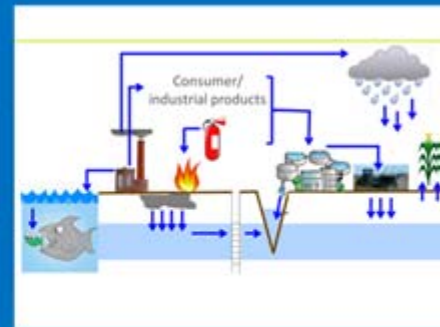


# PFAS Sampling



## Technical Training for Waste Site Cleanup Professionals

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**AECOM**

# Background Levels

## Where Do We Find PFASs?

### FLUOROTECHNOLOGY MAKES IMPORTANT PRODUCTS FOR VITAL INDUSTRIES POSSIBLE

FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemistries by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemistries that offer the same high-performance benefits, but with improved environmental and health profiles.





## Background Levels

### Perfluorocarboxylic Acid Content in 116 Articles of Commerce

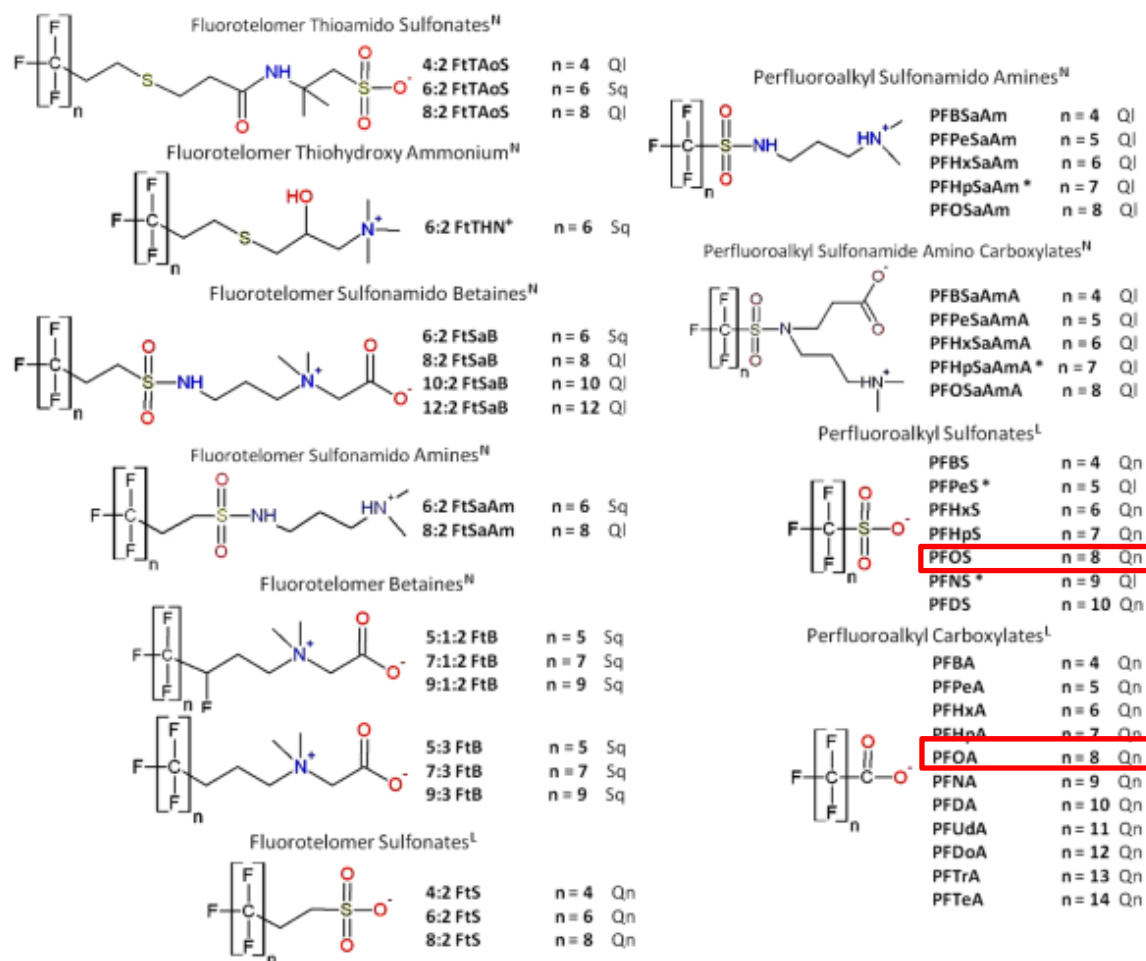
Table 6-1. Comparison of source strengths for total amount of PFCA (TPFCA) in a hypothetical, “typical” American home <sup>a</sup>

