Sampling and Analysis of PFAS Compounds – Lessons Learned and State of the Science

Battelle Bioremediation Conference

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Navy PFAS Investigation Approach

DON PFAS Comprehensive Strategy

- **Addresses issues in the following areas:**
  - **Drinking water on DON installations**
  - **Impacted public and private drinking water off installation**
  - **DON cleanup program**
  - **Aqueous Film Forming Foam (AFFF)**
- **Includes a detailed decision matrix**
  - **PFC DERP Site and AOC Identification, Validation, Prioritization, and Response Process**
  - **Focus on sites with highest potential for current drinking water exposure**

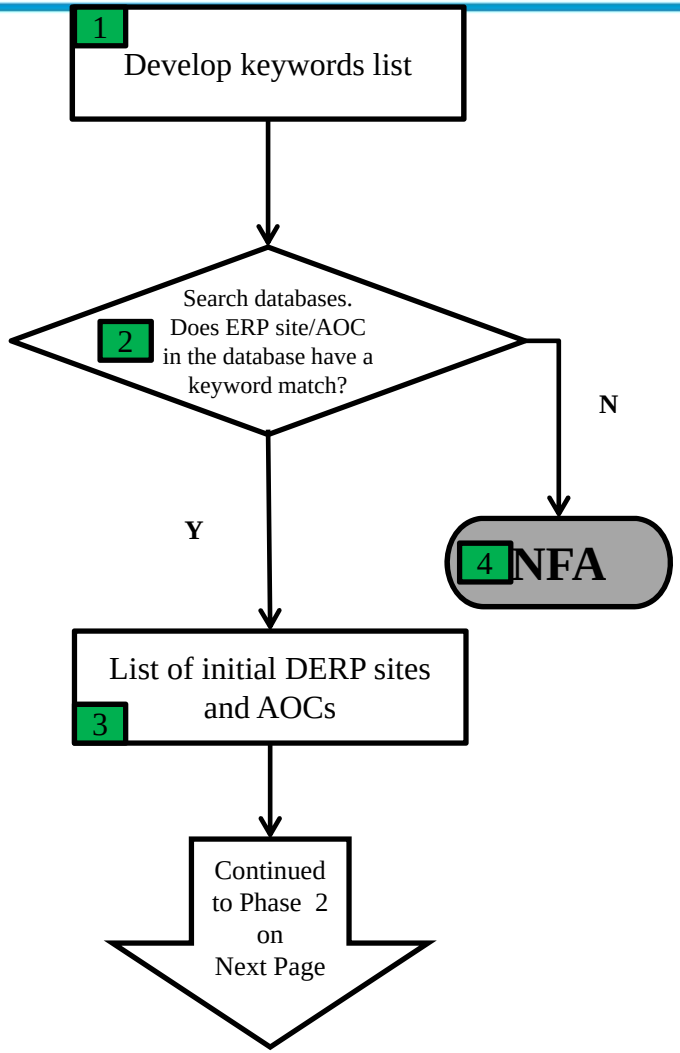
http://www.secnav.navy.mil/eie/pages/pfc-pfas.aspx

PFC DERP Site and AOC Identification, Validation, Prioritization, and Response Process

Phase 1 – Initial DERP Site Identification Database Screening

- Develop list of keywords related to use of PFCs (including AFFF and other specified keywords)
- ER Program (ER,N & BRAC) Databases (NORM, NIRIS, Delayed Disposal Report, Military Fire & Crash Training Sites Table, BRACMIS, GPRA, Flash Card, NOSC.Net, and Other Databases)

Status/Schedule:
COMPLETE



Business Rules:

- Block 1: Develop a list of keywords to perform an initial screening of ERP (ER,N and BRAC) databases. Keywords provide a broad range of sites/AOCs that have the potential for PFC use or release.

  Keywords include but not limited to single or combinations of these words: fire crash training, burn area, plating shop, fire train, fire fight, firefight, burn, hangar, AFFF, foam, plating.

