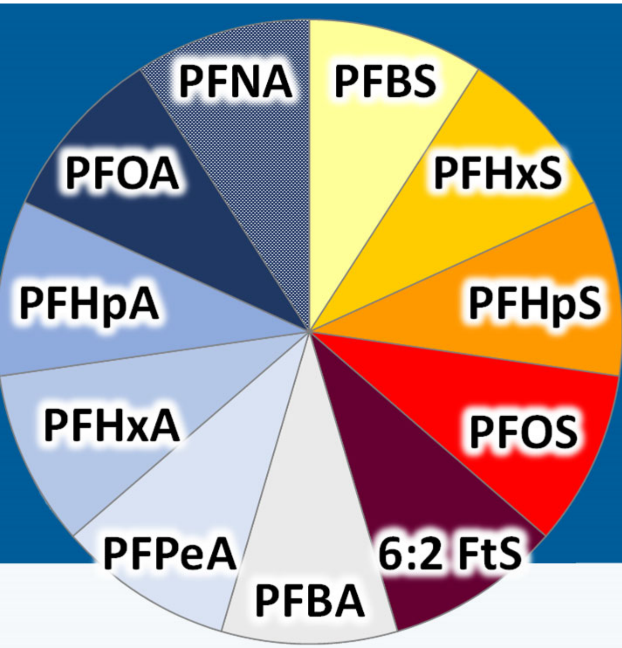
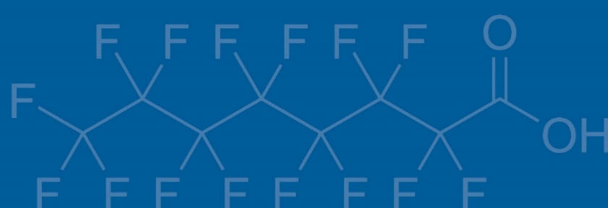
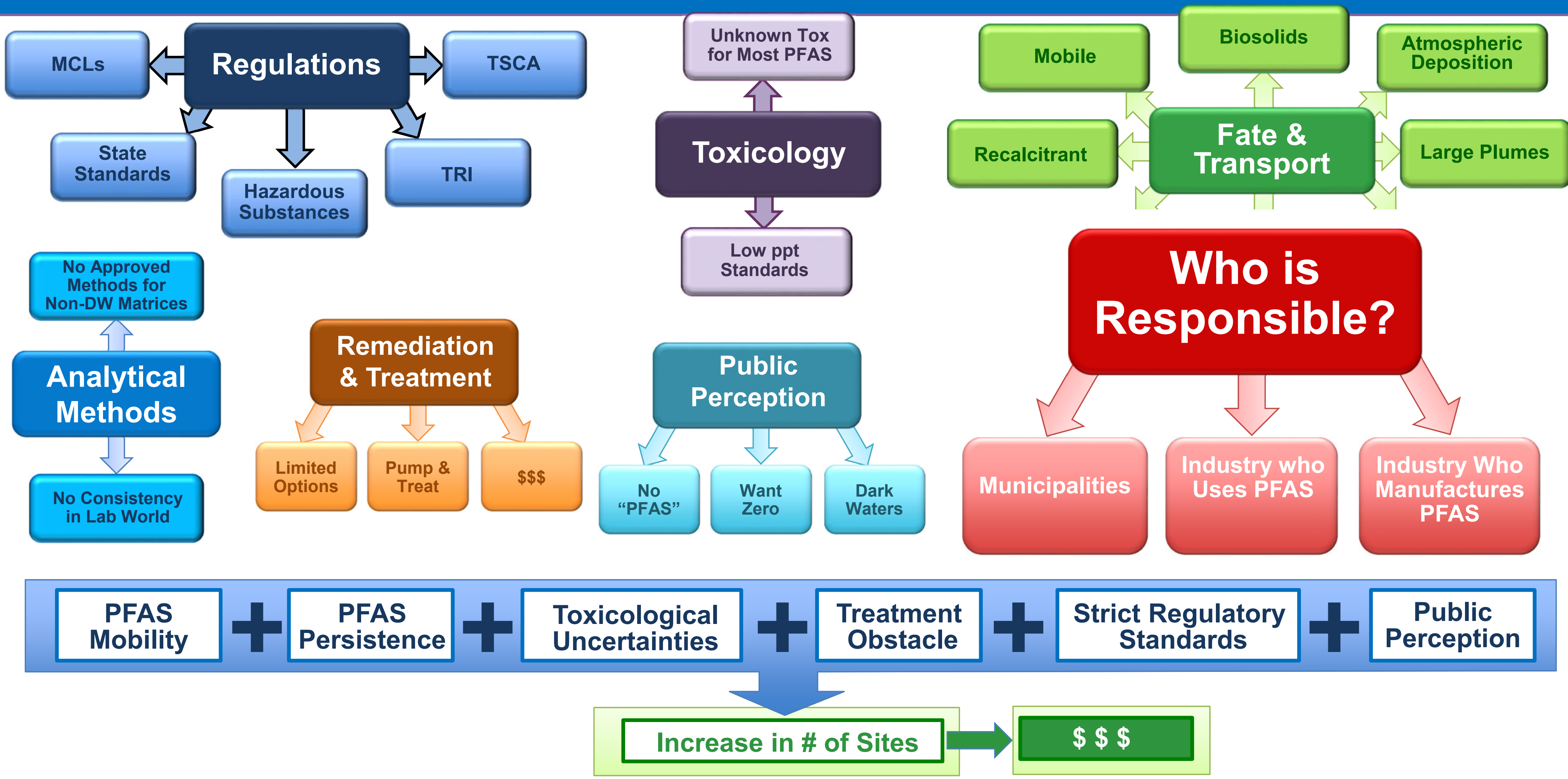


Effects of Variable Analytical Parameter Suites on the Identification of PFAS Sources

