PFAS Forensics: Best Practices for Unwinding Complex PFAS Sources

August 28, 2024

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Effect on Forensics/ Source Identification

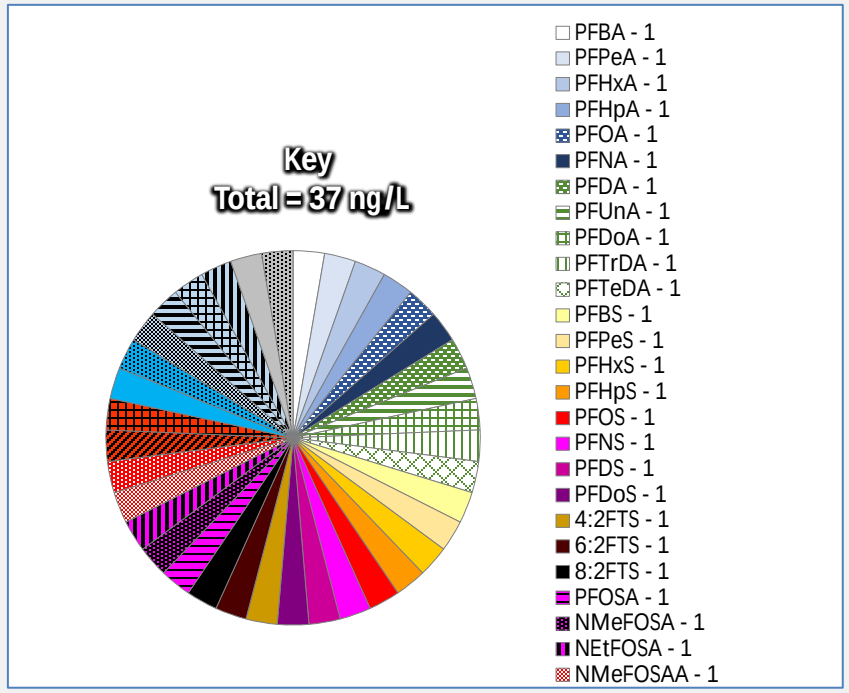
- PFAS Forensics Basic Patterns
- Issues that can Affect the Evaluation of Forensic Data
  - Turbidity
  - Differential F&T rates
  - PFAS Parent Transformation
- PFOS Isomers F&T & Forensics
- Case Study – F&T of Multiple AFFF Releases
- PFAS Mass vs PFAS Concentration

Frisco NC

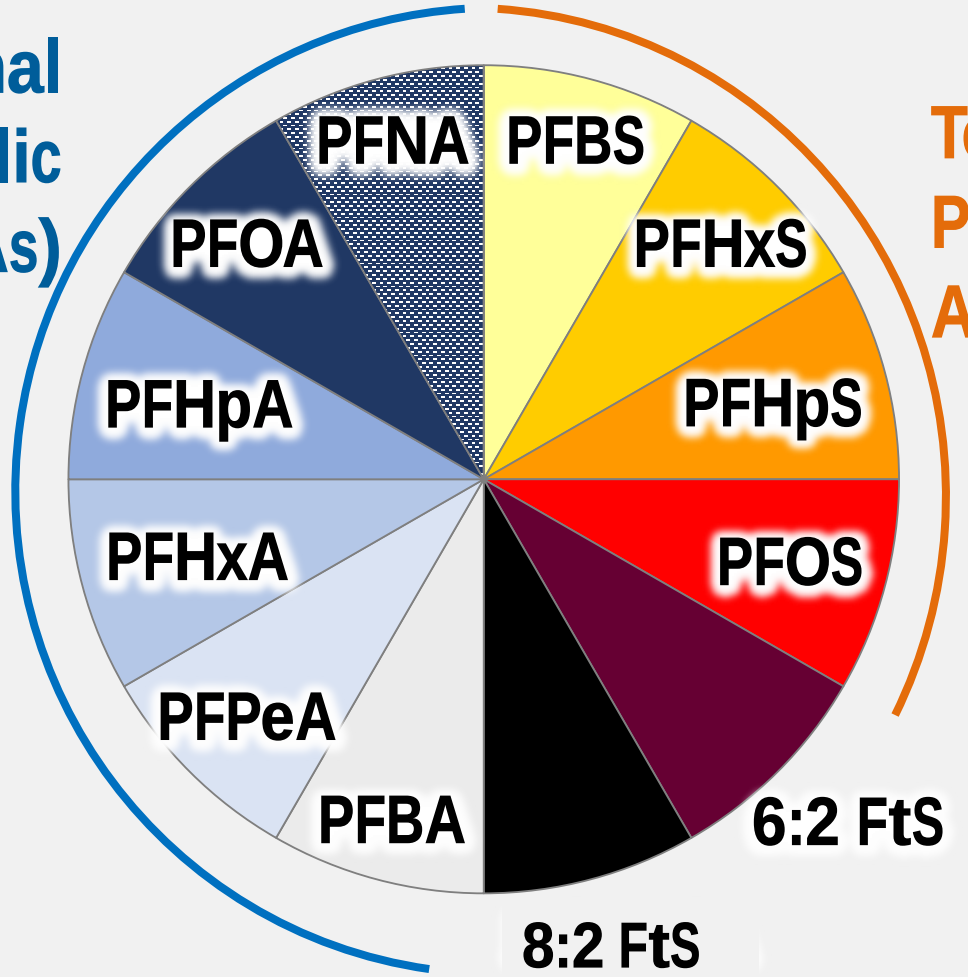
Surf Fishing in 45 Days

And Cell Phones are NOT Combatable with Surf Fishing

Example Analytes for Comparison



Terminal Perfluorocarboxylic Acids (PFCAs)

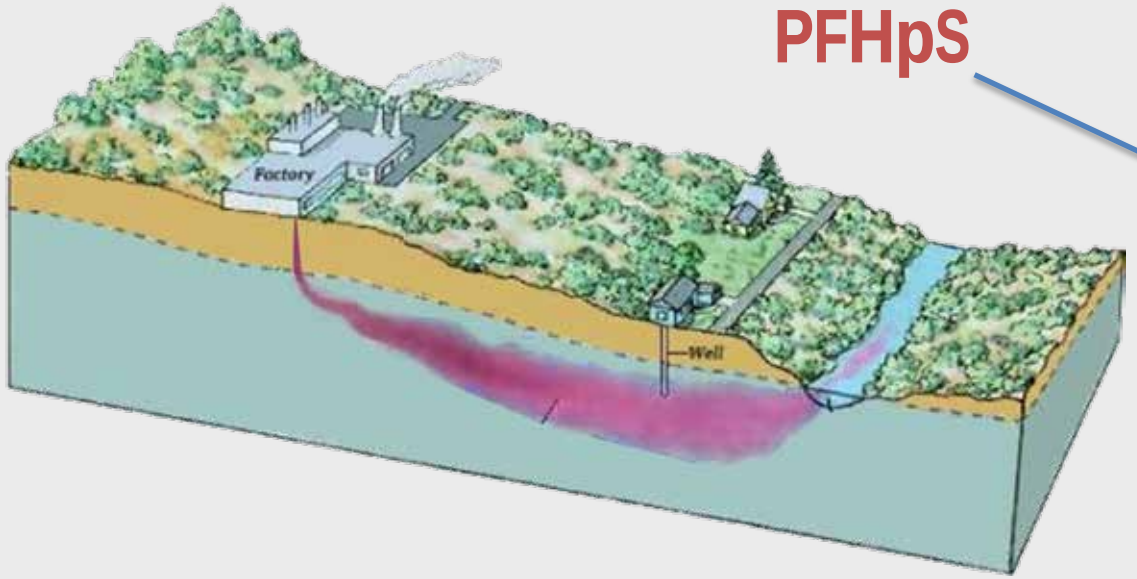


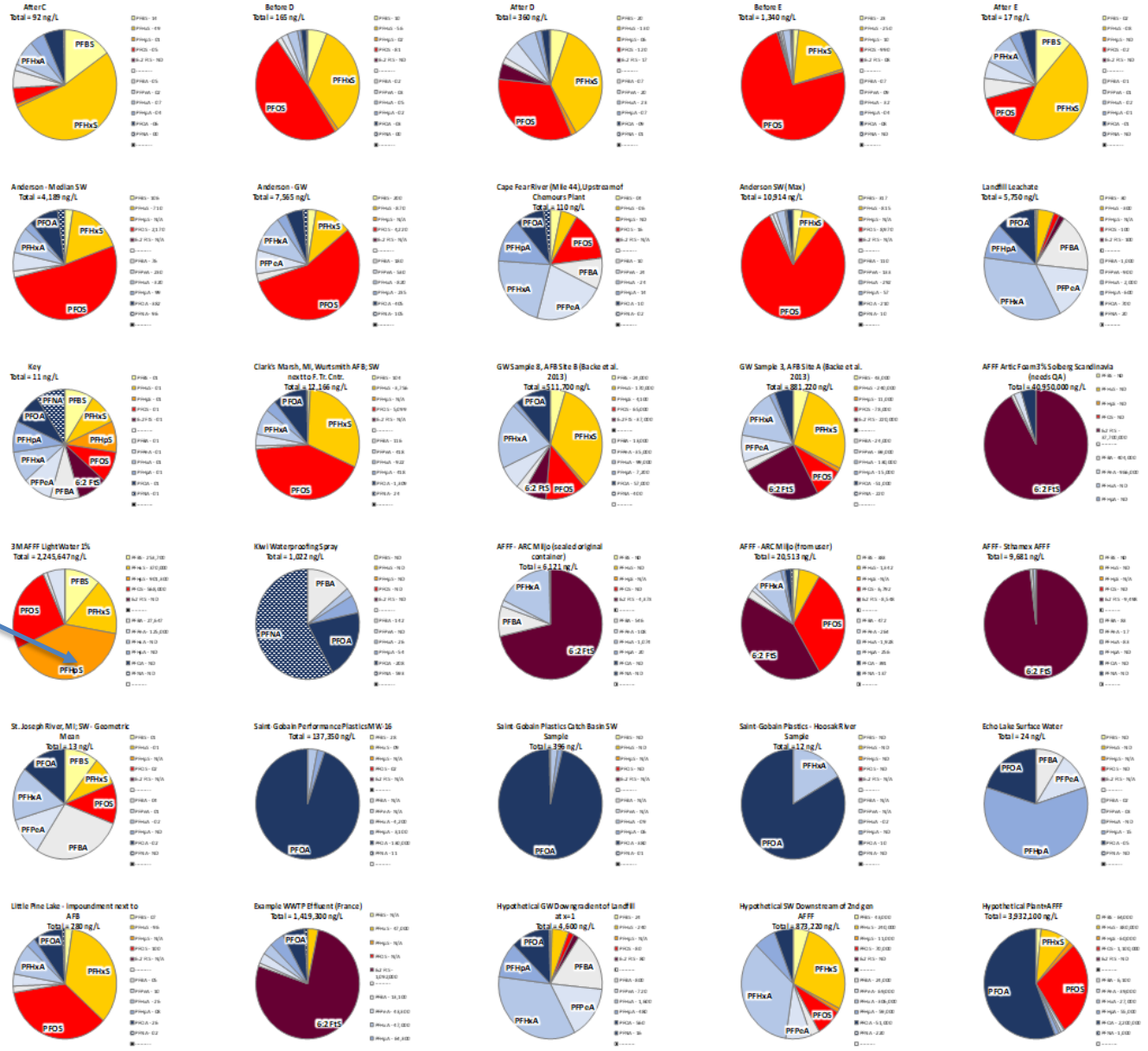
Terminal Perfluorosulfonic Acids (PFSAs)

Select Common Telomers *(transformable)*

Chemical Signatures

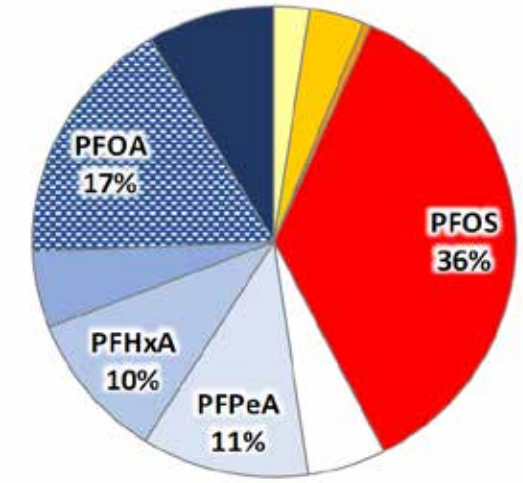
Signatures reflect various source and fate/transport scenarios