Group ID	Article category	TPFCA in article	Article quantity <sup>b</sup>	TPFCA in home (mg)
A	Pre-treated carpeting <sup>c</sup>	48.4 ng/cm <sup>2</sup>	150 m <sup>2</sup>	72.6
B	Commercial carpet-care liquids	12000 ng/g	6 kg <sup>d</sup>	71.8
C	Household carpet/fabric-care liquids and foams	953 ng/g	1 kg	0.95
D	Treated apparel	198 ng/g	2 kg	0.40
E	Treated home textile and upholstery	336 ng/g	5 kg	1.68
F	Treated non-woven medical garments	795 ng/g	0 kg	0
G	Treated floor waxes and stone/tile/wood sealants	2430 ng/g	1 kg	2.42
H	Treated food contact paper	3100 ng/g	0.01 kg	0.03
I	Membranes for apparel	124 ng/g	1 kg	0.12
J	Thread seal tapes and pastes	603 ng/g	0.02 kg	0.01
K	Non-stick cookware	0.028 ng/cm <sup>2</sup>	1 m <sup>2</sup>	0.0003
L	Dental floss and plaque removers	31.3 ng/g	0.005 kg	0.0002
M	Miscellaneous	69.5 ng/g	0	0

<sup>a</sup> The average, single-family home size in the U.S. in 2004 was 2330 ft<sup>2</sup> (<http://www.nahb.org/>). <sup>b</sup> The quantities of articles are rough estimates. <sup>c</sup> Assuming 70% of floor area is carpet; conversion factors for total PFCA are given in supporting information. <sup>d</sup> For one application; dilution factor is considered.

USEPA Study, March 2009  
EPA/600/R-09/033

# Class of PFAS Compounds in AFFF Formulations



**Figure 1.** Target analyte classes, structures, and acronyms. Fluorotelomer PFAS are listed to the left and perfluorinated PFAS are listed on the right.

<sup>L</sup>Legacy classes of PFAS. <sup>N</sup>Newly-identified classes of PFAS. Data quality levels include quantitative (Qn), semi-quantitative (Sq), and qualitative (Ql). \*Indicates analytes analyzed for in AFFF only.

(Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS, Will J. Backe, Thomas C. Day, and Jennifer A. Field, Environ. Sci. Technol., 2013, 47 (10), pp 5226–5234.)

## Sense of Scale

- PFOS/PFOA Health Advisories
  - 70 parts per trillion = 70/1,000,000,000,000
- World Population = 7.4 billion
  - 70 ppt ~ 1 person / 2 world populations



# PFASs Ongoing Evolution





## PFAS Sampling for Water

- What are required and recommended when sampling for PFASs? ✓
- Where to sample for PFASs?
- Which PFASs to analyze for?
- Can we trust the data (cross-contamination)? ✓

### PFAS Sampling



Planning → Field Crew Training → Sampling → Tracking Data Change → Data Interpretation & Reporting  
& Analyses with Time

# Planning for PFAS Sampling

- Example PFAS sampling references
  - USEPA Method 537
  - Perfluorocarboxylic Acid Content in 116 Articles of Commerce, EPA/600/R-09/033
  - Navy Field Sampling Protocols for PFCs
  - Perfluorochemical (PFC) Field Sampling Protocol, Transport Canada, 2013
  - Interim Guideline on the Assessment and Management of Perfluoroalkyl and, Polyfluoroalkyl Substances (PFAS), Department of Environment Regulation, Western Australia, 2016
  - State guidance...
- Contact laboratory
- Develop quality assurance documents
- Conduct field crew training classes
- Site-specific work plan development on sampling strategy

