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PFAS Fingerprinting

Mark J. Benotti, Ph.D.

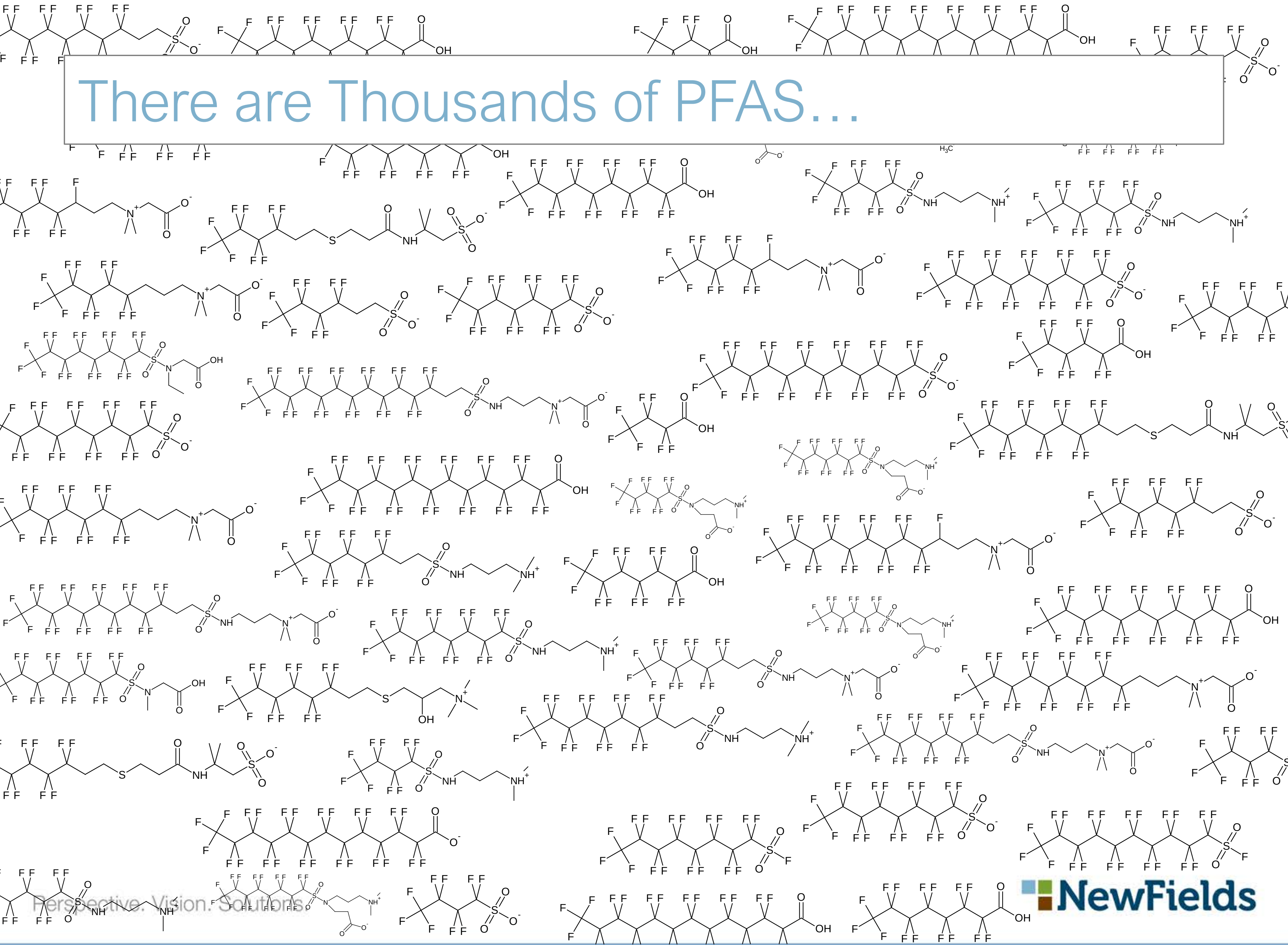
Outline

- Environmental forensics is the practice of interpreting the contaminant "fingerprint" in environmental samples and associating it (or dissociating it) from one or more potential sources.

- Today, I will discuss how PFAS data can help investigators understand the following:

    1) How to look for differences in manufacturing processes
    2) How to look for site-specific evidence for
        1) Environmental fate and transport (DoD case study)
        2) Other potential sources (former refinery case study)
    3) *PFAS forensics is in its nascent stages, so I will also identify future tools that may become available.*

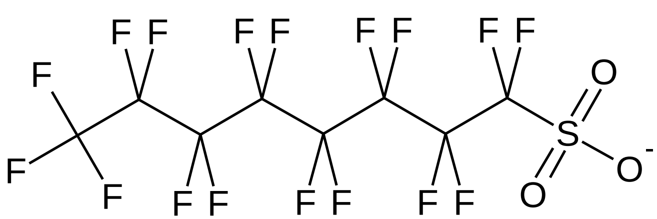
There are Thousands of PFAS…



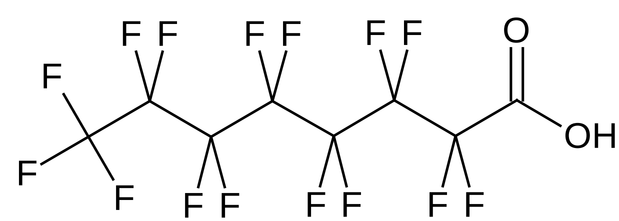
There are Thousands of PFAS…

…but two specific compounds have received the most attention/scrutiny

PFOS (perfluorooctane sulfonate)



PFOA (perfluorooctanoic acid)



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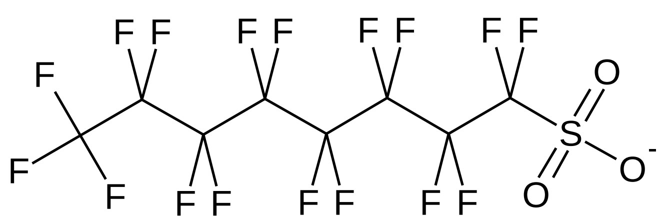
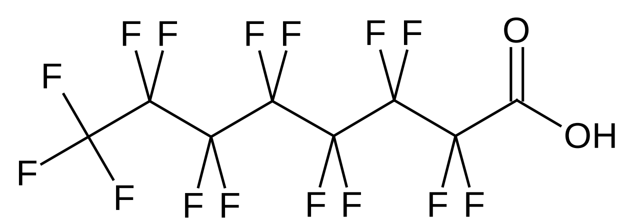


PFOA (perfluorooctanoic acid)



…and only 30-ish can be routinely measured.

Need to "See" Everything to Determine the Extent to Which Two Things are Similar

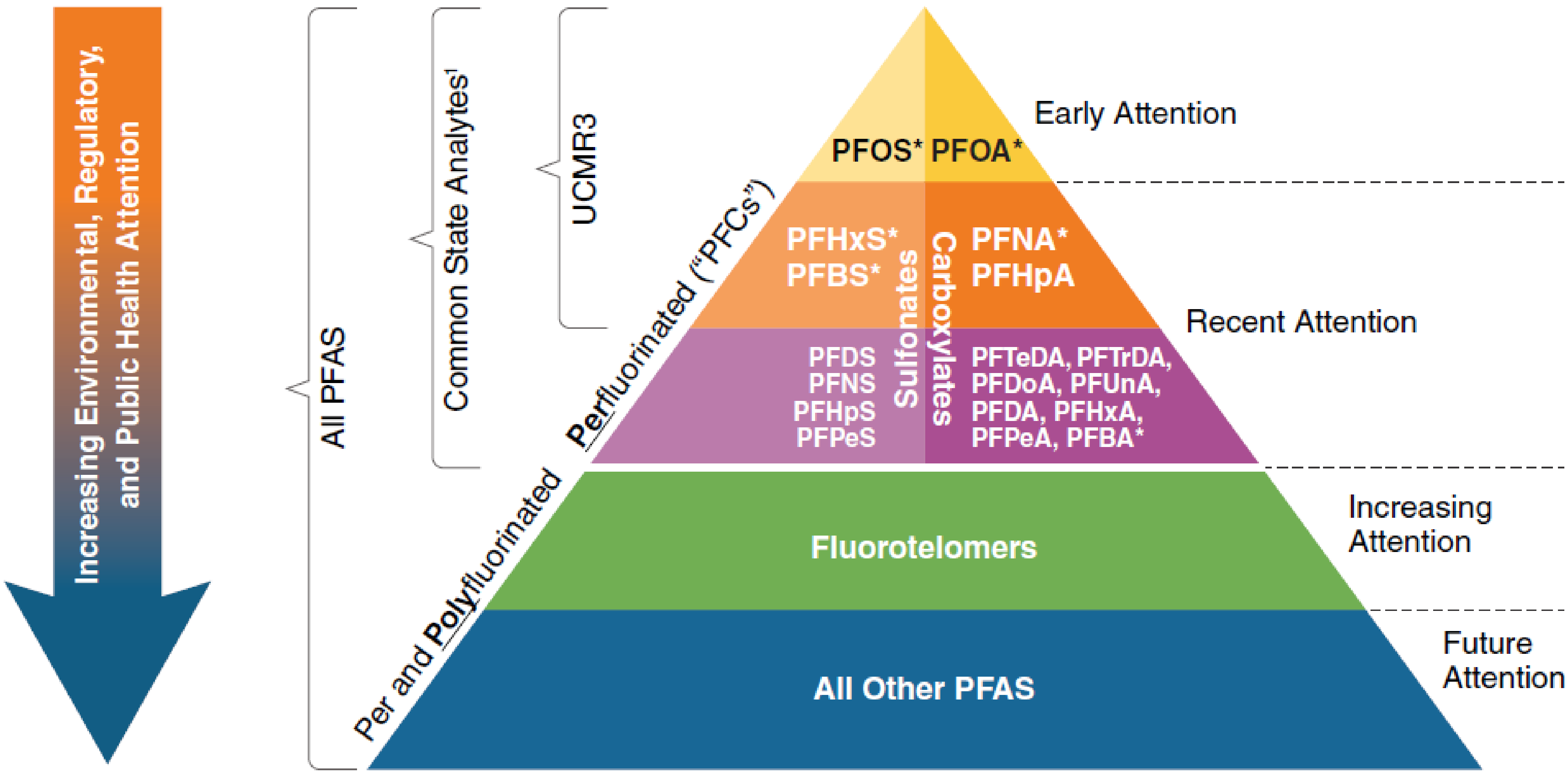
Image 1

Mona Lisa, Leonardo da Vinci, c. 1503-06

Image 2

Portrait of Maddalena Doni, Raphael, c. 1506

Moving Beyond the Tip of the PFAS Iceberg



*Common regulatory criteria or health advisories
[1]Sum of informal poll (NJ, NH, MN)

Thematic and not proportional.
Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

Figure 3-1 from History and Use of Per- and Polyfluoroalkyl Substances (PFAS)
https://pfas-1.itrcweb.org/fact-sheets/

