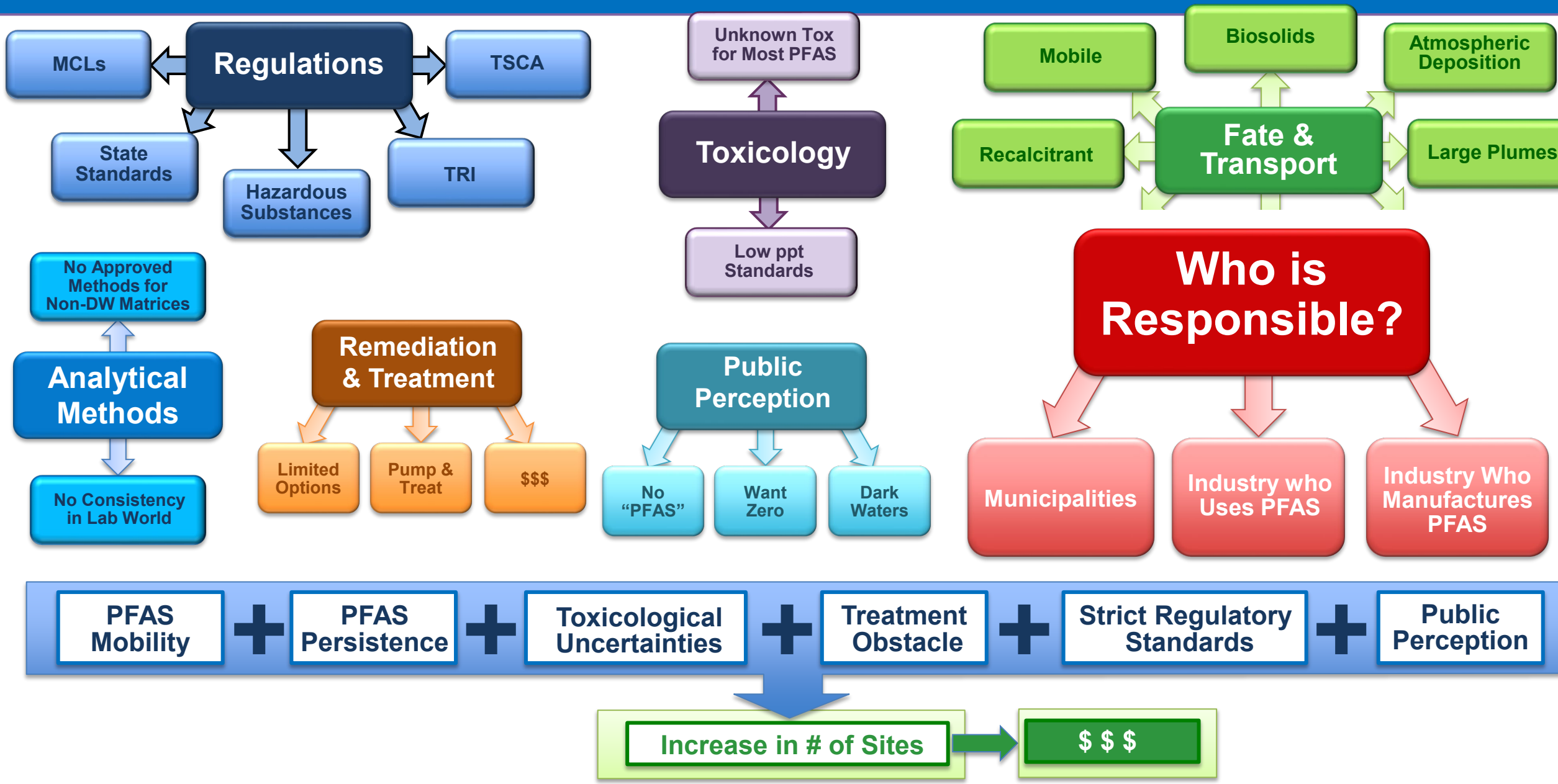
Is That Your PFAS?

Using Forensics to Identify Sources

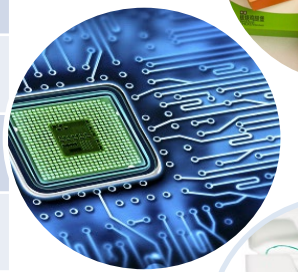
NEWMOA Conference – April 6, 2022

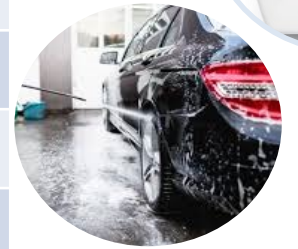
PFAS Uncertainties / Challenges



Industry or Product	How PFAS Used
Fire-fighting Foam	
Metal Plating	Mist suppressant, wetting agent
Textiles, Leather & Apparel	Waterproof clothing & shoes, stain-resistant carpeting
Plastics	Processing aid
Paper & Packaging	Water & oil-resistant paper products
Electronics	Magnetic tapes, cables, wires, circuit boards, semiconductors
Photography	Film, medical diagnostics
Cleaning Products	Alkaline cleaners, car wash products, concrete cleaner
Coatings: waxes, paints, inks, varnish	Paints, floor coverings, polishes
Pesticides	
Medicine	X-ray films, stents, contact lenses
Personal Care Products	Cosmetics, sunscreen, dental floss
Refrigerants	
Building & Construction	Concrete mixtures, coatings for buildings & roofs
Explosives	Infrared tracking flares, warheads
Oil & Gas Industry	Enhance recovery in oil wells, hydraulic oils, gasoline
Mining	Enhance metal recovery from oars, mist suppressant

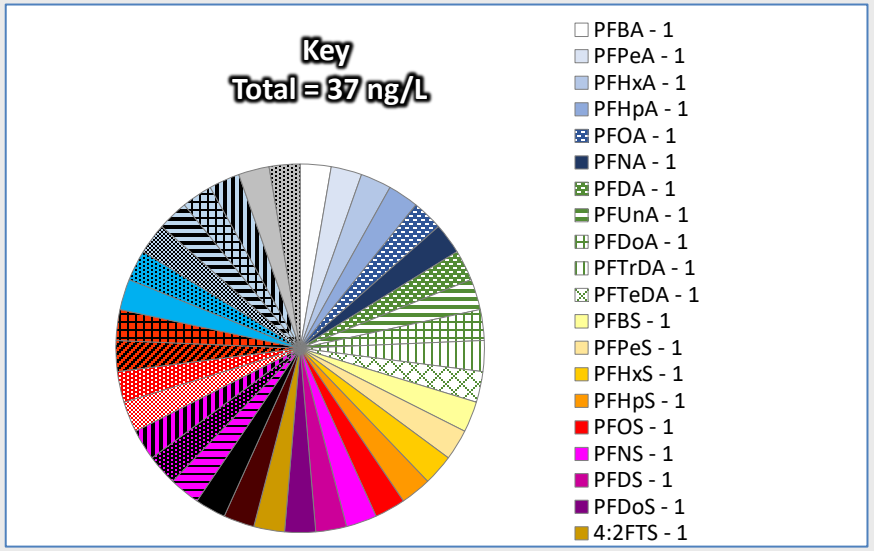




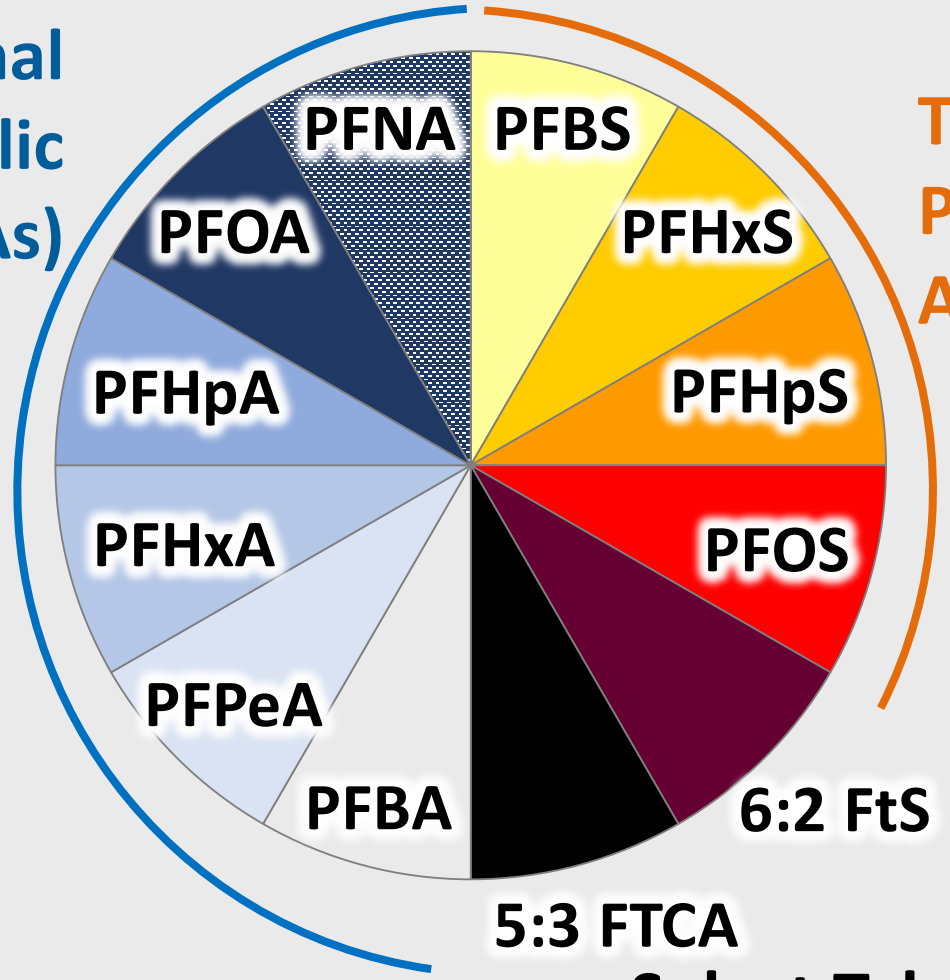


PFAS Forensics: Chemical Signatures

Example Analytes for Comparison



Terminal Perfluorocarboxylic Acids (PFCAs)