June 23, 2021



PFAS Uncertainties / Challenges



Sources of PFAS

Fire-fighting foams

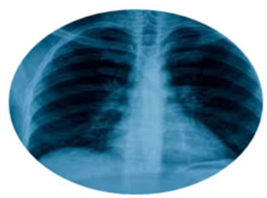
Metal plating

Textiles, leather & apparel

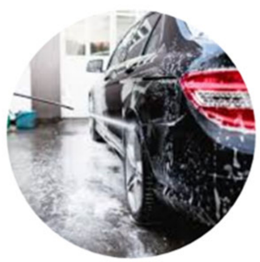
Plastics

Oil & Gas industry

Paper & packaging

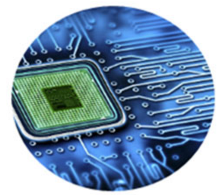


Photography



Cleaning products

Mining



Electronics

Coatings: waxes, paints, inks, varnish

Pesticides

Personal care products

Medicine

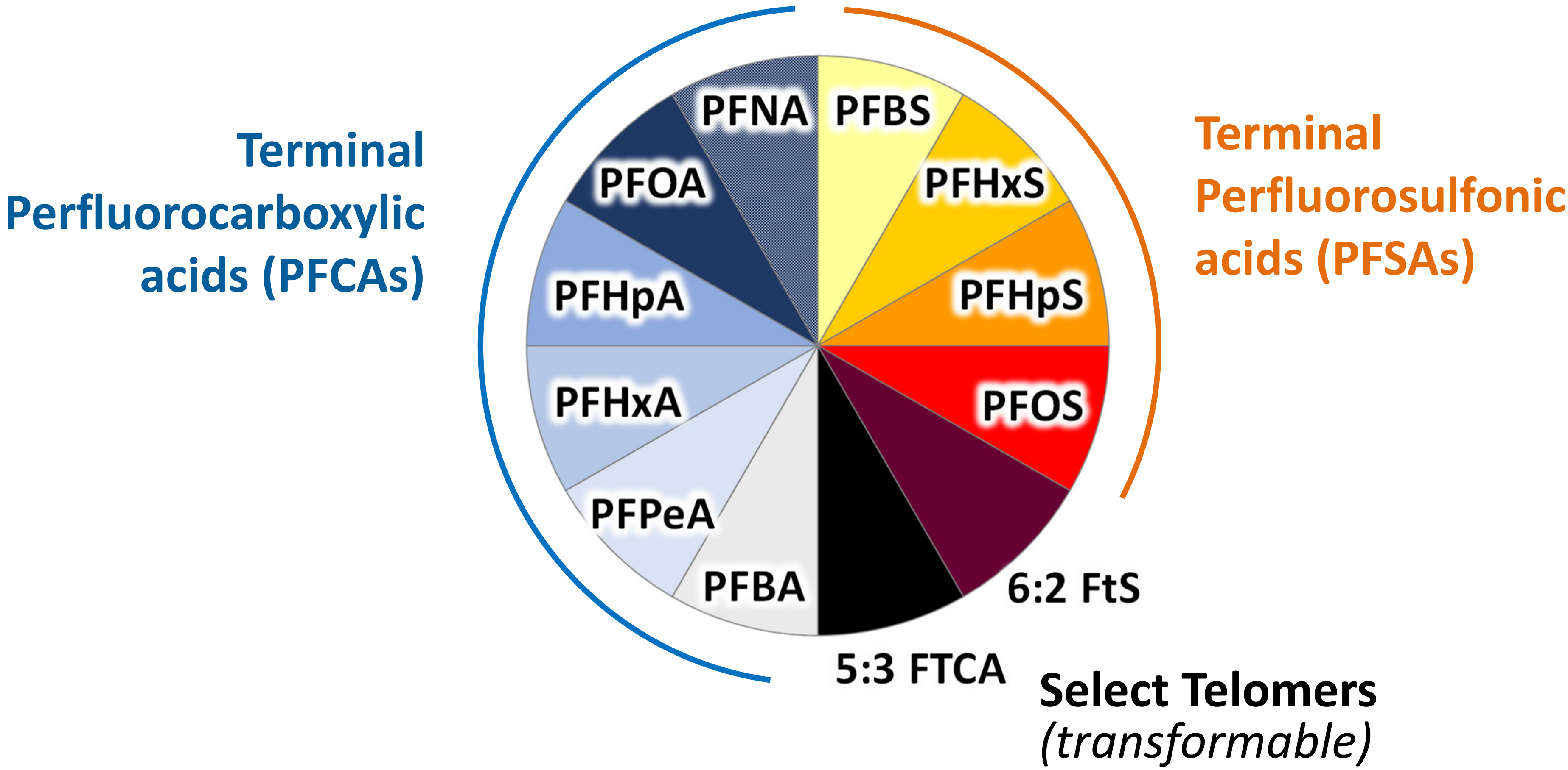
Building & construction

Refrigerants

Explosives

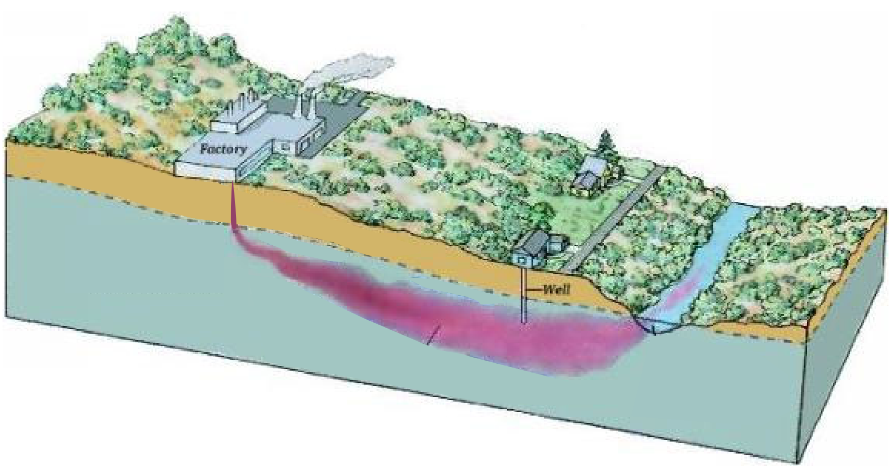
Introduction to PFAS Forensics

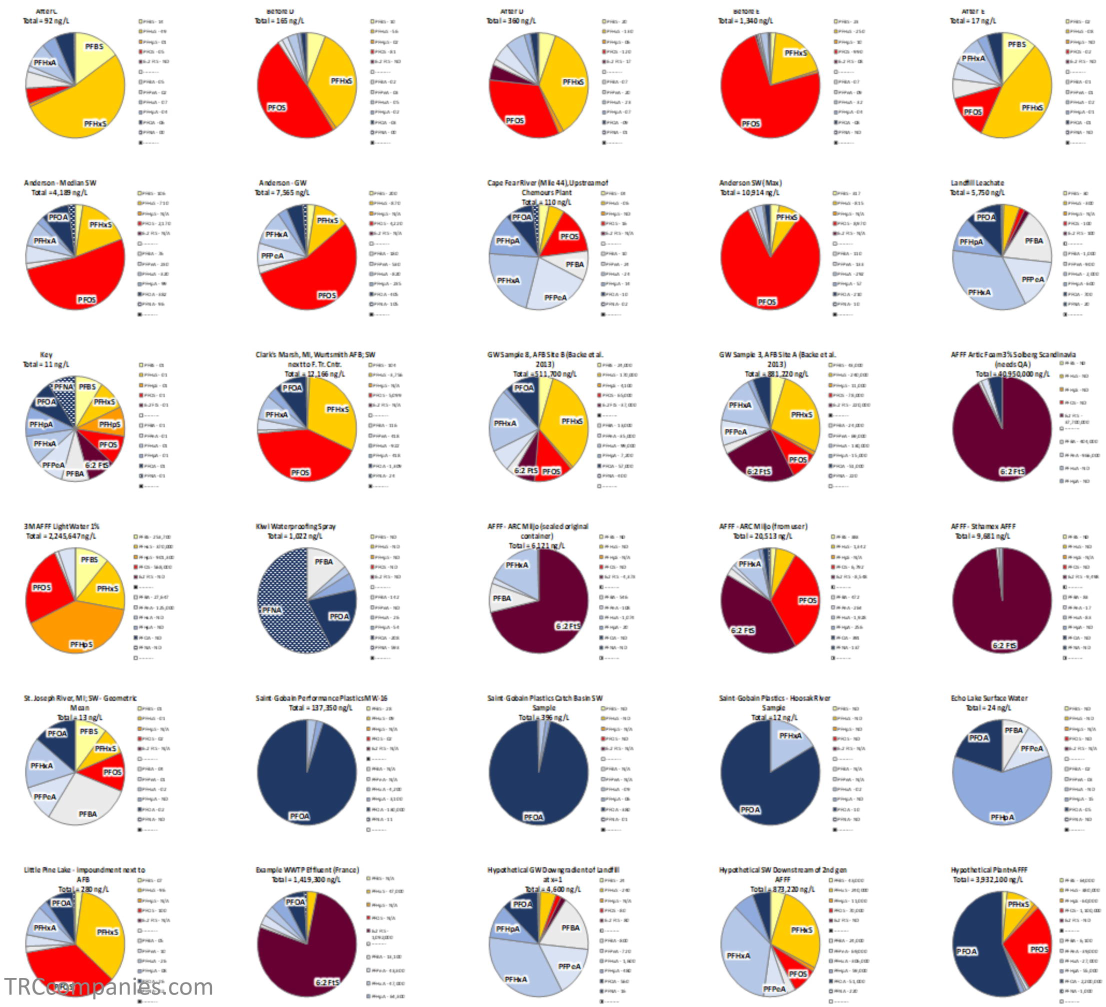
Example Analytes for Comparison



Chemical Signatures

Signatures reflect various source and fate/transport scenarios

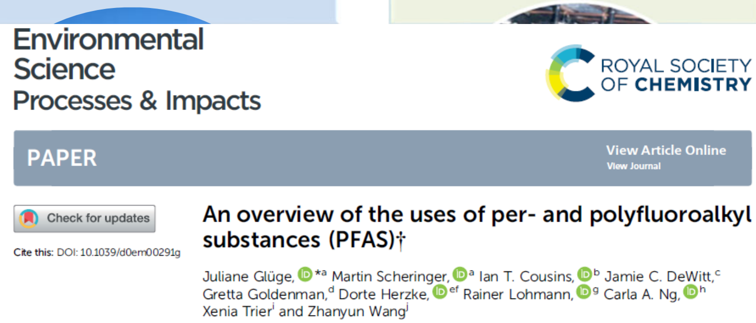




We Understand Signatures

TRC

Paper & Food Packaging	Textile & Leather	AFFF	WWTPs & Landfills	Metal Plating
• **<u>Side-chain fluoropolymers</u>** • PAPs/diPAPs • **<u>NEtFOSE</u>**, **<u>NEtFOSAA</u>**, PFBS, PFOA, PFHxA	• Polymers • Polymer raw materials • PFOA, FTOHs	• PFOA, PFOS, PFHxS • C8 fluorotelomers (8:2 FTS) • C6 fluorotelomers, PFOA	• n:2 FTUCA • n:3 FTCA (5:3FTCA) • n:2 FTSA • EtFOSA	• PFOS • 6:2 FTS, 8:2 FTS • F53B



Environmental Science Processes & Impacts

ROYAL SOCIETY OF CHEMISTRY

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An overview of the uses of per- and polyfluoroalkyl substances (PFAS)†

Juliane Glüge,*[a] Martin Scheringer,[a] Ian T. Cousins,[b] Jamie C. DeWitt,[c] Gretta Goldenman,[d] Dorte Herzke,[ef] Rainer Lohmann,[g] Carla A. Ng,[h] Xenia Trier[i] and Zhanyun Wang[j]

Example Source Signatures

Aqueous Film Forming Foam (AFFF)

Types of Fluorine-Based AFFF

TRC

Legacy 1st Generation AFFF

- PFOS or PFOS"R" based (80%)
- Telomer based (20%)
- PFOA-based (until early 1970s)
- Developed in 1960s
- Production ended in 2002
- Inventory remains in many locations
- **Contains PFOS & PFHxS and possibly PFOA**

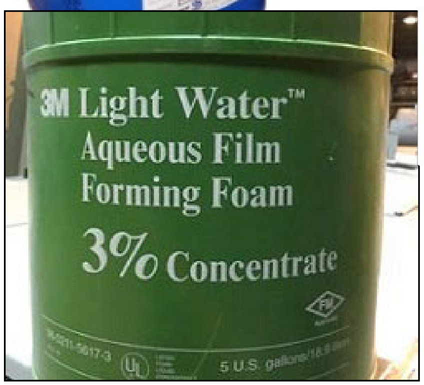
2nd Generation Fluorotelomer & Precursors (ECF) AFFF

- Sold from 1970s - 2016
- Telomers
- PFOS**R** compounds (R= cationic and anionic functional groups) "precursors"
- **PFOSR – transformation to sulfonates**
- **Long-chain fluorotelomers (8:2 FTS) can breakdown to PFOA**

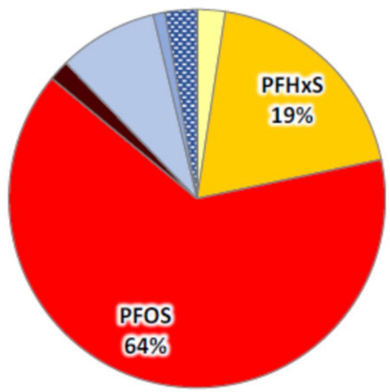
Modern Fluorotelomer AFFF

- Most foam mfrs transitioned to this
- **No PFOS and no breakdown to PFOS**
- **Short-chain fluorotelomers (6:2 and 4:2 FTS)**
- **May contain trace amts of PFOA and PFOA precursors**
- Considered lower in toxicity and reduced BAP

Aqueous Film Forming Foam (AFFF)