Table 5-1. Sample breakdowns by article category

Category ID	Category name	Samples
A	Pre-treated carpeting	9
B	Commercial carpet-care liquids	9
C	Household carpet/fabric-care liquids and foams	12
D	Treated apparel	16
E	Treated home textile and upholstery	14
F	Treated non-woven medical garments	5
G	Treated floor waxes and stone/wood sealants	11
H	Treated food contact paper	5
I	Membranes for apparel	10
J	Thread sealant tapes and pastes	10
K	Non-stick cookware	14
L	Dental floss and plaque removers	8
M	Miscellaneous <sup>a</sup>	7

<sup>a</sup> Includes four car-care products, two boat-care products, one deck cleaner, and one dry sack for outdoor use.

- Regulators
- Project managers
- Field technicians
- Water supply system operation personnel
- Site safety officers



## Many Precautions for Sampling Procedures Don't Have Scientific Data To Prove The Concerns

**BE  
CAREFUL**

VS.

**OVER  
REACT**

Because we believe....

- Extremely low reporting and regulatory limits magnify the importance of cross contamination
- Trace background PFAS levels can be detected
- Uncertainties on the patterns of PFAS released from the PFAS materials remain unknown
- Trace PFAS levels are detected in some drinking water systems

Because we believe...

- Stable chemistry, unlikely to be released under most conditions
- The PFAS levels from cross contamination cannot be quantified
- Manufacturing of PFOA and PFOS have been phased out between 2010-2015

# PFAS Sampling



## The Field Crew



### Do Not Use

### Acceptable Alternatives

Wearing/using personnel hygiene items (cosmetics, lotions, moisturizers)

Do not wear

Sunscreens, insect repellants

Long sleeve, light colored 100% cotton shirts, wide brimmed hats, products that are 100% natural ingredients, DEET, tuck pant legs into socks and/or boots and use duct tape

New or unwashed clothing

Well-washed clothing

Clothing washed in fabric softeners

Clothing not washed with fabric softeners

Treated clothing (waterproof, water resistant, stain-resistant)

Clothing made of synthetic or natural fibers

Treated boots (waterproof, water resistant, stain-resistant)

Steel-toed boots made with polyurethane and polyvinyl chloride (PVC).

Coated Tyvek® suits\*

Tyvek® suits

Handling or prepackaged food products

Do not have at the sampling location, wash hands well after handling, wear powderless nitrile gloves

## Sunscreens and Insect Repellants

- Many manufactured sunblock and insect repellants contain PFASs and should not be brought or used on-site.
- The following products **are acceptable**:
  - Sunscreens - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, and baby sunscreens that are “free” or “natural”
  - Insect Repellents - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellent, Herbal Armor, California Baby Natural Bug Spray, BabyGanics
  - Sunscreen and insect repellent - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion



*“..The highest concentrations of PFOS and PFOA were detected at 0.0671 ng/g and 21.0644 ng/g, respectively. Even though present concentrations are found at ng/g levels, the daily use of sunscreen products is normally several grams. Therefore, a risk assessment of PFOS and PFOA contamination in sunscreen products is an important concern, and more attention needs to be paid to the long-term effects on human health.” - 2015*

*“The concentrations of total PFCA s ranged from not detected to 5.9  $\mu\text{g g}^{-1}$  for cosmetics and from not detected to 19  $\mu\text{g g}^{-1}$  for sunscreens” – Chemosphere, 2013*



# Sampling Equipment

Do Not Use	Acceptable Alternatives
Fluoropolymer bailers or pump bladders	Disposable Equipment Dedicated Equipment (no PTFE parts)
Fluoropolymer tubing, valves and other parts in pumps	High-density polyethylene (HDPE) and silicon materials (i.e. tubing).
LDPE HydraSleeves	HDPE HydraSleeves
Decon 90	Alconox® and Liquinox® soap for decontamination, if needed
Decontamination water from the site	Water used for the decontamination of sampling equipment will be laboratory certified "PFAS-free" water
Glass containers (due to potential loss of analyte through adsorption)	Polypropylene or HDPE sample bottles fitted with an unlined (no PTFE), polypropylene or HDPE screw cap
Waterproof field books	Loose paper on aluminum clipboards
Sharpies (acceptable by EPA checklist)	Ball point pens
Post-it notes	
Blue (chemical) ice*	Ice contained in plastic (polyethylene) bags (double bagged), secured to avoid meltwater from contacting sample containers, overnight shipping
Aluminum foil	Thin HDPE sheeting can be used