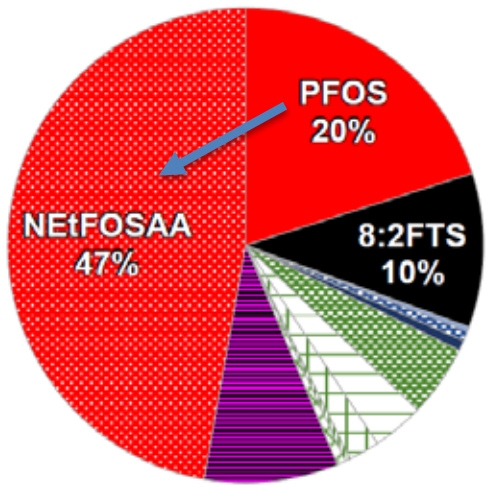


Example of PFAS Forensic Patterns

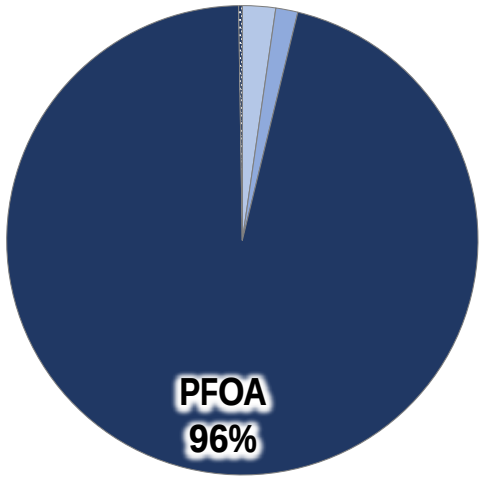
Car Detailing GW



Paper Mill Soil
Total = 572.04 ug/kg

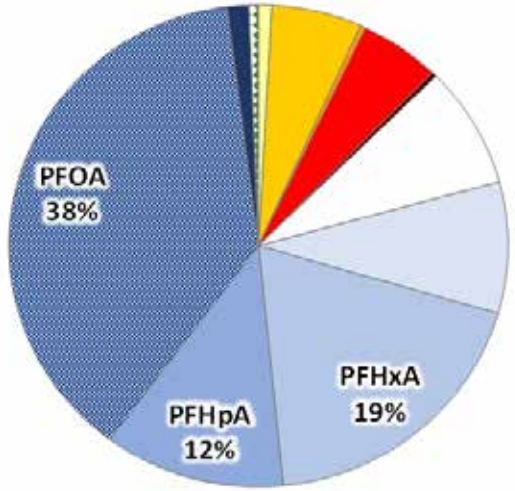


Plastic Manufacturing

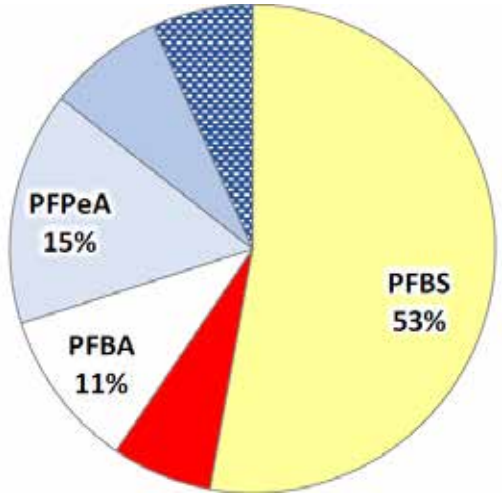


- PFBS - ND
- PFHxS - ND
- PFHpS - N/A
- PFOS - ND
- 6:2 FtS - N/A
- ---------
- PFBA - N/A
- PFPeA - N/A
- PFHxA - 09
- PFHpA - 06
- PFOA - 380
- PFNA - 01
- ---------

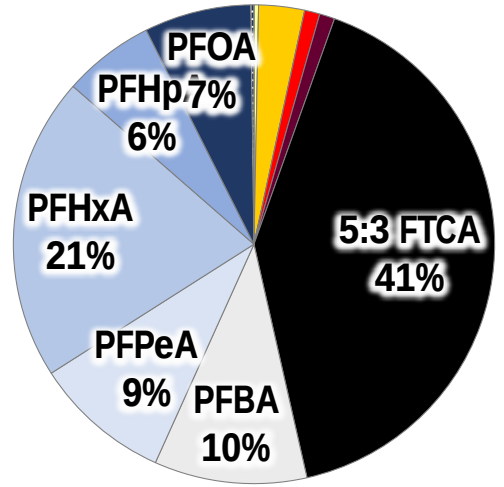
Landfill Groundwater



Private Septic GW



Landfill Leachate

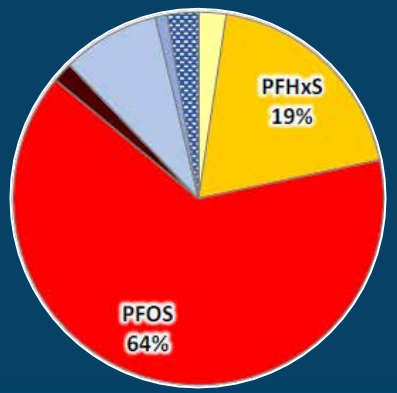


- PFBS - 30
- PFHxS - 300
- ---------
- PFOS - 100
- 6:2 FtS - 100
- 5:3 FTCA - 4,000
- PFBA - 1,000
- PFPeA - 900
- PFHxA - 2,000
- PFHpA - 600
- PFOA - 700
- PFNA - 20
- ---------

Types of Fluorine-Based AFFF

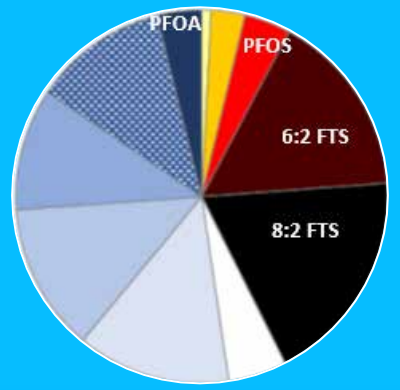
Legacy PFOS-based AFFF

- PFOS or PFOS "R" (PFOS with a functional group; PFOS derivative) based
- Developed in 1960s
- Production ended in 2002
- **Contains PFOS & PFHxS; ratios may vary**



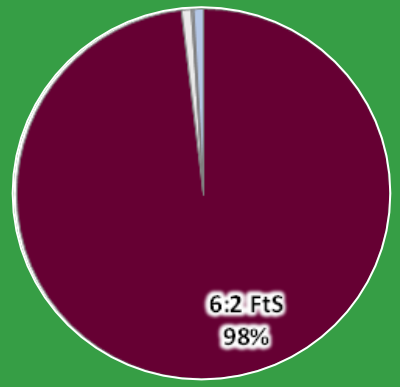
Legacy Fluorotelomer-based AFFF

- Sold from 1970s - 2016
- Mixture of 6:2 FTS and 8:2 FTS
- Fluorotelomer sulfonates can break down to PFCAs
- **Long-chain fluorotelomers (8:2 FTS) can breakdown to PFOA**

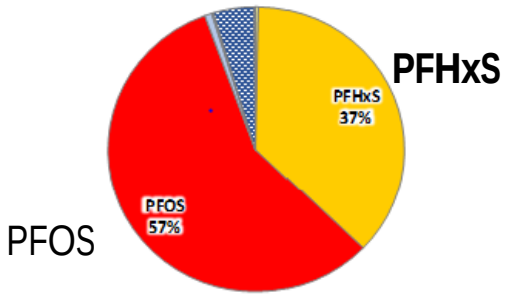


Modern Fluorotelomer AFFF

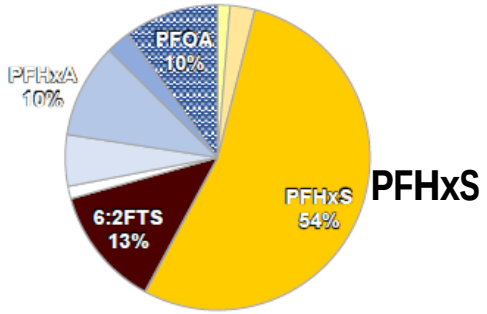
- 2010-Present
- Short-chain fluorotelomer sulfonates (6:2 and 4:2 FTS)
- Can breakdown to shorter chain PFCAs (PFBA, PFPeA, PFHxA, 5:3 FTCA)



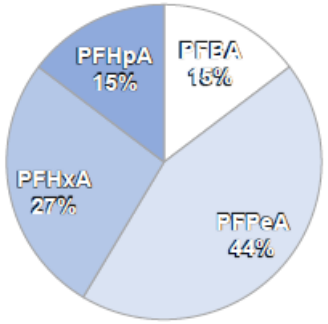
1st Generation
PFOS Based AFFF
2000



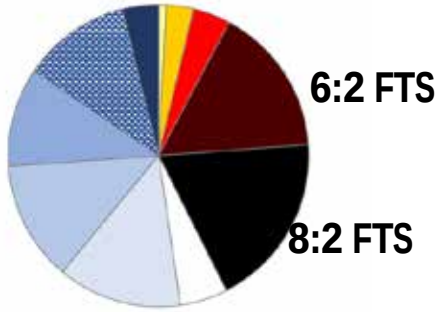
2nd Generation
PFHxS Based AFFF
2008



Clean C6 Soluble
Downgradient GW

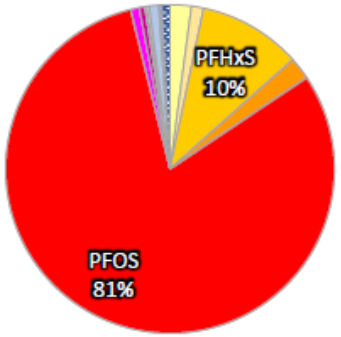


2nd Gen SW Impacted
by Hist 1st Gen Release



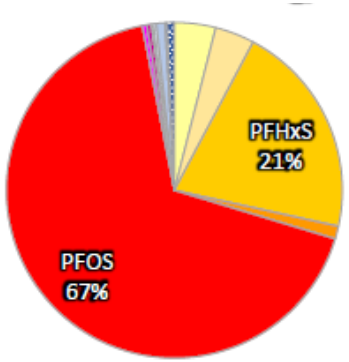
3M AFFF Formulations 1989 to 2001

1989



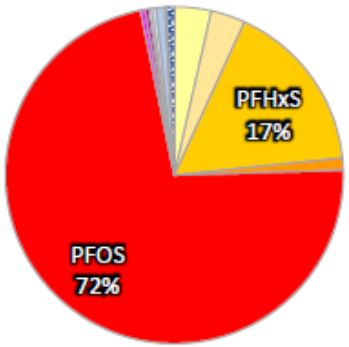
PFOS/PFHxS = 8.1

1993



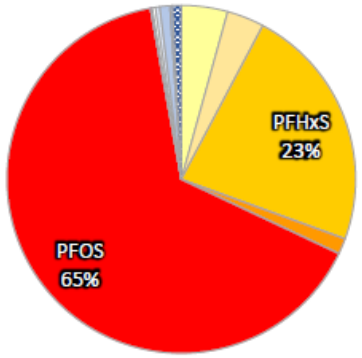
3.2

1993



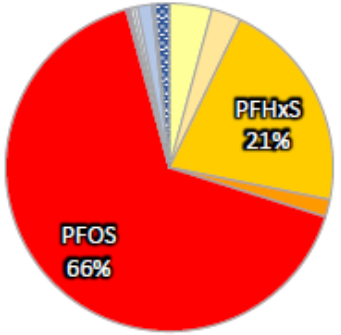
4.2

1998



2.8

2001

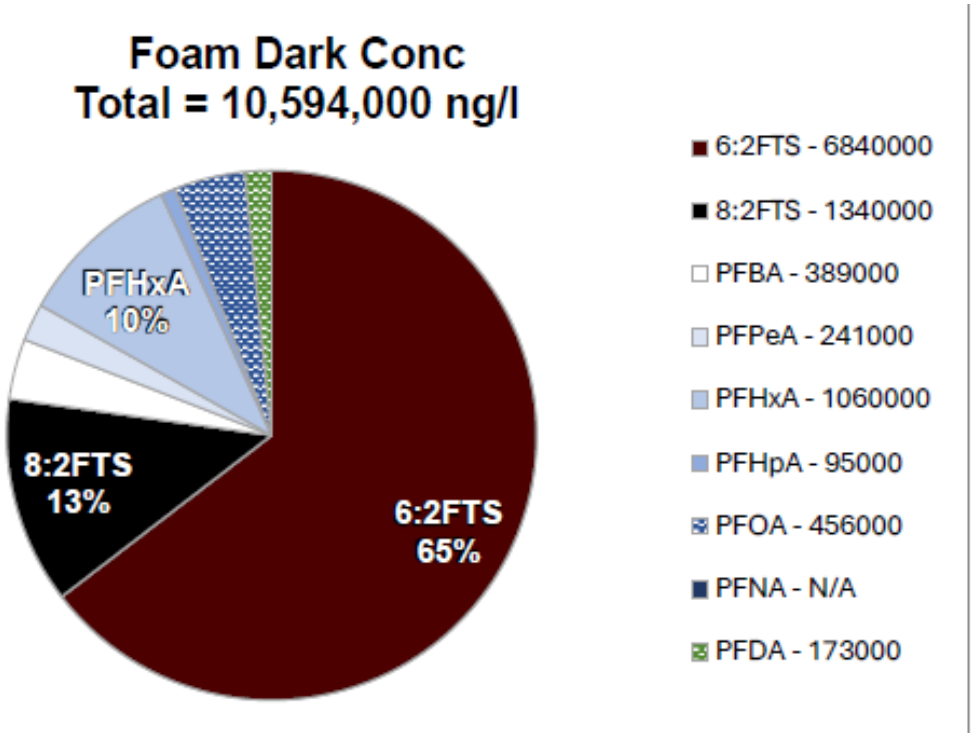


3.1

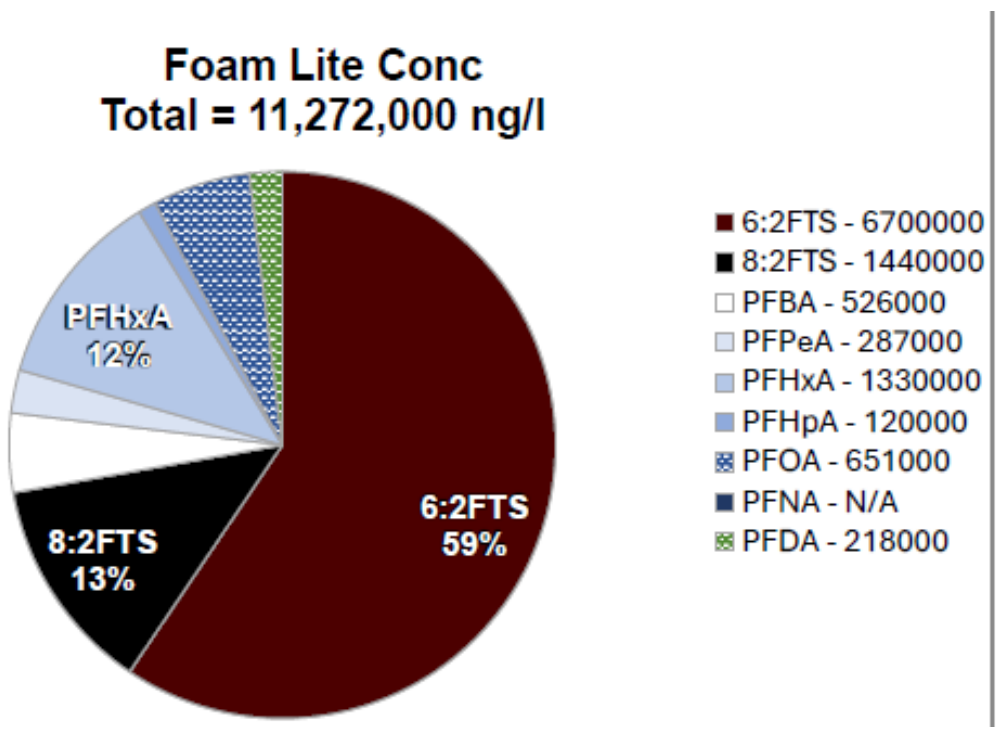
PFOS/PFHxS ranged from 2.4 (release 1996) to 4.2 (release 1990) Airport Surface Water