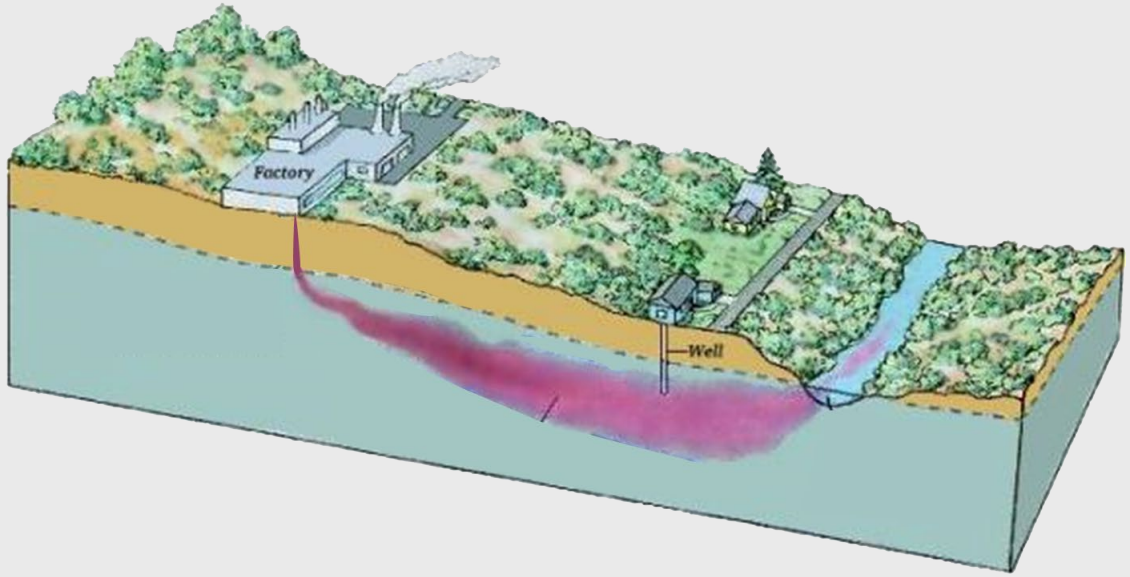


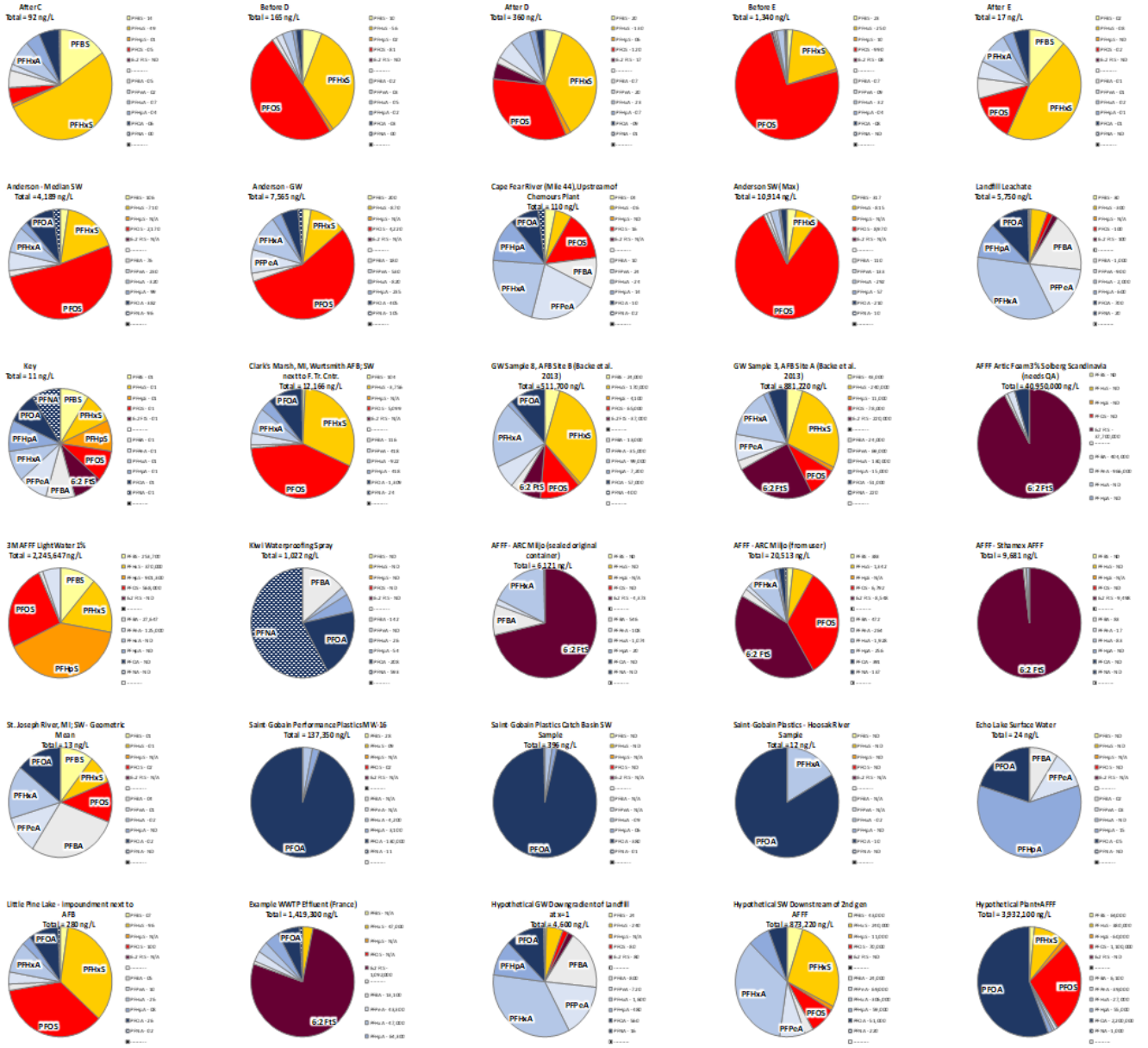
Terminal Perfluorosulfonic Acids (PFSAs)

Select Telomers
(transformable)

Chemical Signatures

Signatures reflect various source and fate/transport scenarios





We Understand Signatures

Paper & Food Packaging

- **Side-chain fluoropolymers**
- PAPs/diPAPs
- **NEtFOSE**, **NEtFOSAA**, PFBS, PFOA, PFHxA

Textile & Leather

- Polymers
- Polymer raw materials
- PFOA, FTOHs

AFFF

- PFOA, PFOS, PFHxS
- C8 fluorotelomers (8:2 FTS)
- C6 fluorotelomers, PFOA

WWTPs & Landfills

- n:2 FTUCA
- n:3 FTCA **(5:3FTCA)**
- n:2 FTSA
- EtFOSA

Metal Plating

- PFOS
- 6:2 FTS, 8:2 FTS
- F53B

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
- 3M "Light Water" (for example)
- Inventory remains in many locations
- Still major source of PFAS at AFFF-impacted sites
- **Contains PFOS & PFHxS; ratios may vary**

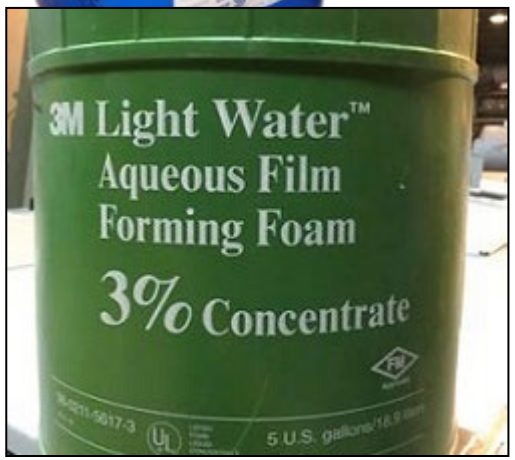
Legacy Fluorotelomer-based AFFF

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

Modern Fluorotelomer AFFF

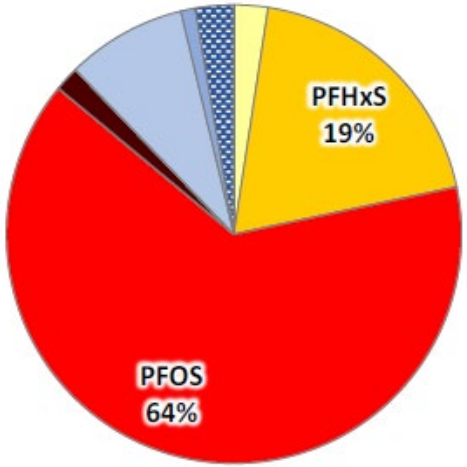
- 2010-Present
- Short-chain fluorotelomer sulfonates (6:2 and 4:2 FTS)
- Can breakdown to shorter chain PFCAs (PFBA, PFPeA, PFHxA, 5:3 FTCA)
- **Does not contain PFOS and no breakdown to PFOS or PFOA**
- **May contain trace amounts of PFOA as manufacturing impurity or byproduct**

Aqueous Film Forming Foam (AFFF)



Data sources:
1. Swedish Chemicals Agency, 2015. Chemical Analysis of Selected Fire-fighting Foams on the Swedish Market 2014.
2. D. Herzke et al., 2009. Survey, screening and analysis of PFCs in consumer products, Swerea IVF project report 09/47.

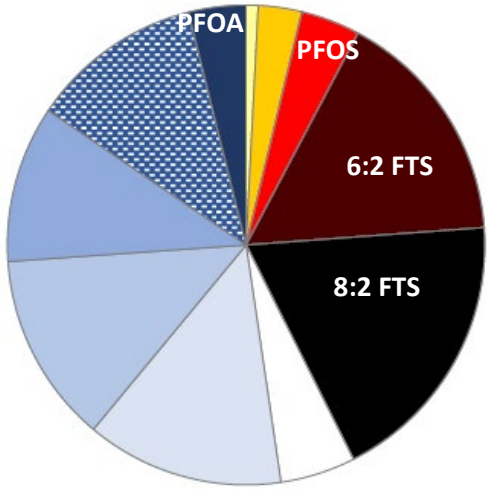
PFOS-Based AFFF



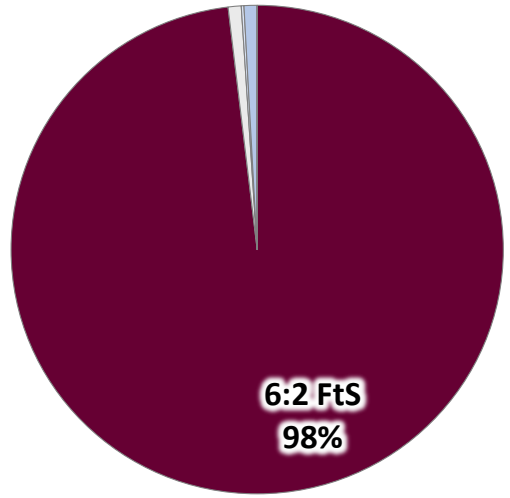
1st Generation

- Note: Typical composition is mainly PFOS and PFHxS
- Different lots may have different ratios of PFOS/PFHxS