- Block 2: The ERP database search will develop an initial "universe" of potential evaluation areas [existing ERP sites (NORM) or AOCs (NIRIS, other databases).
- Block 3: Any ERP site/AOC in the databases with a keyword match will be included as a potential PFC evaluation area for further screening.
- Block 4: ERP sites/AOCs in the databases having no keyword matches will be excluded from further PFC use/release evaluation.

PFC DERP Site and AOC Identification, Validation, Prioritization, and Response Process

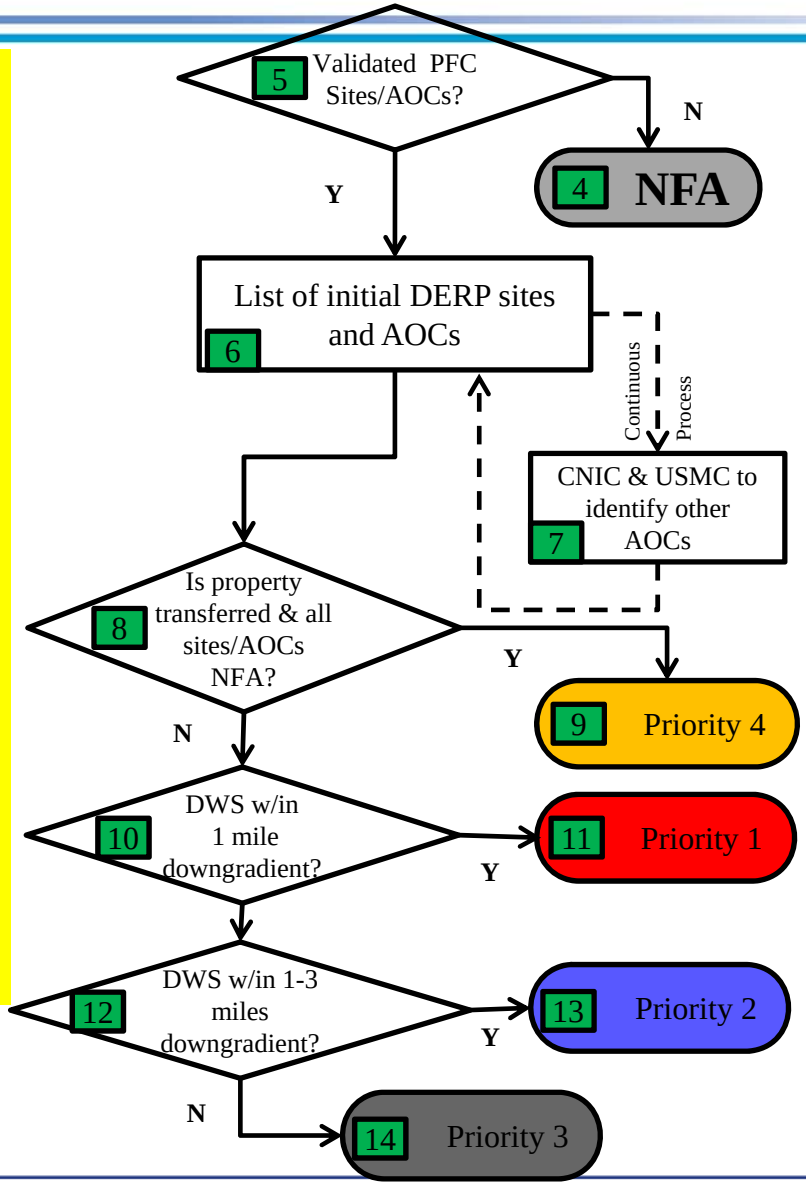
Phase 2 – Site/AOC Validation, Prioritization and Gap Analysis

- Managers and RPMs to validate sites/AOCs progressing from Phase 1
- Prioritize sites/AOCs based on property ownership status, response status, and distance to drinking water sources
- CNIC and USMC to review validated sites/AOC lists per installation with potential release mechanisms and identify additional sites/AOCs for prioritization
- May include limited sampling of groundwater.