Poll Question

AFFF Samples Collected from Hangar



PFHpA 95,000 ng/l
PFOA 456,000 ng/l
Total Detected Appr 11 mg/l



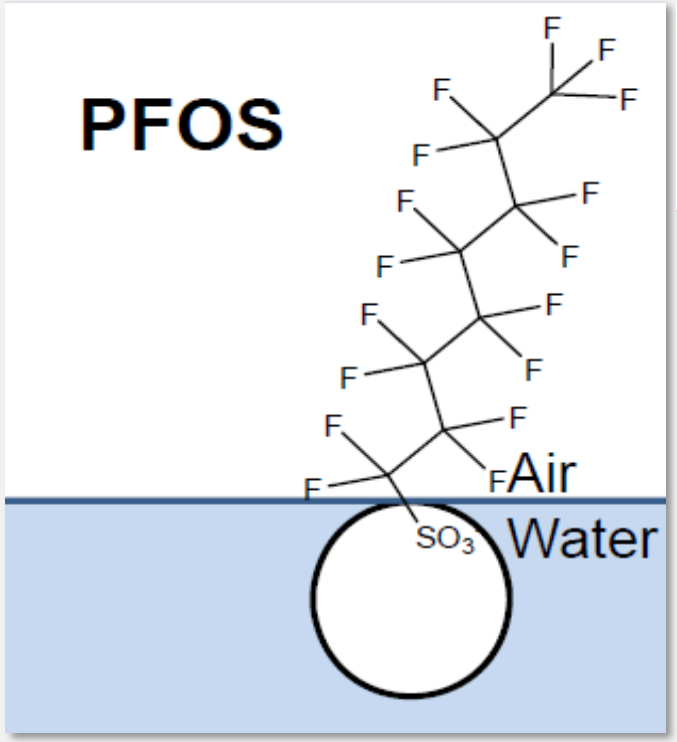
PFHpA 120,000 ng/l
PFOA 651,000 ng/l
Total Appr 11 mg/l

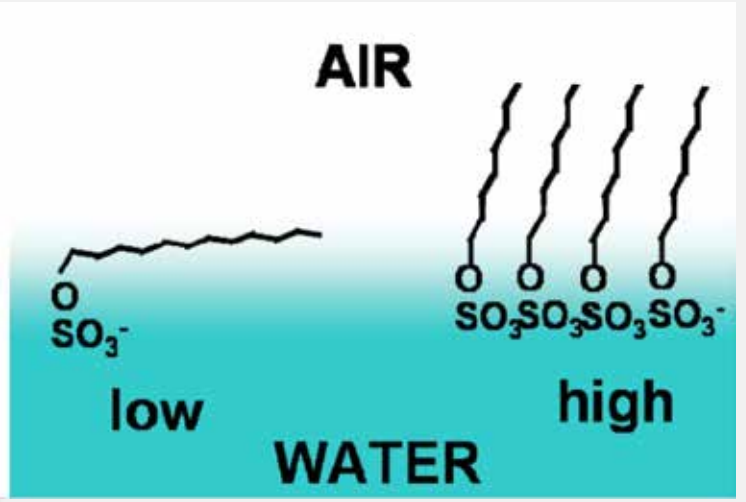
Typical Total PFAS in AFFF ranges from 1% to 5% (10,000 to 50,000 mg/l) missing PFAS mass is the unreported parent compounds 6:2FTSR and 8:2 FTSR

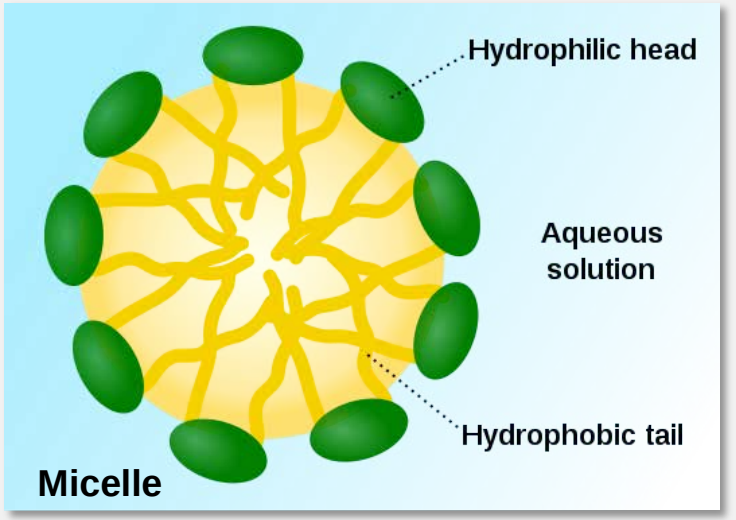
Sampling Procedures & Forensic Considerations

PFAS Properties Affecting Fate & Transport: Partial Hydrophobicity & Surface Partitioning

- Under static conditions PFAS may loosely associate on the water surface and partition between the air/water interface (invisible sheen)
- **AFFF PFAS was designed specifically for this physical property**
- Molecules may self-associate and form micelles with agitation resulting in foaming
- Hemi-micelle soil surface trapping



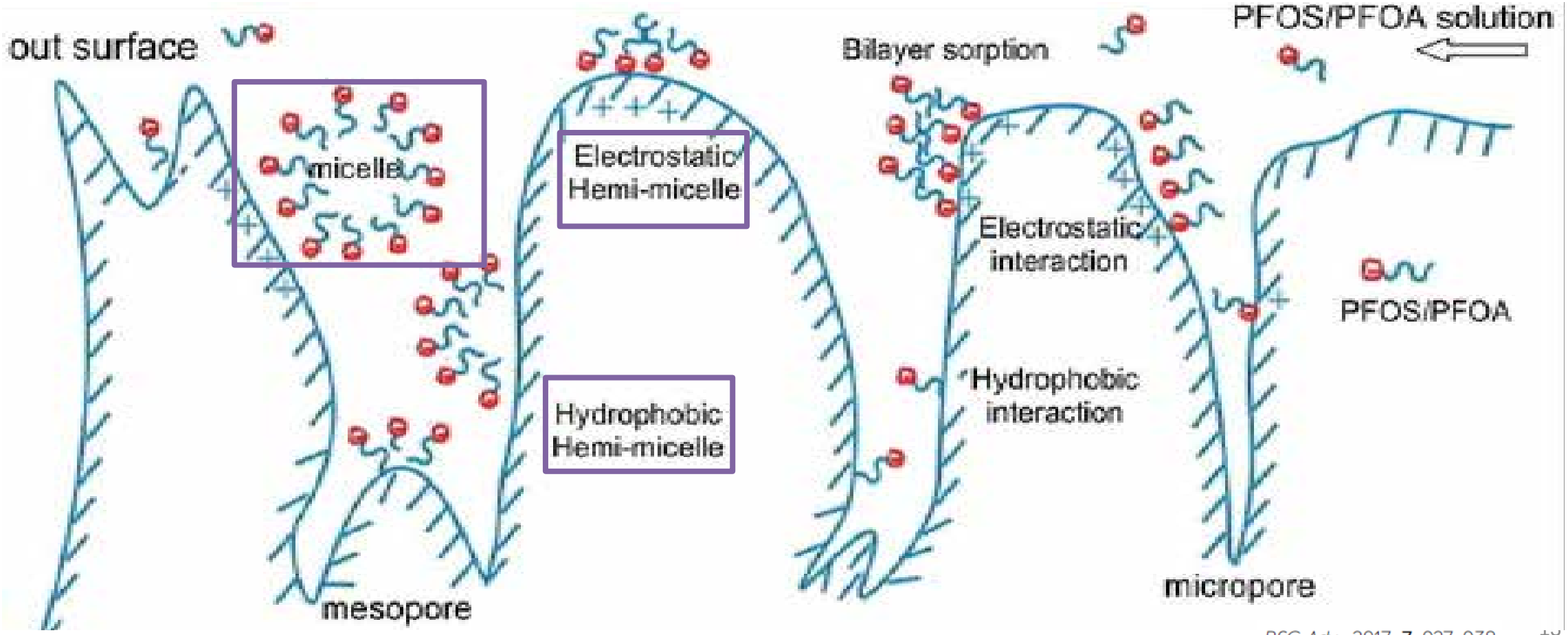




Micelles and Hemi-micelles

Vacuum enhanced lysimeter sampling will probably POP the bubbles releasing far more PFAS than is mobile

AVOID Vacuum Enhanced Lysimeter Sampling



RSC Adv., 2017, **7**, 927–938

Solids in Aqueous Samples

Fate & Transport: Sorption of PFAS to particulates or solids.
Longer-chain PFAS and PFSAs tend to absorb more to solids/particulates.

Aqueous samples with high levels of solids

- PFAS concentrations may vary or not be representative
- Resulting fingerprints or signatures may vary or not be representative

PFAS concentrations and PFAS signatures on samples with elevated solids can be dependent on how lab handles sample.

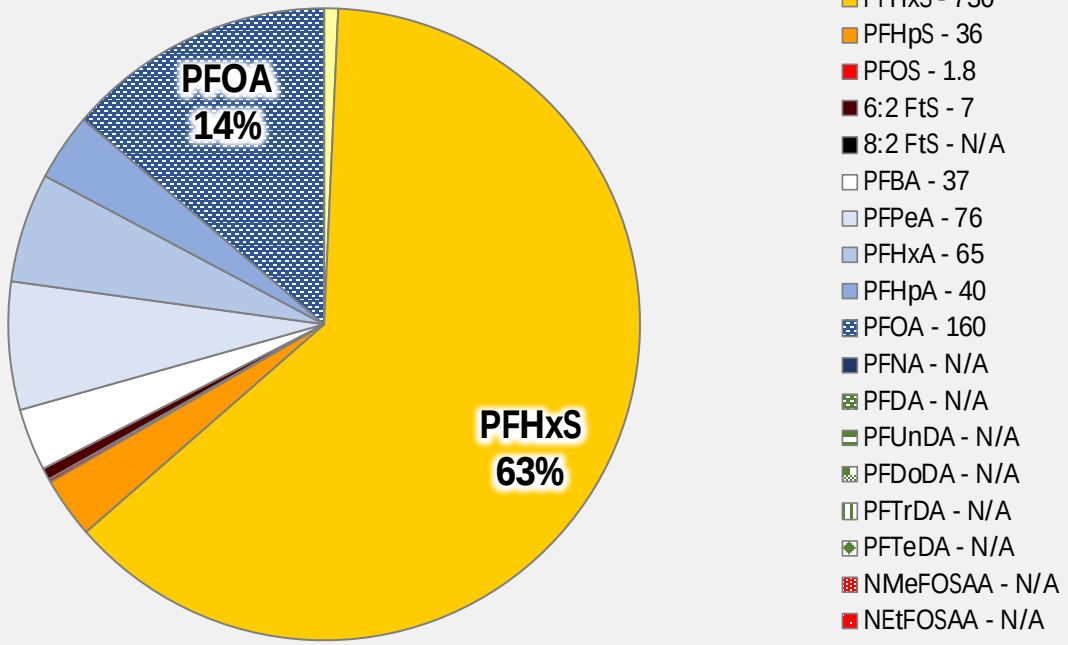
Example PFSAs: PFHxS, PFHpS, PFOS
PFSA = Perfluorosulfonic Acids

Example Longer chain PFCAs: PFOA, PFNA, PFDA
PFCAs = Perfluorocarboxylic Acids

High Biased PFAS Results – Turbidity (AFFF Source)