2nd Generation



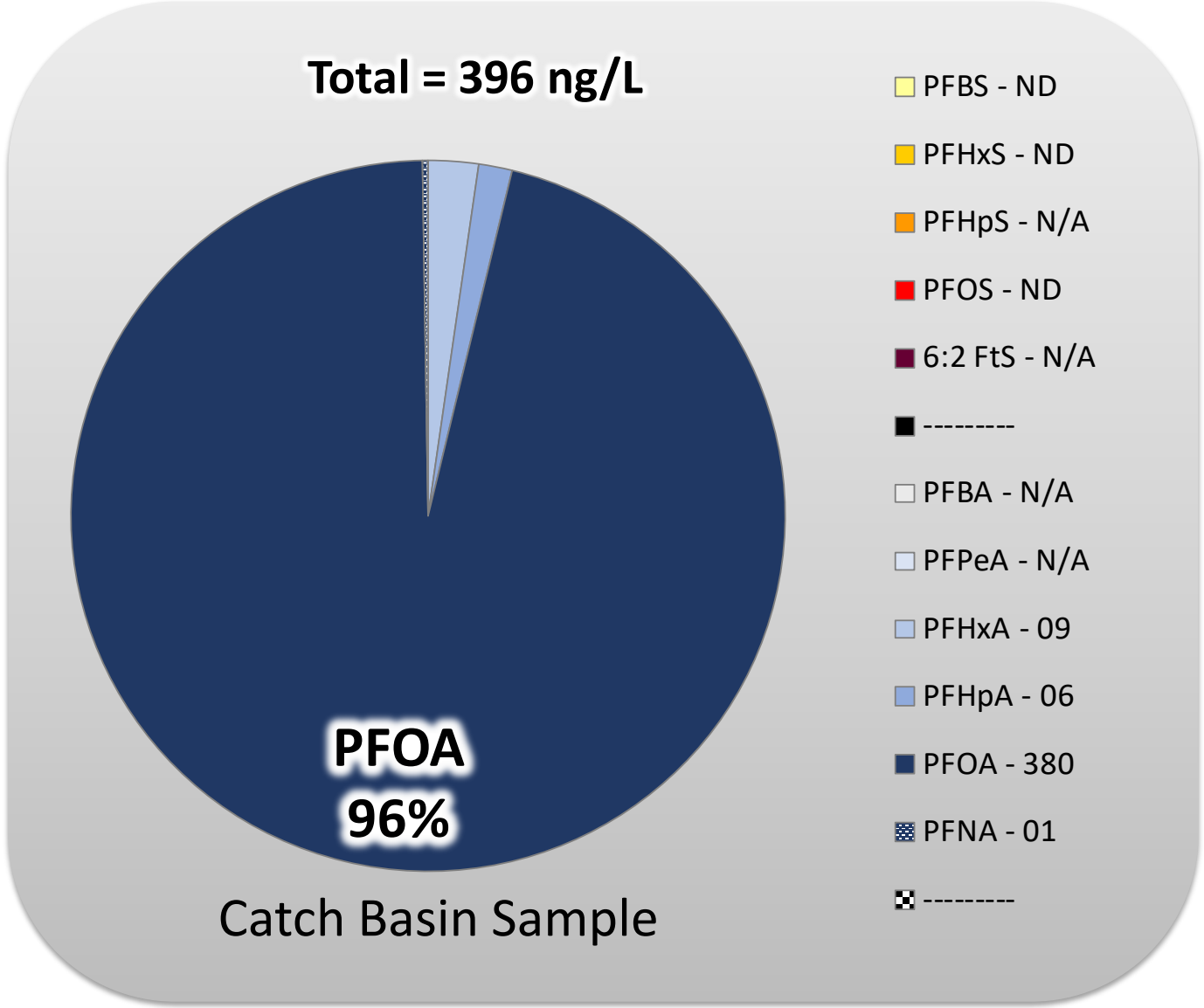
8:2 and 6:2 FTS-Based



Modern Fluorotelomer (6:2 FTS)

Plastics Manufacturing

Site manufactured polytetrafluoroethylene (PTFE) - coated fiberglass

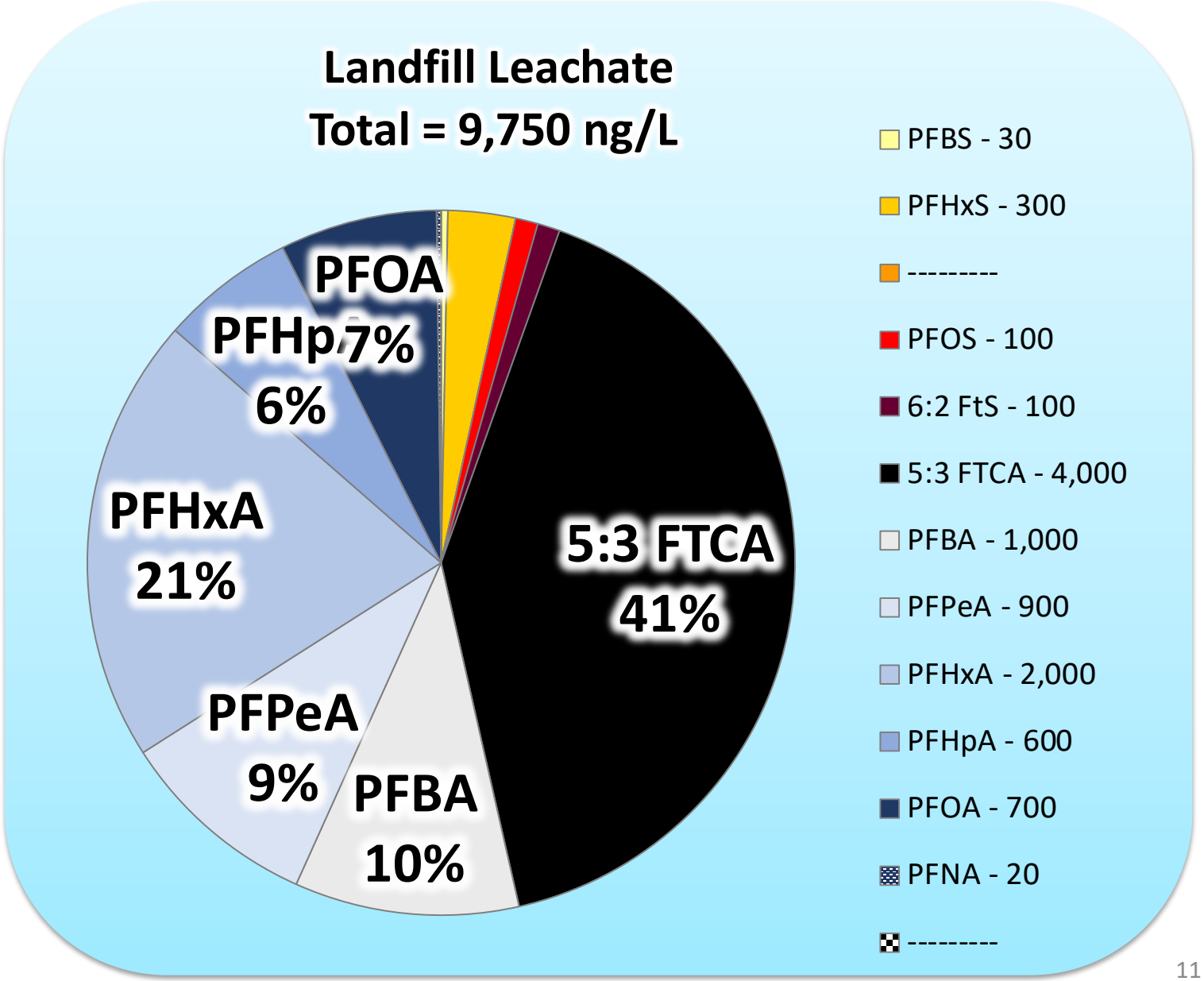


Data source:

1. http://www.dec.ny.gov/docs/administration_pdf/mccdatasummary.pdf

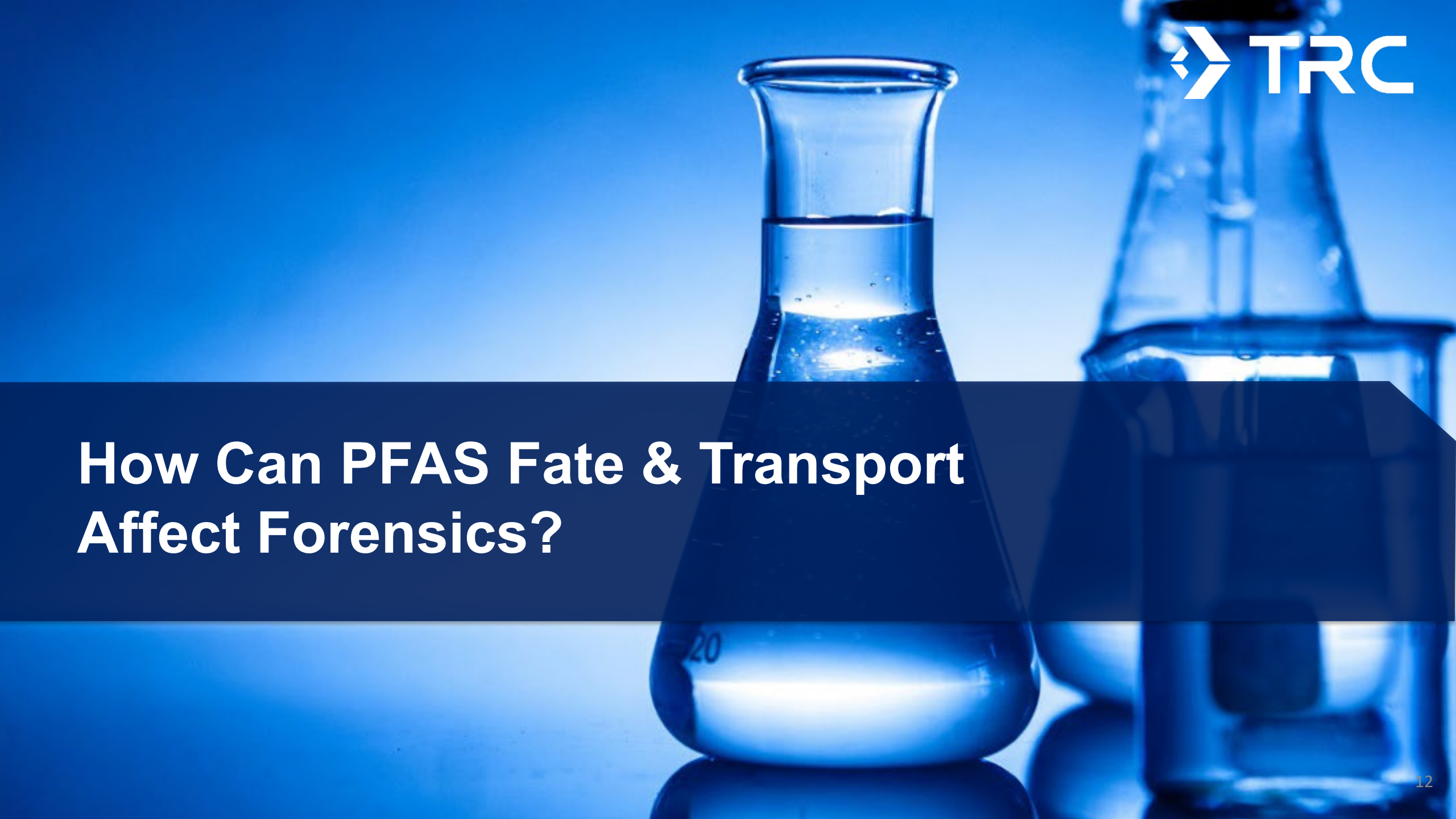
Landfill Leachate

5:3 FTCA telomer appears dominant. Degradation product of other telomers.