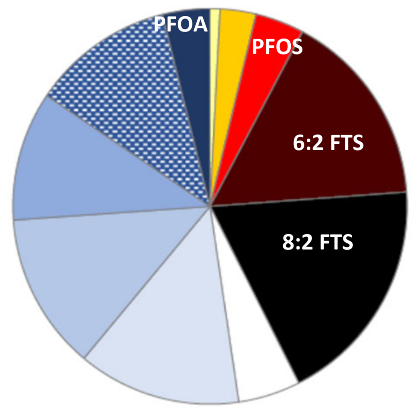
PFOS-Based AFFF



1st Generation

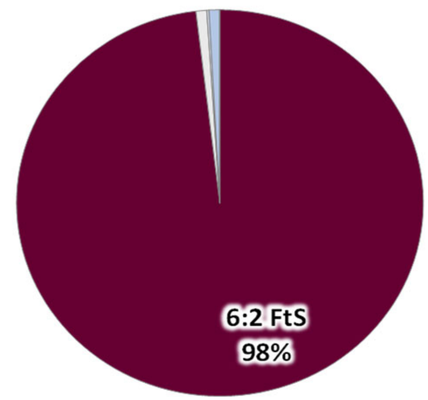
- Note: Typical composition is mainly PFOS and PFHxS

2nd Generation



8:2 and 6:2 FTS-Based

AFFF - Sthamex AFFF
Total = 9,681 ug/kg



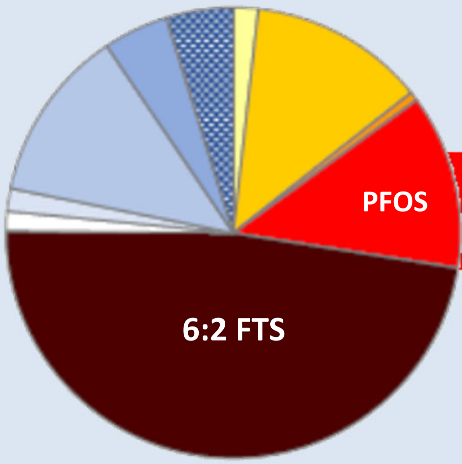
Modern Fluorotelomer

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.

Modern C6/PFOS-Based AFFF Mix from Hangar Release

Pre-TOP Assay

PFAS **100,000 ng/L**



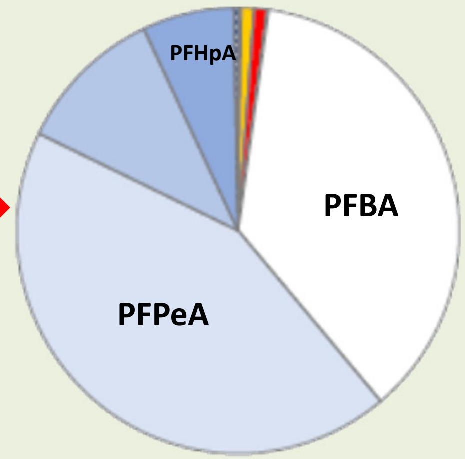
6:2 FTS	40,000
PFOS	10,000
PFPeA	1,300
PFBA	1,100
PFHpA	4,000

Accelerated Weathering

Post-TOP Assay

PFAS **1,200,000 ng/L**

10x increase associated with transformation of 6:2 FTS derivatives

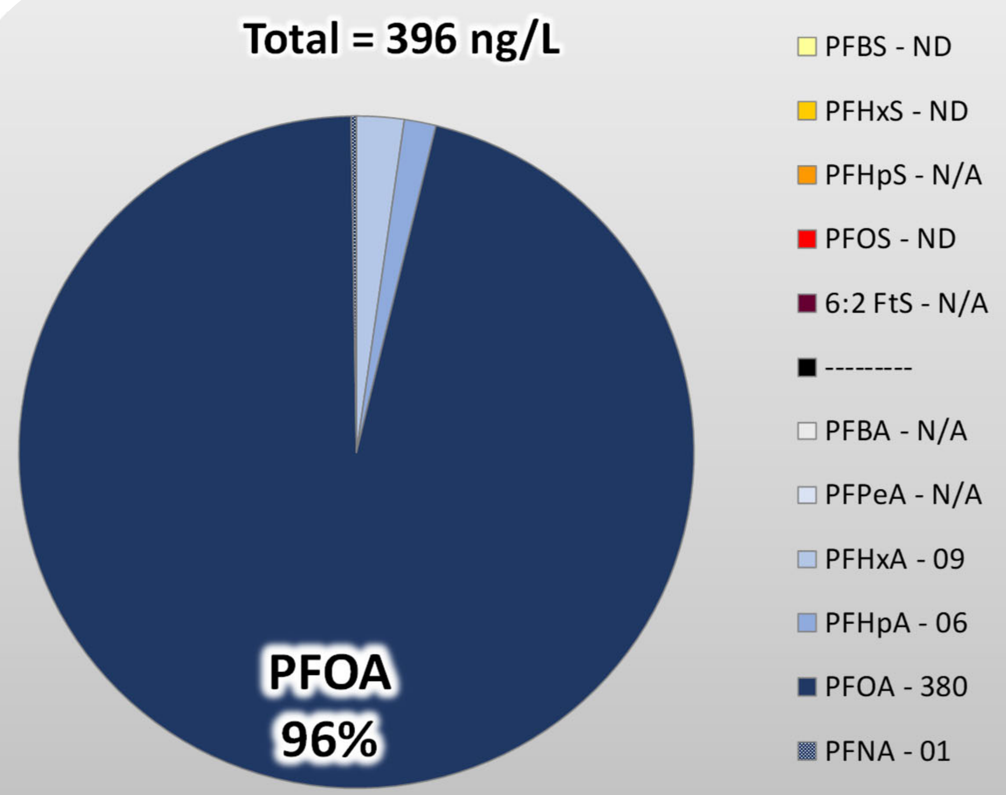


Concentrations ng/L

		Concentration Change
6:2 FTS	1,000	-39,000 ng/L
PFOS	11,000	+ 1,000 ng/L
PFPeA	520,000	+519,000 ng/L
PFBA	400,000	+399,000 ng/L
PFHpA	80,000	+ 76,000 ng/L

Plastics Manufacturing

Site manufactured polytetrafluoroethylene (PTFE) - coated fiberglass



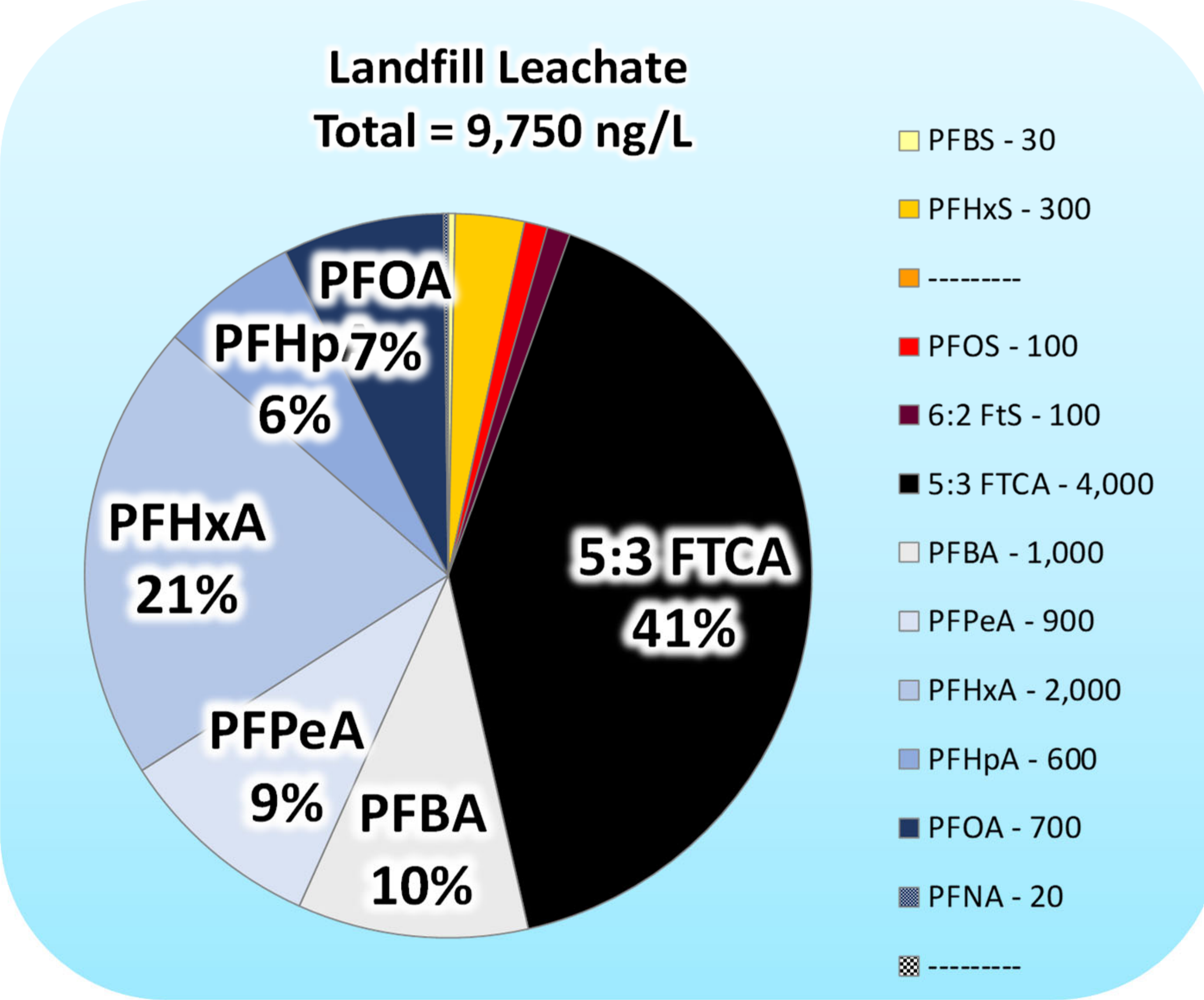
Catch Basin Sample

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.

