River watershed

The Merrimack River and its major tributaries

River map, with major tributaries and selected dams

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Selected rivers

- Androscoggin

- Merrimack

- Connecticut

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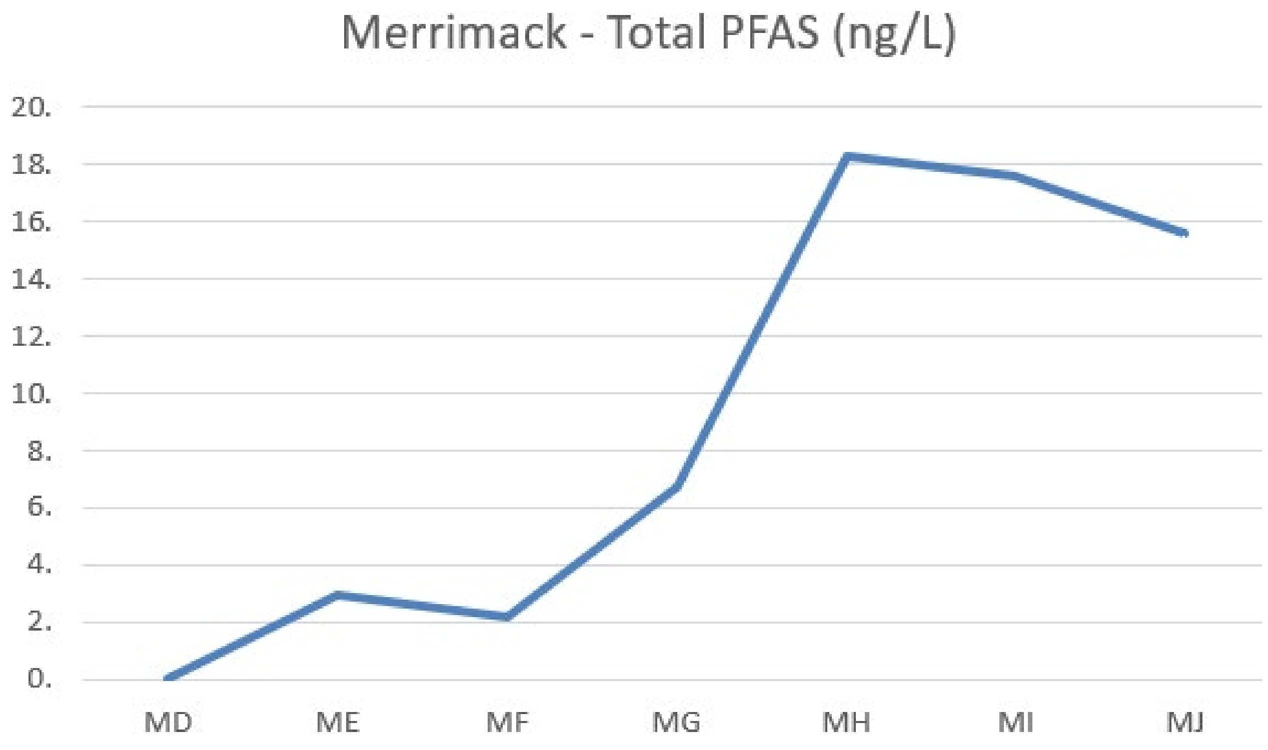
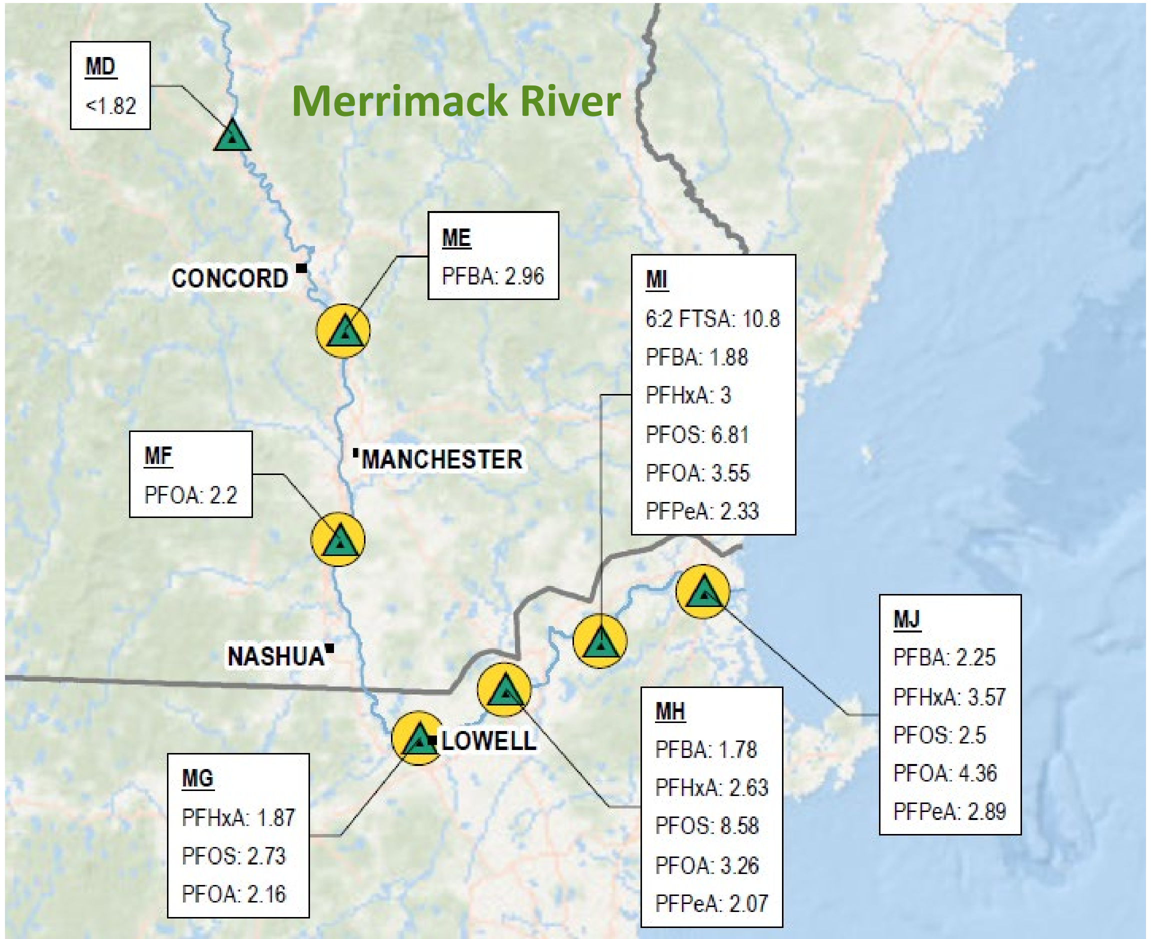
Background PFAS in surface water study