Data source:

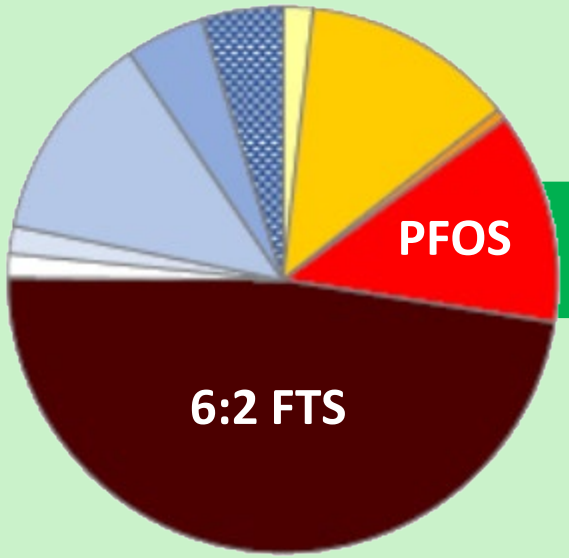
1. Lang et al., 2017. National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate, Environ. Sci. Technol., 2017, 51, 2197−2205 (Data shown for temperate conditions, t>10 yrs)



How Can PFAS Fate & Transport Affect Forensics?

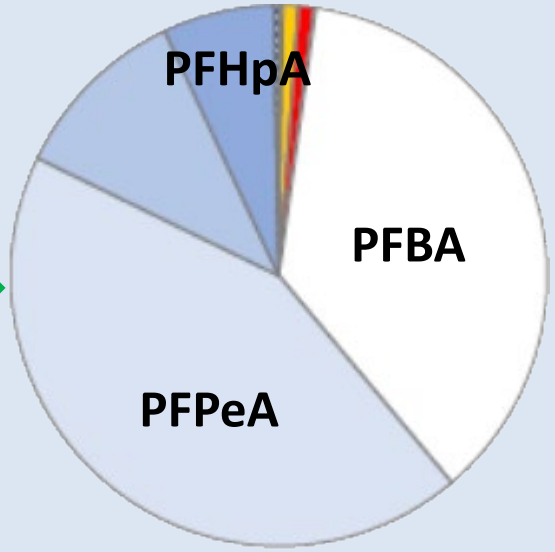
Fate & Transport: PFAS Transformation

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

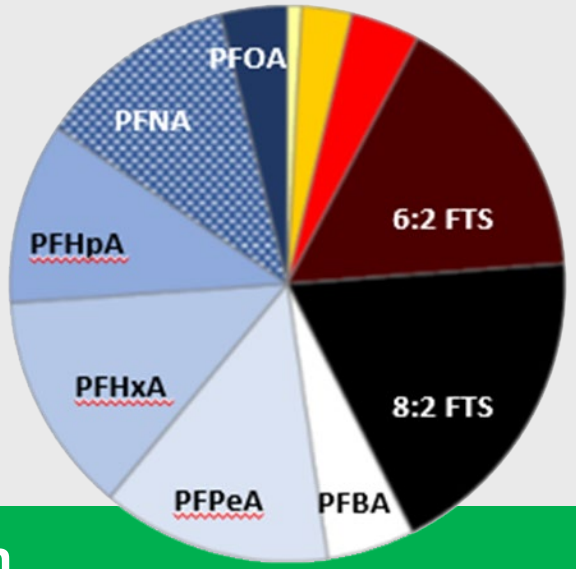
6:2 FTS → PFBA, PFPeA, PFHxA, PFHpA

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

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

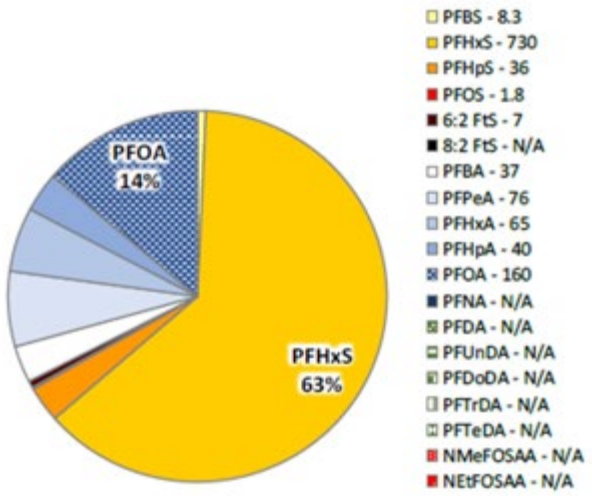
Perfluorocarboxylic acids (PFCAs)



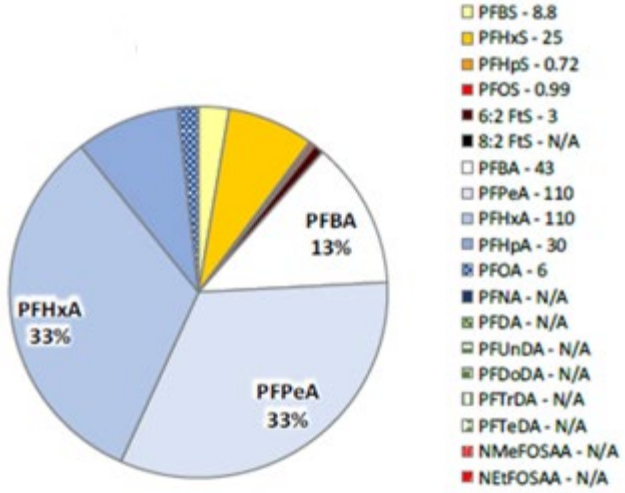
TOP Assay Results	Potential Source Identification
PFBA and PFPeA more prevalent than other PFCAs	Likely 6:2 FTS AFFF
Consistent PFHxA/PFPeA ratio	Likely 6:2 FTS AFFF
High concentration of PFOA with absence of PFHpA	8:2 FTS AFFF likely not main source of PFOA based on aerobic transformation pathway of 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

Fate & Transport: Sorption to Solids

Sample from 1" temporary well turbid



Sample from 2" developed MW clear

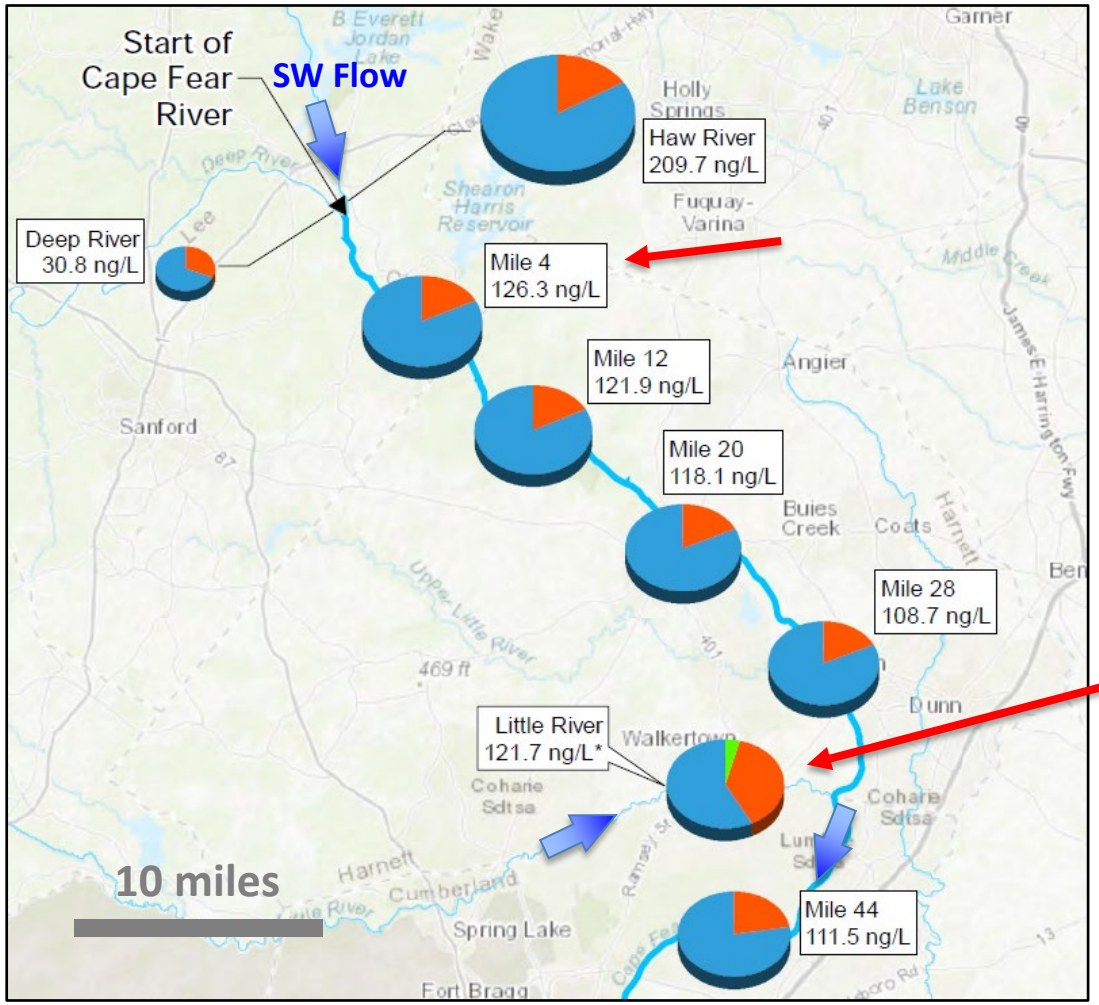


Issue: Chemical sorption of PFAS to particulates or solids. Longer-chain PFAS and PFSAs tend to absorb more to solids.

- Particulates in aqueous samples can interfere with extraction procedure.
- Labs have variable procedures for dealing with this; can vary from lab to lab and within a lab.