Status/Schedule:

- Block 6: Initial list is due 1 June 2016 to DASN(E)
- Block 7: A continuous process; initial validated AOCs to be added to the list by 15 July with additional sites added as discovered.
- Blocks 11, 13, 14, and 9: Initial list is due 31 July 2016 to DASN(E)
- Additional AOCs from CNIC & USMC will be prioritized as they are identified.

Continued to Phase 3 on Next Page



Business Rules:

- Block 5: FEC RPMs to confirm/refute PFCs sites/AOCs based on available data on site history and site operations. RPM is to provide the supporting documentation of "negative" response. For example, a "burn pit" site/AOC for debris disposal and not associated with fire-fighting training can be eliminated. Because some of the required information pertains to on-base and off-base drinking water sources, the RPM will need to coordinate with Environmental Compliance, Public Work, and local municipalities.
- Block 7: Additional areas that have the potential for PFC releases will be identified by facility operations personnel (i.e. hanger, crash site, storage area). Coordinate and work closely with RPMs to identify and validate new AOCs.
- Block 8: Could be identified from NORM, NIRIS, Delayed Disposal Report, Military Fire & Crash Training Sites Table, BRACMIS, GPRA, Flash Card, real estate, & other databases
- Block 10: DWS (Navy, public, and private wells) are located within 1 mile downgradient of sites/AOCs.
- Block 12: DWS (Navy, public, and private wells) are or may be located within 1 - 3 miles downgradient of sites/AOCs.
- Blocks 9, 11, 13, and 14: Refer to rules under Phase 3.

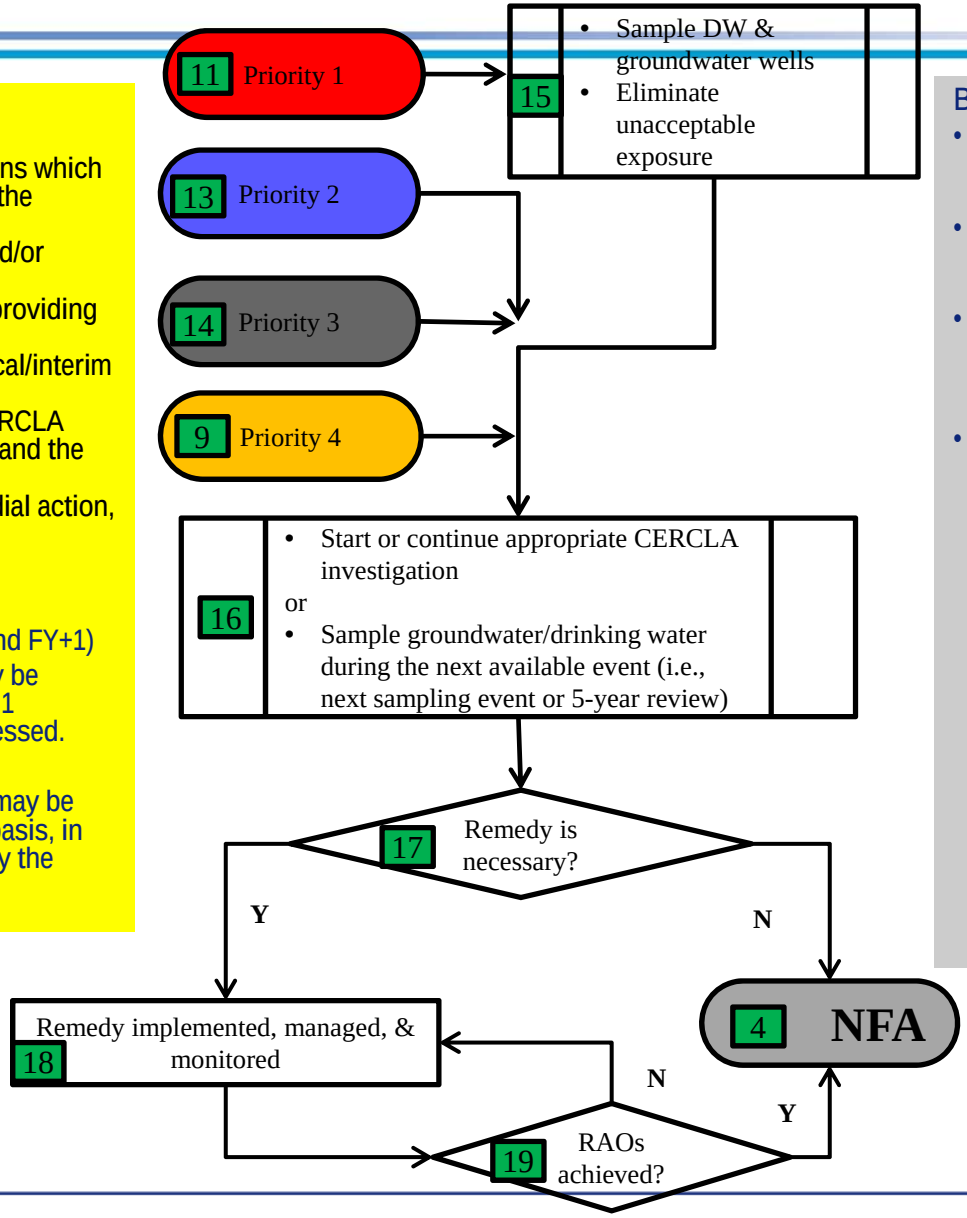
PFC DERP Site and AOC Identification, Validation, Prioritization, and Response Process