Turbidity 1000 NTU

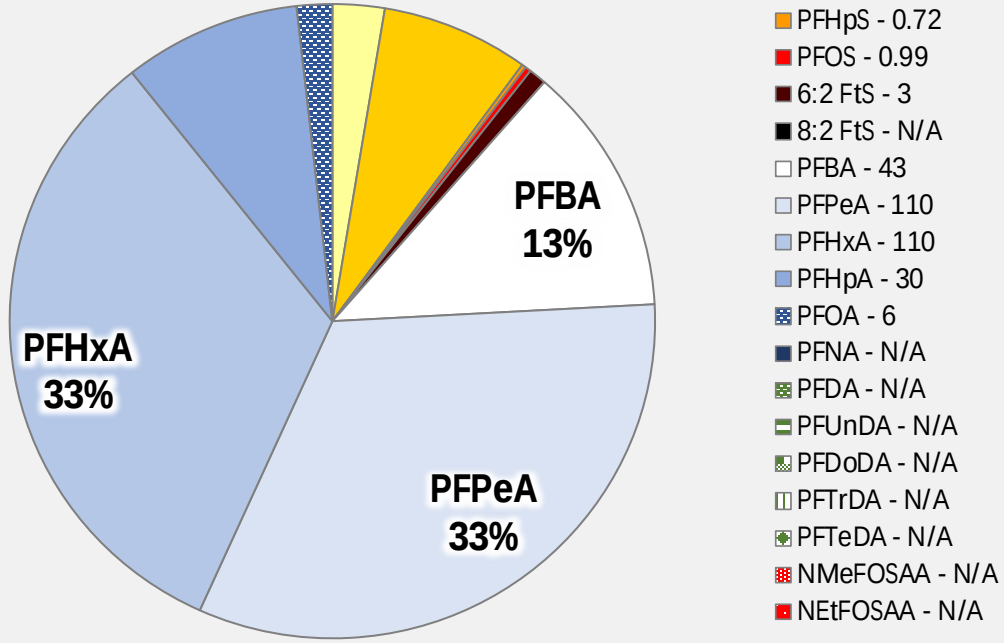
Total – 1,161 ng/L



Total PFAS	1,161 ppt
PFHxS	730 ppt
PFOA	**160 ppt**

Turbidity 25 NTU

Total – 338 ng/L



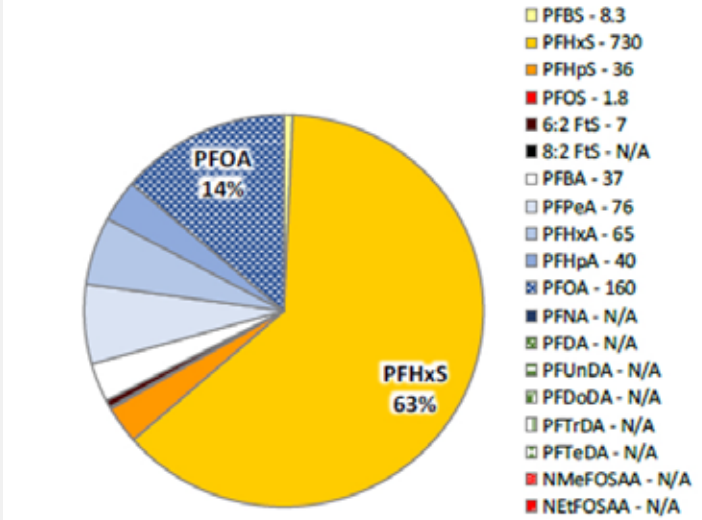
Total PFAS	338 ppt
PFHxS	25 ppt
PFOA	6 ppt

PFOA MCL
10 ppt

PFAS Concentrations and PFAS Signatures Affected by Turbidity

From Turbid to Clear (>10 NTU) to (< 10 NTU)

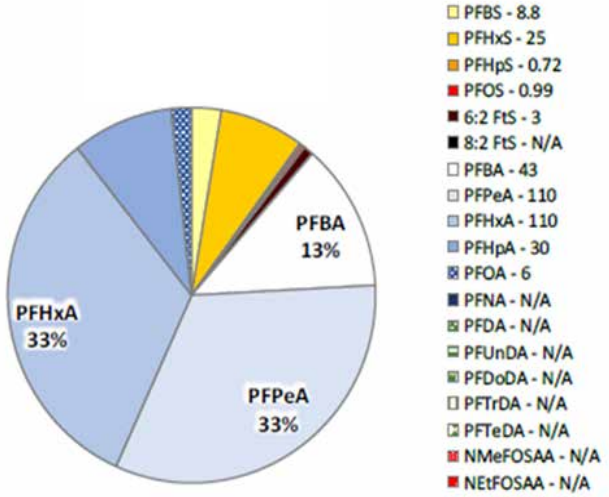
Sample from 1" temporary well turbid



PFOA	160 ppt
PFHxS	730 ppt
Total	1,161 ppt

>1000 NTU

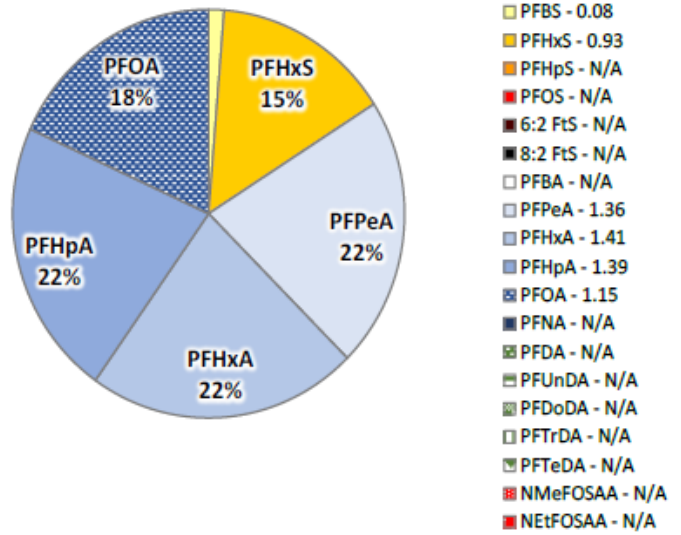
Sample from 2" developed MW clear



PFOA	6 ppt
PFHxS	25 ppt
Total	338 ppt

25 NTU

Sample from 2" grab sampler

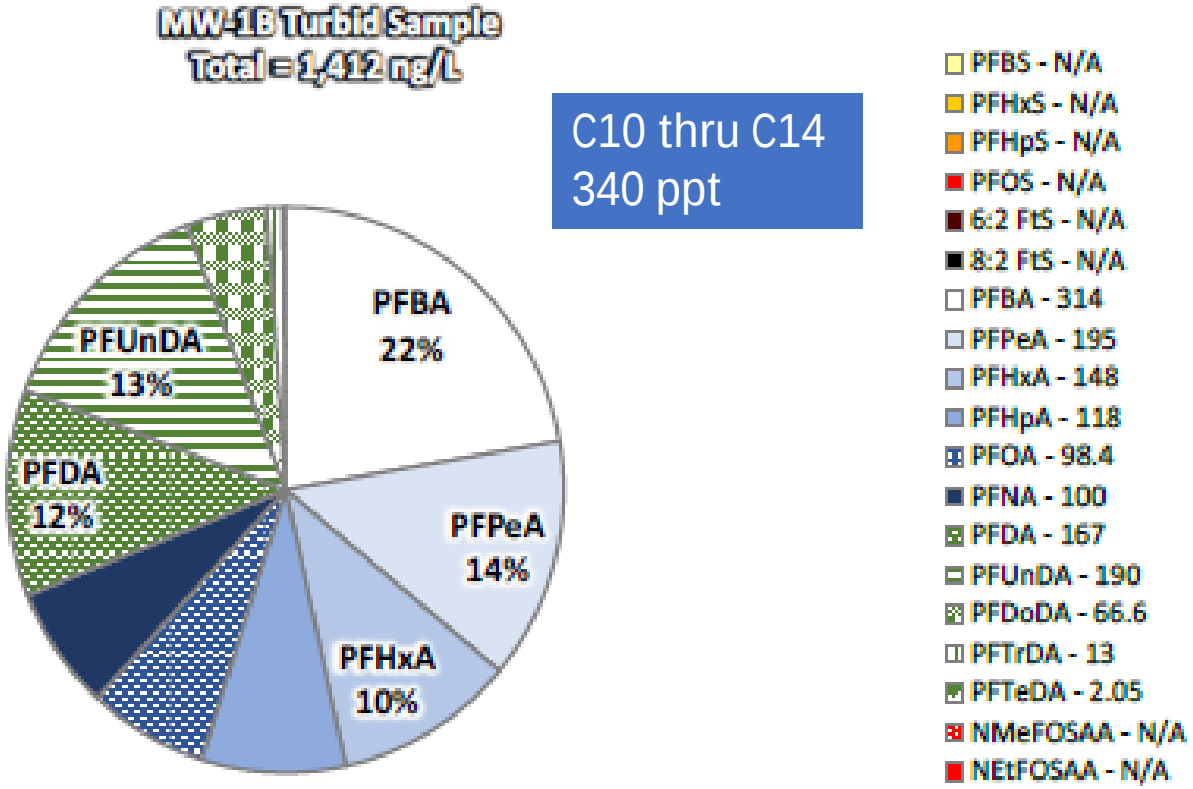


PFOA	1.1 ppt
PFHxS	1.0 ppt
Total	7.0 ppt

2 NTU

High Biased PFAS Results – (PFCA Manufacture)