1. *Floating particulates versus sediment which has settled at the bottom of the container*
2. *Centrifuge and decant*
3. *Just decant*
4. *Rinse the remaining particulates or sediment with methanol and include the methanol rinse in the extraction*
5. *Perform an extraction of the particulate or sediment portion of the sample*
6. *Dealing with particulates that clog extraction cartridges*
7. *Documentation of issues with particulates by laboratory*
8. *Cut-off value for total suspended solids (TSS) causing extraction issues*

Fate & Transport – PFAS Persistence



- Example: Cape Fear River
- Composition and magnitude relatively stable for tens of miles
- Data also suggest:
  - Possible contribution from a downstream source

Key

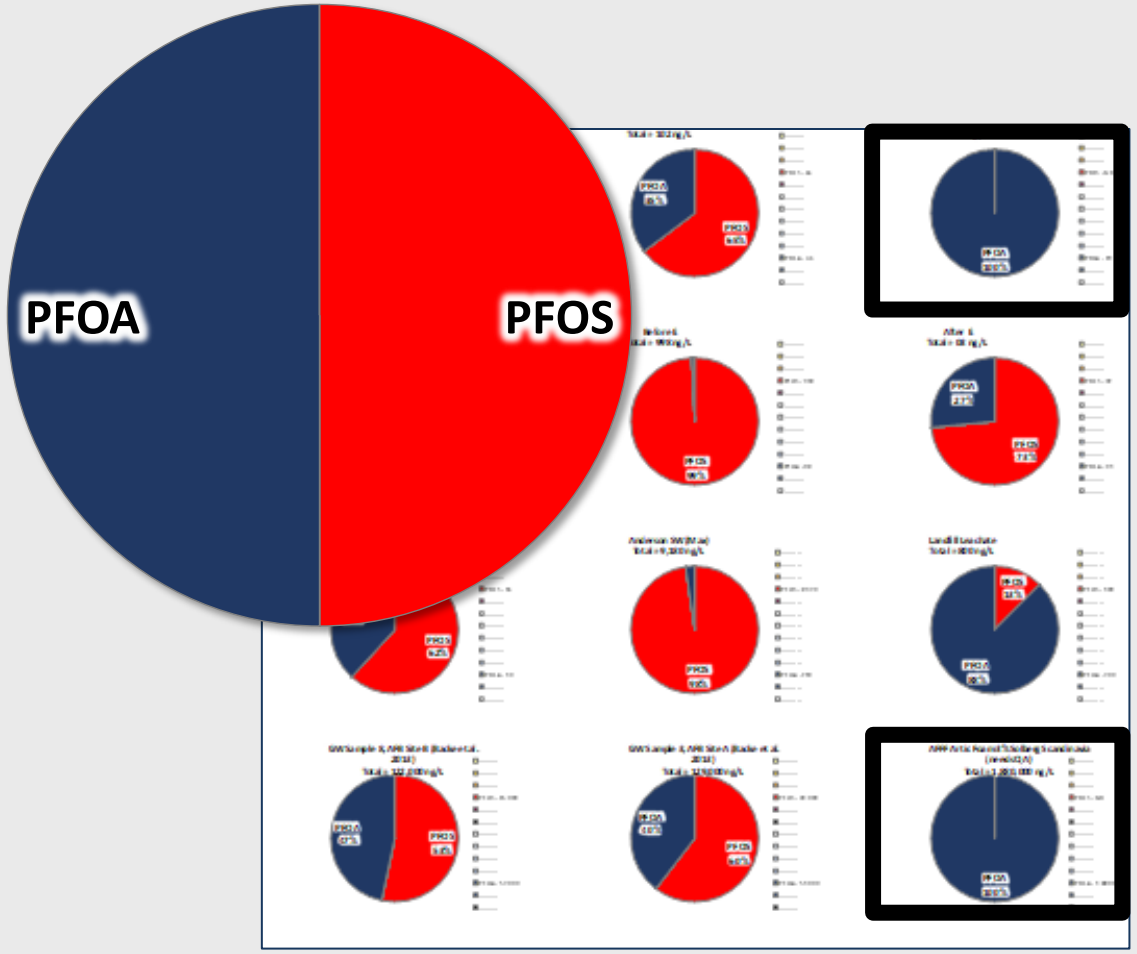
- perfluorocarboxylic acids (PFCAs)
- perfluorosulfonic acids (PFSAs)
- perfluoroalkyl ether sulfonic acids (PFESAs)

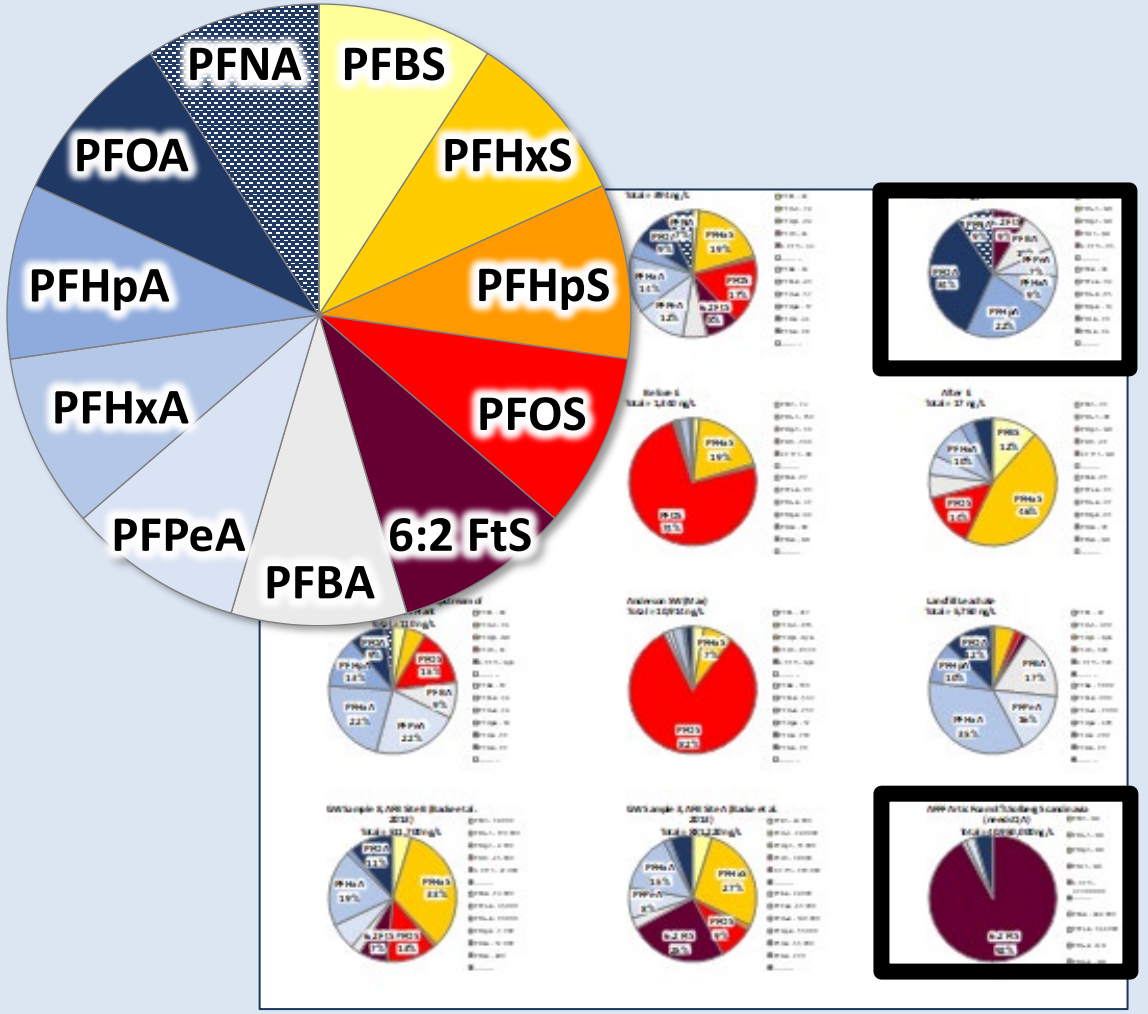
Source:

1. https://www.chemours.com/Fayetteville.../2018-0917-cape-fear-river-pfas-report.pdf.

Preliminary TRC interpretation based on figure only.

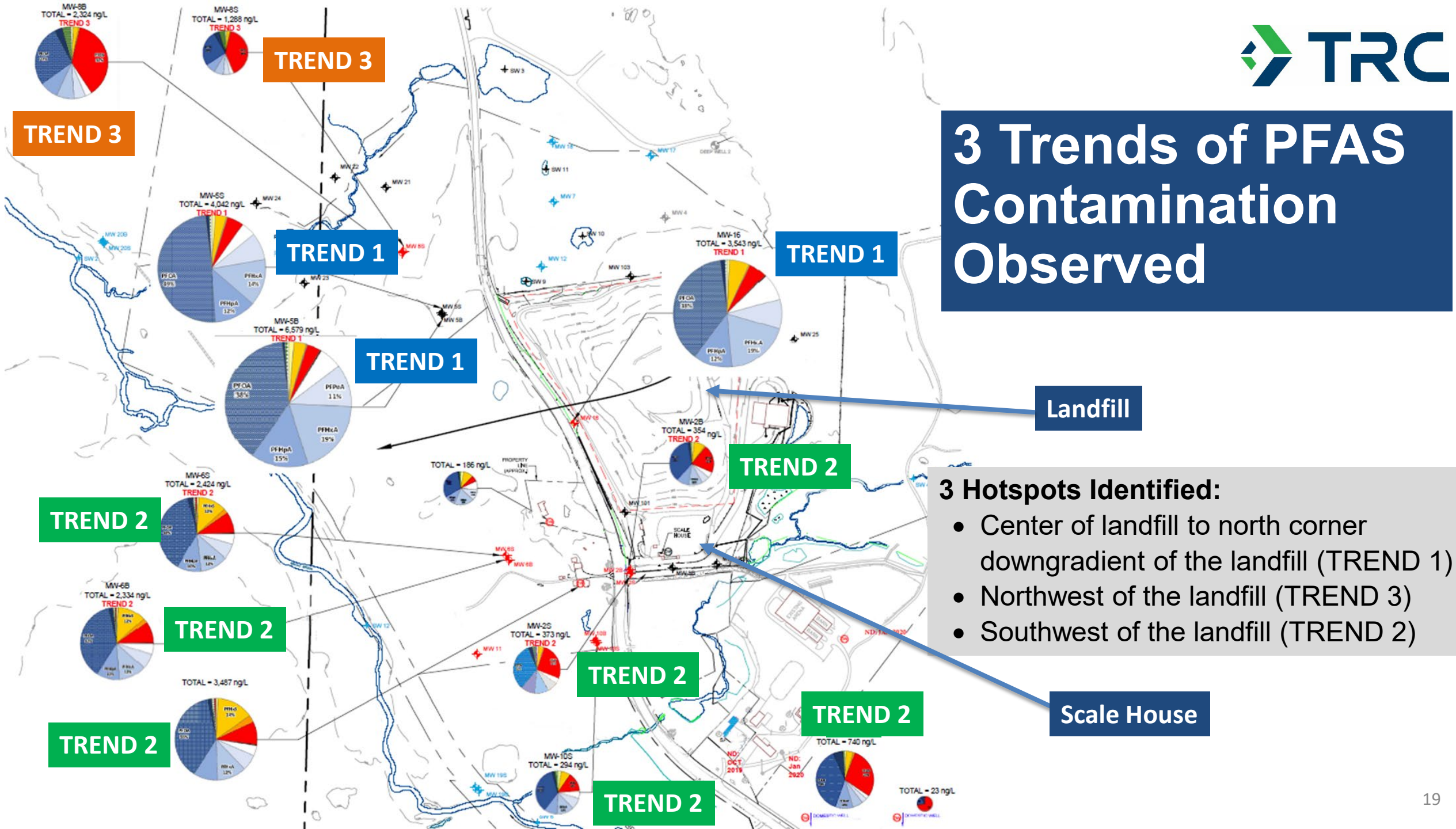
Example Difference Based on Analytes Selected for Signature Evaluation