Phase 3 - Responses

- Layout prioritization of actions which may include one or more of the followings:
  - Sample groundwater and/or drinking water wells
  - Eliminate exposure by providing alternate drinking water
  - Perform other time critical/interim actions
  - Perform appropriate CERCLA investigation to understand the CSM
  - Perform CERCLA remedial action, if necessary

Status/Schedule:

- Block 11: Immediate (CFY and FY+1)
- Block 13: FY+1 to FY+3; May be expedited only after Priority 1 Sites/AOCs have been addressed.
- Block 14: FY+3 to FY+5
- Block 9: FY+5 and beyond; may be expedited on case by case basis, in particular when requested by the regulators/stakeholders.



CY ~ 2016

Business Rules:

- Block 11: PRIORITY 1 – Perform actions per Blocks 15 and 16 and perform time critical actions as necessary.
- Blocks 13 and 14: PRIORITY 2 and PRIORITY 3 – Perform actions per Blocks 15 and 16.
- Block 9: PRIORITY 4 - PFC evaluation pending additional review by ASN/NAVFAC HQ and regulatory request for assessment and may proceed to Blocks 15 and 16.
- Blocks 15 and 16: Develop a CSM to understand GW flow, PFCs migration potential off-base, and aquifer characteristics. This information may be obtained using existing and/or new MWs to verify the presence and level of PFCs in GW. If these results indicate impact to the DWS (downgradient and greater than 1 mile away), the DWS should be sampled with additional "step-out" sampling, if necessary.

  Next step is to initiate the CERCLA site investigation to define nature and extent of the PFC contamination, evaluate risk, and develop remedial alternatives, if necessary. Consider implementation of a removal action to implement a short-term solution to eliminate the use of bottled water.

Navy PFAS Investigation Approach

- **2015 DON PFAS Guidance**
  - **Currently under revision**

- **Provides guidance in the form of Frequently Asked Questions (FAQs) in the following areas:**
  - **Eligibility and Funding**
  - **Investigation and Sampling**
  - **Risk Assessment**
  - **Applicable or Relevant and Appropriate Values**
  - **Remedial Response Considerations**
  - **Land Use Controls**
  - **Five Year Review Issues**