Common Lists of PFAS Analytes

Name	Acronym	Class	CASRN	Common Datasets or Analytical Methods			
				UCMR3	USEPA 537	USEPA 537.1	Laboratory Specific Method, e.g. Alpha
Perfluorobutanoic acid	PFBA		375-22-4				x
Perfluoropentanoic acid	PFPeA		2706-90-3				x
Perfluorohexanoic acid	PFHxA		307-24-4		x	x	x
Perfluoroheptanoic acid	PFHpA		375-85-9	x	x	x	x
Perfluorooctanoic acid	**PFOA**		**335-67-1**	**x**	**x**	**x**	**x**
Perfluorononanoic acid	PFNA		375-95-1	x	x	x	x
Perfluorodecanoic acid	PFDA	Perfluorocarboxylic Acids	335-76-2		x	x	x
Perfluoroundecanoic acid	PFUnA		2058-94-8		x	x	x
Perfluorododecanoic acid	PFDoA		307-55-1		x	x	x
Perfluorotridecanoic acid	PFTrDA		72629-94-8		x	x	x
Perfluorotetradecanoic acid	PFTA		376-06-7		x	x	x
Perfluorohexadecanoic acid	PFHxDA						x
Perfluorooctadecanoic Acid	PFODA						x
Perfluorobutanesulfonic acid	PFBS		375-73-5	x	x	x	x
Perfluoropentanesulfonic acid	PFPeS						x
Perfluorohexanesulfonic acid	PFHxS		355-46-4	x	x	x	x
Perfluoroheptanesulfonic acid	PFHpS	Perfluorosulfonic Acids					x
Perfluorooctanesulfonic acid	**PFOS**		**1763-23-1**	**x**	**x**	**x**	**x**
Perfluorononanesulfonic acid	PFNS						x
Perfluorodecanesulfonic acid	PFDS						x
1H,1H,2H,2H-Perfluorohexanesulfonic acid	4:2 FtS		757124-72-4				x
1H,1H,2H,2H-Perfluorooctanesulfonic acid	6:2 FtS	Fluorotelomer Sulfonates	27619-97-2				x
1H,1H,2H,2H-Perfluorodecanesulfonic acid	8:2 FtS		39108-34-4				x
1H,1H,2H,2H-Perfluorododecanesulfonic acid	10:2 FtS						x
Perfluorooctanesulfonamide	FOSA		754-91-6				x
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	Precursors	-		x	x	x
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA		-		x	x	x
Hexafluoropropylene oxide dimer acid	HFPO-DA		13252-13-6			x	x
Hexafluoropropylene oxide dimer acid	ADONA	"Replacement" PFAS	919005-14-4			x	x
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS		763051-92-9			x	x
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS		756426-58-1			x	x

Differences in Manufacturing

- PFAS was manufactured using electrochemical fluorination (ECF) or telomerization
- Each process produced PFAS containing different chemical signatures that can be used to understand the process by which it was manufactured
    1) Distribution of perfluorinated carbon chain
    2) Presence of branched/linear isomers

PFOS and PFOA Manufacture by ECF

ECF was licensed by 3M in the 1940s and used by 3M to manufacture PFOS in the United States until 2001

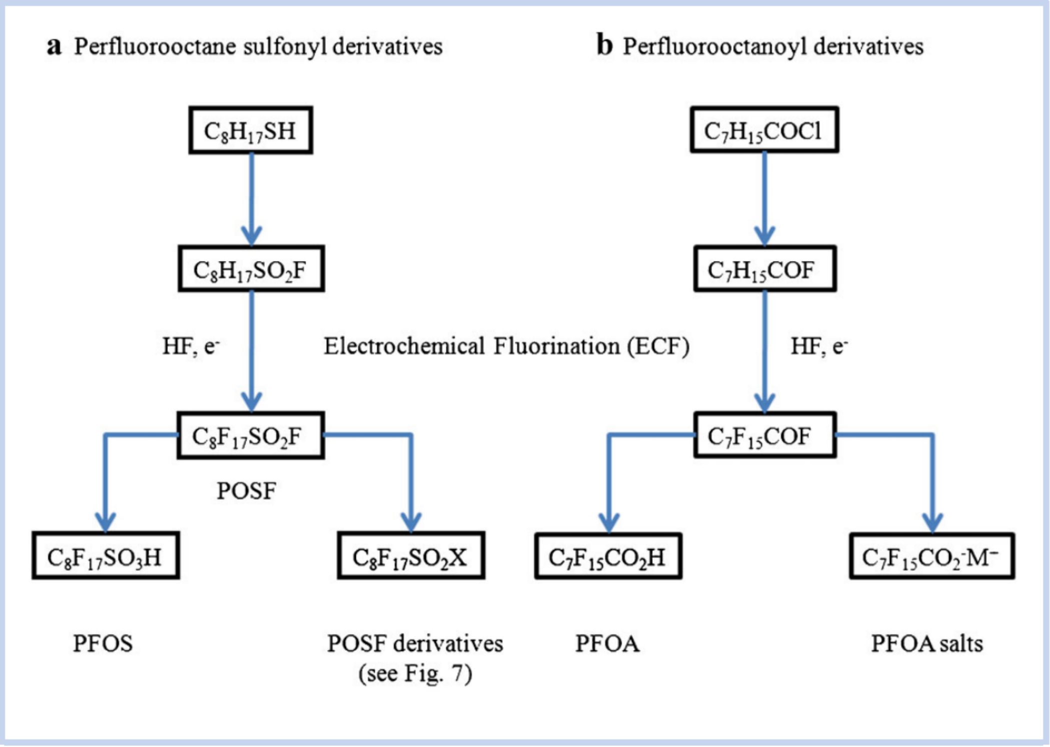


Figure 1. Synthesis, by electrochemical fluorination, of building blocks leading to PFOS, PFOA, and derivatives.

<u>Process produced:</u>

- Even and odd-number perfluorinated carbon chains
- Linear and branched isomers

Figure from Buck, R.C., J. Franklin, U. Berger, J.M. Conder, I.T. Cousins, P. de Voogt, A.A. Jensen, K. Kannanm S.A. Maybury, and S.P.J. van Leeuwen, 2011, Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins, Integrated Environmental Assessment and Management, Vol. 7, No. 4, pp. 513–541

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PFOA Manufacture by Telomerization

Telomerization was developed in the 1970s and yields straight carbon chain isomers.

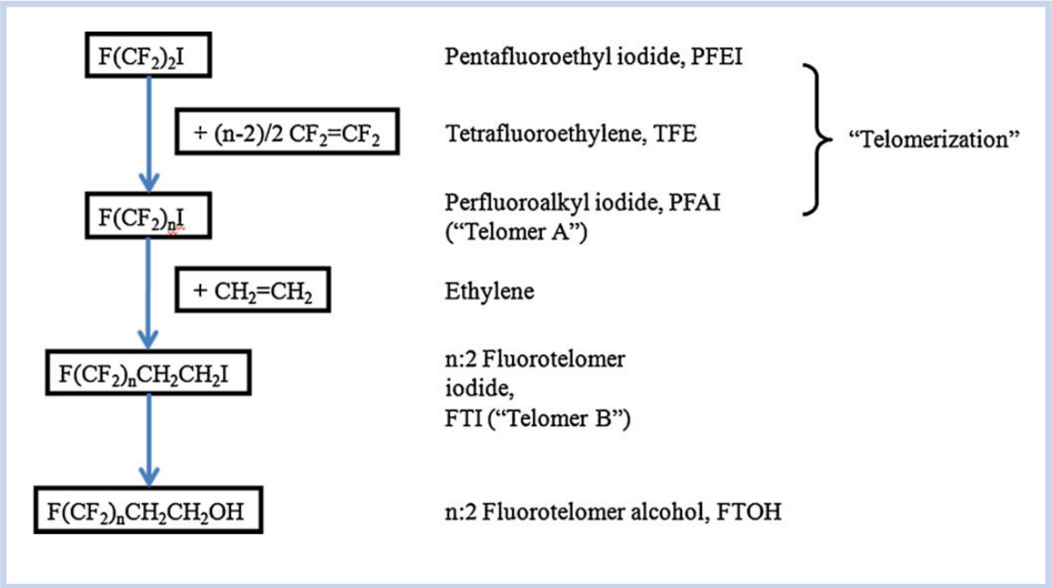

Figure 2. Synthesis, by telomerization, of building blocks leading to fluorotelomer alcohols.

<u>Process produced:</u>

- Even number perfluorinated carbon chains
- Predominantly linear isomers
- *Not used for PFOS*

Figure from Buck, R.C., J. Franklin, U. Berger, J.M. Conder, I.T. Cousins, P. de Voogt, A.A. Jensen, K. Kannanm S.A. Maybury, and S.P.J. van Leeuwen, 2011, Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins, Integrated Environmental Assessment and Management, Vol. 7, No. 4, pp. 513–541

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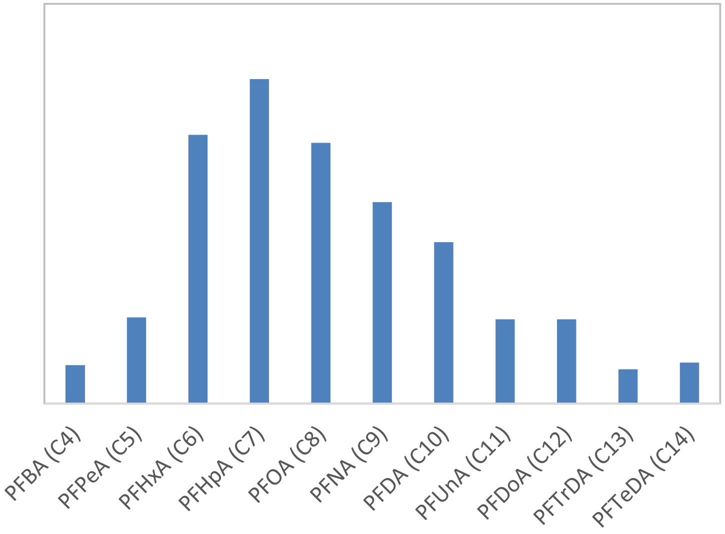
Differences in PFAS Manufacture 1 – Distribution of Perfluorinated Carbon Chains

- The distribution of carbon chains can reflect how the PFAS was manufactured
  - ECF-produced PFAS is reflective of the chemical stocks used in manufacture, and therefore can have a distribution of both odd- and even-numbered carbon chains
  - Telomerization-produced PFAS is constructed with C_2F_4 building blocks, or “taxogen”, and therefore exhibits predominantly even-numbered carbon chains

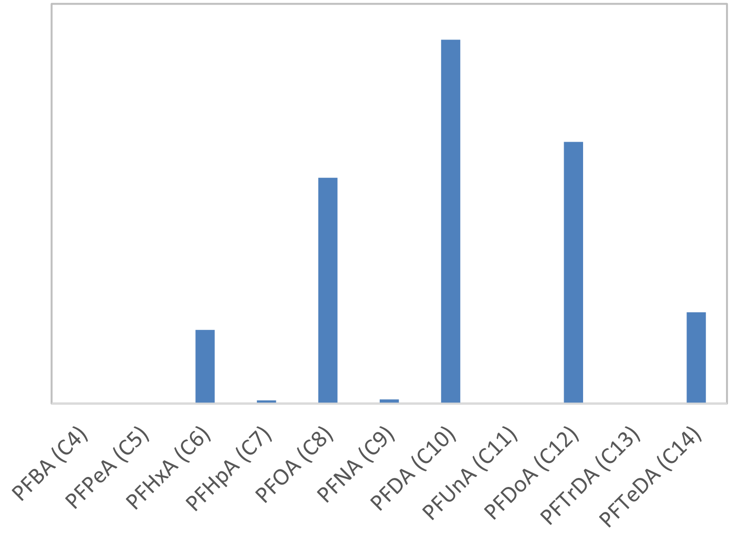
Differences in carbon chain distribution due to manufacturing* of PFCAs as impurities in FCMs

The ECF-produced FCM has both even- and odd-numbered PFCA impurities, whereas the telomerization-produced FCM has only even-numbered

Example FCM manufactured using **ECF**



Example FCM manufactured using **telomerization**



Benotti, M.J., L.A. Fernandez, G.F. Peaslee, G.S. Douglas, A.D. Uhler, and S. Emsbo-Mattingly, "A Forensic Approach for Distinguishing PFAS, submitted to Environmental Forensics

*both of these materials are no longer used

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PFAS Carbon Chain Distribution – Take Home

- Perfluorinated carbon chains dominated by even-numbered structures are an indication of manufacture by telomerization
- Perfluorinated carbon chains dominated by even- and odd-numbered structures *may* be an indication of manufacture by ECF
    - *Or it could be weathered telomerization-produced PFAS, because even-numbered telomerization-produced PFAS can biotransform to both even- and odd-numbered PFCAs*[1]

[1]Harding-Marjanovic, K.C., E.F. Houtz, S. Yi, J.A. Field, D.L. Sedlak, L. Alvarez-Cohen, 2015, Aerobic biotransformation of fluorotelomer thioether amido sulfonate (lodyne) in AFFF-amended microcosms" Environmental Science & Technology, 49(13): 7666-74