## Sample Collection

- Prior to collection of samples, field personnel must wash their hands and wear a new set of nitrile gloves
- Do not filter samples
- *Shaker Test: A small portion of the sample (~10-25 mL) should be shaken by the sample collector on site. If foaming is noted within the sample, this should be documented when samples are submitted for analysis*
- Field QA/QC Samples !!
  - Field blanks (bottle to bottle)
  - Equipment blanks (rinsate)
  - Trip or travel blank

PFOA Site	FS/DUP	EB/FB	EB hits >RL
A (landfill)	209	32	0
B (landfill)	77	21	2
C (landfill)	99	21	3
D	637	22	0
E	823	34	0

AFFF Site Sample Type	Samples Analyzed	PFAS detected	# detections	PFAS Analytes detected	Result (min- max)
Field Blank	11	No	0	0	0
Equipment Blank	115	Yes	3	PFOS, 6:2 FTS	0.011-0.02 µg/L

## Drilling, Well Redevelopment, Surface Water Sampling

- Don't use detergent to decon drilling equipment, scrub with a plastic brush and rinse thoroughly in tap water, then triple-rinse in distilled or deionized water
- Use PFAS-free drilling fluids
- Don't re-use PVC well material which has been used previously at sites where PFAS is known or suspected to be present
- Collect representative water sample used during drilling activities
- Purged groundwater must be drummed, transported and managed properly
- Surface water must be collected by inserting a capped sampling container (polypropylene or HDPE) with the opening pointing down to avoid the collection of surface films
- Soil and sediment core samples must be collected directly from single-use PVC liners that must not be decontaminated or reused at different locations