Navy PFAS Investigation Approach

Progress

- 16 Priority 1 (with drinking water exposure) installations sampled to date

FEC	# of Installation
HPAC	8
MPAC	3
LANT	2
MIDLANT	38
SOUTHEAST	23
SOUTHWEST	31
NORTHWEST	8
WASH	14
TOTAL	**127**

PFAS Analytes

- **Initially 2015 DON Guidance recommended reporting only PFAS with vetted toxicity values**
  - **PFOA, PFOS (EPA Lifetime Health Advisory)**
  - **PFBS (EPA Superfund RfD)**

- **DON Guidance currently undergoing revision.**
  - **Report PFAS included in EPA Method 537 (14 PFAS)**
  - **To aid in CSM development, additional PFAS can be analyzed and reported if there are promulgated State values**

Critical Sampling Considerations

- Cross contamination issues
  - Example table of precautions listed in UFP-SAP
- Use of Field Reagent Blank
- Consideration of IDW
- Detection Limit

Table 1. Summary of Prohibited and Acceptable Items for PFC Sampling

Prohibited Items	Acceptable Items
Field Equipment	
Teflon® containing materials (Teflon® synonyms include: Polytetrafluoroethylene; Poly[ethylene tetrafluoride]; Polytetrafluoroethene; Tetrafluoroethene polymer; Tetrafluoroethylene homopolymer; Ethene; tetrafluoro-; and homopolymer. Commercial names include: PTFE; Aflon; Algloflon; Chromosorb T; Fluon; Fluo-kem; Fluoroflex; Fluoroplast 4; Halon G 80; Heydeflon; Polifen; Politef; and Tarflen)	High-density polyethylene (HDPE) and Low density polyethylene (LDPE) materials
LDPE sample containers	HDPE sample containers and acetate liners
Teflon® tubing	Silicon or HDPE tubing
Waterproof field books not manufactured by Rite in the Rain	Rite in the Rain products or loose leaf paper (non-waterproof)
Plastic clipboards, binders, or spiral hard cover notebooks	Aluminum field clipboards or with Masonite
	Sharpies®, pens
Post-It Notes	
Chemical (blue) ice packs	Regular ice
Excel Purity Paste TFW Multipurpose Thread Sealant Vibra-Tite Thread Sealant	Gasoils NT Non-PTFE Thread Sealant Bentonite
Equipment with Viton Components (need to be evaluated on a case by case basis, Viton contains PTFE, but may be acceptable if used in gaskets or O-rings that are sealed away and will not come into contact with sample or sampling equipment.)	
Field Clothing and PPE	
New clothing or water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™	Well-laundered clothing, defined as clothing that has been washed 6 or more times after purchase, made of synthetic or natural fibers (preferable cotton)
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex™	Boots made with polyurethane and PVC, well-worn or untreated leather boots, leather boots with boot covers
Tyvek®	Reflective safety vests, Cotton Clothing, synthetic under clothing, body braces
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling, unless the products are applied to body parts that will be covered by clothing.	**Sunscreens** - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are "free" or "natural" **Insect Repellents** - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics, Deep Woods Off **Sunscreen and insect repellant** - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion

Myth Busting

- **Some precautions listed in the "things to avoid" sampling procedures need to be validated, but precautions such as frequent changing of gloves and aggressive decontamination cannot be emphasized enough. Equipment blanks and field blanks are especially important when dealing with such low detection levels/action levels.**

- **While there have been upwards of 300 PFAS compounds described at AFFF-impacted sites, the majority of these are at very low concentrations (single-digit ppt range, or 10's of ppt range at sites where PFOS is approaching the ppm range); a much smaller number of PFASs such as PFOS, PFHxS, and the fluorotelomer sulfonates can be several orders of magnitude higher in concentration.**

Myth Busting

- **Verify with laboratory whether branched and linear forms are summed (or reported separately)**

- **Since PFAS accumulate at the water/air interface, the sampling approach should draw from the water column (rather than near the surface or excluding the surface)**