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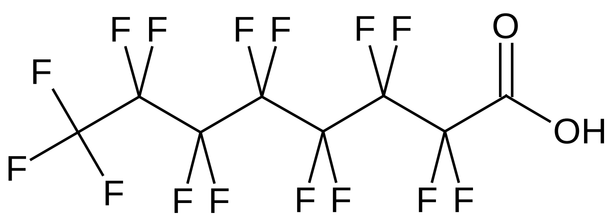
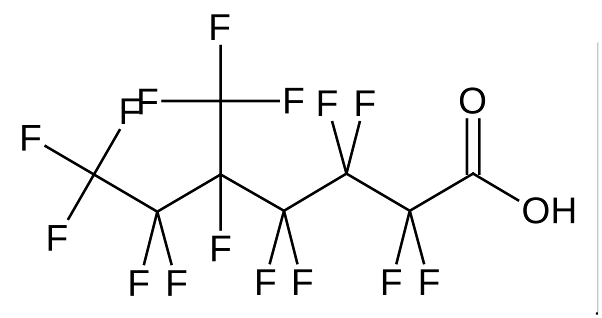
Differences in PFAS Manufacture 2 – Isomers

- Isomers are compounds with the same chemical formula but a different arrangement of atoms.
  - e.g., linear PFOA (or n-PFOA) vs 4-m PFOA



vs



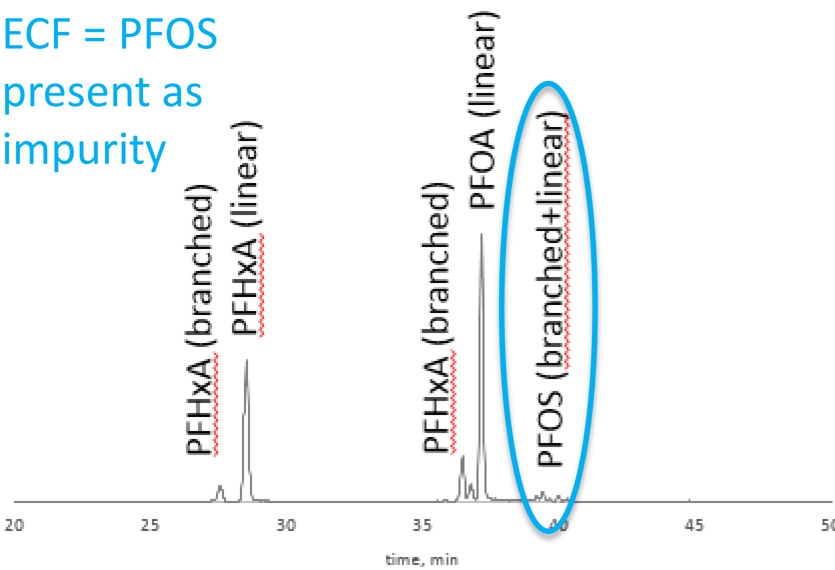
- There is only one linear isomer but many potential branched isomers of both PFOA and PFOS
- *Manufacture by ECF produced both linear and branched isomers, whereas manufacture by telomerization predominantly produced linear isomers*

Differences in PFHxA, PFOA and PFOS data resulting from differences in FCM manufacturing*

1) PFOS was only produced by ECF – so it is present as an impurity in the ECF-manufactured material and not in the telomerization produced material

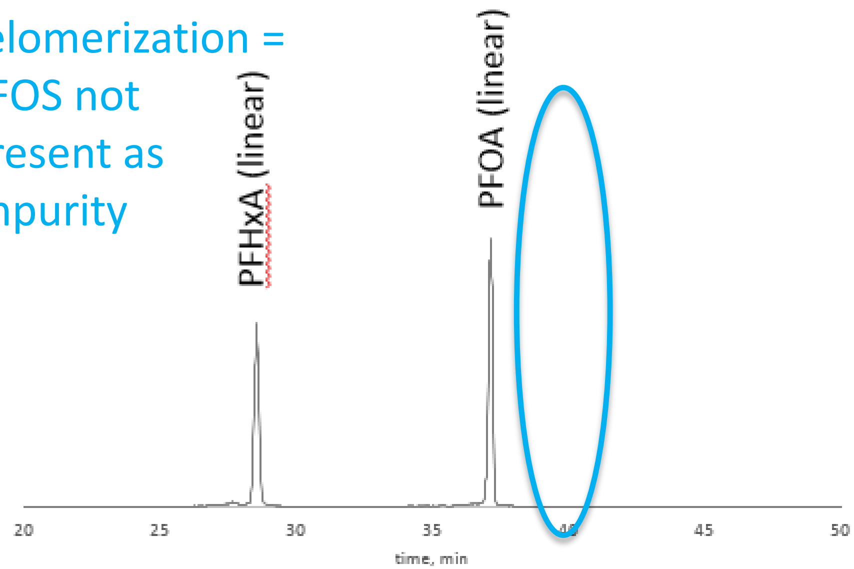
<u>Example FCM manufactured using **ECF**</u>

ECF = PFOS present as impurity



<u>Example FCM manufactured using **telomerization**</u>

Telomerization = PFOS not present as impurity



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*both of these materials are no longer used

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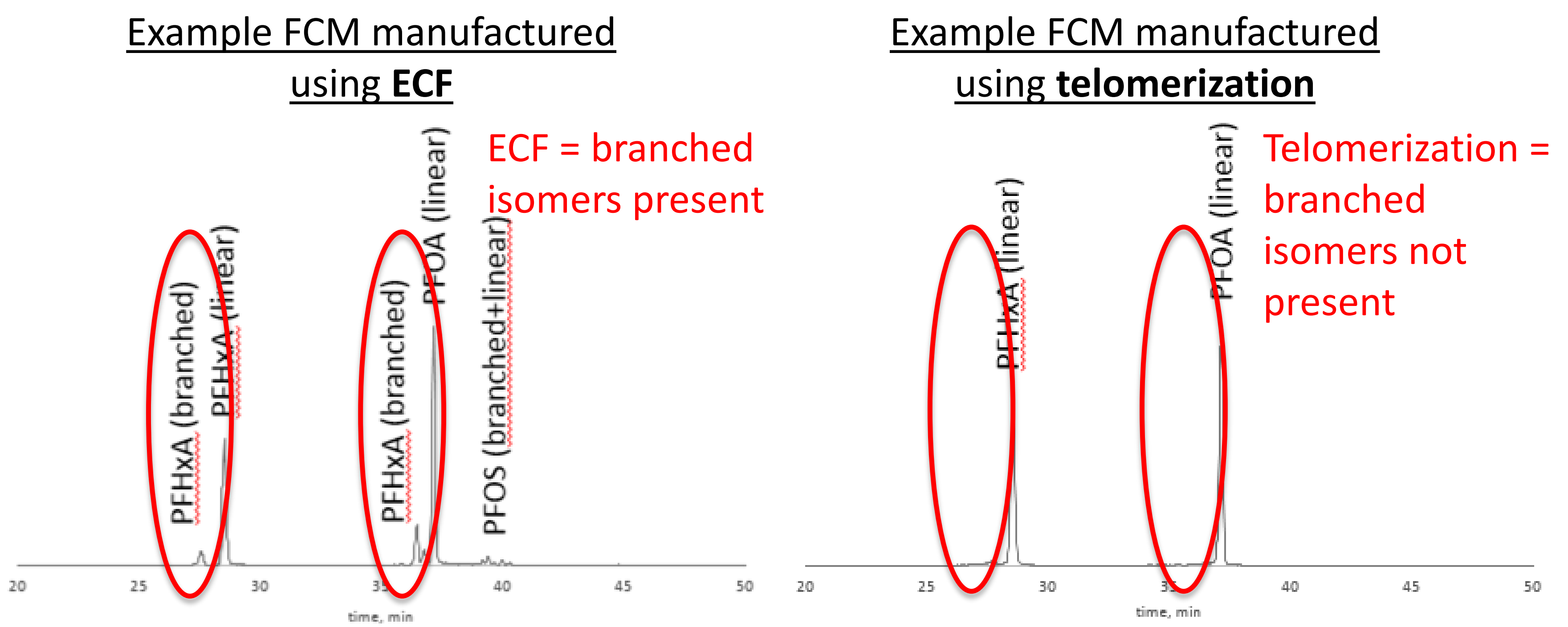
Differences in PFHxA, PFOA and PFOS data resulting from differences in FCM manufacturing*

2) Branched isomers of PFHxA and PFOA are present in ECF-manufactured material and not in the telomer-produced material



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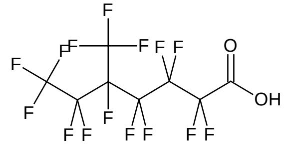
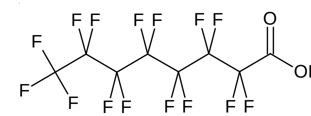
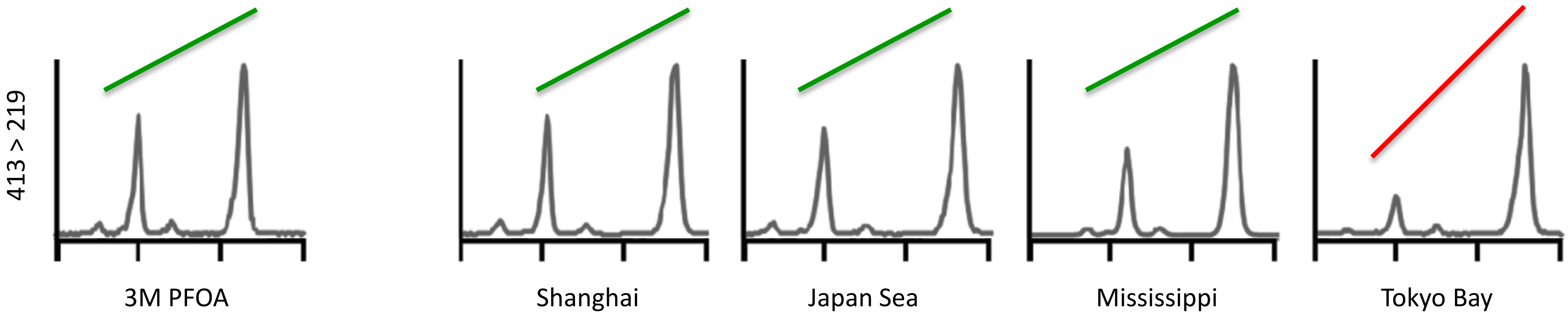
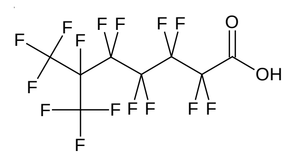
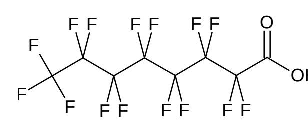
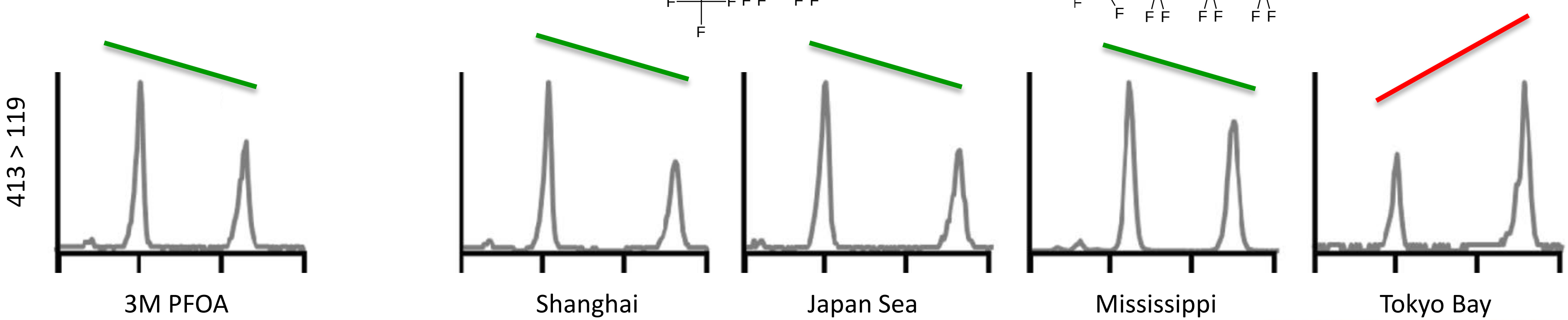
The use of isotope distributions may go beyond ECF vs. telomerization