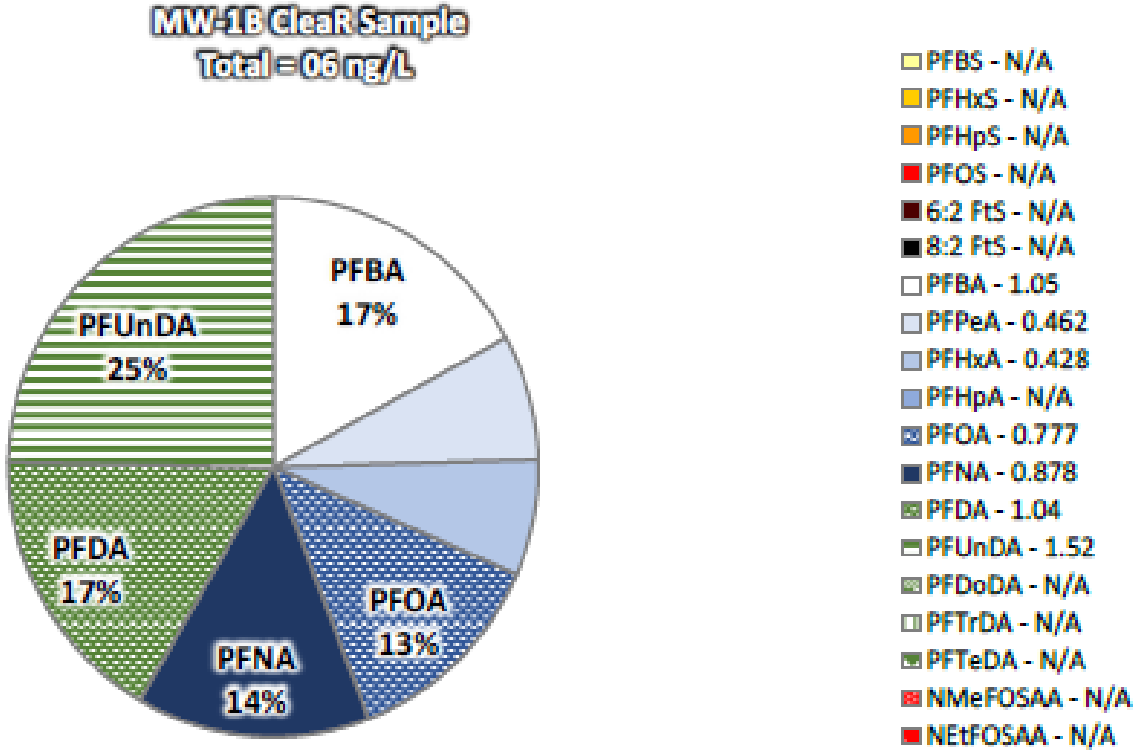
Turbidity 830 NTU



C10 thru C14
340 ppt

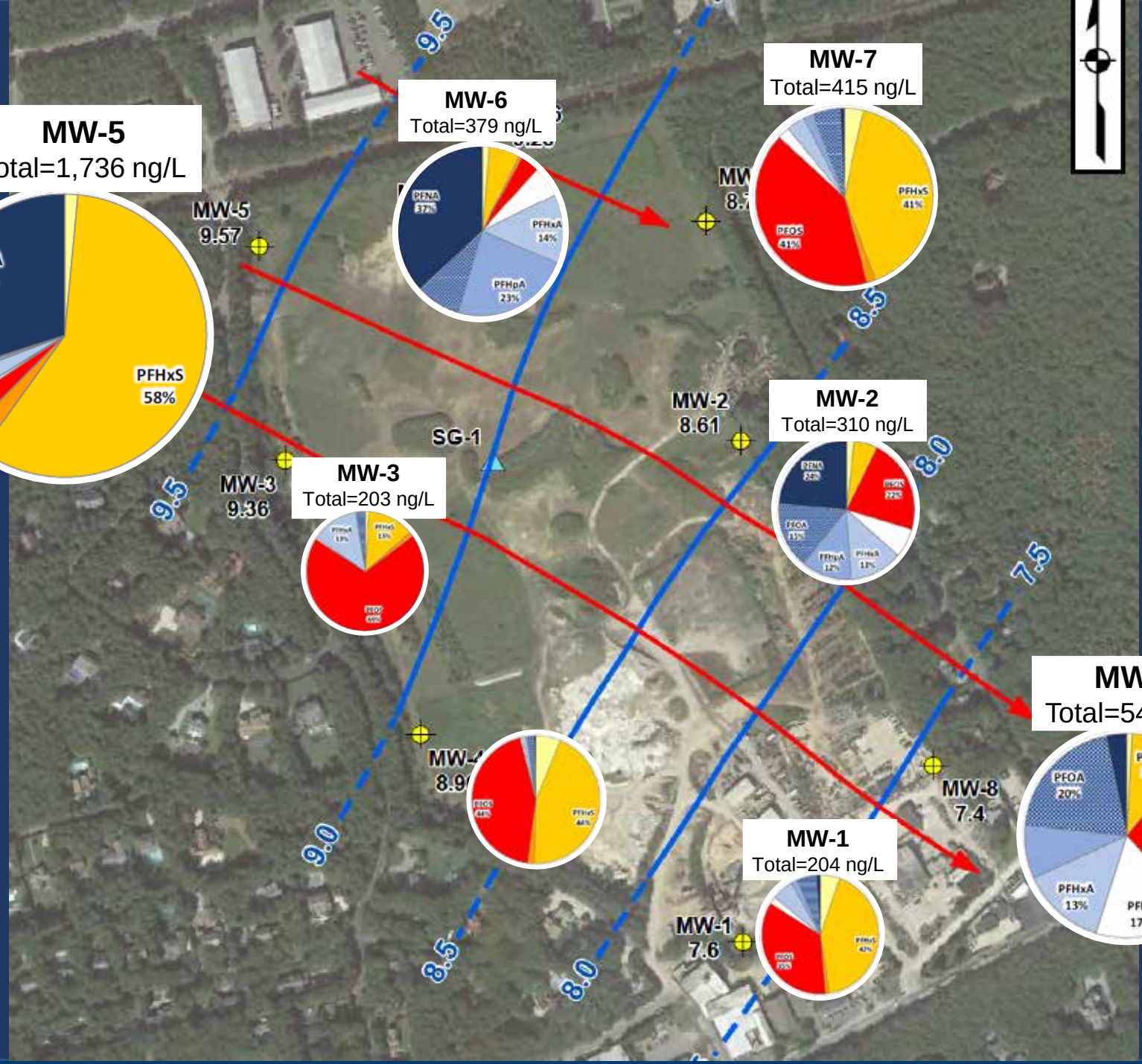
Total PFAS 1,412 ppt
PFOA 160 ppt
PFNA 100 ppt

Turbidity 18 NTU



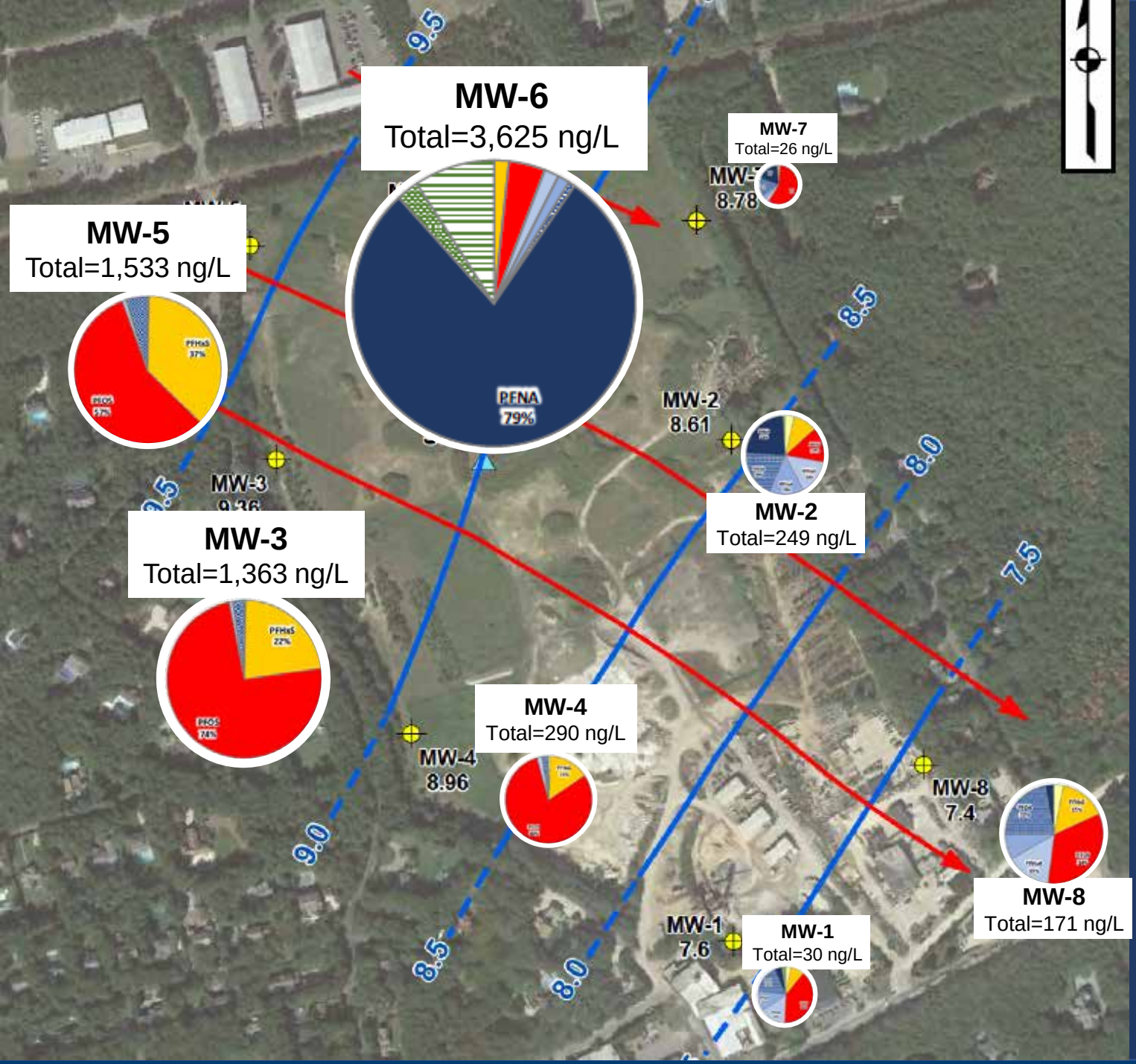
Total PFAS 6.0 ppt
PFOA 0.777
PFNA 0.878

PFOA & PFNA MCLs as low as 4 ppt



1st Round Collected with Bailer

June 2018 Alpha report

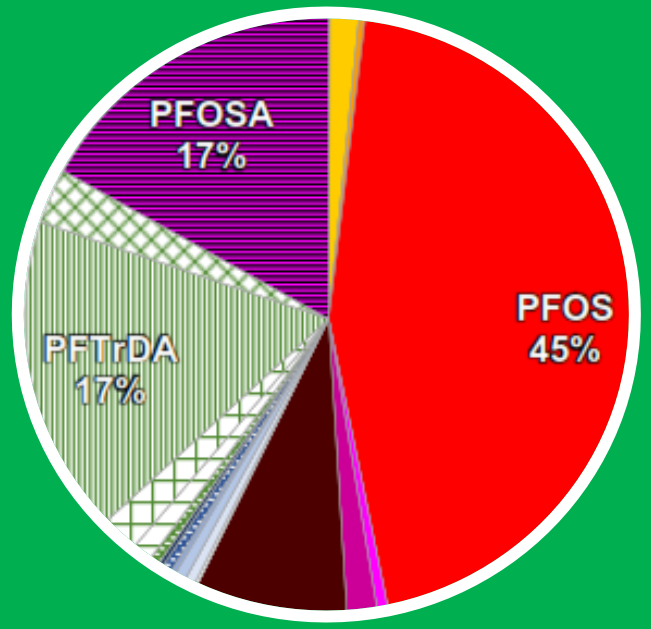


Second Round

Low flow sampling; no turbidity criteria; less than 3 volumes purged

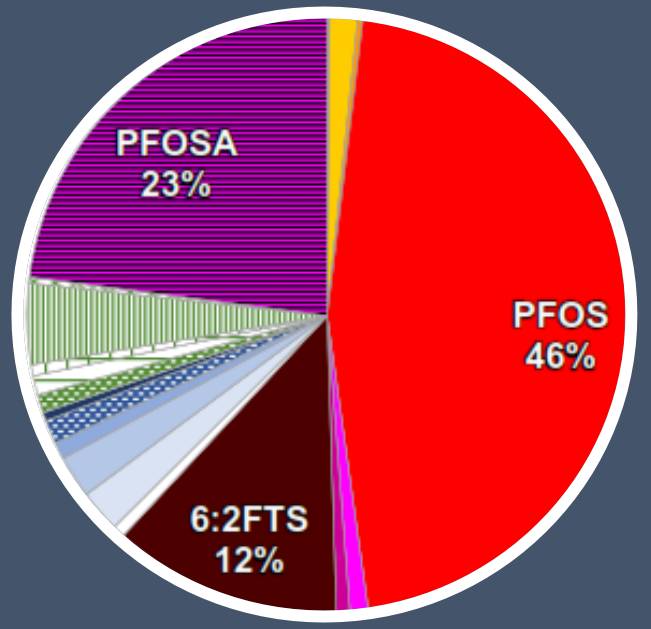
Fire Training Area Surface Soil – Exposed to Elements for > 20 Years

SOLVENT EXTRACTION
Surface Soil
Total = 289.84 ug/kg



31 ug total PFAS mass extracted from 100 g of soil

WATER EXTRACTION (SPLP)
Surface Soil
Total = 4359.5 ng/L



10 ug total PFAS mass leached from 100 g of soil

- 30% of PFAS mass flushed off soil during SPLP mixing
- Well installation will also disturb soil and increase flushing of insoluble PFAS from smear zone soils into sampled water

PFAS F&T Properties & Forensic Considerations

Need to Consider Fate and Transport Phenomena

Transformation

Retention of PFAS in source area soil

Chemical retardation due to sorption to organic carbon

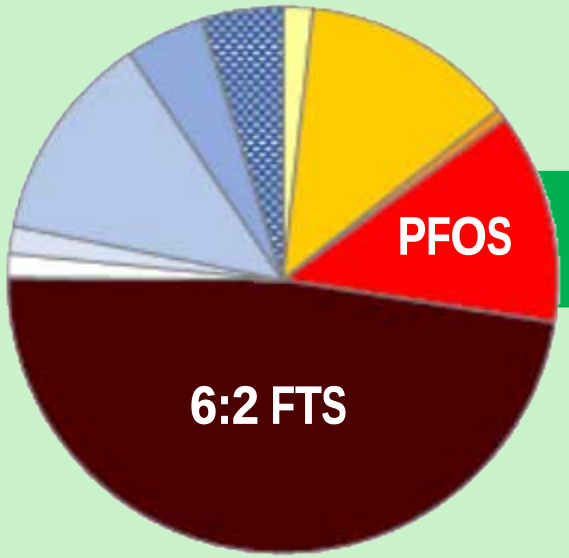
Preferential adsorption of linear isomers

PFAS persistence

Mixing/Dilution/ Co-mingling

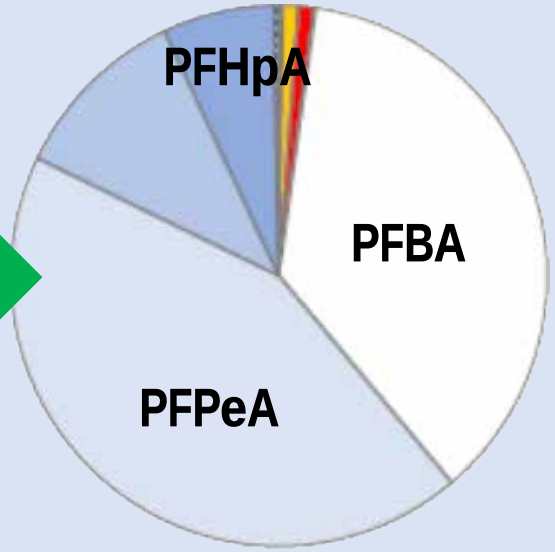
Fate & Transport: C6 PFAS Transformation

Pre-TOP Assay
Total PFAS **100,000 ng/L**



Accelerated Weathering

Post-TOP Assay
Total PFAS **1,200,000 ng/L**



Concentrations ng/L	Pre-TOP	Post-TOP
6:2 FTS	40,000	1,000
PFOS	10,000	11,000
PFPeA	1,300	520,000
PFBA	1,100	400,000
PFHpA	4,000	80,000

Issue: Thousands of PFAS **precursor** compounds can transform in the environment to the persistent PFAS

Example Polyfluoroalkyl Precursors:

- N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)
- N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)
- 6:2 Fluorotelomer sulfonic acid (6:2 FTSA)
- 8:2 Fluorotelomer sulfonic acid (8:2 FTSA)
- 4:2 Fluorotelomer sulfonic acid (4:2 FTSA)
- 10:2 Fluorotelomer sulfonic acid (10:2 FTSA)
- N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)
- N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)
- N-Methyl perfluorooctane sulfonamide (MeFOSA)
- N-Ethyl perfluorooctane sulfonamide (EtFOSA)