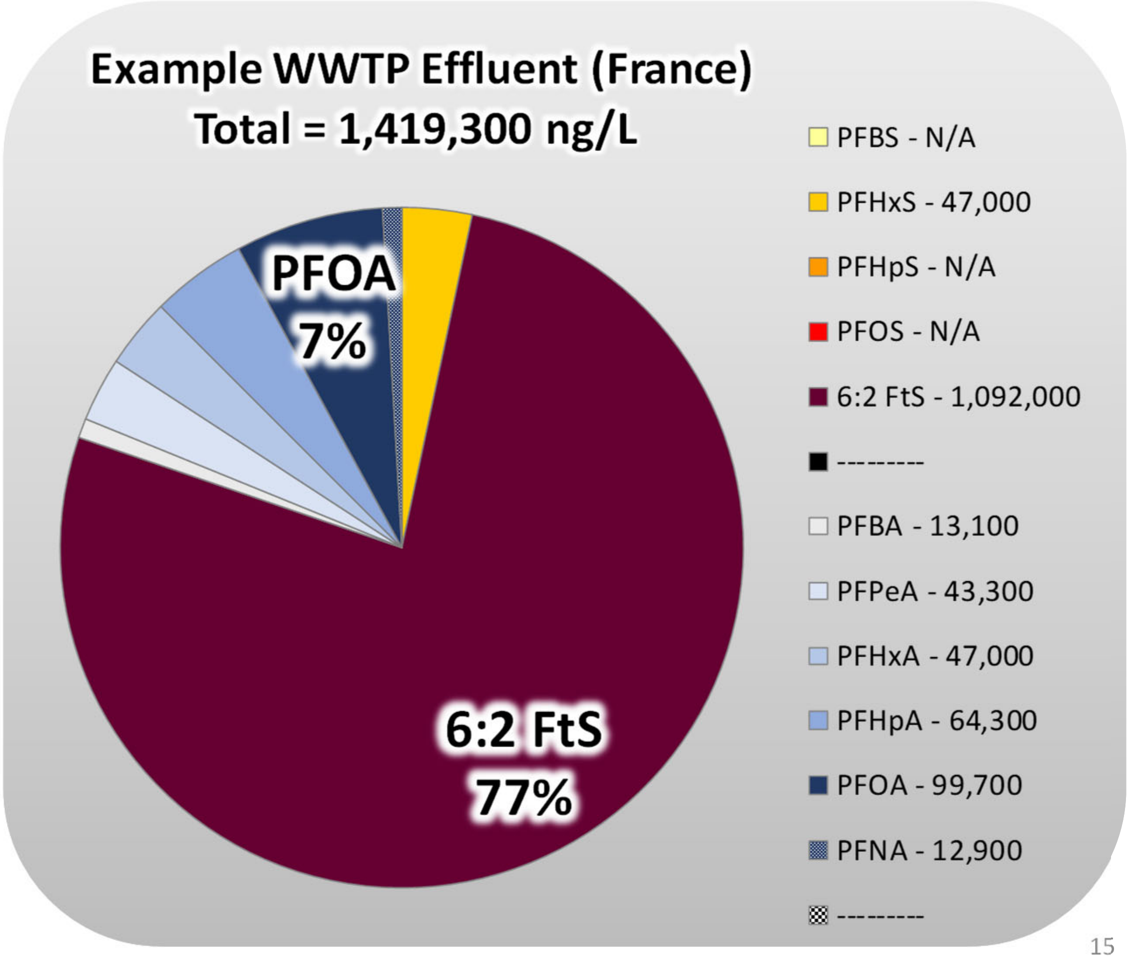


Data source:

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)

WWTP Effluent

Composition is highly variable and depends on influent sources (e.g., chrome plating)



Data source:

1. X. Dauchy et al., 2017. Mass flows and fate of per- and polyfluoroalkyl substances (PFASs) in the wastewater treatment plant of a fluorochemical manufacturing facility, Science of the Total Env. 526 (2017) 549-558.

Groundwater and Surface Water Signatures

Need to Consider Fate and Transport Phenomena

TRC

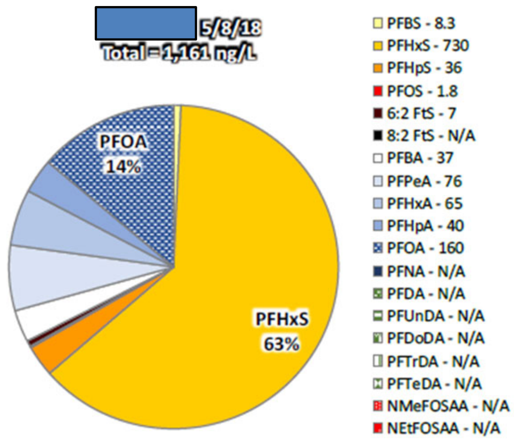
Examples:

- Degradation (e.g., 6:2 FTS, 8:2 FTS → PFBA, PFPeA, PFHxA, PFHpA, PFOA)
- Retention of PFAS in source area soil
- Chemical retardation due to sorption to organic carbon
- Mixing/Dilution
- Plume commingling

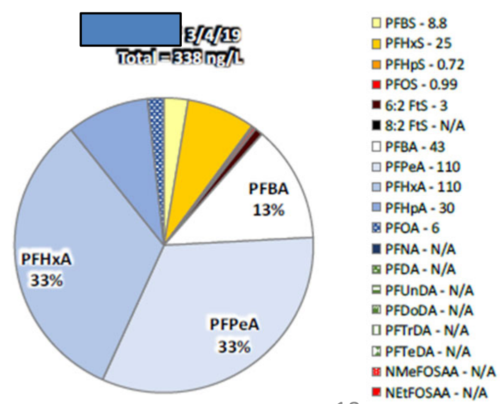
How Do Labs Deal With Solids in Aqueous Samples?

- The following samples *contain* non-settleable particulate matter which plugged the solid-phase extraction column.
- The following samples *were decanted* prior to preparation due to excessive sediment in bottle.
- The following sample *was decanted* prior to preparation due to having floating sediment particles and also some wood material.
- The following sample *was centrifuged* prior to spiking and the extraction due to the color being a dark yellow with floating material instead, which we cannot decant.
- Samples have fine sediment at the bottom of the bottle *and mixed in with the sample water.*
- *Due to residual amounts of sediment in the sample, the sample container was placed in the oven and dried after extraction, and the weight was then recorded. The container was then extracted per the SOP.*