- **There is as of yet no official method for analysis of PFAS other than for drinking water (though EPA is developing a method for non-drinking water media with a list of 24 PFAS), so each laboratory uses their own method for analyses of the other matrices. This can result in inter-lab variability and inaccurate results. Special attention should be paid to QC for non-DW PFAS samples, such as consideration of submission of PT samples, additional blanks and replicates (e.g. beyond the 10%), etc.**

PFC DERP Site and AOC Identification, Validation, Prioritization, and Response Process Acronyms

Acronyms:

AFFF	Aqueous film-forming foam
AOC	Area of concern
BRAC	Base Realignment and Closure
BRACMIS	BRAC Management Information System
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFY	Current fiscal year
CNIC	Commander Navy Installations Command
CSM	Conceptual site model
DERP	Department of Defense Environmental Restoration Program
DW	Drinking water
DWS	Drinking water system
ER,N	Environmental Restoration, Navy Account
ERP	Environmental Restoration Program
FEC	Field Engineering Command
FY	Fiscal year
GPRA	Government Performance and Results Act
HQ	Headquarters
MW	Monitoring well
NAVFAC	Naval Facilities Engineering Command
NFA	No further action
NIRIS	Naval Installation Restoration Information Solution database
NORM	Normalized database; used for ER,N and BRAC accounts budgeting
NOSC.Net	Navy On-Scene Coordinator; NAVSEA-hosted database to track releases
PFC(s)	Perfluorinated chemical(s)/compound(s)
RPM	Remedial Project Manager
USMC	United States Marine Corps

QUESTIONS?

Per- and Polyfluorinated Alkyl Substances Method Validation Update for Non-Drinking Water Samples

May 23, 2017

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Drinking Water Method 537

- Six per- and polyfluorinated alkyl substances (PFAS) under the 3rd Unregulated Contaminants monitoring rule (UCMR3)
- Eight additional PFAS not listed on UCMR3
- Finished (treated) drinking water samples; potable groundwater

Non-DW Sample Methods

- Focus on:
  - Simplicity
  - Robustness
  - Production lab use
  - Minimizing sample transfers, extractions, filter steps, chemical additions (e.g. pH adjustments)

- Find a balance among sensitivity, ease of implementation, and monitoring requirements

PFAS Method Validation

- **24 PFAS (including all target analytes in EPA Method 537)**
- **Methods under consideration for water (all using LC/MS/MS)**
  - Direct injection
  - Solid phase extraction (with and without radio-labeled internal standard correction)
- **Target Detection Limit: 10 ng/L**
- **Publish draft method in fall 2017**
- **Evaluating Soil Methods**

PFAS - Sampling and Storage

- **Sampling/Storage**
  - Holding time studies
  - Sample vessel materials (glass, polycarbonate, high-density polyethylene)
  - Standard operating procedures for field sampling
    - Initial focus on groundwater

Questions? Comments?

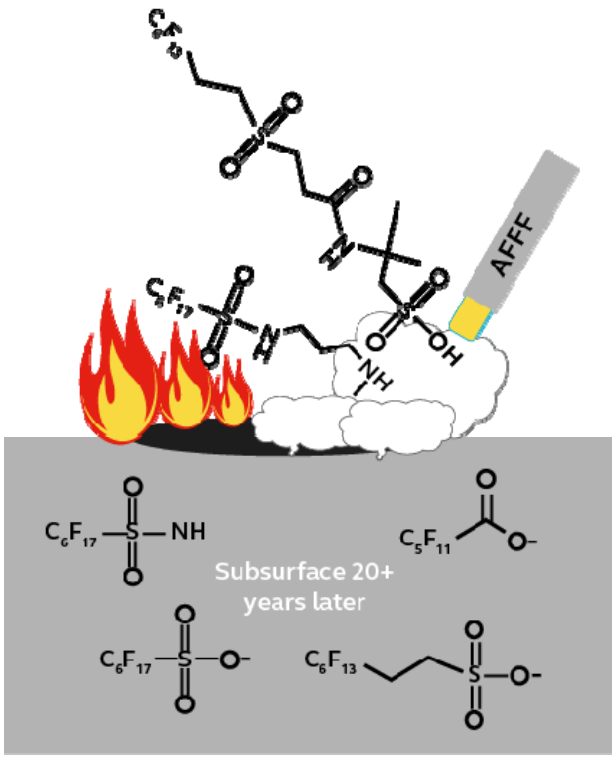
- **Contacts:**
  - OLEM-Schatzi Fitz-James: fitzjames.schatzi@epa.gov
  - Region 3- Cynthia Caporale: caporale.Cynthia@epa.gov
  - ORD-Chris Impellitteri: Impellitteri.Christopher@epa.gov
  - Communications-Michelle Latham: latham.michelle@epa.gov