1) Relative abundance of 4m-PFOA  to n-PFOA 



2) Relative abundance of 5m-PFOA  to n-PFOA 



Figures modified from Benskin et al., 2010

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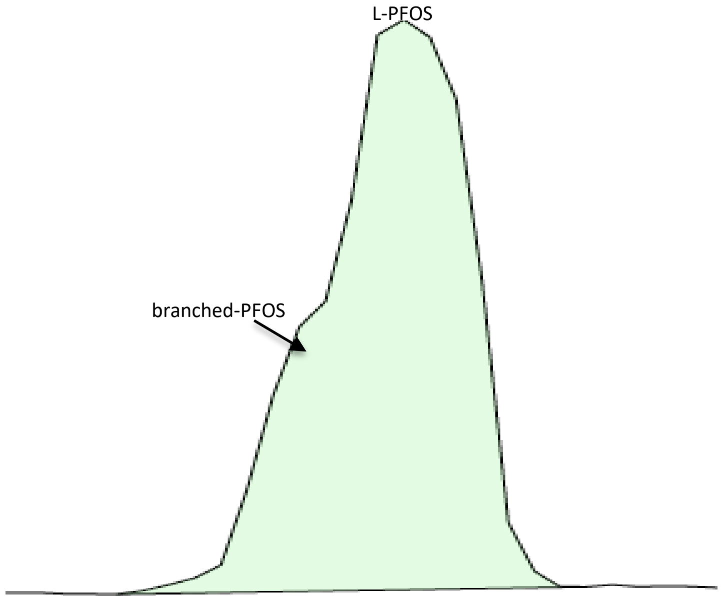
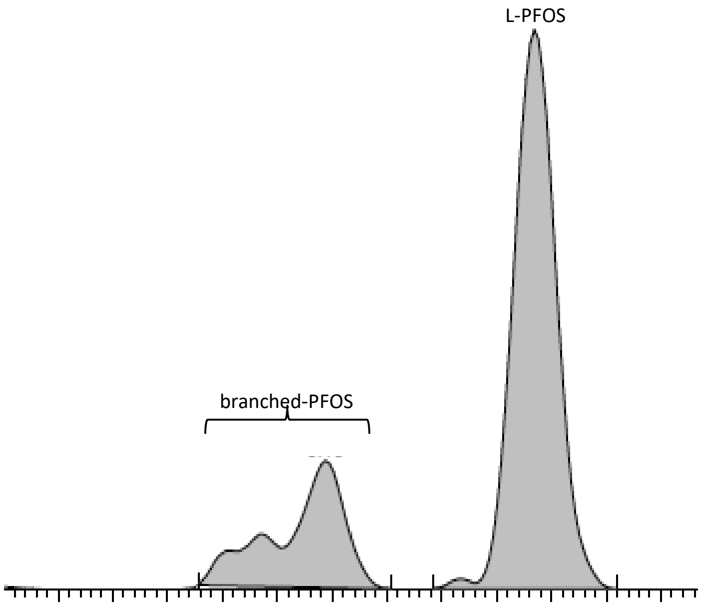
Be Careful Interpreting PFAS Isomer Data

Interpreting branched vs linear isomer data from laboratories that maximize throughout or use older equipment can be challenging

Lab with method designed to maximize sample throughput



Lab ensuring that branched and linear PFOS isomers are separated



In Practice Things Are Different

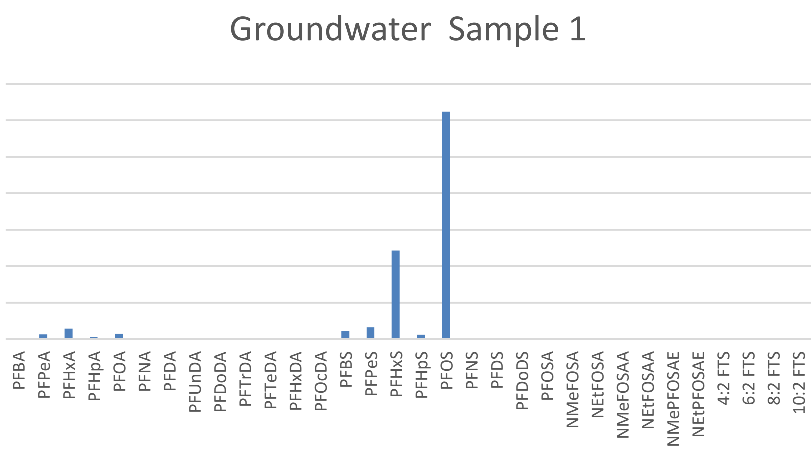
- We do not have a library of source materials to compare data to (yet)
- We are often handed data after samples have been collected and analyzed so we don't have a say about which PFAS analytes are measured
- And source areas are often known to be a mix of both ECF- and telomerization-produced materials (think AFFF source areas with a long history of firefighting training)
- How do we go about investigating these types of data?

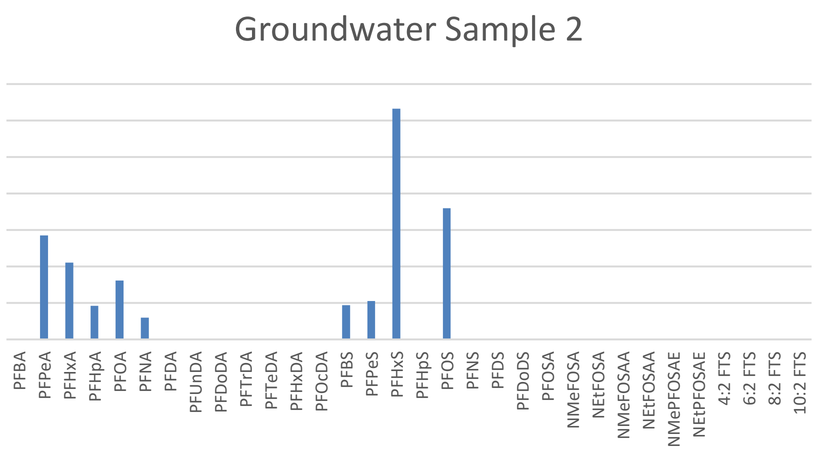
PFAS Isomer Data – Take Home

- The presence of isomers indicates influence by ECF-manufactured PFAS, which was manufactured by 3M before 2001
- A complete or near lack of branched isomers means manufacturing by telomerization which was manufactured by various companies since the 1970s
- These data may be of limited value at sites with ongoing releases of both ECF- and telomerization-produced PFAS, such as most AFFF-training sites
- *Take care interpreting isomer data – when in doubt, work with a chemist with experience with the equipment (LC-MS/MS systems) used to generate these data*

"Static" Approaches to PFAS Forensics

Visually compare samples to one another?





Use "established" diagnostic ratios differences?

	Sample 1	Sample 2
% PFCAs	6.6	40.4
% Long Chain PFSAs (C6+)	94.1	83.2

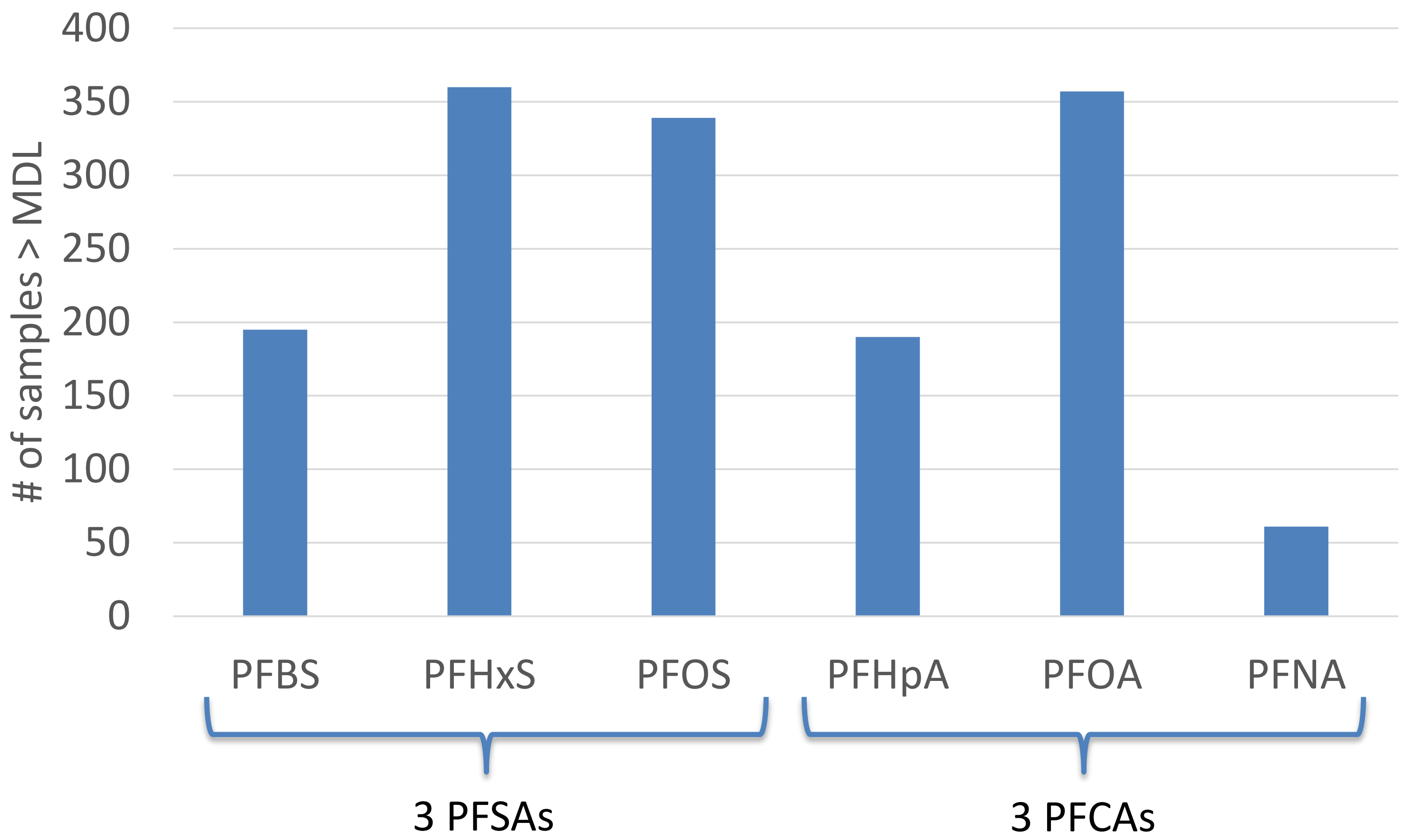
Principal Component Analysis (PCA)

PCA is a multivariate statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components.