Sample from 1” temporary well turbid

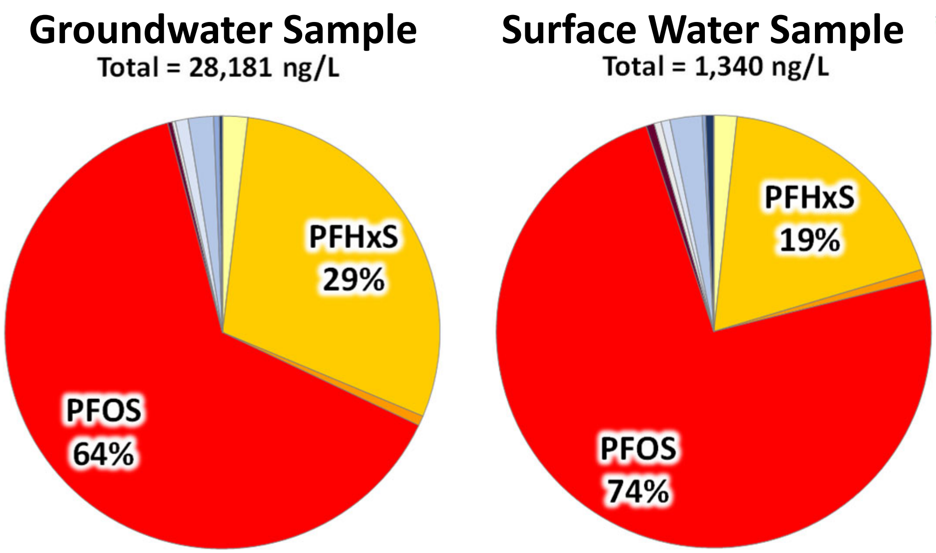


Sample from 2” developed MW clear

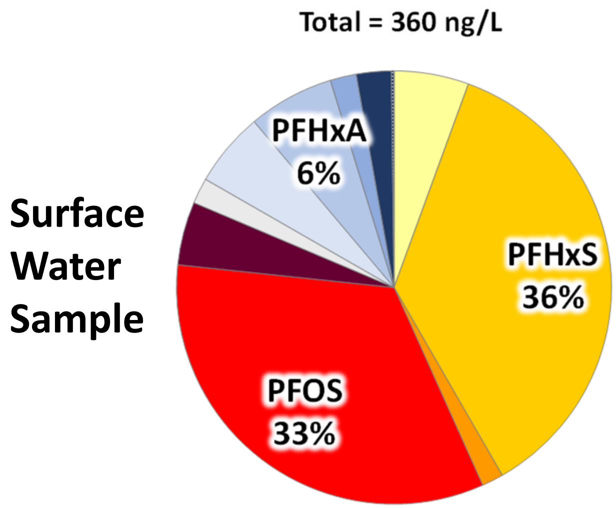


AFFF Releases

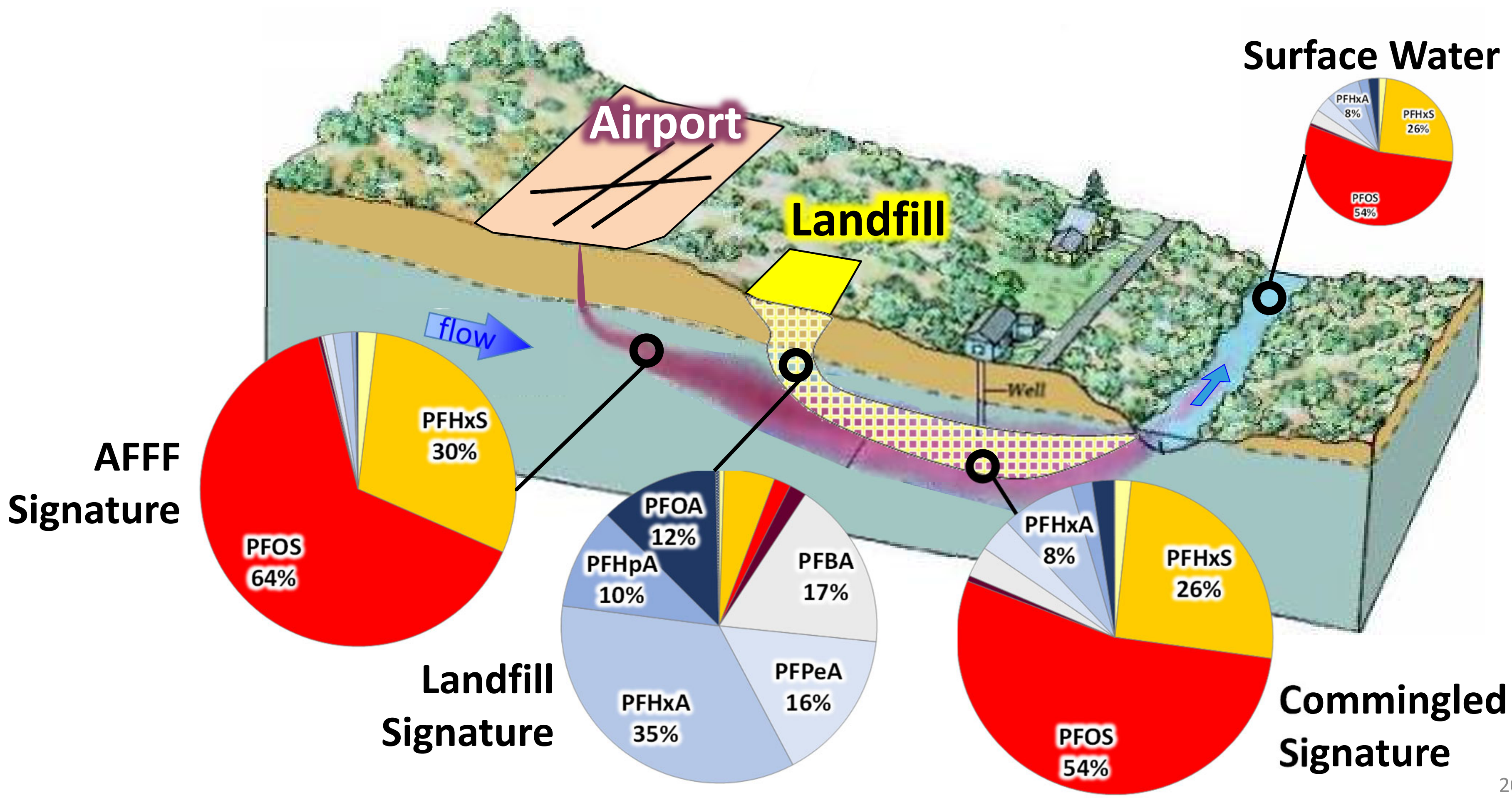
- Surface water very similar to groundwater signature from 1st generation AFFF



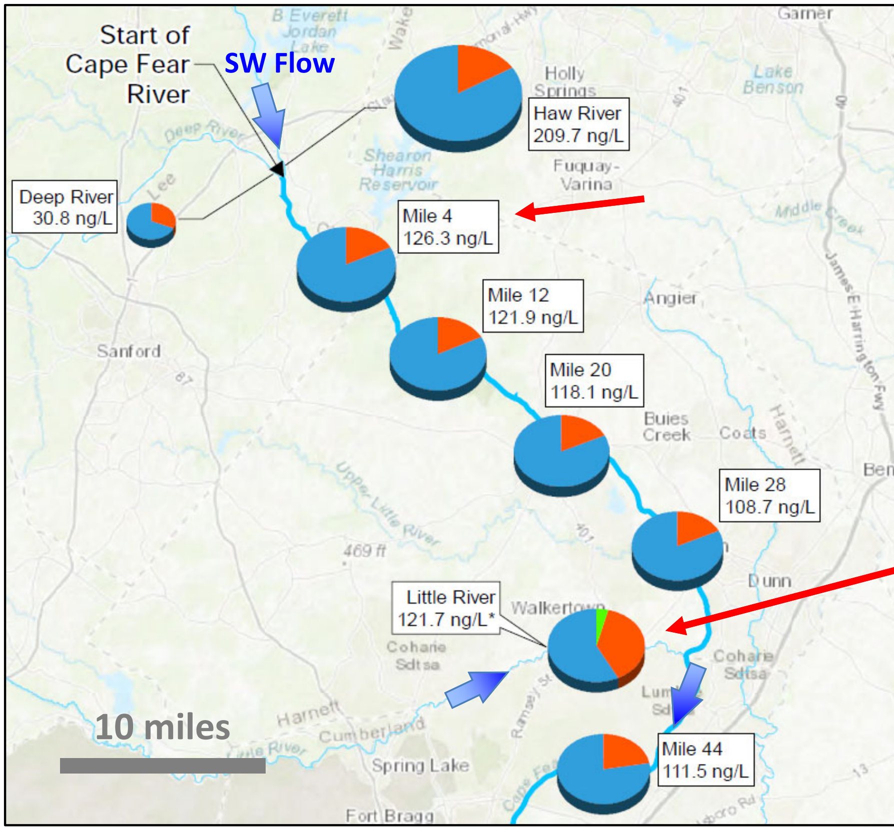
- Other surface water sample may be from combined 1st and Modern Fluorotelomer AFFF



Commingled Plumes



Surface Water – PFAS Persistence



Source:

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

Preliminary TRC interpretation based on figure only.

- 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)

Surface Water – Dilution

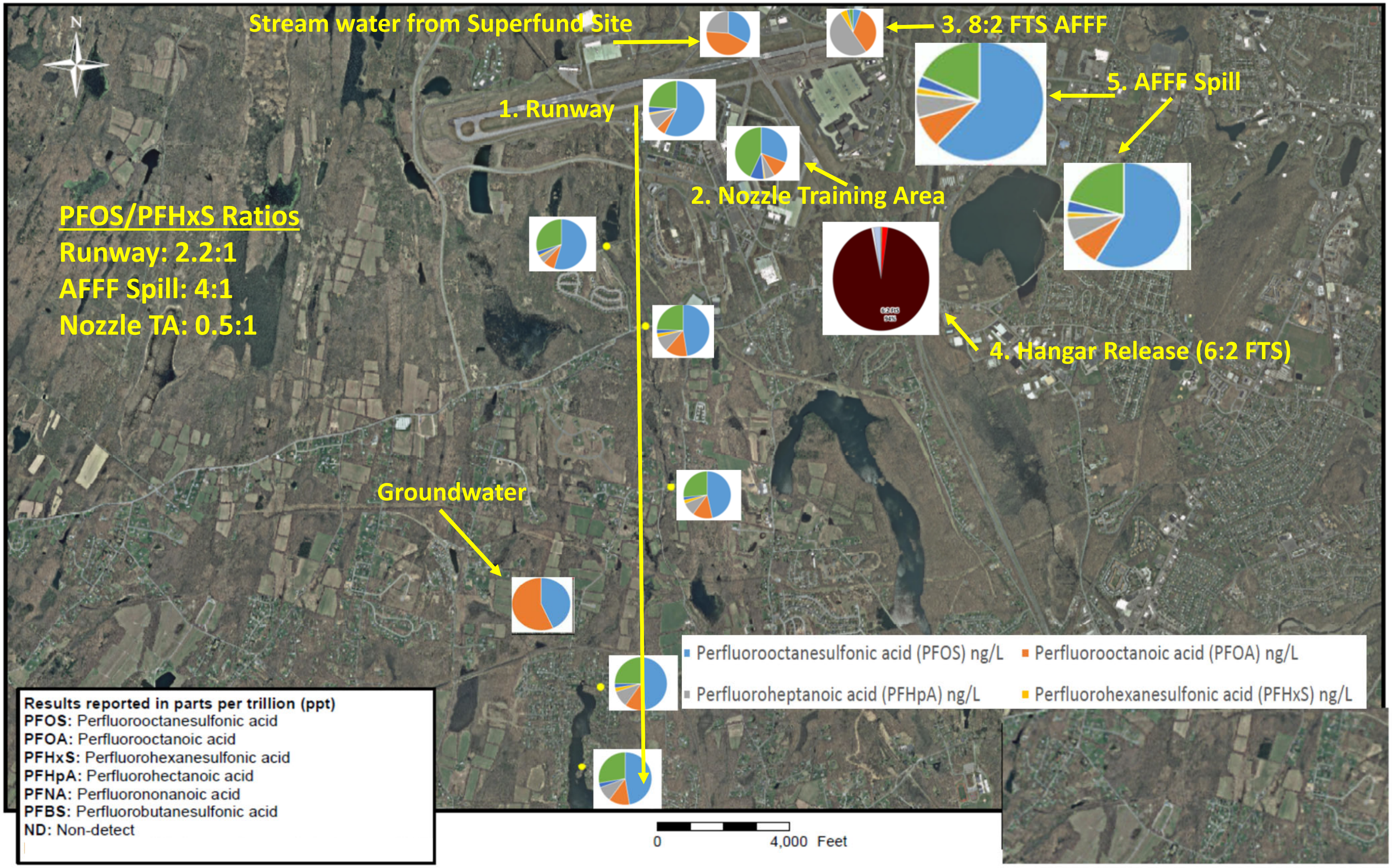
- WWTP effluent impacts lessoned due to dilution
- Lakes can be points of retention and mixing

Table 5. T-PFAA Concentrations in WWTP Effluents and Downstream Receiving Waterbodies and Estimated Concentrations Based on Effluent Dilution Model Results.