- Increasing total [PFAS] with population density, but no drinking water standard exceedances





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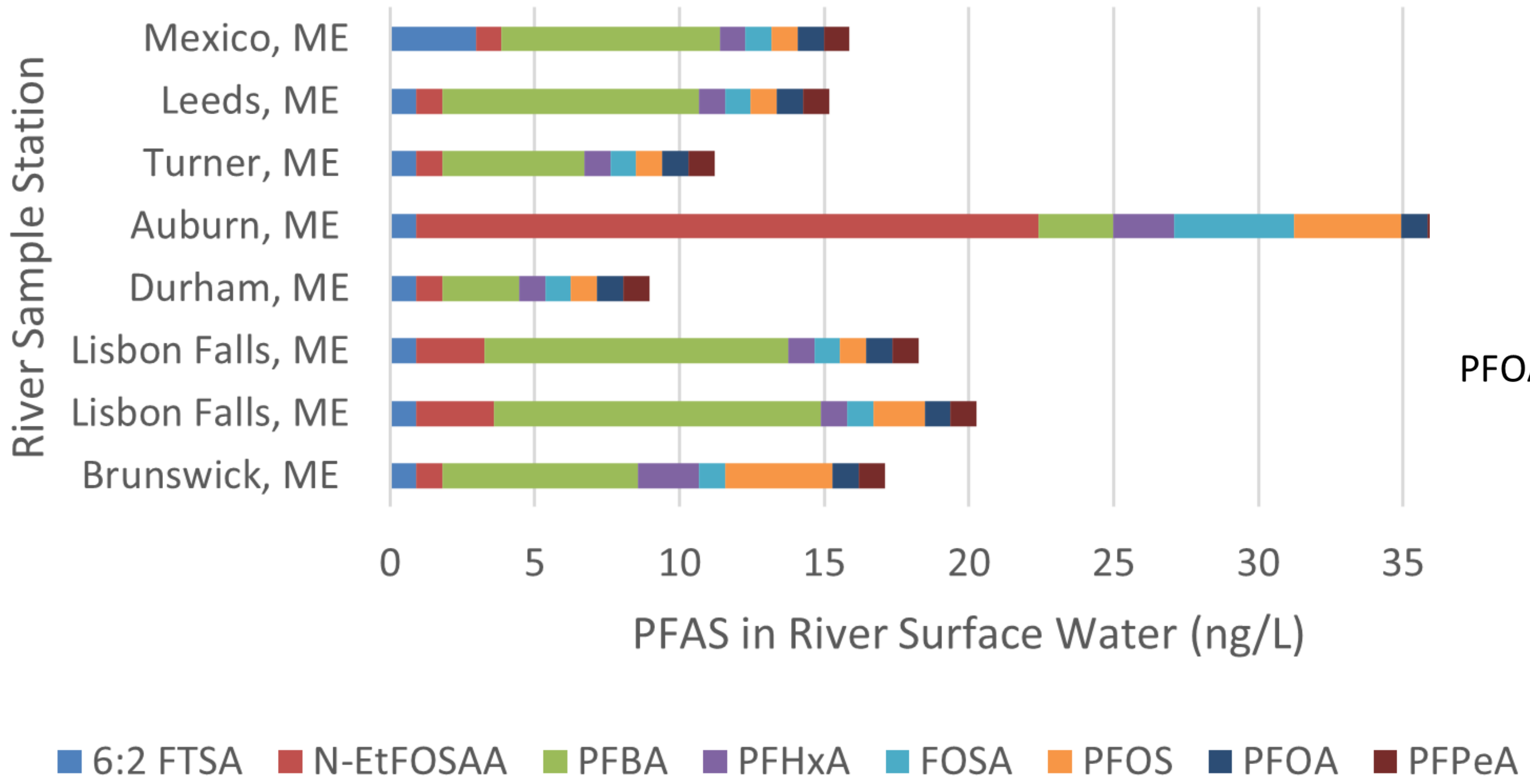
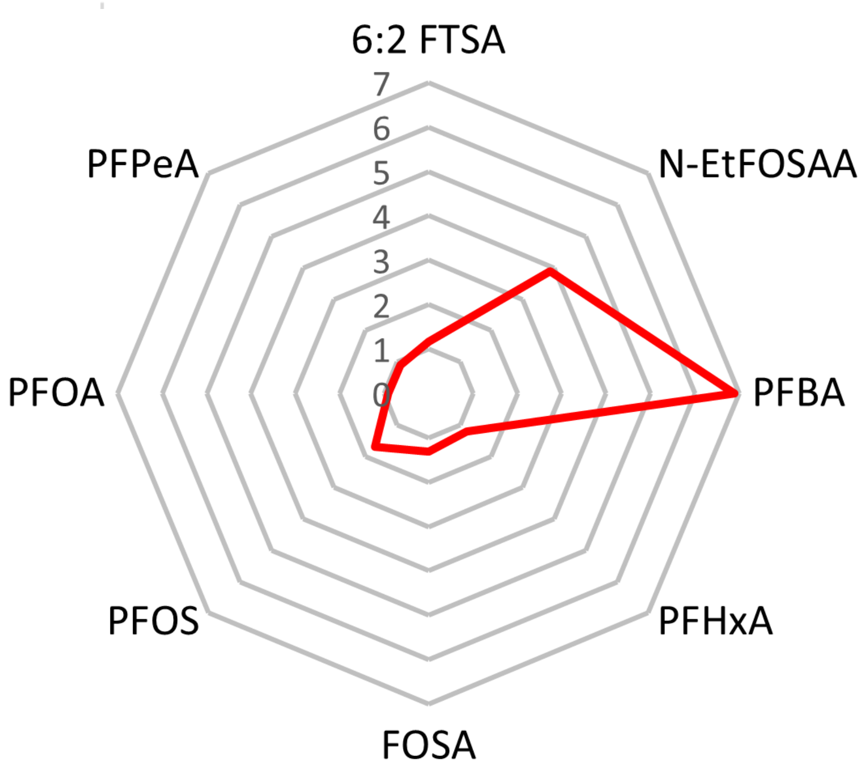