Case Study: Landfill

- 11 groundwater samples with concentrations >100 ppt total PFAS selected for evaluation
- 4 potable well samples
- Samples analyzed for 23 PFAS and TSS
- Objectives of forensics analysis:
  - To differentiate on-site landfill sources versus off-site sources of PFAS
  - To determine if there was information on potential sources
  - To identify hot spots of PFAS within landfill
  - To identify need to gather additional information and/or to sample/install additional monitoring wells

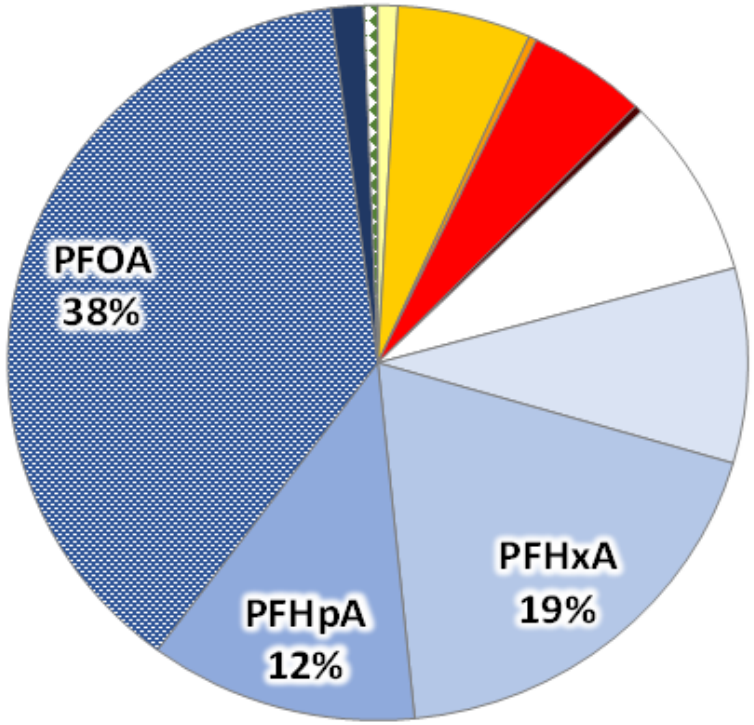


3 Trends of PFAS Contamination Observed

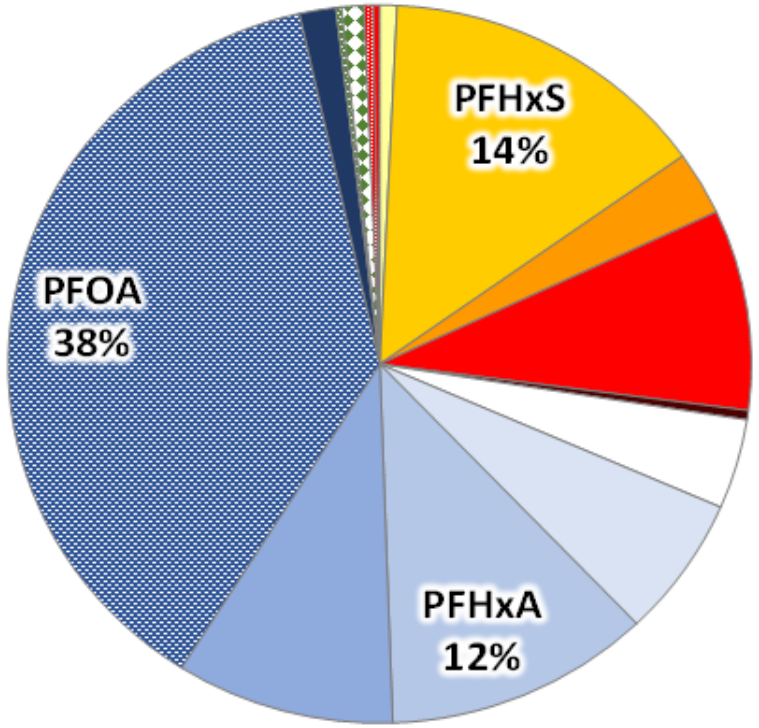
3 Hotspots Identified:

- Center of landfill to north corner downgradient of the landfill (TREND 1)
- Northwest of the landfill (TREND 3)
- Southwest of the landfill (TREND 2)