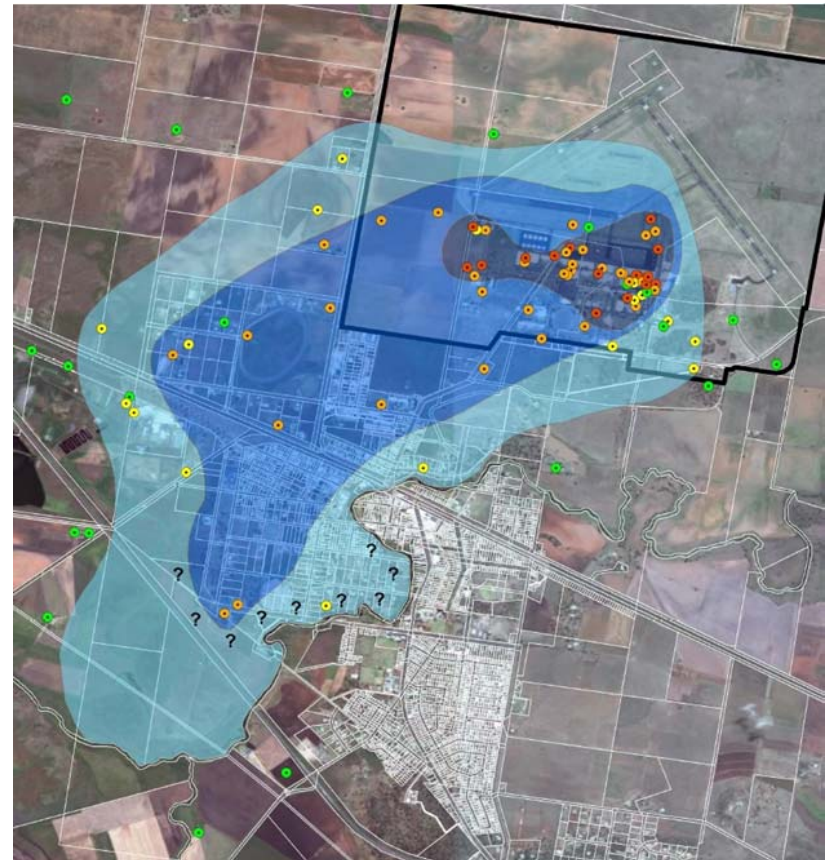
## Additional Considerations

- No food or drink shall be brought on-site, with the exception of bottled water and hydration drinks (i.e., Gatorade® and Powerade®) and available for consumption only in the staging area.
  - When field personnel require a break to eat or drink, they should remove their gloves and coveralls and move to an appropriate location (preferably downwind). When finished, field personnel should then tidy up and put their coveralls and gloves back on prior to returning to the work area.
  - Visitors to the site are asked to remain at least 30 feet from sampling areas.
-



## Recommended PFAS Sampling Strategy

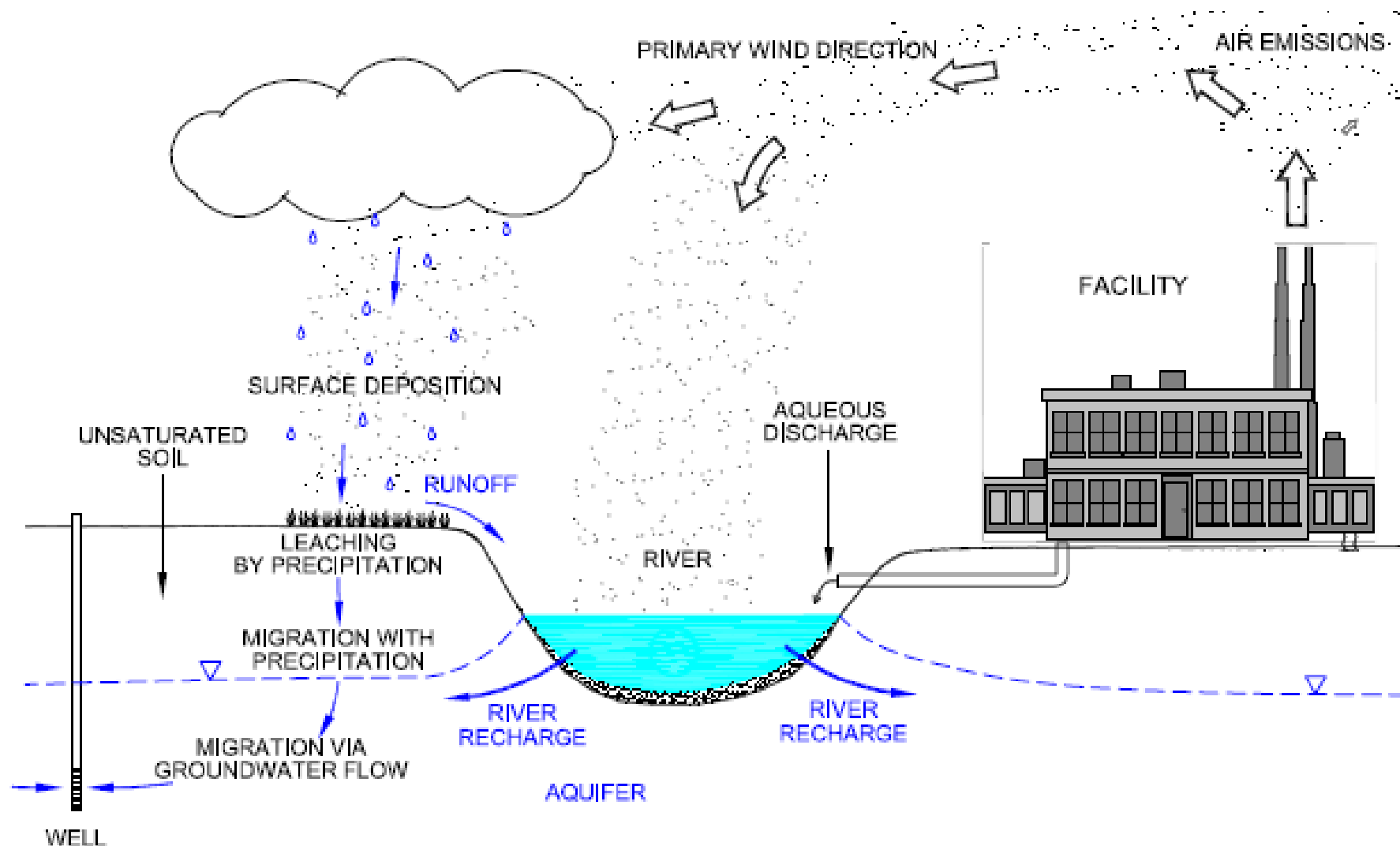
1. Drinking water
2. Surface water
3. Groundwater
  - 1) upgradient well(s).
  - 2) furthest downgradient of the interpreted or known source.
  - 3) downgradient to source
  - 4) the wells closest to the interpreted or known source are sampled last.