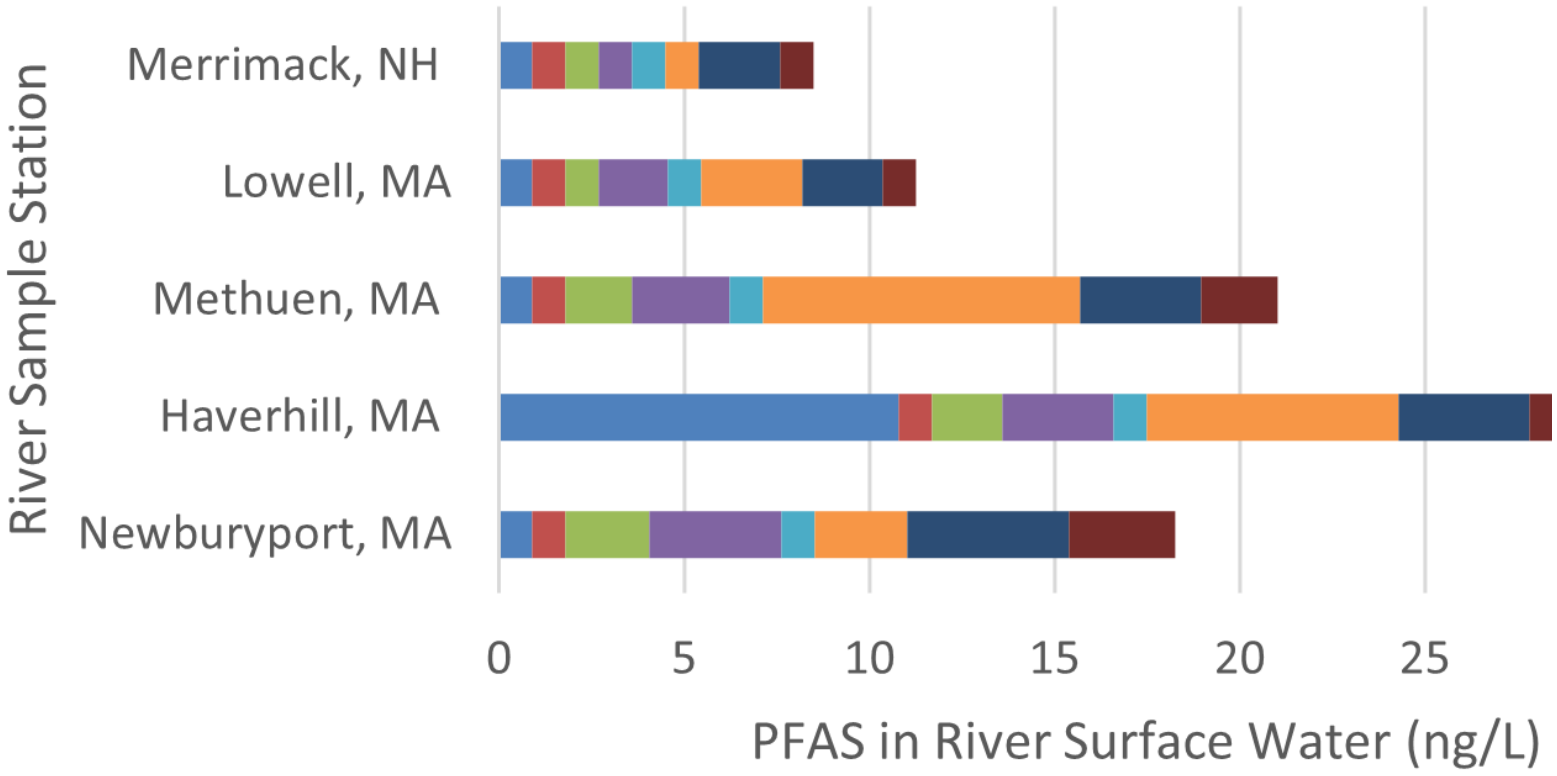
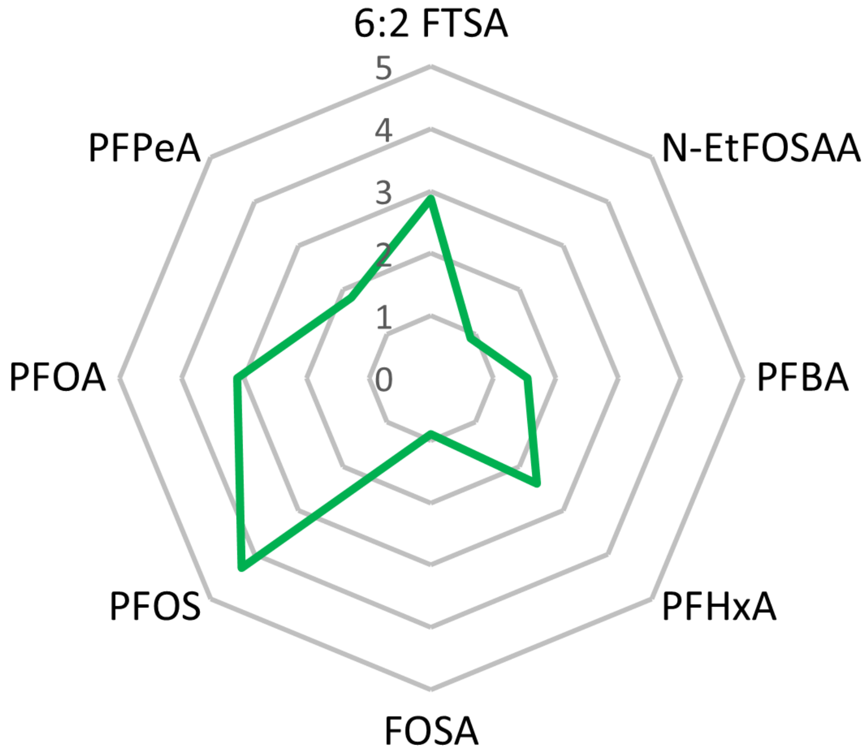
PFAS concentration and distribution: Androscoggin River