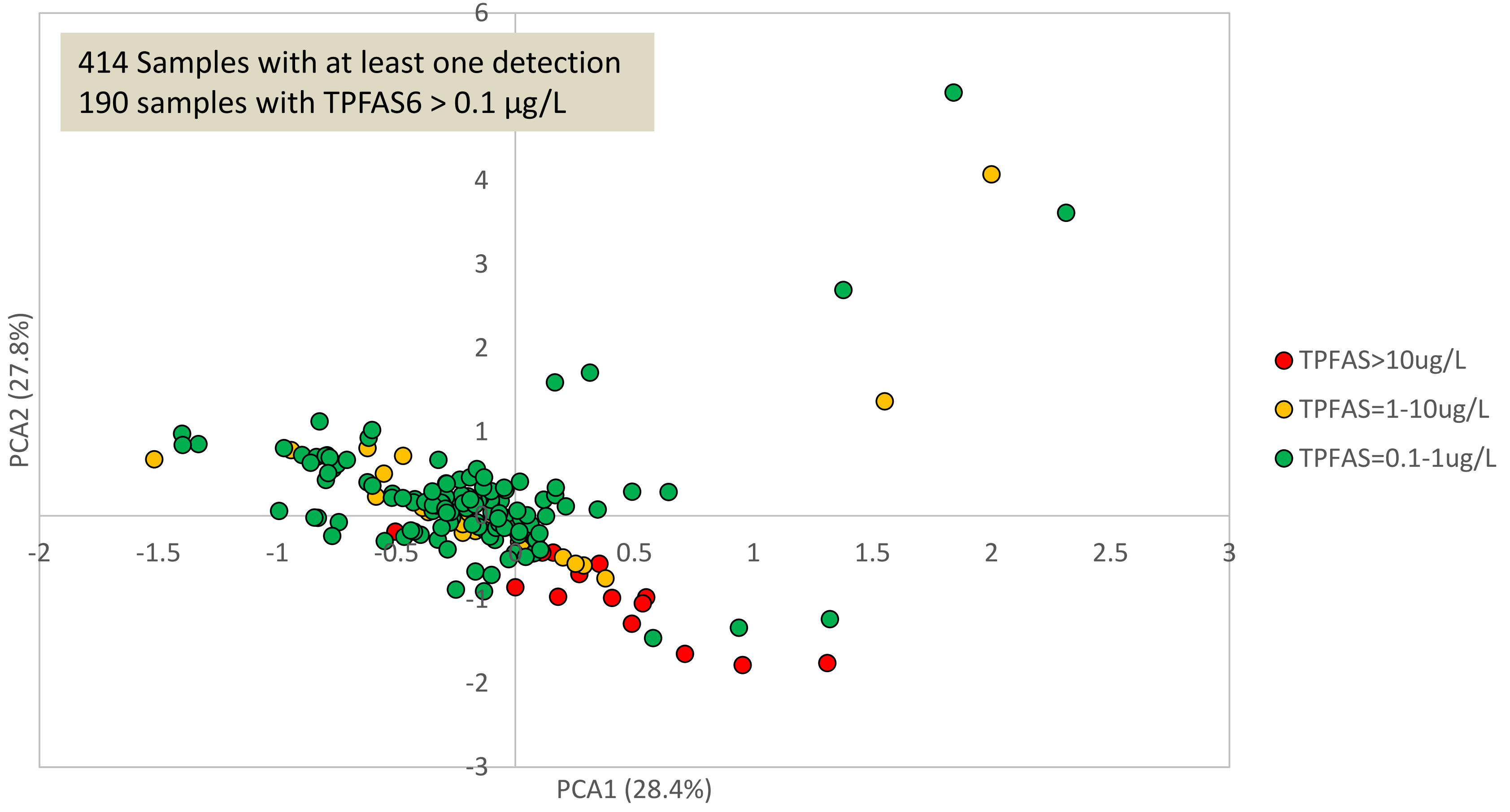
Translation – PCA identifies and graphically shows the most important features of data that describe similarities and differences between sample chemistries within a dataset.

Site 1: DoD Site

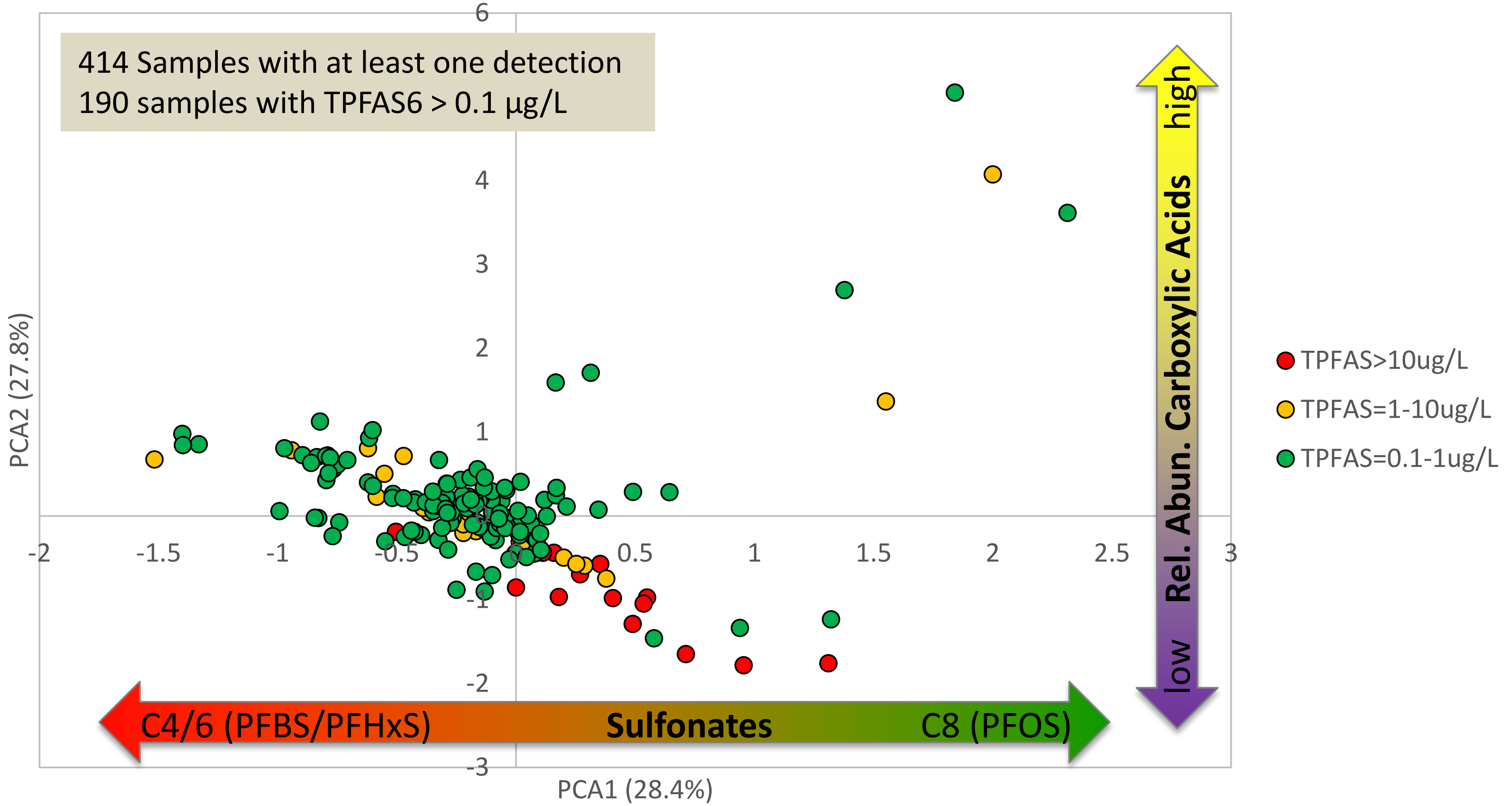
414 groundwater samples with at least one detection



DoD Site PCA Results (TPFAS > 0.1 µg/L)



Sulfonate Chain Length and Rel. Abundance of Carboxylic Acids are Most "Important" Features



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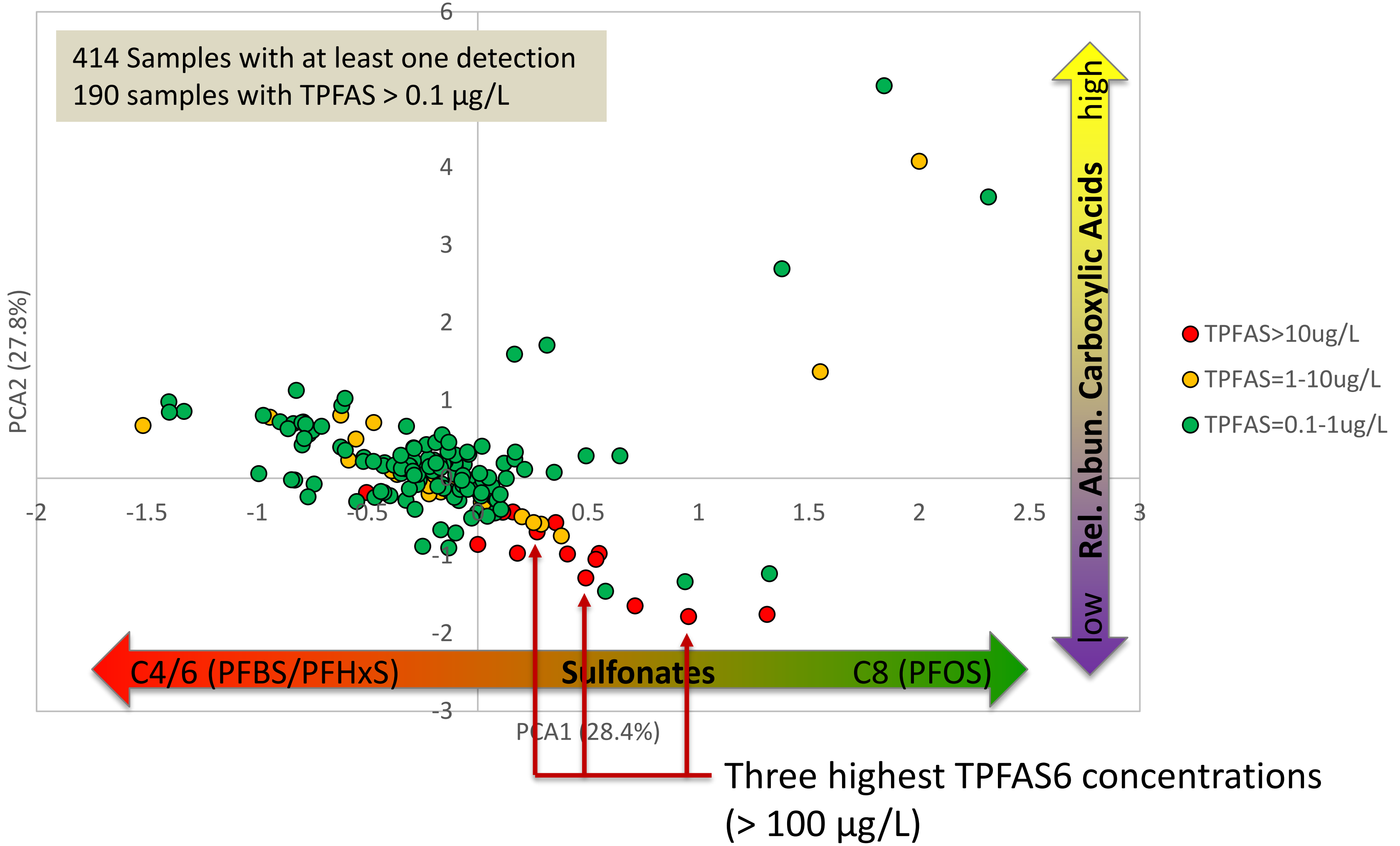
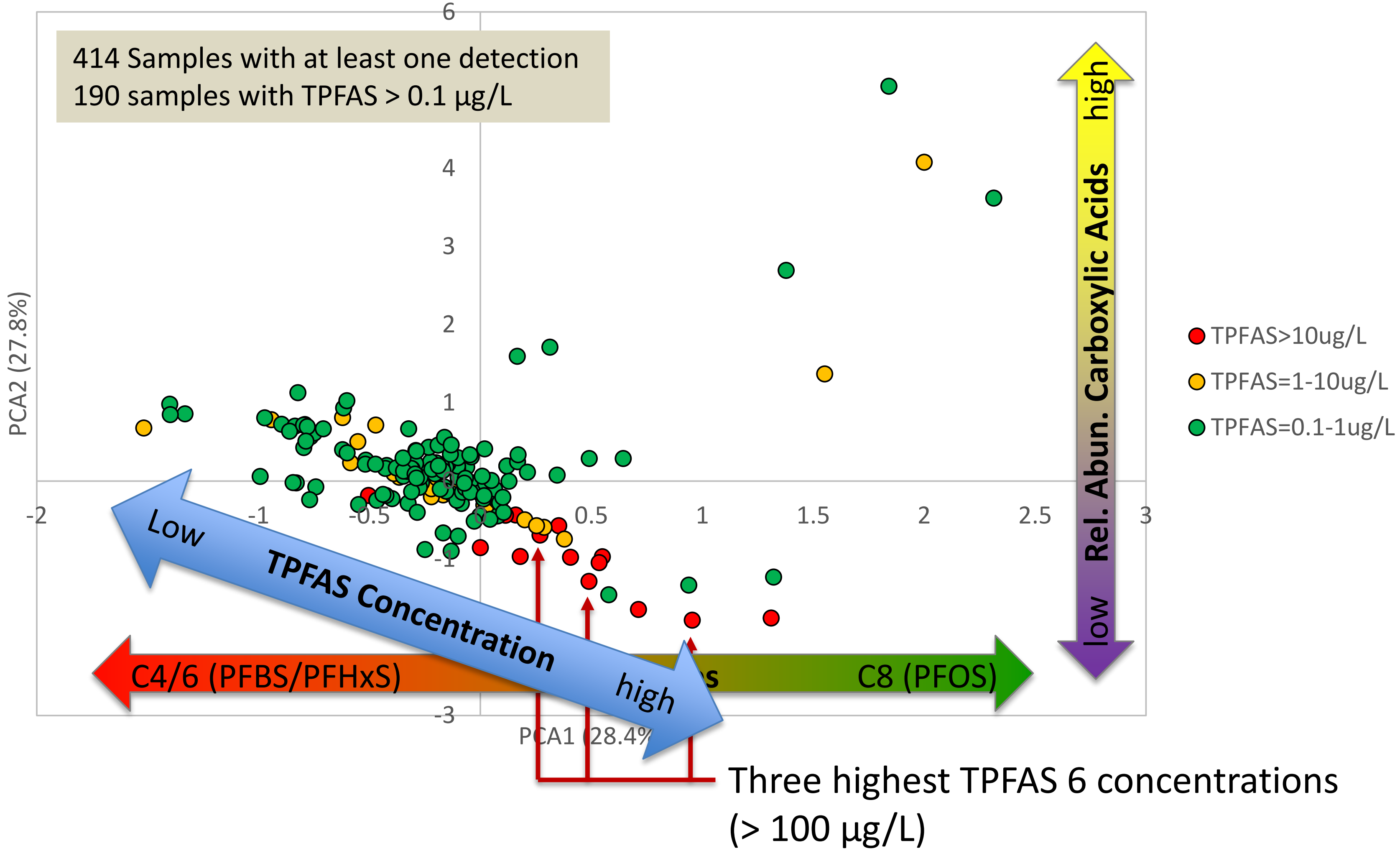
Highest TPFAS6 Conc. Defines One End of Data Cloud