Large dilute plume intercepting multiple sensitive receptors

# Multiple Transport Mechanisms

## PFOA Releases From a Fluoropolymer Manufacturing Facility



# Environmental Conditions PFASs at AFFF Release Sites

## Groundwater Flow

Fire Training Area

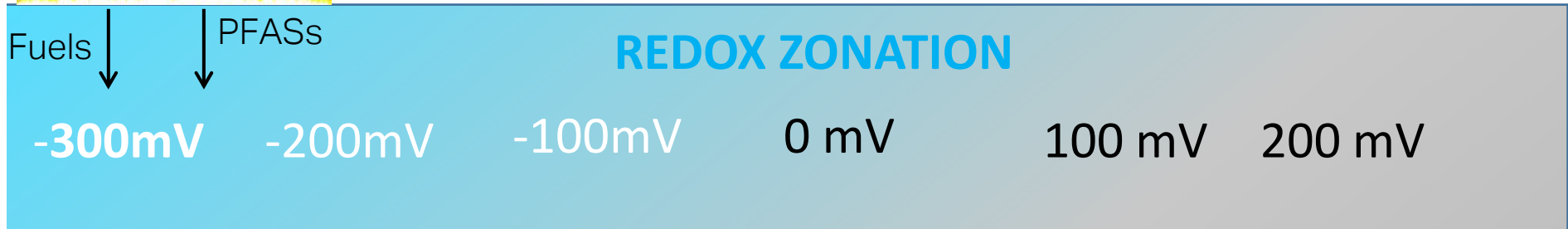


High BOD  
PFASs extend  
anaerobic zone

Hydrocarbons  
biodegrade  
rapidly

Precursors Oxidize &  
Dead End at  
PFOS/PFOA

Shorter chain  
PFASs become  
more mobile



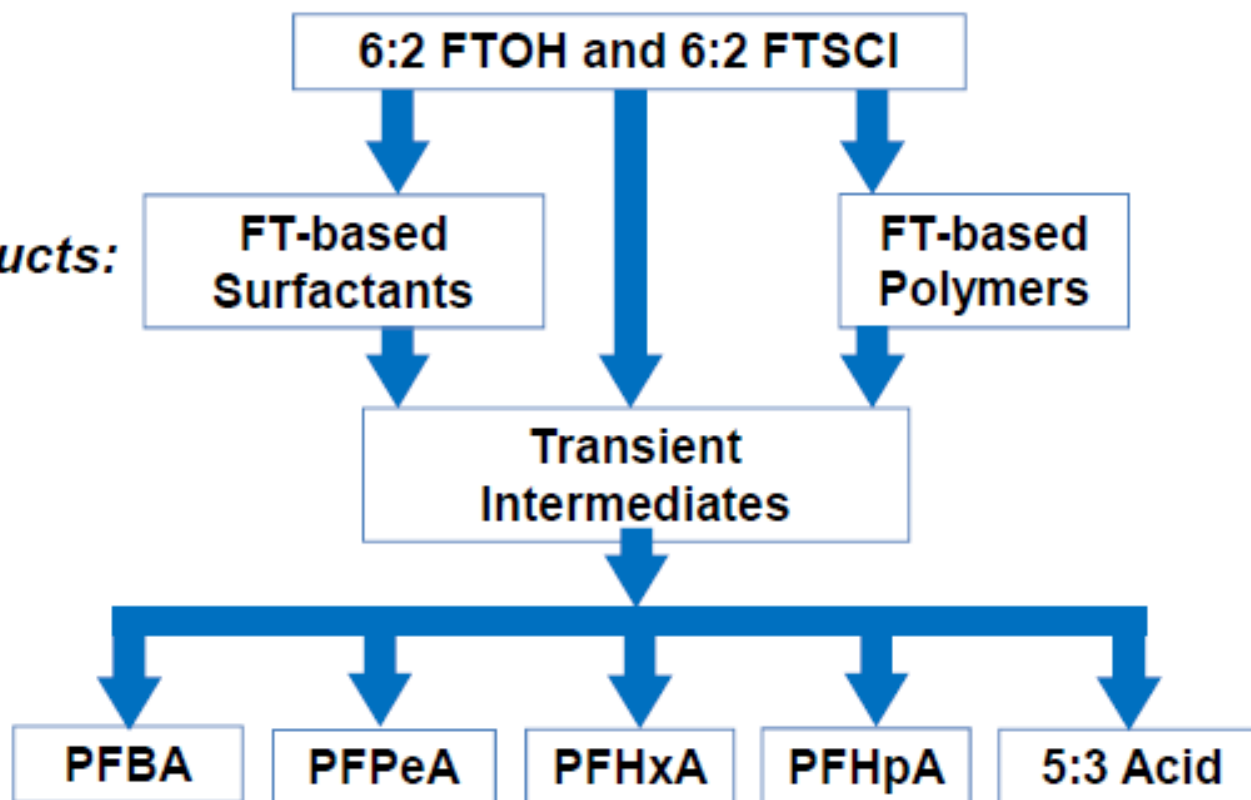
# Precursors Biotransformation

## 6:2 Fluorotelomer Biotransformation Pathways Converge

*Raw materials:*

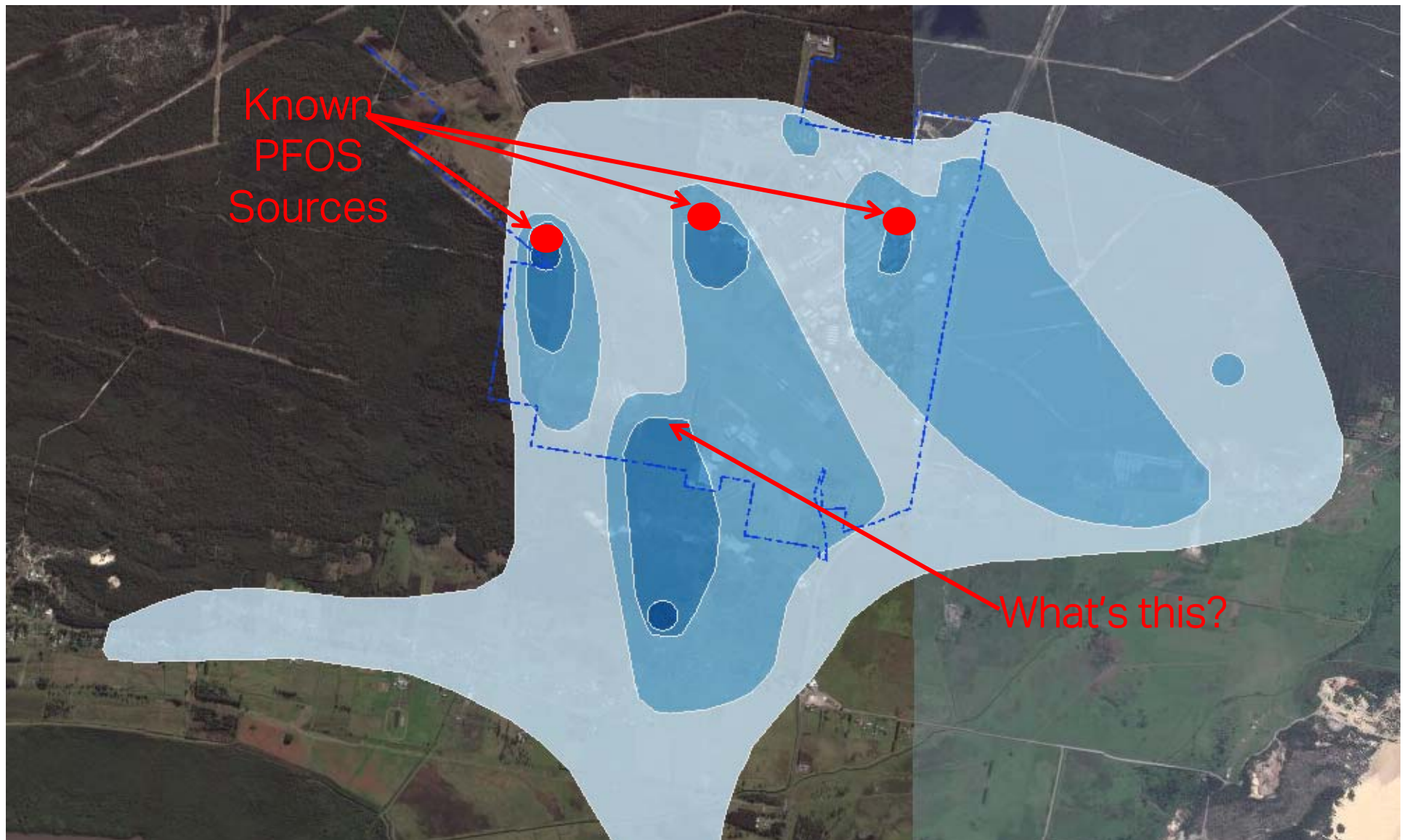
*Commercial products:*

*Terminal products:*





## AFFF Precursor Oxidation Impact on PFOS Concentrations



## How PFAS Data Can Change with Time

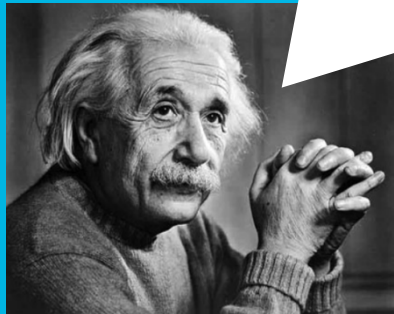
- Contaminated Sites with Potential PFAS Impact