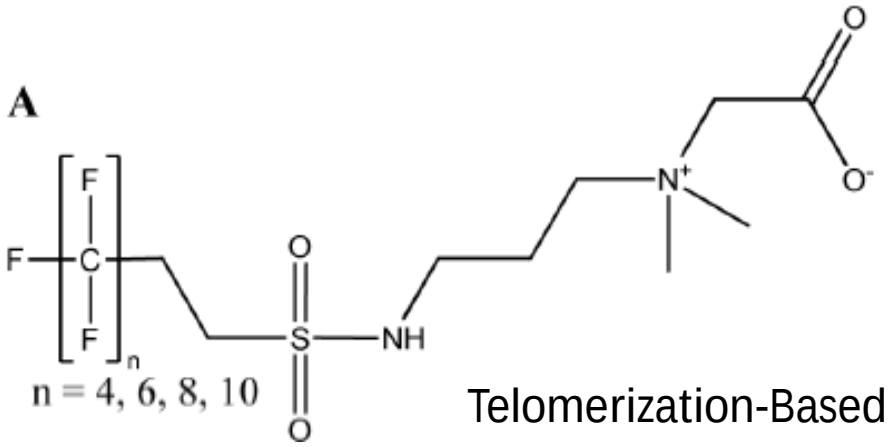
TOP = Total Oxidizable Precursor

Rules of Thumb

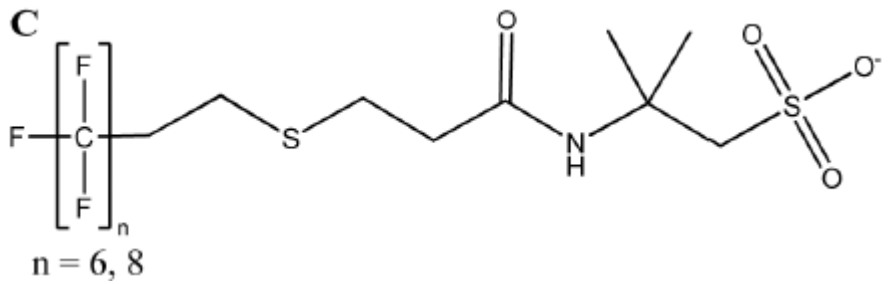
6:2 FTS → PFBA, PFPeA, PFHxA, PFHpA

8:2 FTS → PFBA, PFPeA, PFHxA, PFHpA, PFOA

Telomerization-Based Fluorinated Surfactants Parent Compounds

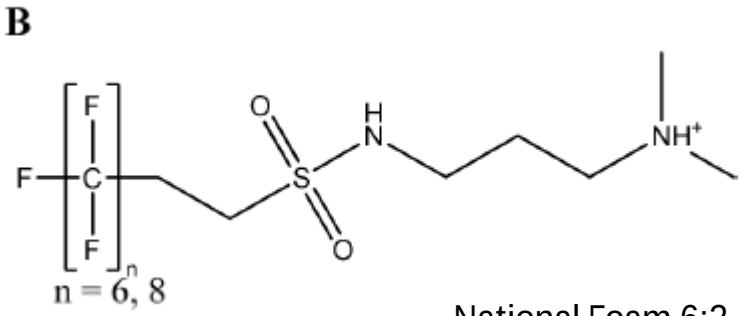


National Foam 4:2, 6:2, 8:2, 10:2 fluorotelomer sulfonamide with dimethyl quaternary amine and carboxylic acid functional groups



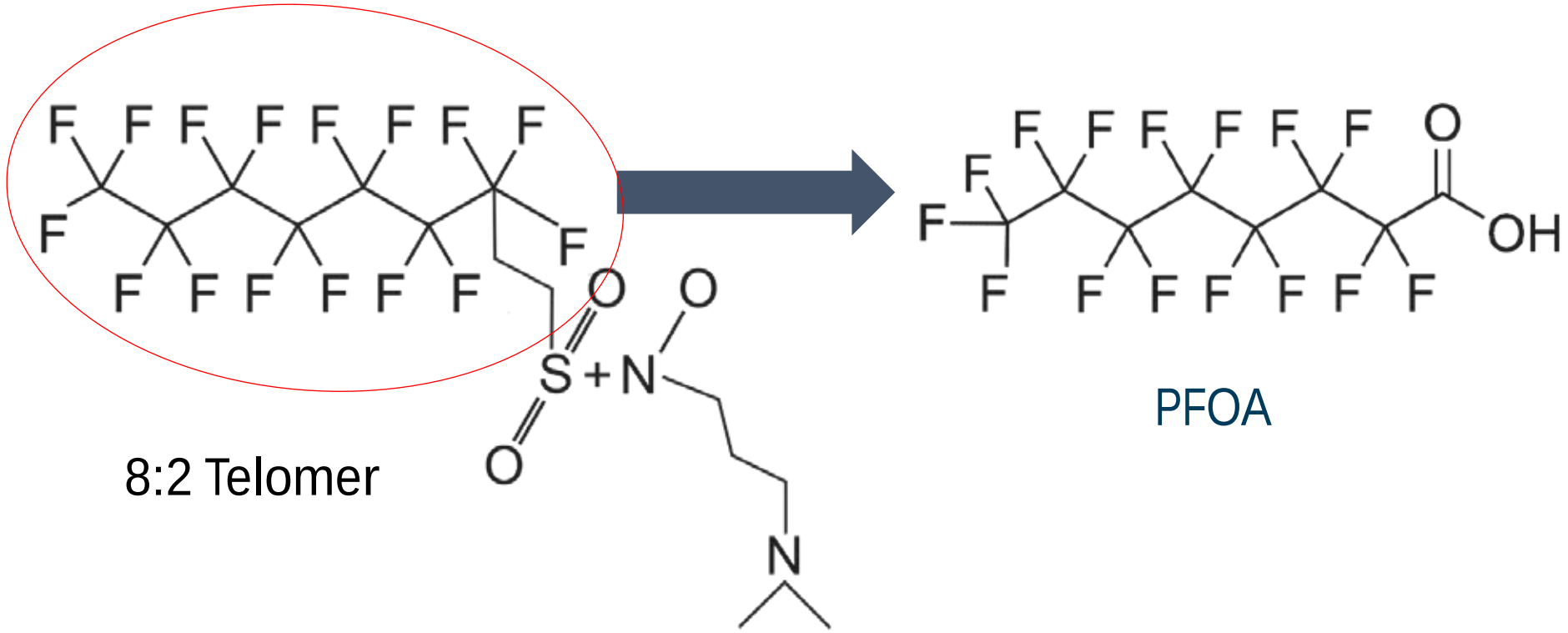
Chemguard / Angus / Ansul 6:2, 8:2 fluorotelomer thioether amido sulfonate

Telomerization-Based Fluorinated Surfactants



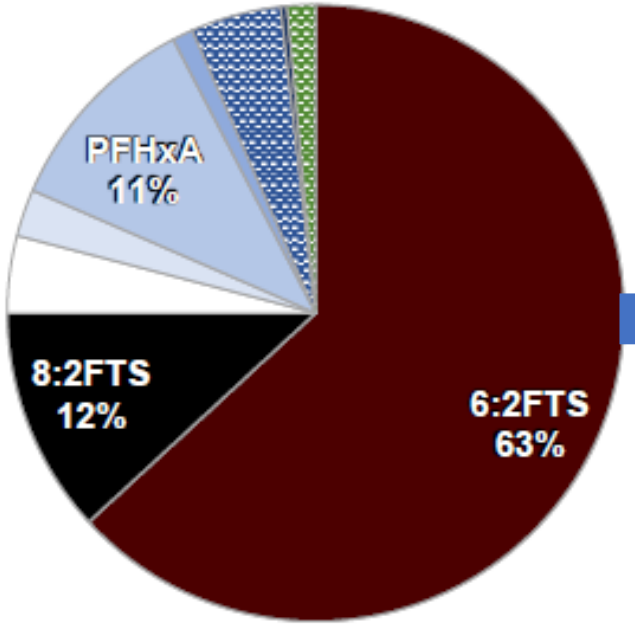
National Foam 6:2, 8:2 fluorotelomer sulfonamide with dimethyl quaternary amine without terminal acetic acid functional group

Transformation of Poly-Fluoroalkyl Substances to PFOA



Fate & Transport: 2nd Generation AFFF PFAS Transformation

Foam Lite Conc Pre
Total = 10,134,000 ng/l

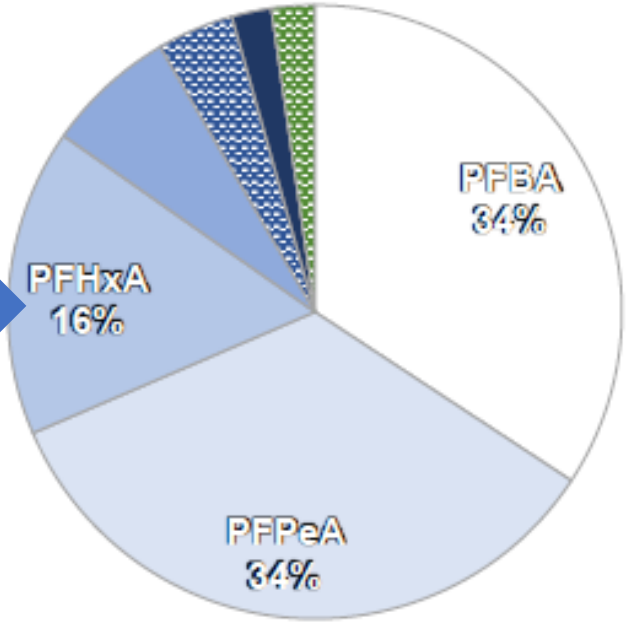


PFHpA 110,000 ng/l
PFOA 480,000 ng/l
Total 10,134,000 ng/l

Complete transformation
strong oxidation (TOP assay)

Under natural aerobic conditions
transformation occurs but at slower rate

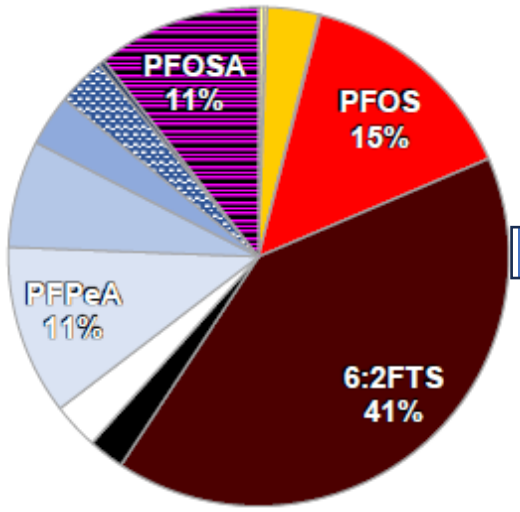
Foam Lite Conc Post
Total = 3,210,000,000 ng/l



PFHpA 220,000,000 ng/l (2,000 x)
PFOA 130,000,000 ng/l (270 x)
Total 3,210,000,000 ng/l (320 x)

Actual total PFAS concentration is 3,210 mg/l
Majority is 6:2FTSR (parent compound) with lessor amounts of 8:2 FTSR