Distribution of Most Samples Describes Subsurface Transport



Spread In Data Cloud Explained by Migration

Class	Analyte	# Carbons	K_{OC} *
PFCAs	PFHpA	7	43
	PFOA	8	78
	PFNA	9	229
PFSAs	PFBS	4	62
	PFHxS	6	112
	PFOS	8	631

- *Shorter chain more mobile than longer chain PFAS*
- *PFCAs more mobile than PFSAs*

*from Guelfo, J.L., Higgins, C.P. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol*. **2013.** 47, 4164–4171.

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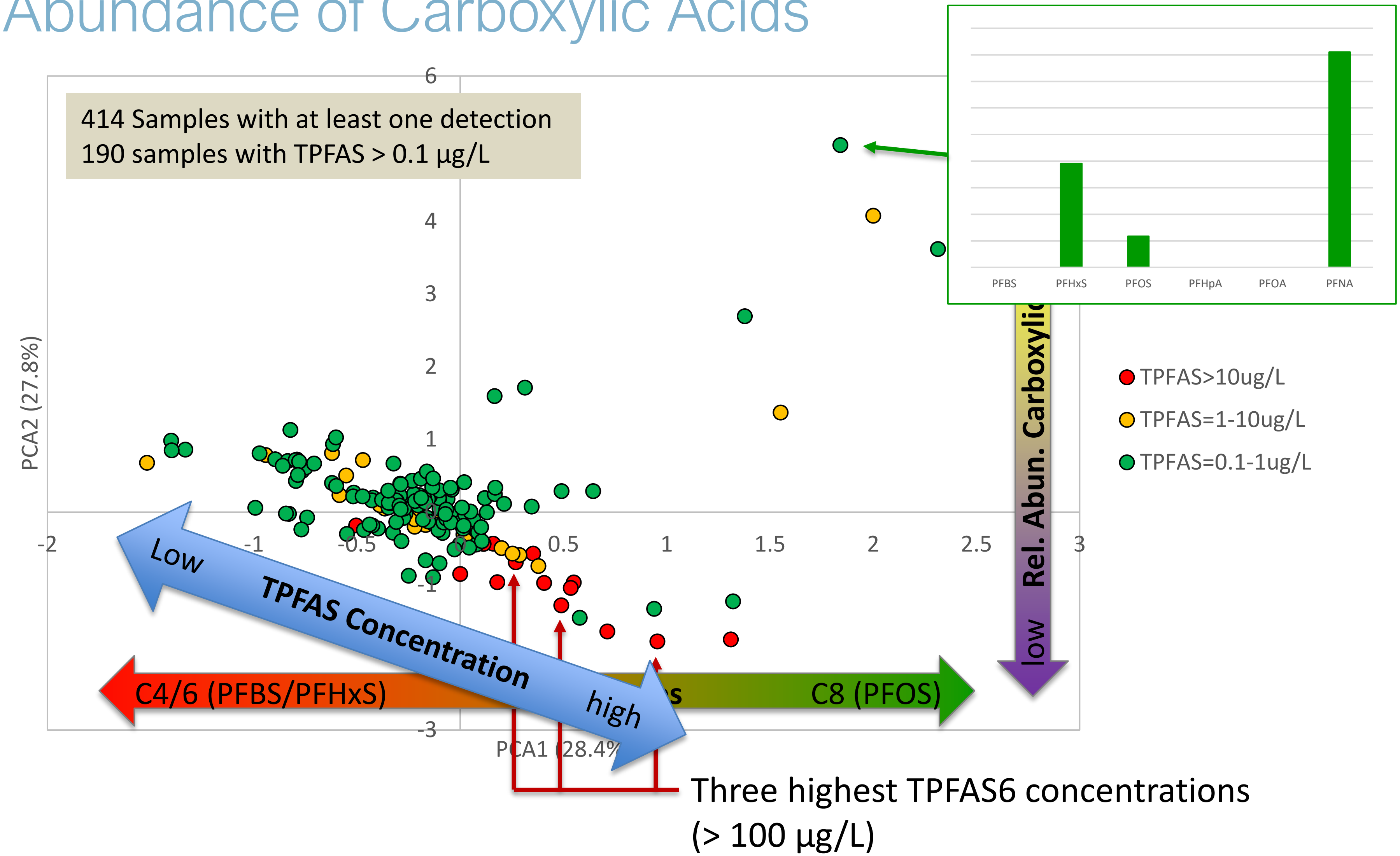
Outliers are Often Defined by High Relative Abundance of Carboxylic Acids



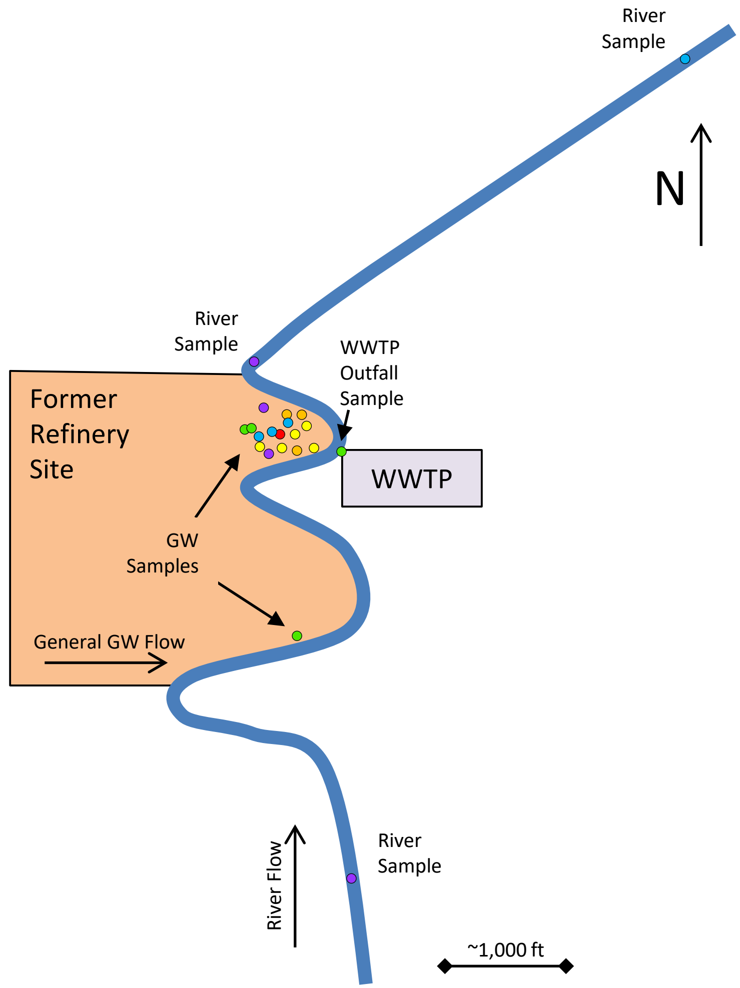
Observations from DoD Site

- Whichever data are used, the patterns of data are explained by
    1. the relative amounts of long vs. short chain PFSAs (i.e., transport) and
    2. the relative abundance of PFCAs
- PCA of existing data does not explicitly identify different sources*
    - PCA can help identify how similar samples are to those from a source area or where signatures are inexplicably different and *may* be due to other sources
    - PCA cannot be done in a vacuum, it should be used as one of *multiple lines of evidence* in any forensic investigation