  - Active AFFF uses and unprotected storage
  - Remediation induced conditions can alter biotransformation of PFAS precursors (McGuire et al, ES&T, 2014), such as:
    - Air/oxygen sparging
    - Pump and treat
    - In-situ chemical oxidation
  - Surface and groundwater investigation program (uses of PTFE materials for VOC sampling)
- Off-Site Sampling
  - Private well installation
  - Cross contamination from household and personal use items which may contain PFASs

## PFAS Sampling– Summary

- Identify sources of cross contamination in the field and lab environments
  - Evaluate sampling protocols including field equipment and clothing in the field and collect blanks
  - At PFAS impacted sites, practice consistently to avoid cross contamination early for site-wide investigation program
  - Use a lab with proven PFAS experience and understanding of potential PFAS contamination sources and PFAS analytical issues
  - Document field practice changes to account for potential data variations between PFAS sampling events
  - Need scientific data to document the PFAS impact from the personal protection and field equipment, remove or add precautions when more science evolves
-

# Thank You!

“The significant problems  
we face cannot be solved  
at the same level of  
thinking we were at when  
we created them.”



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**Perfluoroalkyl carboxylates:**  
 Examples:  
 $m=2$  PFBA  
 $m=4$  PFHxA  
 $m=6$  PFOA

**Perfluoroalkane sulfonates:**  
 Examples:  
 $m=3$  PFBS  
 $m=5$  PFHxS  
 $m=7$  PFOS

**Per + Poly = Per & polyfluoro alkyl substances (PFAS)**

**Polyfluoroalkyl substances:**  
 $m=5$  6:2 FtS  
 $m=7$  8:2 FtS





**Technical Training for Waste Site Cleanup Professionals**

## Q & A



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