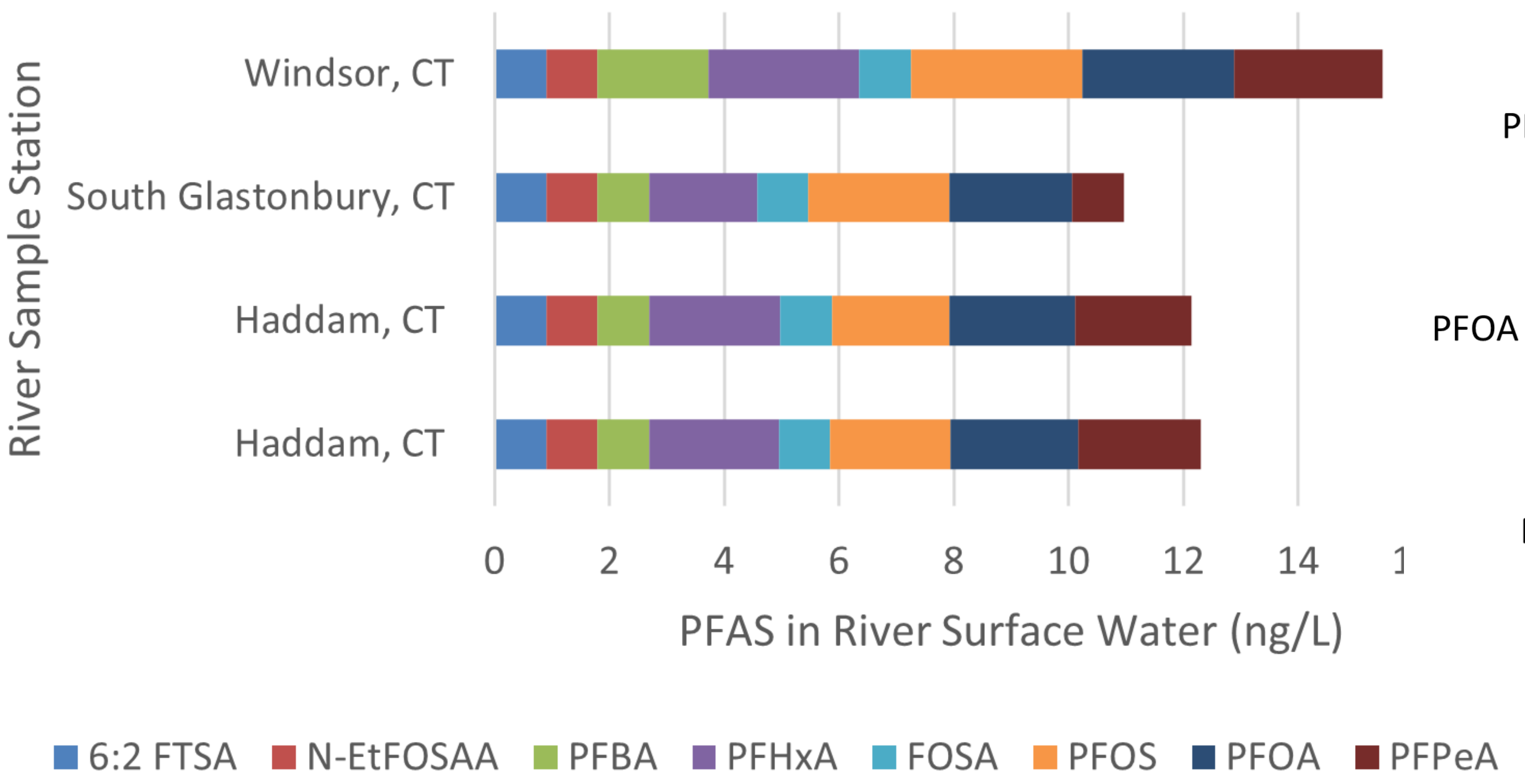


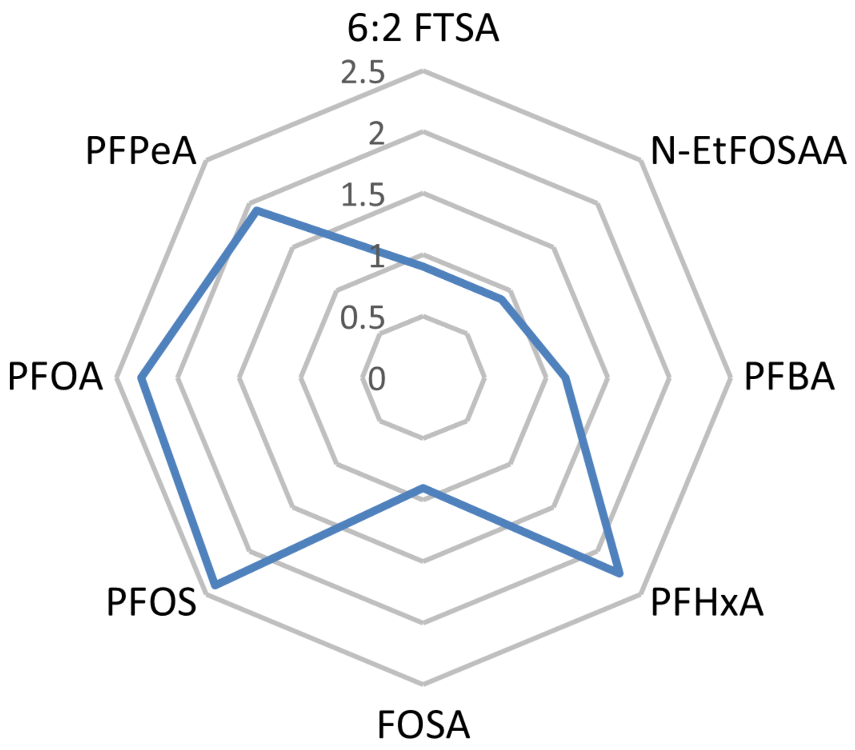
PFAS concentration and distribution: Merrimack River