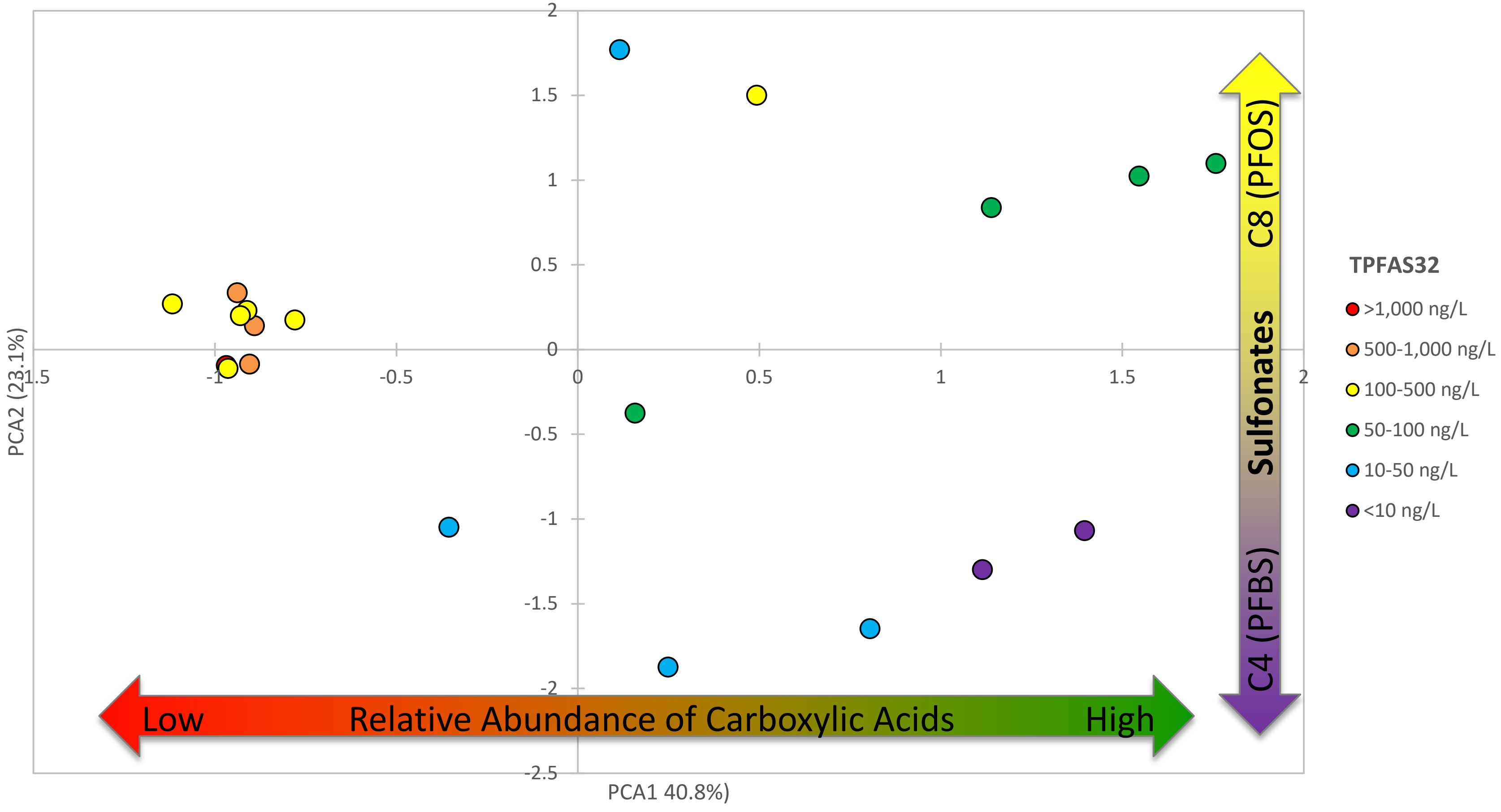
*it's possible that it could if source materials or multiple source areas are included in the analysis

Former Refinery Site

- Refinery closed in late 1990s
- Firefighting training area and at least one fire where AFFFs were used
- AFFF plume communicating with a river where PFAS has been detected
- Proximate WWTP discharging to river



Former Refinery Site PCA Results



Perspective. Vision. Solutions.

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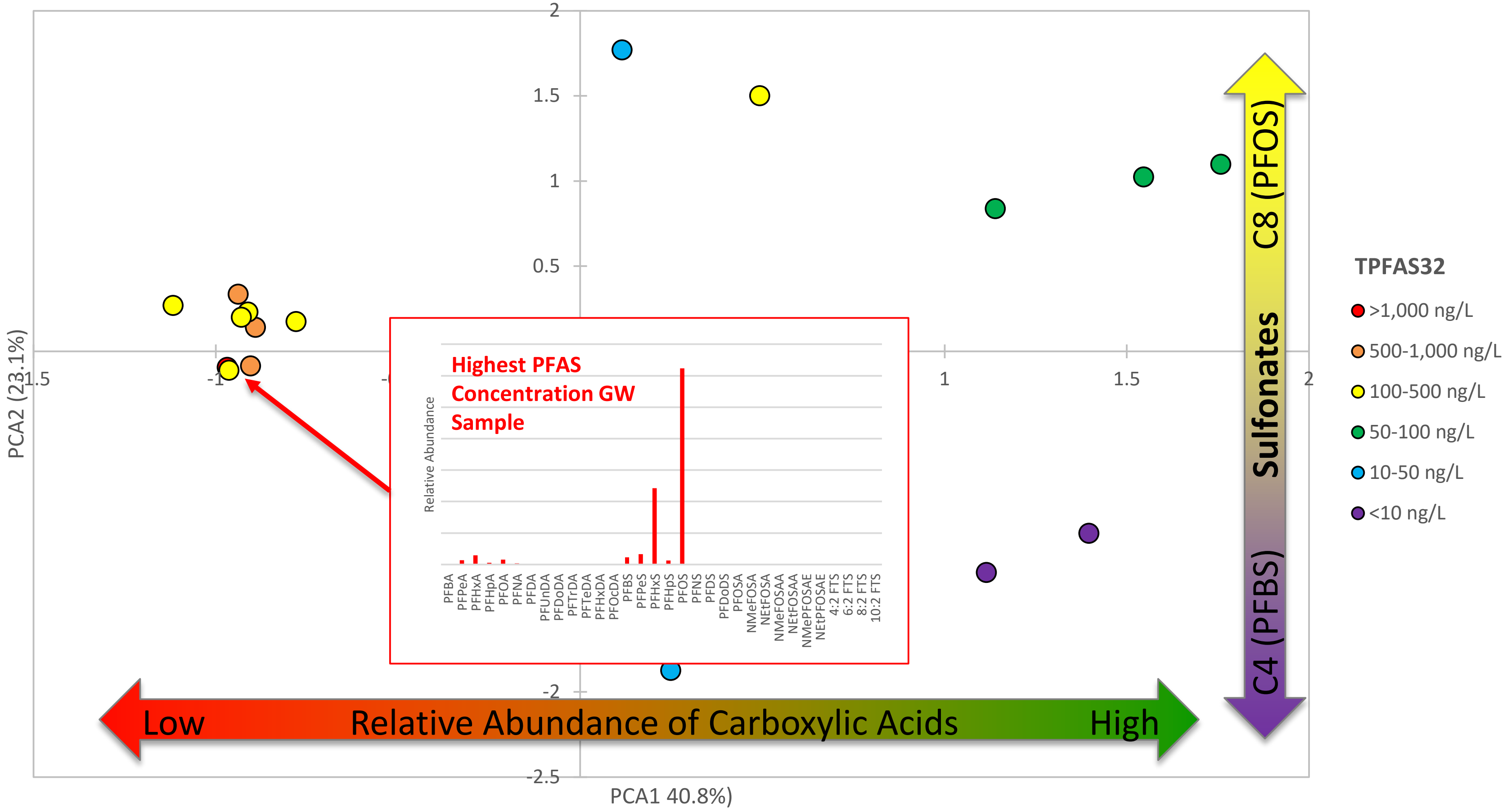
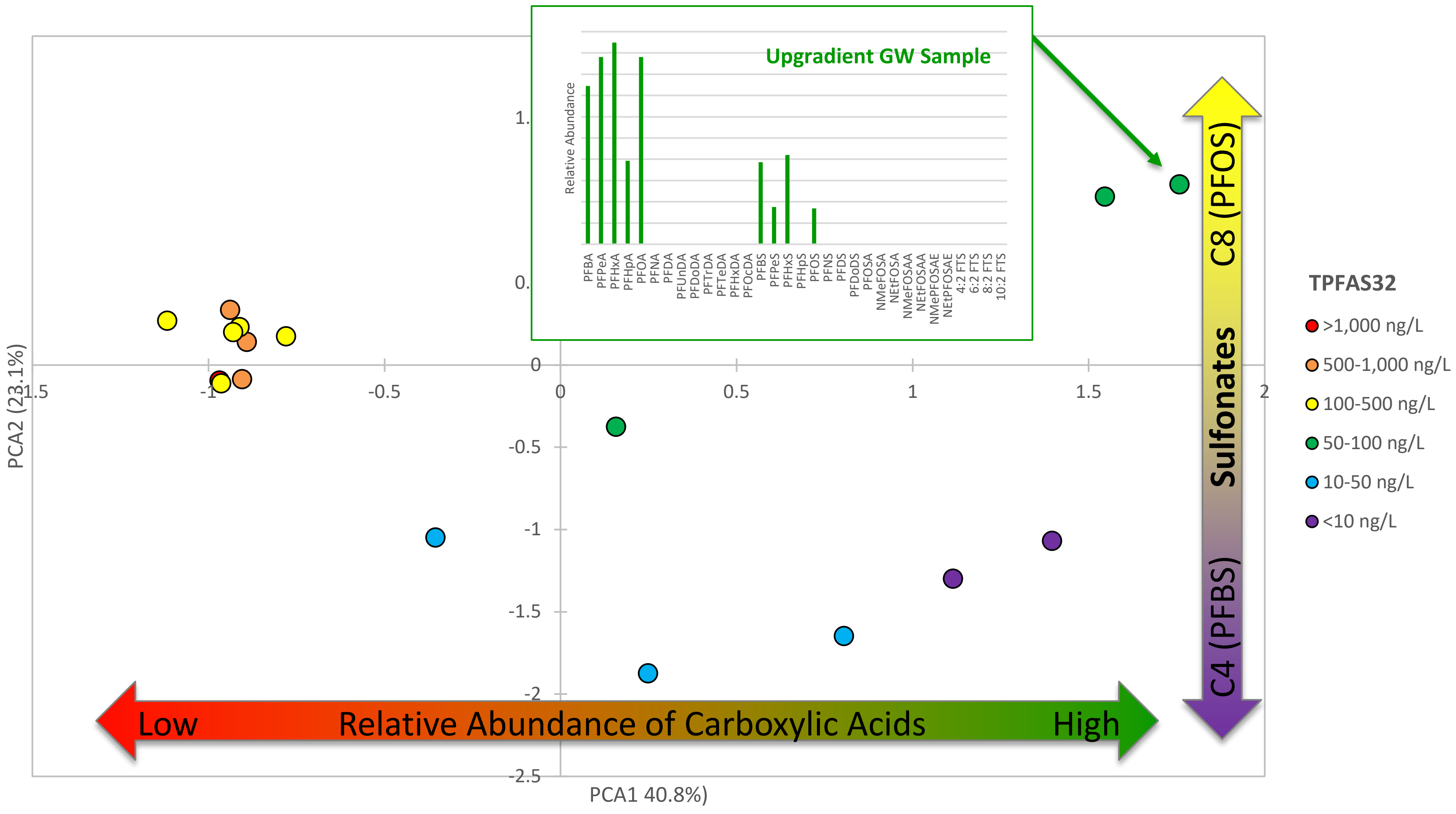
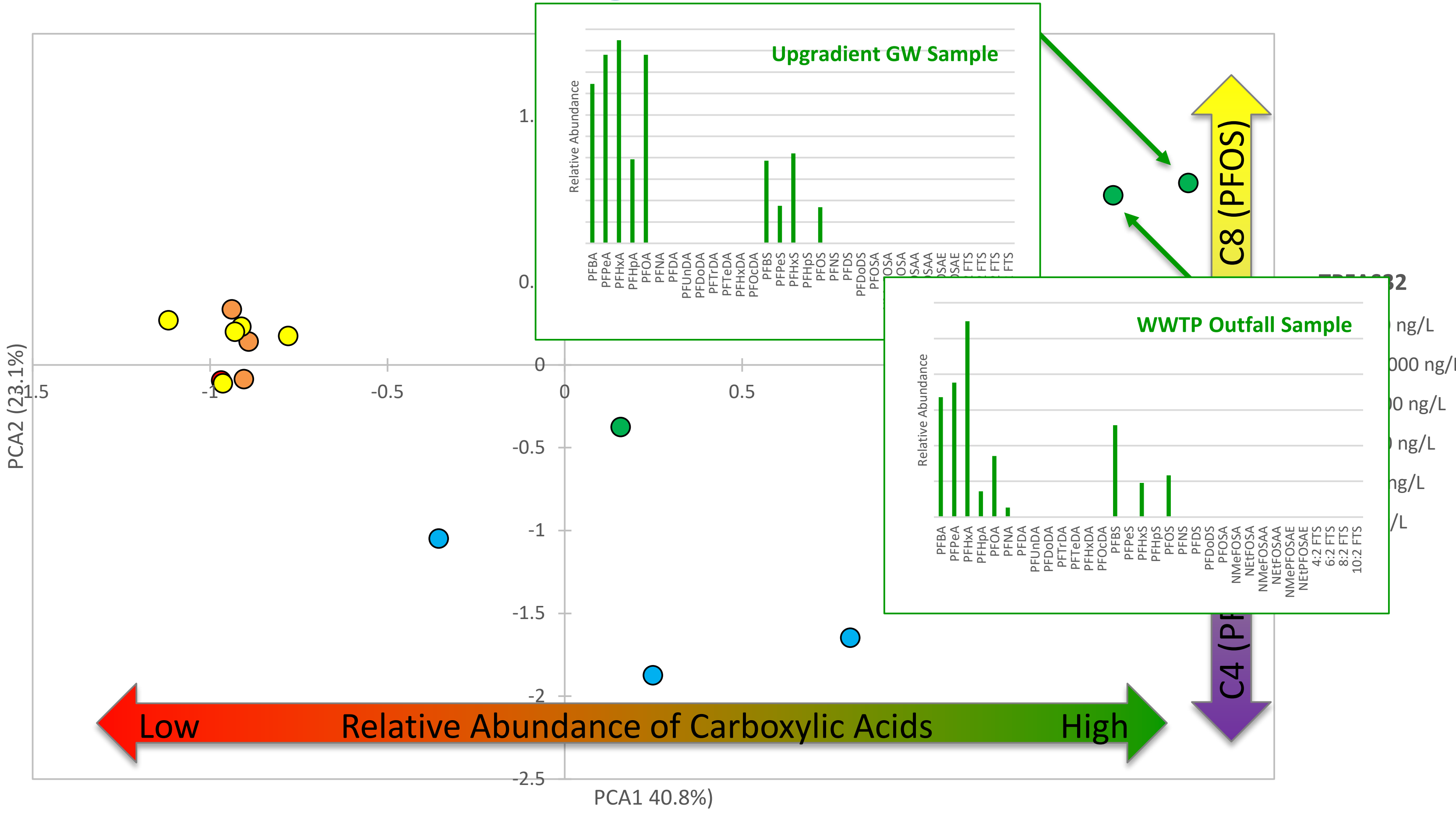
Most Samples Within the AFFF Plume Have a Similar PFAS Signature