Standard PFAS Analyses

- **US EPA Method 537: Analysis for selected PFAS in drinking water**
  - 12 PFAAs and 2 Precursors:
    - PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUA, PFDoA, PFTrA, PFTeA
    - PFBS, PFHxS, PFOS
    - N-EtFOSAA, N-MeFOSAA
- **Method 537 has been adapted with more analytes to other media**
  - Up to 39 analytes (laboratory dependent)
  - PFAS LOD in GW ~ 2 to 10 ng/L
  - Soil with LODs as low as 0.2 µg/kg
  - Availability of standards and other factors limit the number of PFAS that can be measured with a single method
- **Quality Systems Manual (QSM) 5.1 has guidelines for GW and soil; new EPA methods are under development for these media**

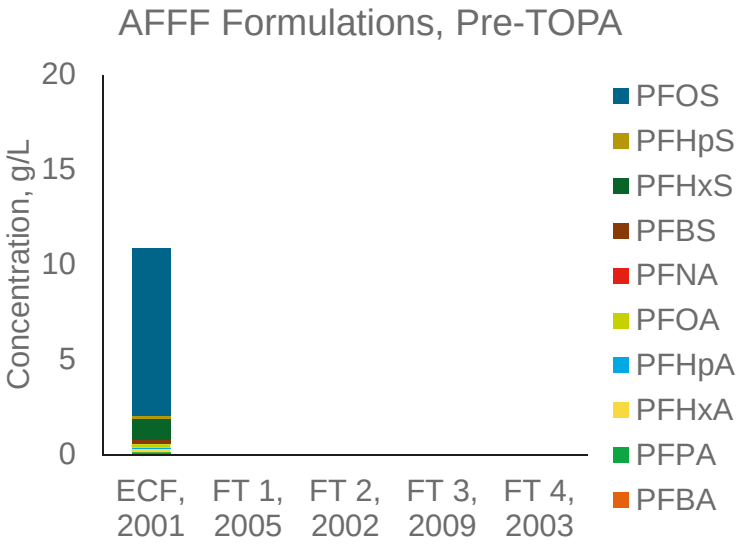
Expanding Analytical Tool Box for PFAA Precursors