PFAS concentration and distribution: Connecticut River





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Soil Investigation – Suspected AFFF Release

Discreet Soil Samples

- Using Sonic Drilling cores

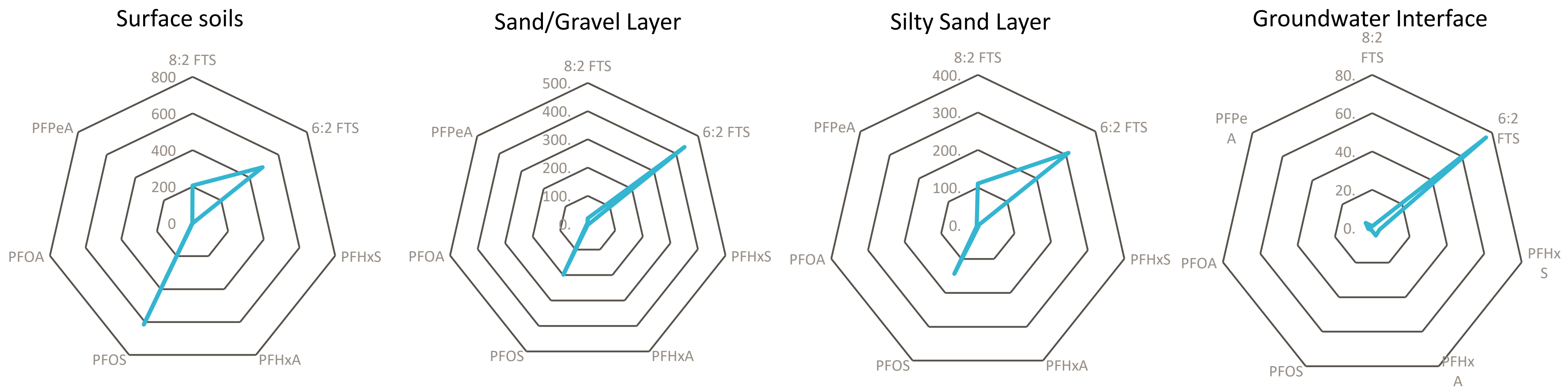
PFAS Targeted Analysis – Project Specific List

- EPA Method 537.1 Modified – (DOD QSM 5.3)

Study Results

- Demonstrated Attenuation
- Interbedded Sands/Silty Clays
- Consistent with log KOC and soil type

Soils Investigation - Radar Diagrams by Depth/Soil Type



Depth Below Ground Surface

Summary conclusions

To mitigate risk and control impact from releases requires:

- Identification and differentiation between multiple sources
- Use of multiple lines of evidence including:
  - Determination of the source materials through direct or indirect analysis,
  - Understanding hydrogeologic and geochemical conditions,
  - Evaluation of the potential for transformation of non-target analytes.

Use of Visual Tools enables efficient evaluation of potential sources

- Assist in identifying point sources and/or discharge areas
- Can differentiate between contributing sources within co-mingled plumes

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Thank you for Your Attention!

Questions and Discussion?

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