Upgradient GW Sample is Enriched in PFCAs



WWTP Outfall Sample and Upgradient GW Sample Have Similar PFAS Signatures



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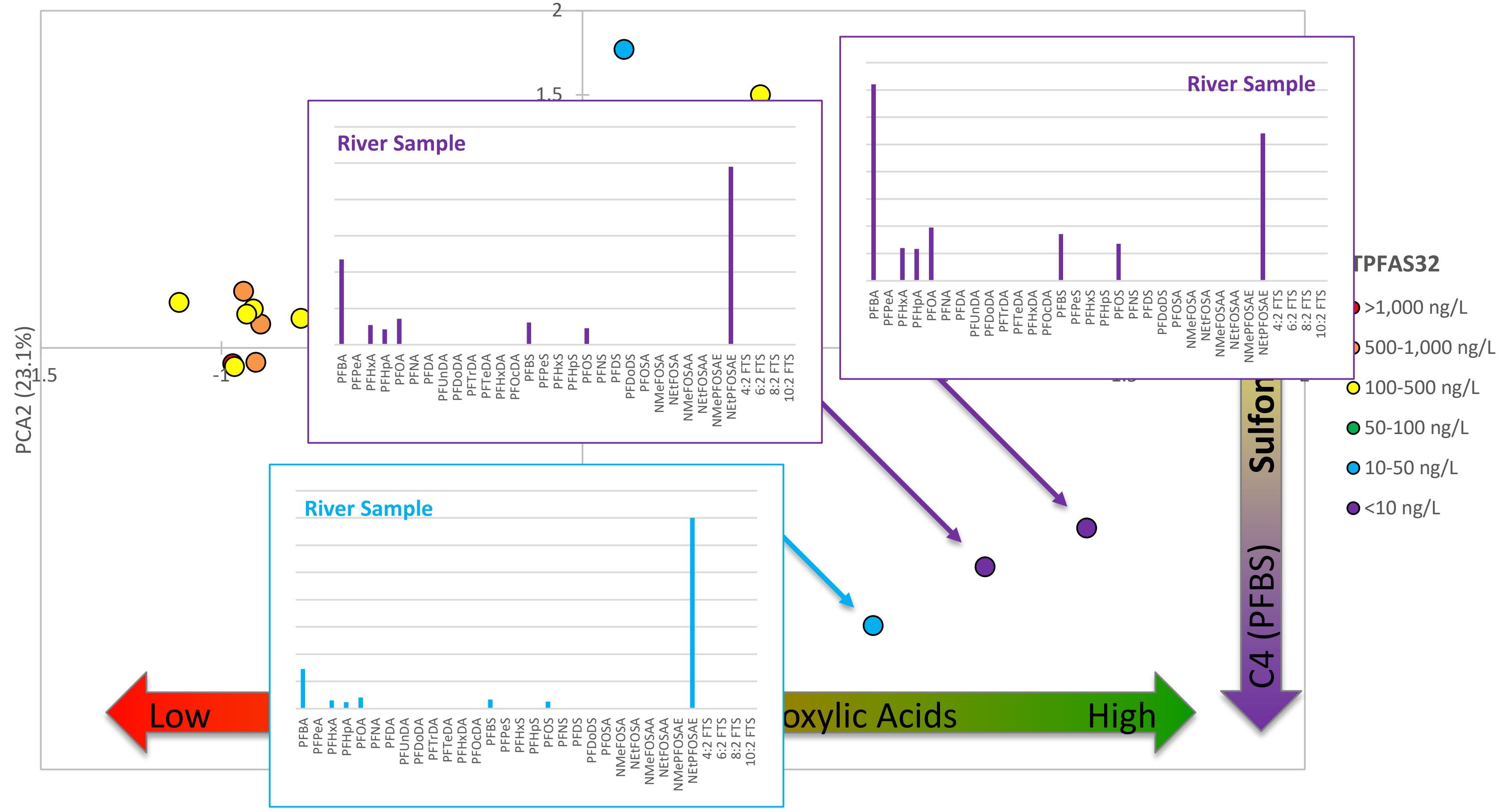
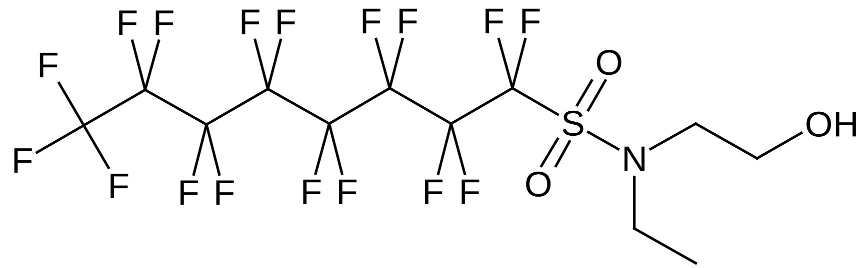
River Samples Also Enriched in PFCAs and NEtPFOSE



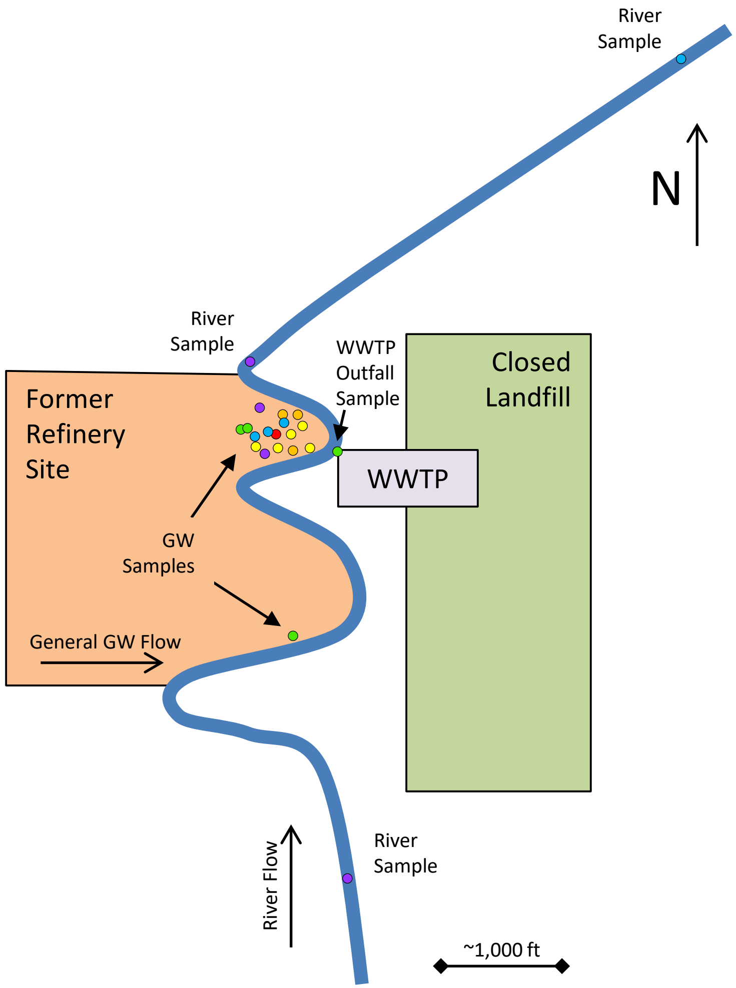
NEtPFOSE



- N-ethyl perfluorooctosulfonoamidoethanol
- PFOS “precursor”
- More volatile than other PFAS
- Primarily used to treat paper
- *Not found in AFFF source area*
- *Also an indicator of a landfill PFAS source*

PFAS Signature Observations

- AFFF plume has unique signature and is migrating towards river
- Groundwater along river and away from plume and WWTP effluent enriched in PFCAs
- River enriched with NEtPFOSE which likely stems from landfill



Our Proposed Approach to PFAS Forensics

Follow the a tiered approach similar to what is used for petroleum forensics

- Tier 1: Screening
- Tier 2: Regulatory Compliance
- Tier 3: Diagnostic Ratios and Patterns

Leverage these tools to compare environmental samples to a **library of source materials**

- The following slides provide examples of the types of forensic information how such information will be applied

A Forensic Approach To PFAS

A Forensic Approach for Distinguishing PFAS Materials

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Details of this tiered approach, as well as examples of the types of information that may be observed in source materials, are presented in the forthcoming publication in Environmental Forensics

A Forensic Approach for Distinguishing Per- and polyfluoroalkyl Substances (PFAS)

Abstract:

The widespread detection of per- and polyfluoroalkyl substances (PFAS) in the US and the ongoing proliferation of environmental regulations has prompted the need for a forensic approach for the source attribution of PFAS materials. Current LC-MS/MS standard methods are sensitive and robust, but only characterize a small fraction of the total potential PFAS signature. Other, more powerful analytical tools such as QToF-MS exist, and have been used to characterize some of the unknown or "non-target" fraction of PFAS, but these methods are expensive and not widely available. This paper presents a tiered approach to PFAS forensics based on standard methods and/or other relatively inexpensive methodologies. The approach outlined herein is broken into three tiers, including 1) a screening method to assess the general characteristics of the bulk PFAS signature; 2) a standard method to sensitively measure PFAS compounds of regulatory interest; and 3) a method for resolving the isomer patterns of select PFAS compounds. The combination of these readily accessible methods is illustrated herein with different source materials, including aqueous film forming foam (AFFF) concentrate samples and food contact materials (FCMs). The tiered PFAS forensic approach bridges the gap between ground breaking academic methods and production laboratory throughput for the purpose of rapidly characterizing samples from large or complex study areas.

Keywords: PFAS, forensics, source attribution, AFFF, food contact materials, LC-MS, LC-MS/MS

Subject classification codes: include these here if the journal requires them

Final Thoughts

- *Some* forensic information may be available from PFAS data collected using "standard methods"
  - PCA or other multivariate tools can show how similar or dissimilar signatures may be
    - *But need to understand and be able to explain trends*
    - Often may not identify different sources, but may identify where PFAS signature cannot be explained by source area signature
- For suspected or purported sources, a more comprehensive analysis of PFAS will reveal additional forensic information
  - follow a tiered approach (screening → conc. of individual compounds → diagnostic ratios and isomer profiles)
- Compare results to a library of source signatures analyzed as both pure materials and in soil/groundwater

Questions?

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