Wastewater Treatment Plant	Receiving Waterbody	Season	WWTP Discharge Flow (cfs)	Receiving Waterbody Flow (cfs)	WWTP T-PFAA effluent concentration (ng/L)	Measured T-PFAA conc. in receiving waterbody (ng/L)
Marine Park (Flowing stream)	Lower Columbia River	spring	16.2	229,000	42.1	< 2
		fall	13.9	117,000	41.8	< 2
Pullman	South Fork Palouse River	spring	3.3	23	61.4	16.6
		fall	4.0	3.9	48.1	73.5
Spokane Riverside	Spokane River	spring	49.5	12,335	91.8	< 2
		fall	38.4	1,405	71.4	9.37
Sumner	Puyallup River	spring	2.7	3,353	68.9	< 2
		fall	2.7	1,071	116	< 2
Medical Lake (Stagnant waterbody)	West Medical Lake	spring	0.4	---	107	153
		fall	0.5	---	125	170

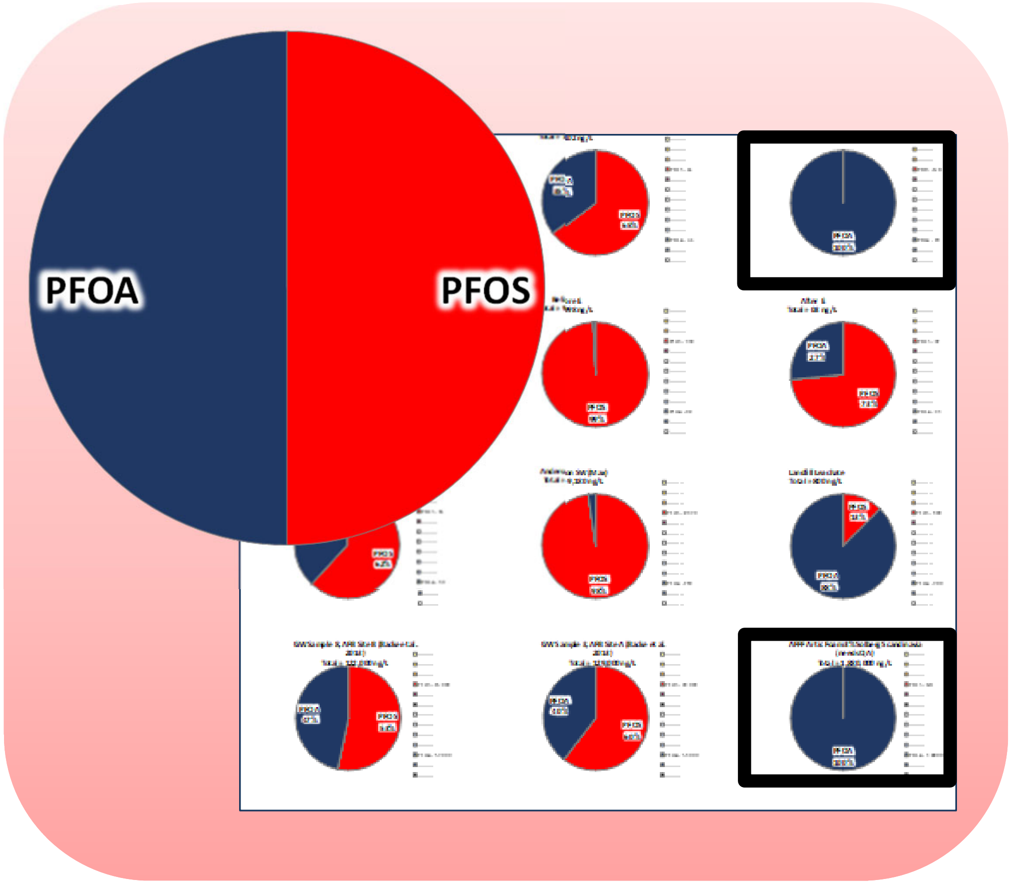
Source:

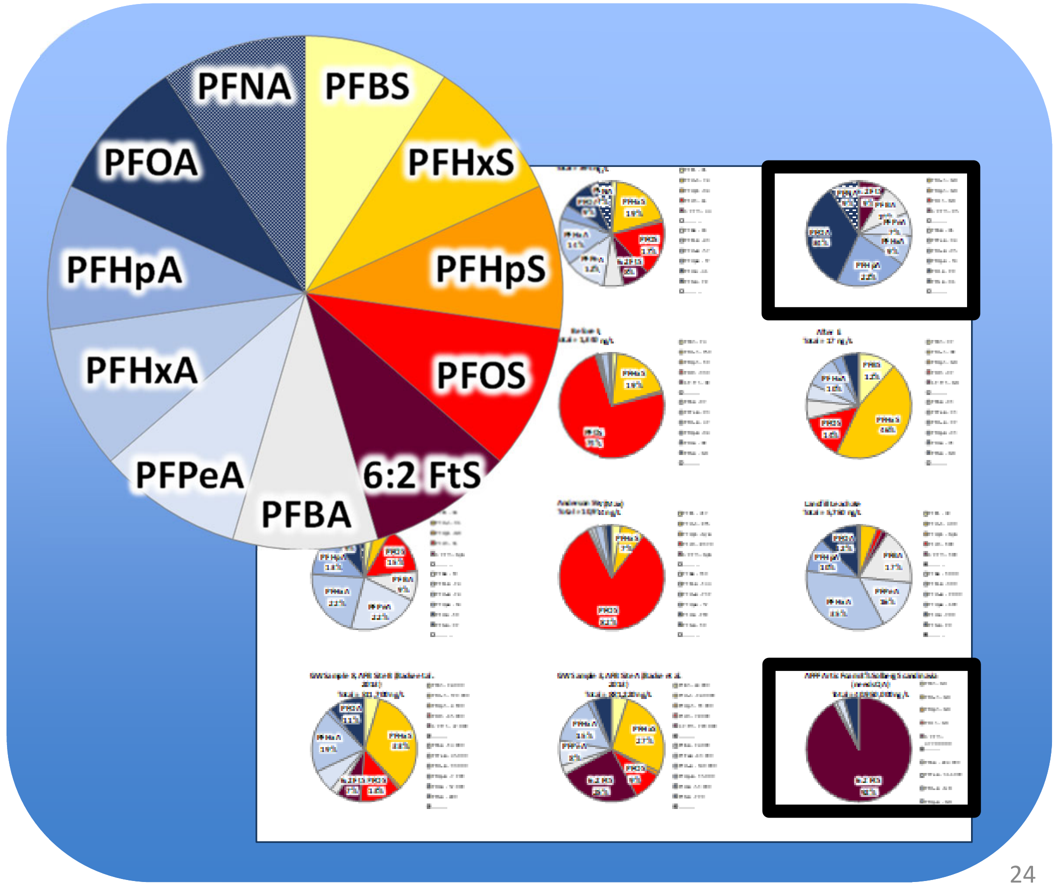
1. Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Rivers and Lakes, 2016, Department of Ecology, State of Washington, Publication No. 17-03-021, September 2017



Stream water from Superfund Site
3. 8:2 FTS AFFF
1. Runway
5. AFFF Spill
2. Nozzle Training Area
PFOS/PFHxS Ratios
Runway: 2.2:1
AFFF Spill: 4:1
Nozzle TA: 0.5:1
4. Hangar Release (6:2 FTS)
Groundwater
Perfluorooctanesulfonic acid (PFOS) ng/L
Perfluorooctanoic acid (PFOA) ng/L
Perfluoroheptanoic acid (PFHpA) ng/L
Perfluorohexanesulfonic acid (PFHxS) ng/L
Results reported in parts per trillion (ppt)
PFOS: Perfluorooctanesulfonic acid
PFOA: Perfluorooctanoic acid
PFHxS: Perfluorohexanesulfonic acid
PFHpA: Perfluorohectanoic acid
PFNA: Perfluorononanoic acid
PFBS: Perfluorobutanesulfonic acid
ND: Non-detect
0
4,000 Feet

Example Difference Based on Analytes Selected for Signature Evaluation





Multiple Lines of Evidence Needed

Chemical Signatures / Fingerprints	**Operational history** (e.g., manufacturing dates; PFOS/PFOA phase-outs)
Isomer profiling (linear vs. branched; telomerization vs. ECF)	**High resolution mass spectrometry methods** (QTOF)
Chain lengths, including ratios* (PFCA/PFSA, PFOA/PFOS, rel abundance PFCA, PFSA)	**Statistical methods** (differentiating different sources; PCA, geospatial analyses)
Source PFAS patterns (including development of a library)	**Timing of release** (e.g., AFFF)

***Ratios can get tricky: mixtures of sources, partitioning (F&T), shift in market towards shorter chains, biotransformations**

Takeaway Messages

- Chemical signatures can be a useful forensic tool.
- The choice of PFAS selected for signature evaluation must be considered.
- Very large group transformation intermediates present 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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ACKNOWLEDGMENTS:
Mike Eberle, TRC

Thank you

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PER- and POLYFLUOROALKYL SUBSTANCES

TECHNICAL and REGULATORY UPDATE

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INTRODUCTION

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THE PFAS PUZZLE

- Lack of federal regulation
- Non-uniformity of state regulation
- Non-uniformity of test methods
- Lack of environmental test methods
- Variety of compound lists
- Thousands of PFAS compounds
- Low DLs vs contaminated matrices
- Ultra restrictive field sampling guidance

By leading the way for PFAS testing Pace Analytical® helps to reduce confusion and provide guidance through the above challenges.