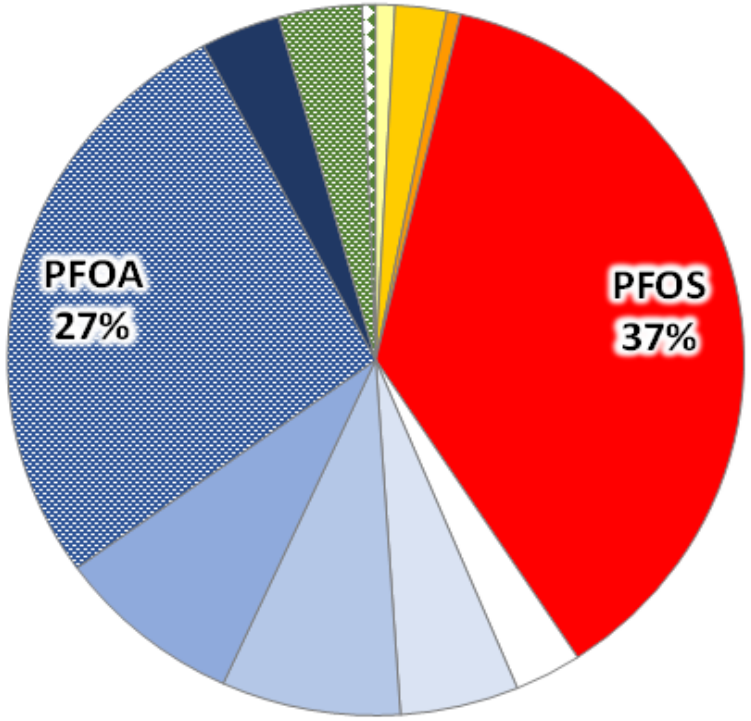
Three Patterns



TREND 1



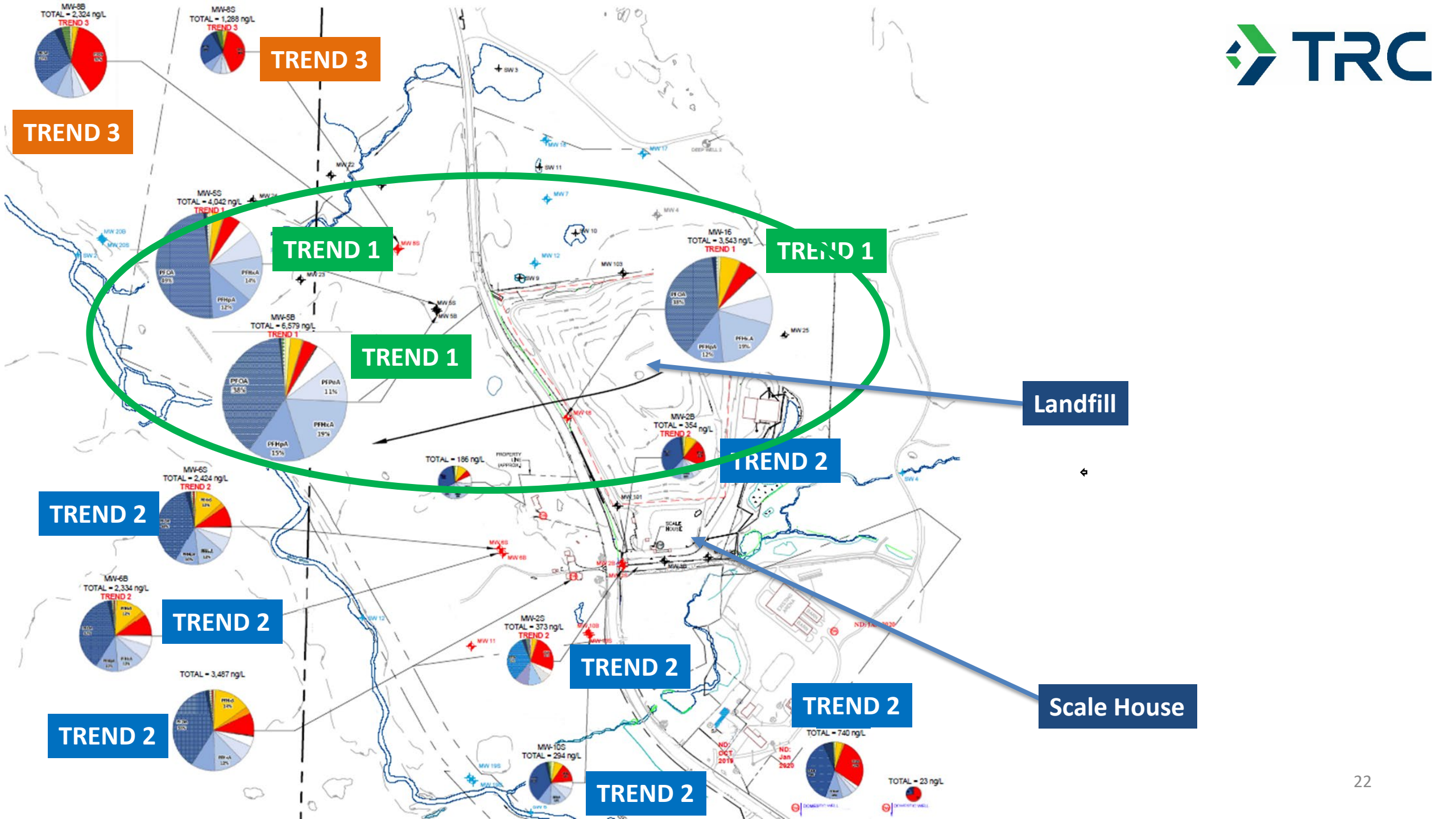
TREND 2



TREND 3

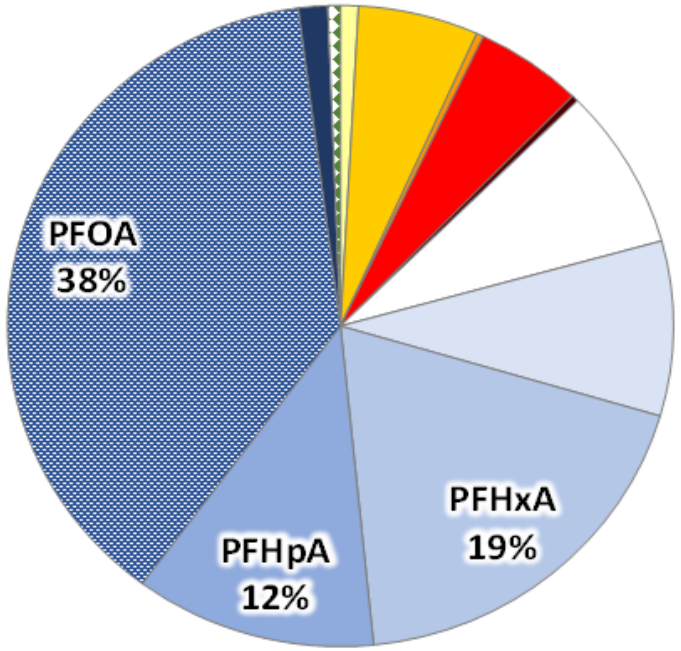
Diagnostic Ratios

- PFCAs relative abundance to total PFAS
- PFSAs relative abundance to total PFAS
  - values >0.5 may be potential indication of legacy AFFF source (e.g., AFFF produced prior to 2002)
- PFCA/PFSA ratio
- PFOA/PFOS ratio
  - values <1 may be indication of potential legacy AFFF source (AFFF produced prior to 2002)

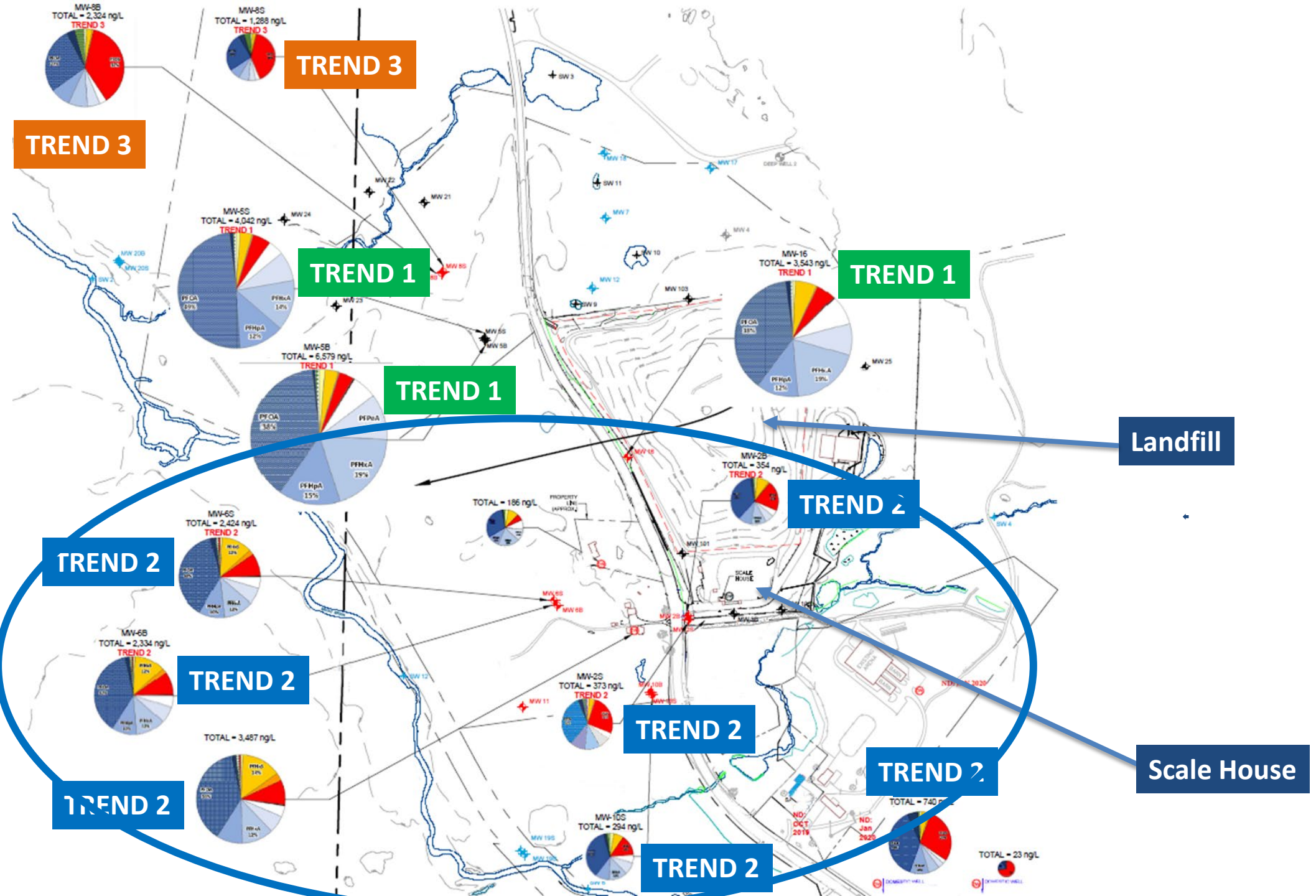

MW-8B
TOTAL = 2,324 ng/L
TREND 3
MW-8S
TOTAL = 1,288 ng/L
TREND 3
TREND 3
TREND 3
MW-5S
TOTAL = 4,042 ng/L
TREND 1
TREND 1
MW-5B
TOTAL = 6,579 ng/L
TREND 1
TREND 1
MW-16
TOTAL = 3,543 ng/L
TREND 1
TREND 1
Landfill
MW-2B
TOTAL = 354 ng/L
TREND 2
TREND 2
TOTAL = 186 ng/L
MW-6S
TOTAL = 2,424 ng/L
TREND 2
TREND 2
MW-6B
TOTAL = 2,334 ng/L
TREND 2
TREND 2
MW-2S
TOTAL = 373 ng/L
TREND 2
TREND 2
Scale House
TOTAL = 3,487 ng/L
TREND 2
MW-10S
TOTAL = 294 ng/L
TREND 2
TREND 2
TOTAL = 740 ng/L
TOTAL = 23 ng/L

Trend 1

Trend 1			
Diagnostic Ratios	**MW-1** Edge of landfill	**MW-2S** Downgradient	**MW-2B** Downgradient
PFCAs relative abundance	0.868	0.894	0.902
PFSAs relative abundance	0.130	0.107	0.095
PFCA/PFSA ratio	6.74	8.42	9.62
PFOA/PFOS	7.24	9.90	10.82



- MW-1 likely landfill source and MW-2S/MW-2B likely signature downgradient of MW-1
- Mixing of landfill leachate in groundwater creating consistent signature: confirms plume from landfill moving off-site
- PFCA/PFSA ratio increases with distance downgradient from landfill
- PFAS signatures rich in PFCAs indication of landfill source
- PFOA at concentrations >PFOS with absence of fluorotelomers indicates unlikely an AFFF source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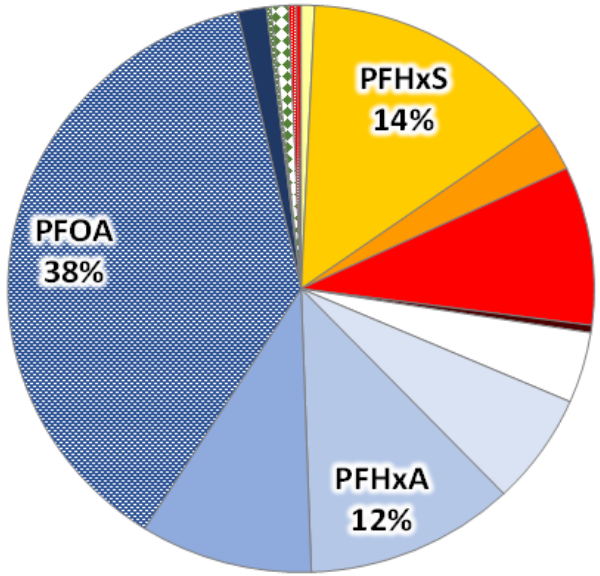
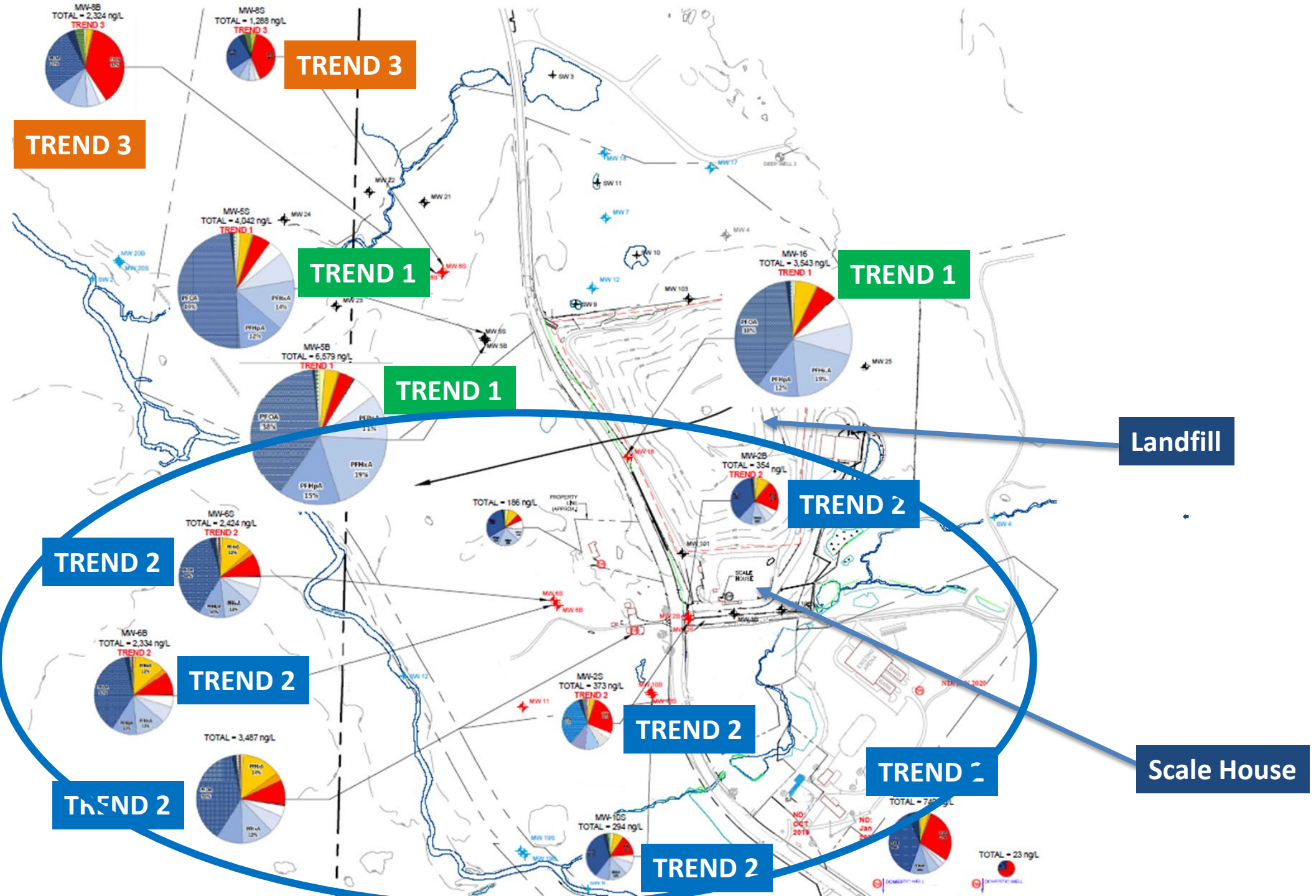
TREND 2
TREND 2
MW-10S
TOTAL = 294 ng/L
TREND 2
TOTAL = 740
TOTAL = 23 ng/L