MW-2

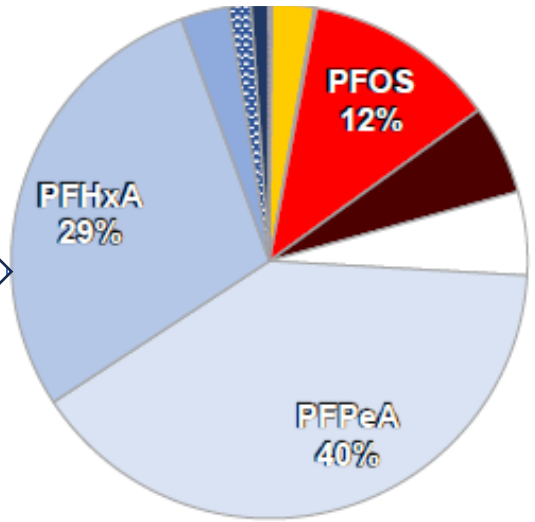


Foam Dark Conc
Total = 10,594,000 ng/l

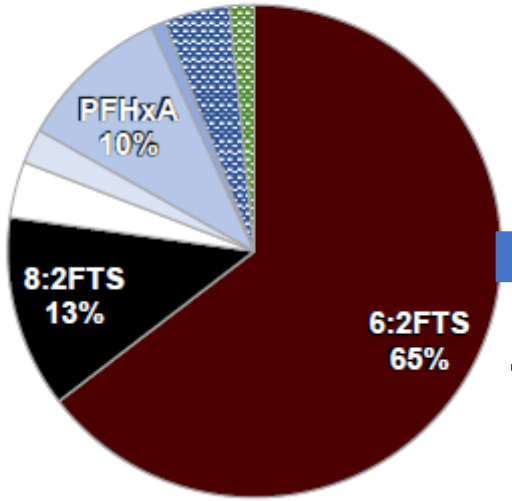
GW Flow

Natural Telomer Transformation

MW-7

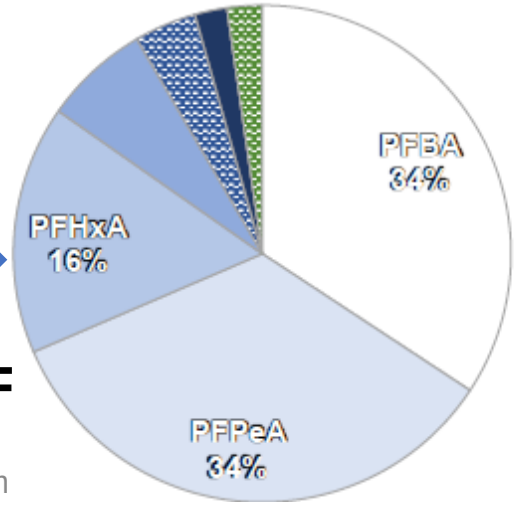


Foam Lite Conc Post
Total = 3,210,000,000 ng/l



Pre & Post TOP Assay Results

Accelerated Telomer Transformation of Source AFFF

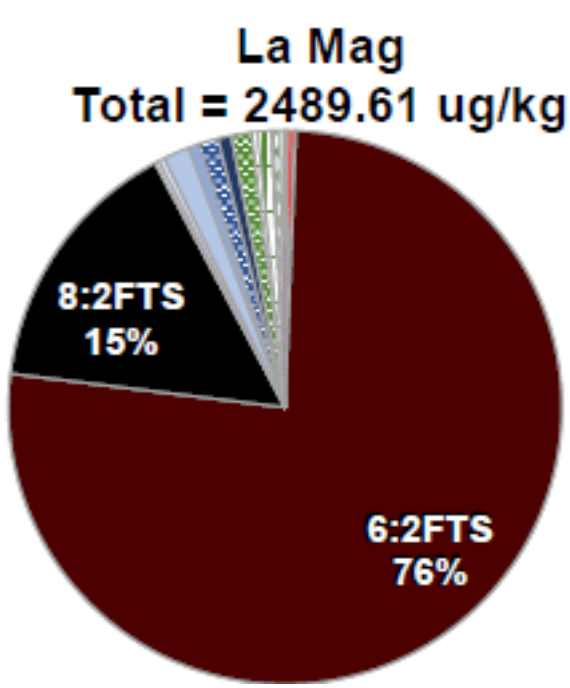


TRCcom

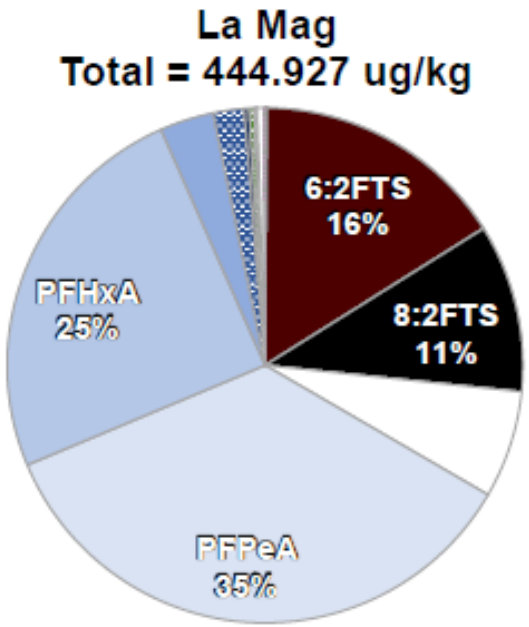
Fate & Transport: 2nd Generation AFFF PFAS Transformation

Under natural mildly oxidizing conditions only minor concentrations of PFBA formed compared to the much larger % of PFBA formed after TOP assay

Example of 2nd Gen AFFF Natural Transformation in GW: La Magnetic Rail Accident 2nd Generation Telomer Based AFFF



GW Flow



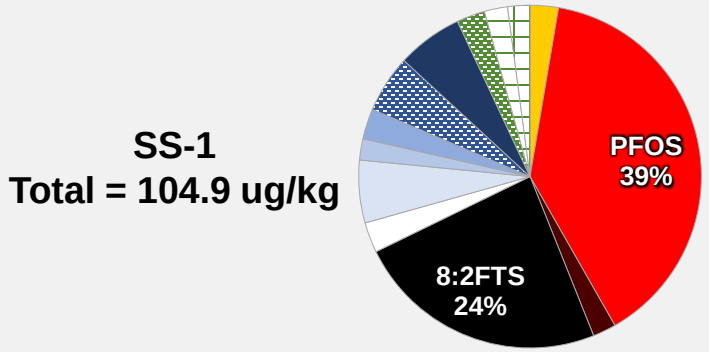
Near Source GW (anaerobic)

Downgradient GW (aerobic)

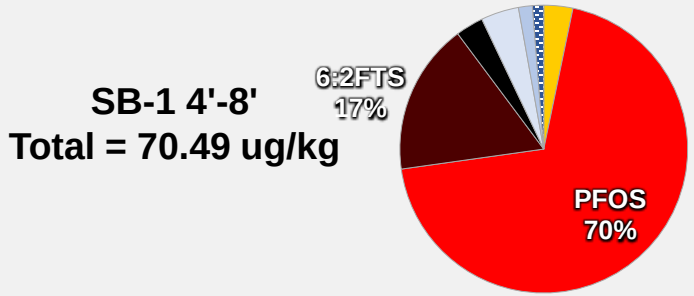
Preferential Migration of the More Soluble Branch Chained PFOS Isomers

Telomer transformation products in surface soil – equilibrium between generation and flushing of the far more soluble trans products

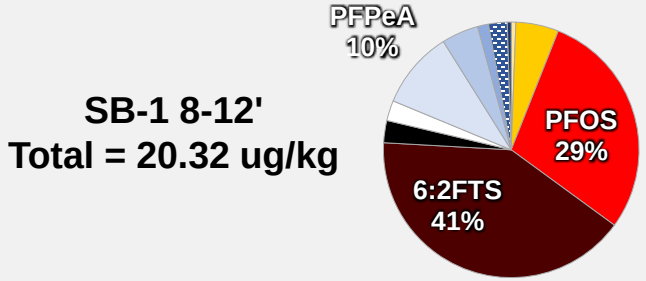
8:2 FTS AFFF
less penetration into soil column and similar F&T properties as PFOS so probably released after PFOS -AFFF



PFOS
Linear 93%
Branched 6%



PFOS
Linear 84%
Branched 16%



PFOS
Linear 69%
Branched 32%

0’

Depth (ft)

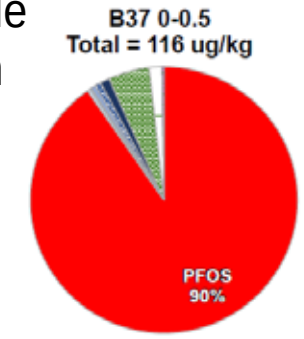
32’

Normal PFOS Isomer Trend PFOS is enriched with the more mobile branch chained isomers with depth

Parent Compound Trans & Preferential Migration of the More Soluble PFAS

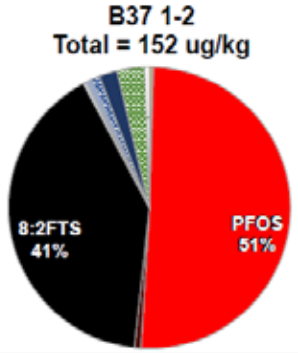
Sample Depth

0.5’

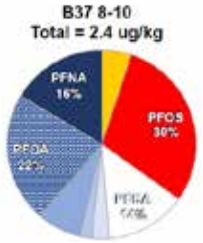


1 – 2’

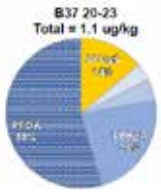
8 – 10’



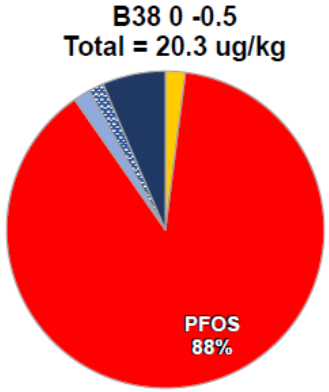
20 – 21’

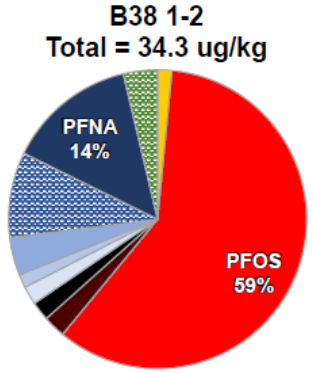


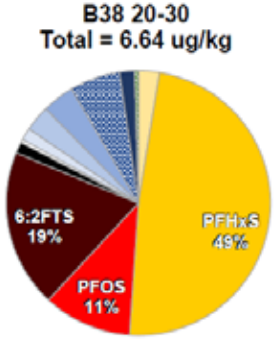
20 – 30’



Complexity of PFAS leaching factors under natural condition is extremely complex, current laboratory analytical leaching tests were not designed, tested, and/or certified by anyone – research is ongoing







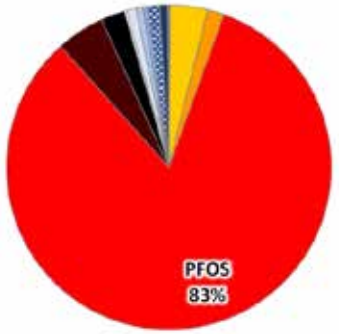
PFOS / PFHxSA AFFF mix?

PFHxSA low solubility

Aerobic Transformation

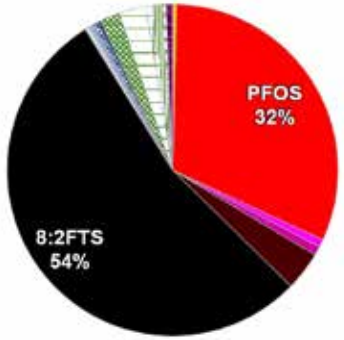
To PFHxS soluble

FTA 1990s to Mid 2000s 1st and 2nd Generation AFFF (100 feet)



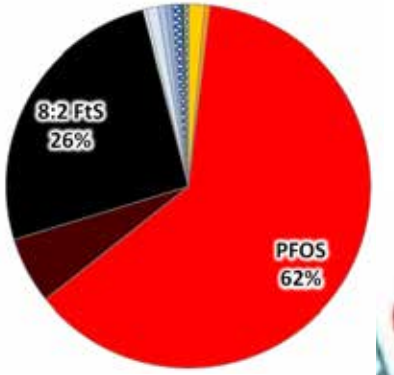
Surface Soil

Aerobic shallow telomers transformation



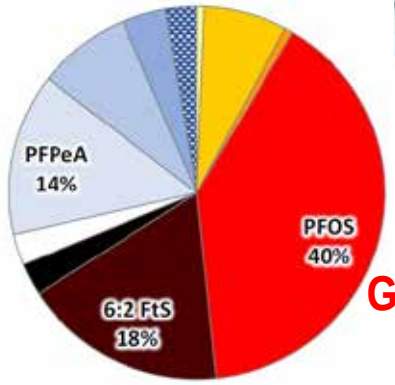
Sub Slab Soil

Anaerobic – from residual HCs and cover stable telomers

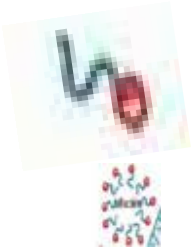


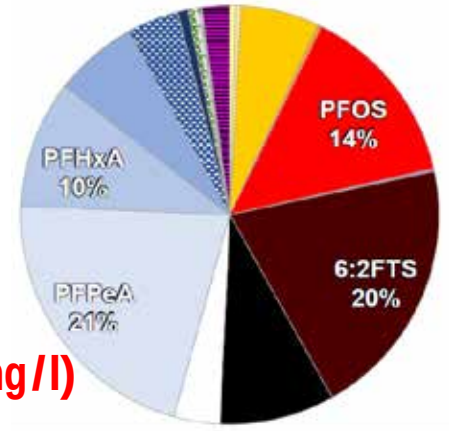
Soil Smear Zone

ND



Partitioning of Micelles to hydrated molecules





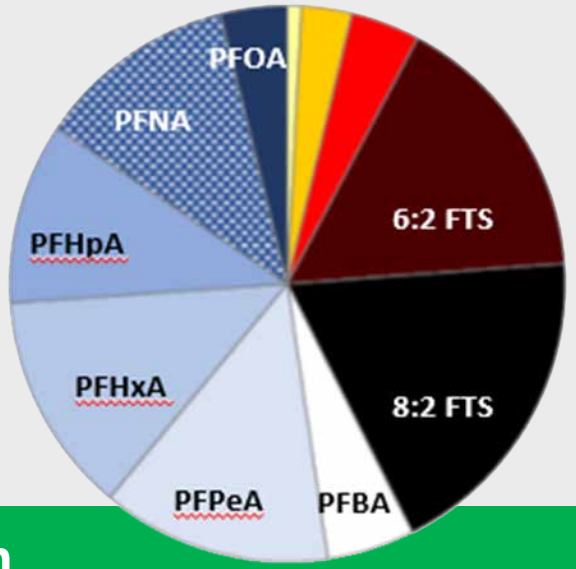
GW Smear Zone (high TSS)

Downgradient GW (TSS 35 mg/l)

Fate & Transport: PFAS Transformation
TOP Assay and AFFF: Some Simple Tips on Interpretation