AGENDA

1. SOURCES
2. TEST METHODS
3. REGULATORY UPDATE
4. FIELD SAMPLING and RESOURCES
5. PROJECT SET-UP WITH THE LAB

PER- AND POLYFLUOROALKYL SUBSTANCES - PFAS

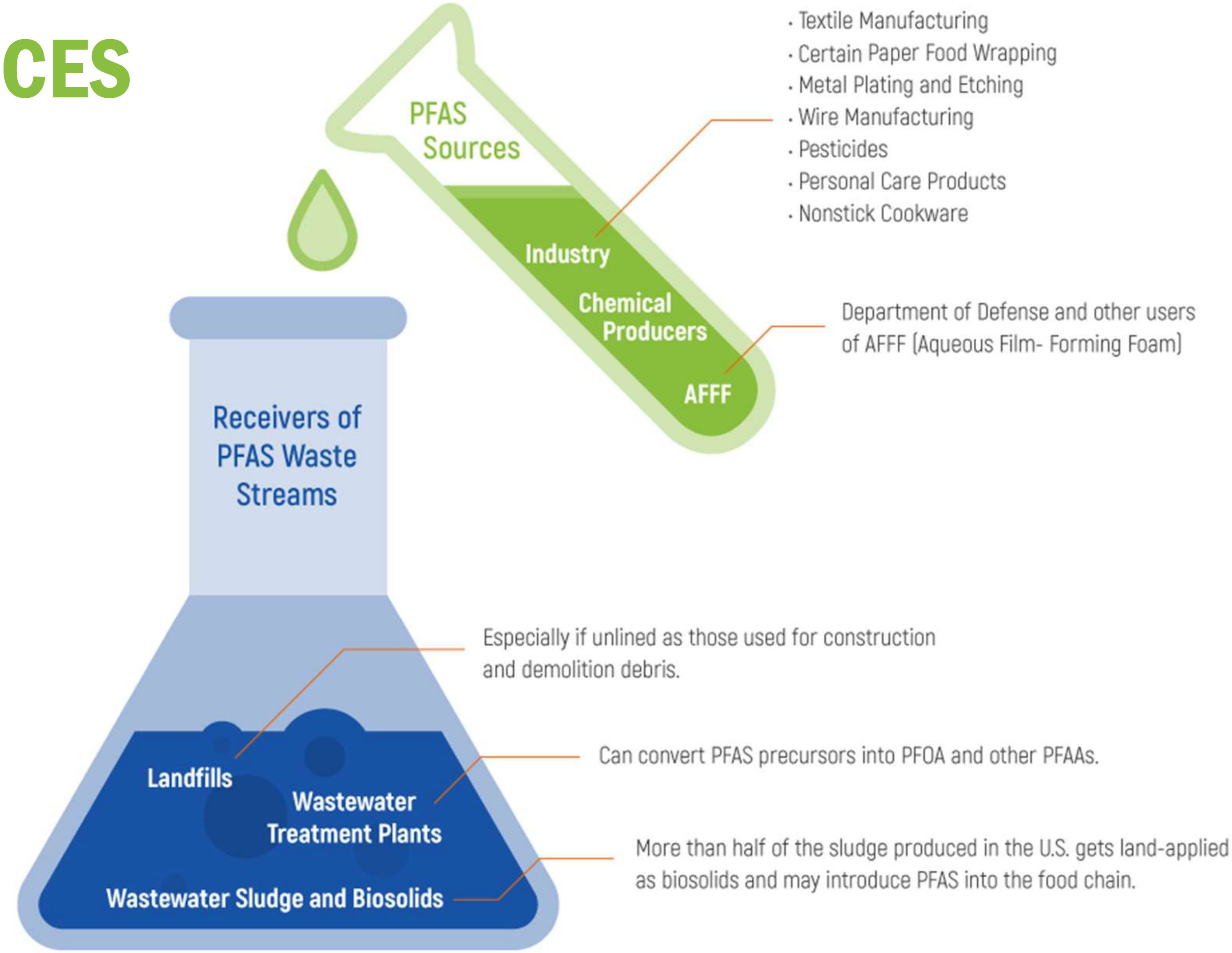
- Per- and polyfluoroalkyl substances (PFAS) are a large, diverse group of manufactured compounds used in a variety of industries:

Aerospace, automotive, apparel, food packaging, fire-fighting foams, non-stick coatings/cookware, wire, carpeting and metal plating

- Entirely man-made
- Documented health effects
- Bioaccumulative
- Hydrophilic

The P*FAST*® Mobile Lab is housed in a self-contained, climate-controlled trailer ready for mobilization and quick set up.

SOURCES


PFAS Sources
Industry
Chemical Producers
AFFF
· Textile Manufacturing
· Certain Paper Food Wrapping
· Metal Plating and Etching
· Wire Manufacturing
· Pesticides
· Personal Care Products
· Nonstick Cookware
Department of Defense and other users of AFFF (Aqueous Film- Forming Foam)
Receivers of PFAS Waste Streams
Landfills
Wastewater Treatment Plants
Wastewater Sludge and Biosolids
Especially if unlined as those used for construction and demolition debris.
Can convert PFAS precursors into PFOA and other PFAAs.
More than half of the sludge produced in the U.S. gets land-applied as biosolids and may introduce PFAS into the food chain.

SOURCES - PROJECT SET UP WITH THE LAB

Are there any potential sources of PFAS contamination upstream:

- Airport, refinery, fire training area – AFFF impacts
- Lined Landfill – leachate; unlined landfill – groundwater, surface water
- Textile, paper food packaging, polymers, plastics, leather goods, pesticides, personal care products, non-stick cookware, wire, insulation producers
- Metal plating and etching
- PFAS chemical producers

SOURCES

PFAS Production Facilities

Due to the solubility and persistence of many PFAS, environmental release mechanisms associated with these facilities include:

- Air emission and dispersion
- Spills
- Disposal of manufacturing wastes and wastewater

Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas but potentially over the surrounding area.

SOURCES

Industrial companies that use PFAS in their products

- Aqueous Film Forming Foam (AFFF)
- Textiles and Leather: factory and consumer applied coating to repel water, oil, and stains
- Paper Products: surface coatings to repel grease and moisture
- Metal Plating and Etching: corrosion prevention, wear reduction, surfactant, fume suppressant
- Wire Manufacturing: coating and insulation
- Pesticides, cleaning products, polishes, photo processing

SOURCES – RECEIVERS OF PFAS

Solid Waste Facilities

- PFAS production facilities waste disposal
- Secondary manufacturing sites waste disposal
- Municipal solid waste facilities
    - Consumer and industrial PFAS-containing waste
    - Leachate
- Unlined landfills such as C&D

SOURCES – RECEIVERS OF PFAS

Wastewater Treatment

Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate, firefighting foam, and industrial effluent results in the discharge of PFAS to Wastewater Treatment Plants (WWTPs).

WWTP Operations

- Conventional sewage treatment methods do not remove or treat PFAS
- Conventional treatment processes can change PFAS concentrations
  - Increase in PFAA due to transformation of precursor PFAS

SOURCES – RECEIVERS OF PFAS

WTTP Biosolids

- PFAS have been found in domestic sewage sludge
- More than half of the sludge produced in the United States is applied to agricultural land as biosolids
- Application of biosolids as a soil amendment can result in a transfer of PFAS to soil
- PFAS can enter the food chain through the use of biosolids-amended soil
- PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS contaminated biosolids

TEST METHODS

Characteristic	EPA 537.1	EPA 533	PFAS by ID
Matrix	Drinking Water	Drinking Water	All matrices
Compounds	18	25	NA
Holding Times, days	14/28	28/28	28/28
Extraction	Solid Phase (SPE)	Solid Phase (SPE)	Solid Phase (SPE)
Quantification	Internal Standard (IS)	Isotope Dilution (ID)	Internal Standard (IS)
Notes		Developed for UCMR 5 and additional PFAS. Cannot replace 537.1.	Labs required to modify 537, DoD QSM B-15 or other methods as 537/533 are prescriptive methods.

TEST METHODS

Characteristic	MPCA Guidance	WDNR Guidance	DoD QSM B-15	OW 1600/EPA 8328 (under development
Matrix	Non-potable Water, Solids, Biota	Non-potable Water, Solids, Biota	Non-potable Water, Solids	Non-potable Water, Solids, Biota
Compounds	33	33	25/24*	24
Holding Times, days	28/30	28/28	28/28	14/28
Extraction	Solid Phase (SPE)	Solid Phase (SPE)	Solid Phase (SPE)	Solid Phase (SPE)
Quantification	Isotope Dilution (ID)	Isotope Dilution (ID)	Isotope Dilution (ID)	Isotope Dilution (ID)
Notes			*25 in water, 24 in solids	Currently in multi-lab validation step with final method by late 2021-2022.

TEST METHODS

Characteristic	TOP Assay	True-TOF™, AOF, EOF, TF
Matrix	Non-potable Water, Solids	Non-potable Water, Solids
Compounds	Up to 40	1 (total)
Holding Times, days	28/28	28
Extraction	Solid Phase (SPE)	Varies
Quantification	Isotope Dilution (ID)	NA
Notes	Non-Targeted method designed to quantify total of all PFAS precusor chemicals.	Non-Targeted Combustion Ion Chromatography method designed to quantify all PFAS present

REGULATORY UPDATE - FEDERAL

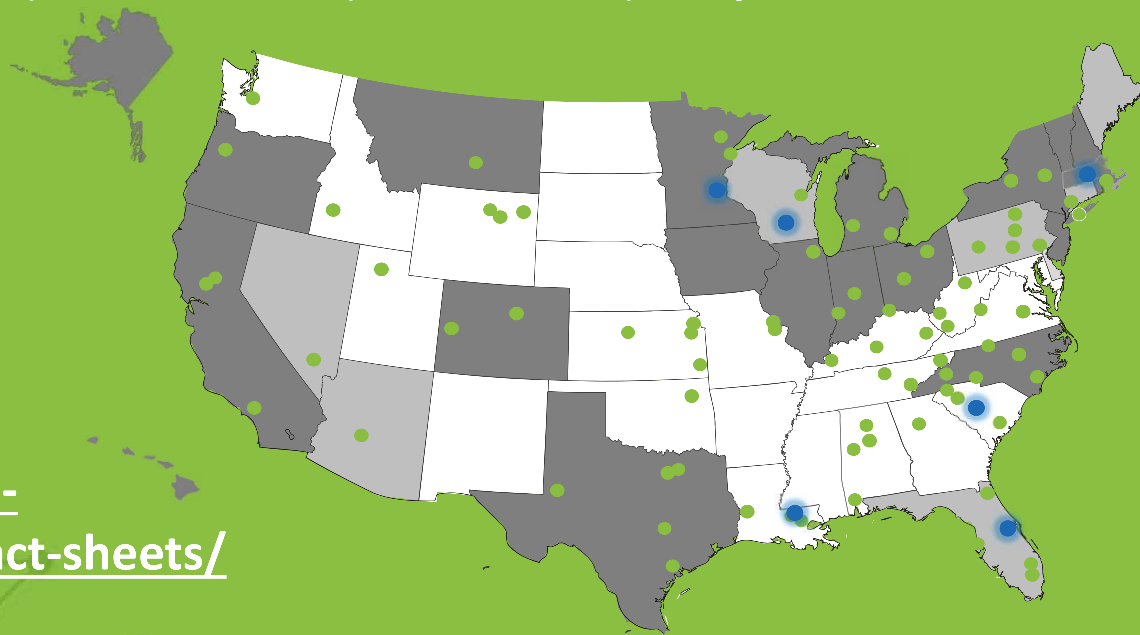
- 176 PFAS added to EPA’s Toxics Release Inventory (TRI)
- Final regulatory determination to set PFOA and PFOS limits for Public Water Systems
- DoD set MCLs for PFOA and PFOS for all Public Water Systems that serve all installations worldwide in 2020
- Some observers believe that EPA is fast-tracking implementation of enforceable limits for PFOA and PFOS under SDWA