Trend 2

Trend 2							
Diagnostic Ratios	**MW-2S**	**MW-2B**	**MW-6S**	**MW-6B**	**PW 1**	**MW-10S**	**PW 2**
PFCAs relative abundance	0.683	0.673	0.735	0.735	0.709	0.748	0.649
PFSAs relative abundance	0.320	0.333	0.256	0.258	0.282	0.259	0.354
PFCA/PFSA ratio	2.16	2.06	2.90	2.87	2.53	2.97	1.85
PFOA/PFOS	1.26	1.73	4.09	3.93	4.16	2.49	1.32

- PFAS concentrations at wells MW-2S/MW-2B (closest to landfill source) lower than concentrations at side-gradient wells MW-6S/MW-6B
- PFCA/PFSA ratio increases with distance downgradient from MW-2S/MW-2B well couplet
- Potential sources of plume include the scale house septic system
- PFSA relative abundance higher than TREND 1: need to determine if the PFOS/PFHxS-richer groundwater is associated with the landfill or another source, such as the scale house area

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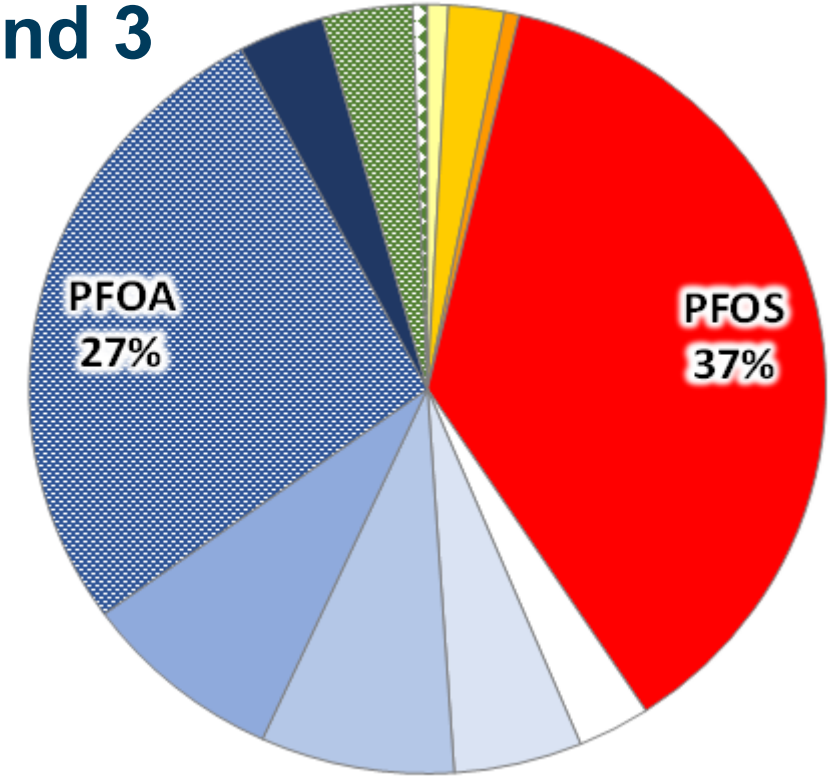
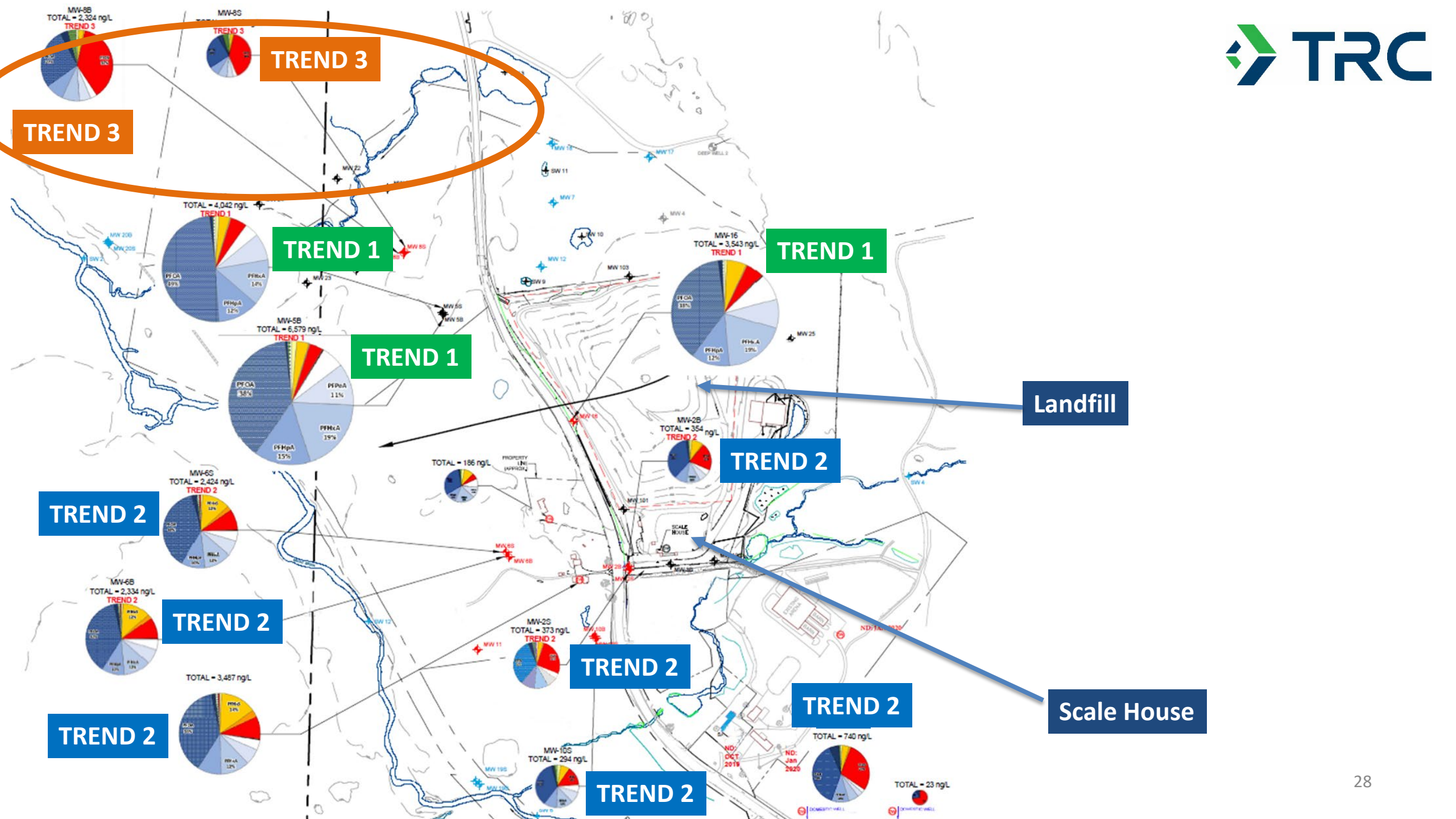
TREND 2
TOTAL = 23 ng/L

Trend 3



Trend 3		
Diagnostic Ratios	**MW-8S**	**MW-8B**
PFCAs relative abundance	0.555	0.586
PFSAs relative abundance	0.449	0.417
PFCA/PFSA ratio	1.25	1.42
PFOA/PFOS	0.65	0.73

- Pattern observed at TREND 3 wells not a landfill source.
- Higher concentrations of PFOS: higher likelihood of different source (e.g., possible liquid source such as use of AFFF or a chemical poured into a septic system, composting facility, etc.).
- TREND 3 likely another upgradient source as PFOS-rich downgradient groundwater results are generally not associated with landfills


MW-8B
TOTAL = 2,324 ng/L
TREND 3
MW-8S
TREND 3
TREND 3
TREND 3
TOTAL = 4,042 ng/L
TREND 1
TREND 1
MW-5B
TOTAL = 6,579 ng/L
TREND 1
TREND 1
MW-16
TOTAL = 3,543 ng/L
TREND 1
TREND 1
Landfill
MW-2B
TOTAL = 354 ng/L
TREND 2
TREND 2
TOTAL = 186 ng/L
MW-6S
TOTAL = 2,424 ng/L
TREND 2
TREND 2
MW-6B
TOTAL = 2,334 ng/L
TREND 2
TREND 2
MW-2S
TOTAL = 373 ng/L
TREND 2
TREND 2
Scale House
TOTAL = 3,487 ng/L
TREND 2
TREND 2
MW-10S
TOTAL = 294 ng/L
TREND 2
TOTAL = 740 ng/L
TOTAL = 23 ng/L

Takeaway Messages

- Chemical signatures can be a useful forensic tool.
- The choice of PFAS selected for signature evaluation must be considered.
- Very large group of transformation intermediates presents a challenge to data interpretation.
- An integrated, multiple lines-of-evidence approach is always warranted.
- High-quality hydrogeologic evaluation is critical.
- Signatures cannot be evaluated in isolation.

Questions?

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Thank you