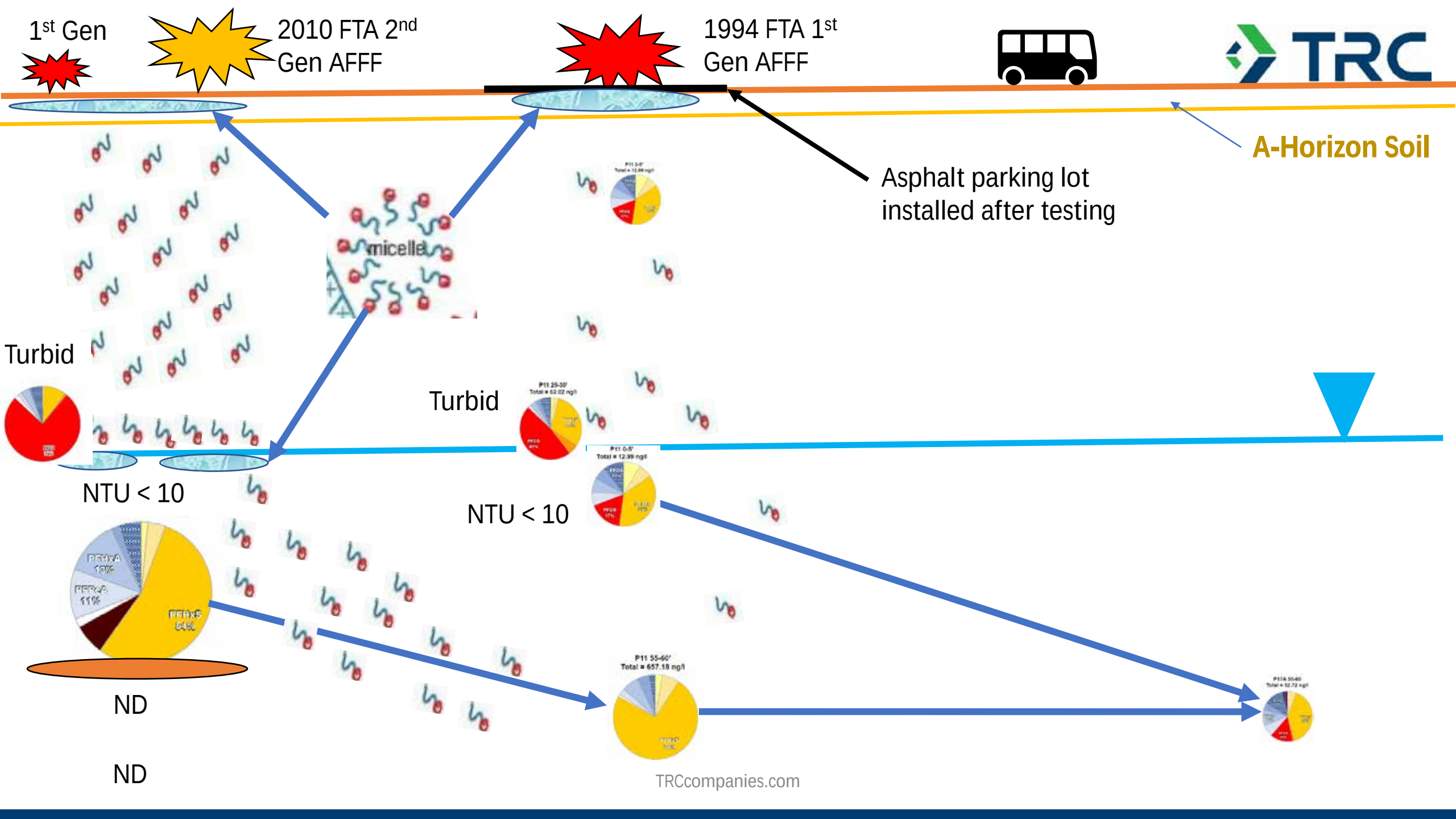
Rules of Thumb	
6:2 FTS →	PFBA, PFPeA, PFHxA, PFHpA
8:2 FTS →	PFBA, PFPeA, PFHxA, PFHpA, PFOA

Perfluorocarboxylic acids (PFCAs)



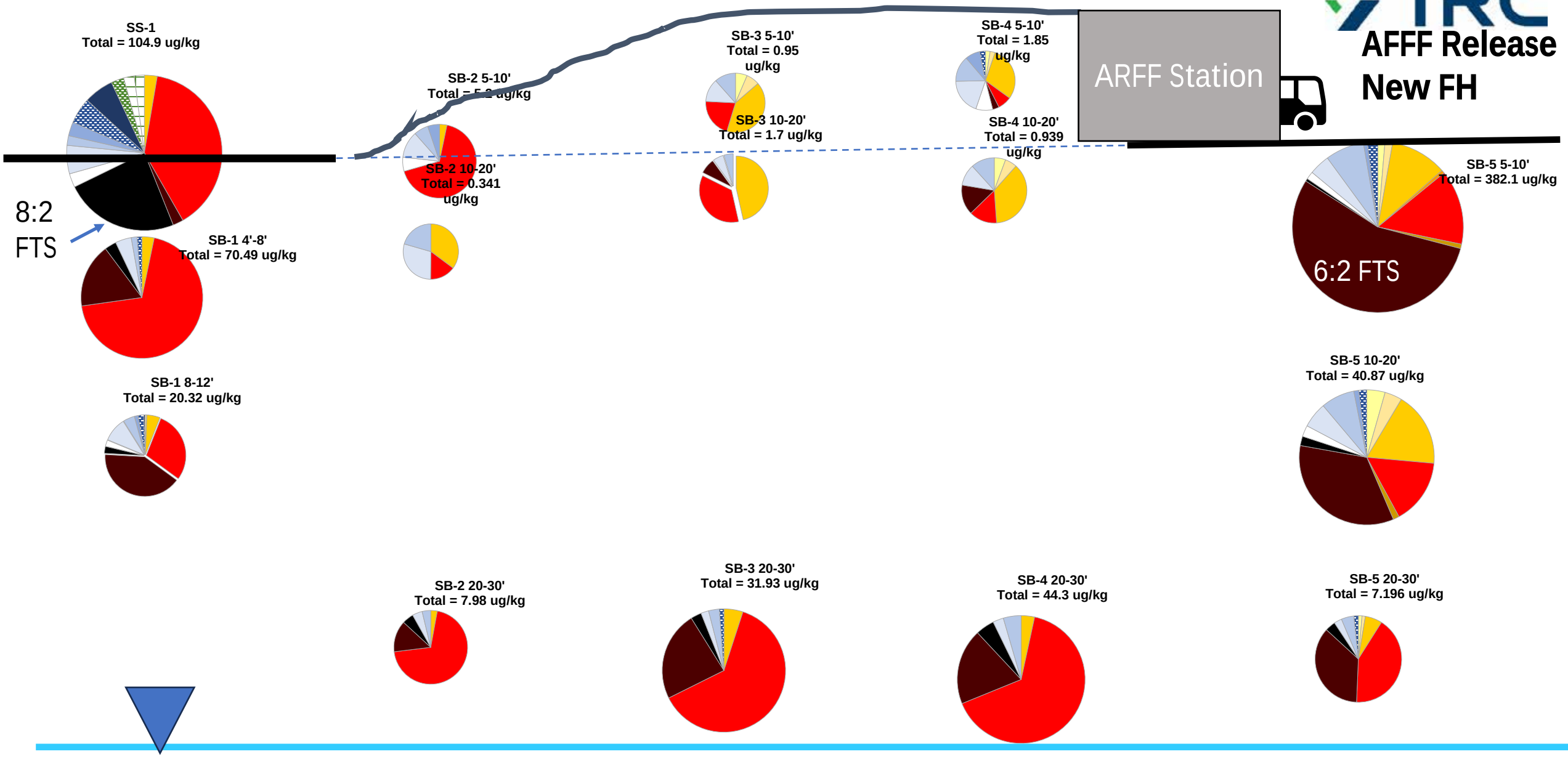
TOP Assay Results	Potential Source Identification
PFBA and PFPeA more prevalent than other PFCAs	Likely 6:2 FTS AFFF
Consistent PFHxA/PFPeA ratio	Likely 6:2 FTS AFFF
High concentration of PFOA with absence of PFHpA	8:2 FTS AFFF likely not main source of PFOA based on aerobic transformation pathway of 6:2 FTS which shows consistent ratios of PFHxA to PFPeA
Presence of PFHpA and PFOA	May indicate presence of 8:2 FTS
Increase in PFHxS/PFOS ratio	Likely ECF-based Legacy AFFF

Case Study – Four AFFF Source in Comingled Plume with Local Production Wells


1st Gen
2010 FTA 2nd Gen AFFF
1994 FTA 1st Gen AFFF
A-Horizon Soil
Asphalt parking lot installed after testing
micelle
Turbid
NTU < 10
Turbid
NTU < 10
PFHxA 19%
PFPeA 11%
PFHxS 64%
ND
ND
P11 55-60' Total = 657.18 ng/l

AFFF PFAS F&T/Forensics
Soil Results Airport AARF Station

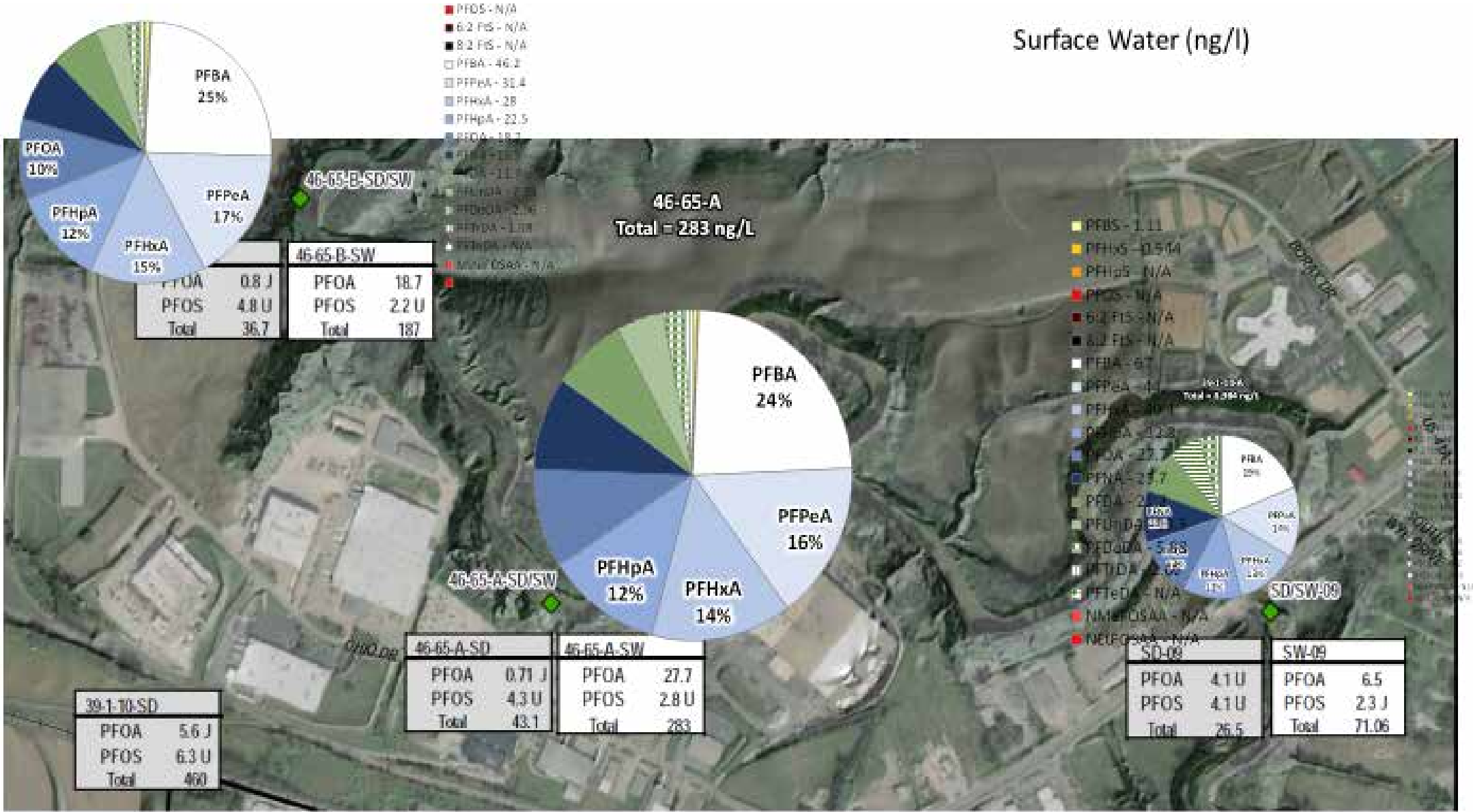
AFFF Release Old FH



AFFF Release
New FH

PFAS Forensics Soil/Sed & GW Results are like Apples and Rabbits
Stream Sediment and SW

Stream Surface Water Impacted by PFAS Manufacturing SW Soluble PFCAs (C4 – C10)



Stream Sediment Impacted by PFAS Manufacturing – SED Insoluble PFCA (C11 – C14)

Concentration vs Mass Contributions

Low Flow Rates; Different PFAS Concentrations

	Outfall 008		Outfall 009	
	Low Flow: 3.3 gpm		Low Flow: 0.3 gpm	
	Concentration (ng/L)	Mass Flow Rate (ug/hour)	Concentration (ng/L)	Mass Flow Rate (ug/hour)
PFOS	68	51	270	18
PFOA	22	6.8	46	3.1
PFHxS	96	72	270	18
		Total ug/hr: 130		Total ug/hr: 39

- Two outfalls with different flow rates and different PFAS concentrations
- Outfall 008: Lower concentrations of PFAS but higher contribution of PFAS mass
- Flow rate matters!

Takeaway Messages

- Chemical signatures can be a useful forensic tool.
- Aqueous samples: Understand how collected, level of particulates/turbidity, how lab handled sample.
- AFFF: understand characteristics of different AFFF and transformation products.
- Flowing water bodies: use mass versus concentration for forensics analyses.
- Signatures cannot be evaluated in isolation.

Questions?

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www.TRCcompanies.com

ACKNOWLEDGMENTS:

Liz Denly, TRC

Thank you