REGULATORY UPDATE - FEDERAL

- President Biden’s Environmental Plan stipulates that his administration will move to designate PFAS as hazardous substances and accelerate toxicity studies
- EPA issued “Interim PFAS Strategy” for wastewater and stormwater regulated under the National Pollutant Discharge Elimination System (NPDES)
- EPA plans to test the nation’s water systems again for PFAS during UCMR 5, and this time will include all small systems that serve >3,300 consumers

REGULATORY UPDATE - STATE

So far 25 states have established standards/guidance for PFAS in drinking water, groundwater, surface water, wastewater, and/or soil:

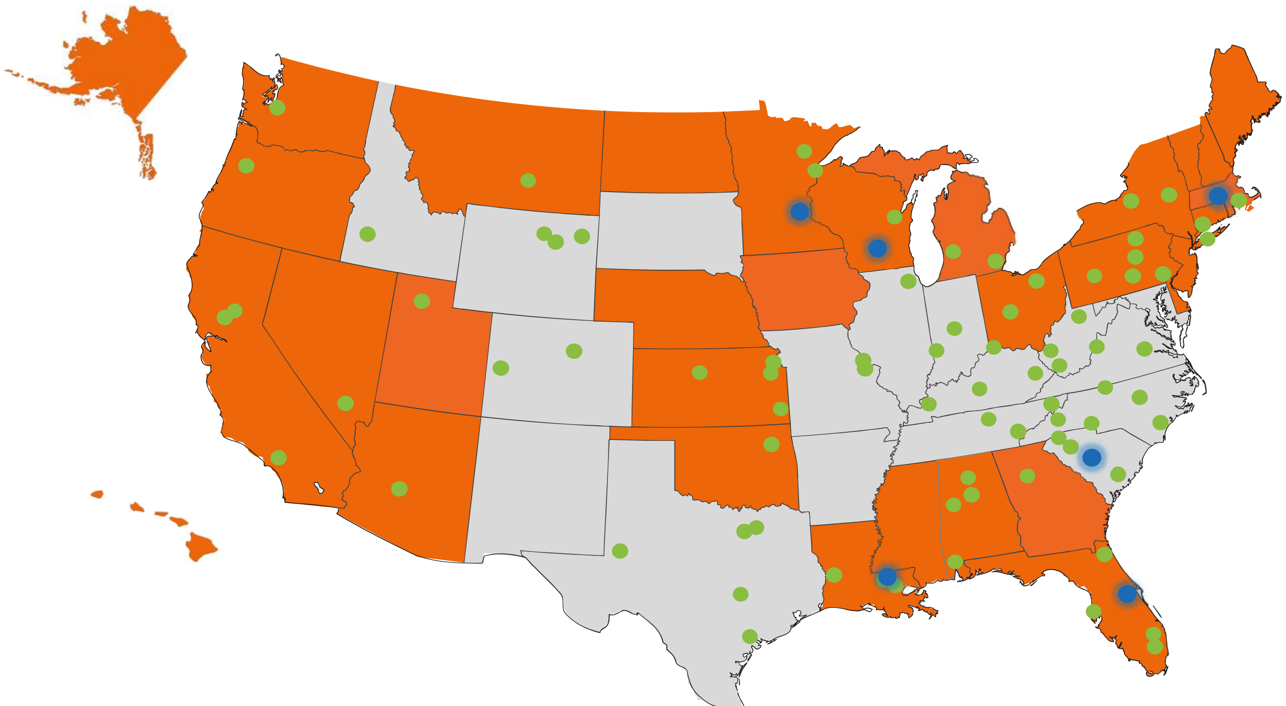


Promulgated limits issued

Guidance levels issued

See https://pfas-1.itrcweb.org/fact-sheets/

CERTIFICATIONS



PFAS certification not available and not required for non-DoD projects

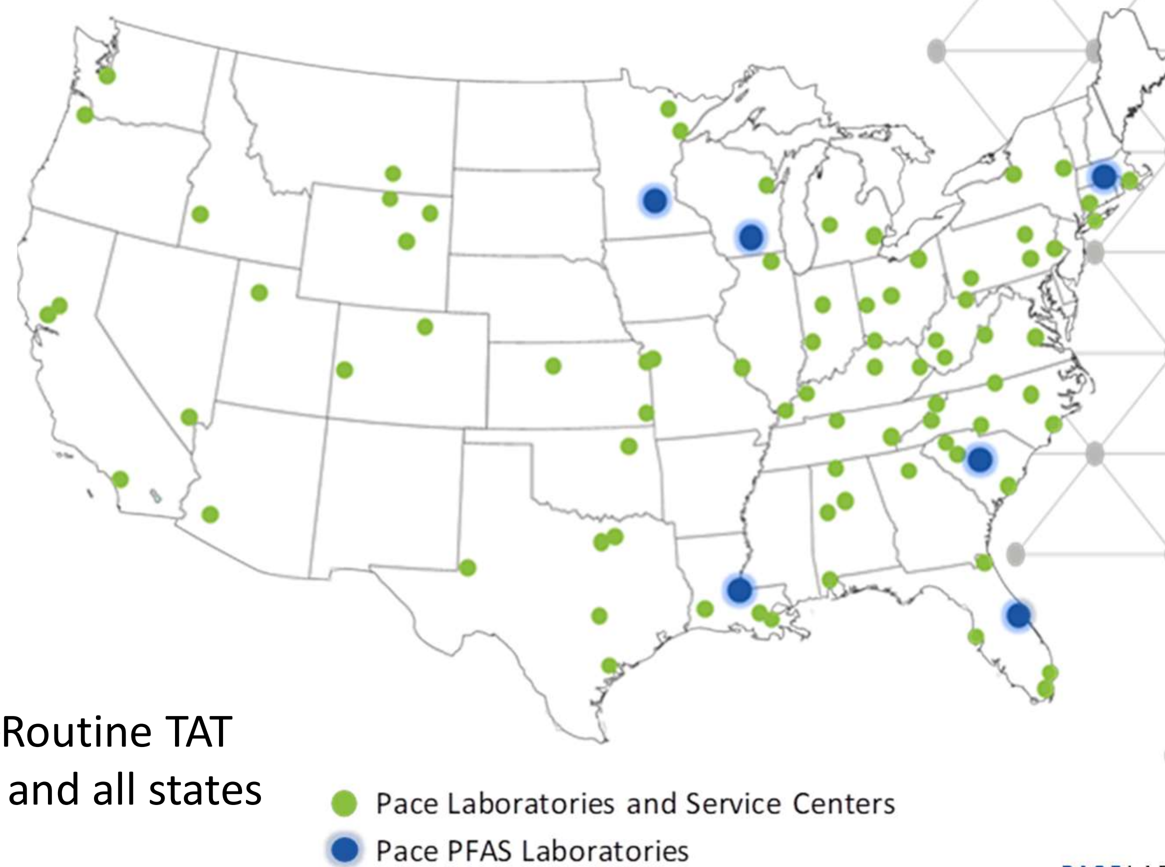
PFAS Certified

Pace PFAS lab

Pace Gulf Coast and SC are PFAS DoD ELAP accredited throughout the U.S.

PFAS AT PACE ANALYTICAL

- AFFF
- Leachate
- Biota
- Solid Waste TCLP/SPLP
- Sediment
- Soil
- Sludge/Biosolids
- Wastewater
- Non-potable Water
- Potable Water
- TOP Assay
- True-TOF™
- TAT – Emergency Responses–Routine TAT
- DoD ELAP Accreditation, TNI, and all states
- P*FAST*® Mobile Lab



PFAS TAKE-AWAYS

- Carefully consider your objectives.
- Compound list and test method selection are critical.
- Sample collection is key to getting good data.
- Pace Analytical® is your PFAS partner, not simply your lab.

Pace Analytical®
ENVIRONMENTAL SCIENCES

ADDITIONAL RESOURCES

Visit:

- **PFAS.com**
- **PACELABS.COM | Search: PFAS**

Thank you for attending

SPECIALTY SERVICES

LD SAMPLING GUIDE

Polyfluoroalkyl Substances (PFAS) und in a variety of sources, including ipment typically used to collect soil, oundwater, surface water, sediment, and drinking water samples. Due to this concern, as well as the need for very low reporting limits, special handling and care must be taken when collecting samples. To avoid PFAS sample contamination, Pace Analytical® has developed this Guide of recommendations for collecting PFAS samples for testing and analysis.

BEST PRACTICES FOR PFAS SAMPLE COLLECTION

- Wash hands and use new nitrile gloves for each sample collected
- Groundwater, surface water, or drinking water samples should not be filtered as the glass fiber on the filter can potentially absorb PFAS
- Collect the PFAS sample first, prior to collecting samples for any other parameters into any other containers. This avoids contact with any other type of sample container, bottles or package materials
- Do not place the sample bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap

When the labeled sample is collected, place the samples in an individual sealed plastic bag parate from all other sample parameter es

es must be chilled during shipment and ive at the lab at <6 C +/-2

FIELD REAGENT BLANKS (FRB)

When sampling for PFAS, it is recommended that field reagent blanks be collected during sampling to check for residual PFAS during the sample collection process. The purpose of the FRB is to ensure that PFAS measured in the field samples were not inadvertently introduced into the sample during sample collection and/or handling.

Analysis of the FRB is required only if a field sample contains a method analyte or analytes at or above the MRL. The FRB is processed, extracted, and analyzed in exactly the same manner as a field sample. FRBs include a container filled with preserved water and an empty unpreserved container (per EPA methodology). To collect the FRB, simply pour the preserved water into the empty unpreserved container at the time a sample is collected in the field.

FRBs are required by EPA Method 537, but the number of FRBs to collect (for each site, for each representative sample, or not at all) is at the discretion of the customer and/or regulator overseeing the project.

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