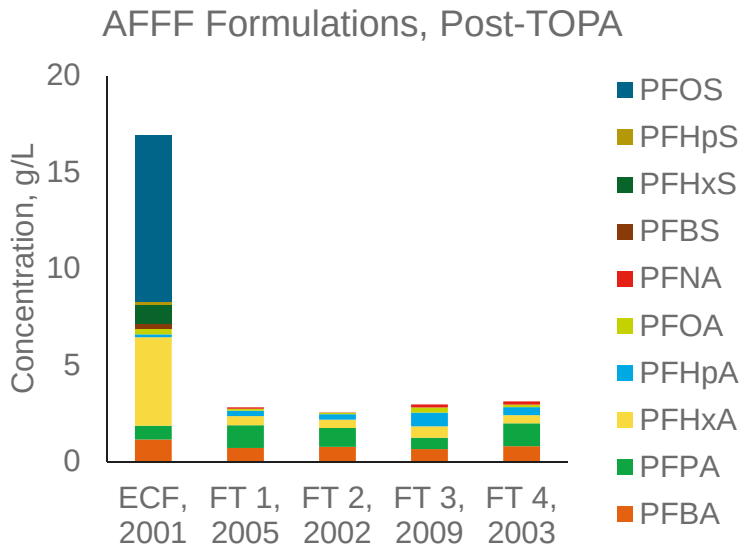
- **Total oxidizable precursor (TOP) Assay**
  - Initial LC-MS/MS analysis with re-analysis following oxidative digest
  - Detection limits to ~ 2 ng/L (ppt)
  - Commercially available in UK, Australia, US & Canada
- **Particle-induced gamma emission (PIGE) Spectroscopy**
  - Isolates organofluorine compounds on solid phase extraction, measures total fluorine
  - Detection limits to ~ 15 ug/L (ppb) F
  - Commercially available in US
- **Adsorbable organofluorine (AOF)**
  - Isolates organofluorine compounds with activated carbon and measures F by combustion ion chromatography
  - Detection limits to ~ 1 ug/L (ppb) F
  - Commercially available in Germany, Australia
- **LC-QTOF (Quantitative Time of Flight)**
  - Tentative identification of PFAS through exact mass measurement
  - Commercially available in U.S.



TOP Assay Applied to AFFF Formulations:

Many formulations appear PFAS-free until precursors are revealed by TOP Assay





FT = Fluorotelomer-based AFFF

ECF = Electrochemical Fluorination- based AFFF

TOP Assay Applied to Groundwater

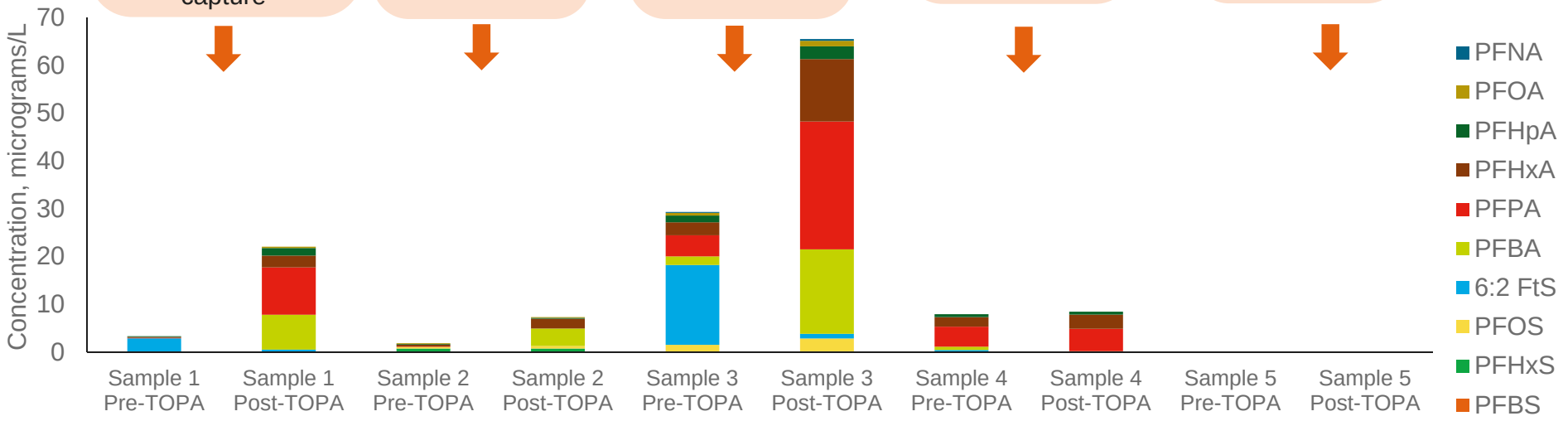
Sample 1 **Key use of TOP Assay and Expanded Analyte List** – both indicate significant PFAS mass that conventional analysis does not capture

Sample 2 **Key use of TOP Assay**– indicates significant PFAS mass that conventional analysis does not capture

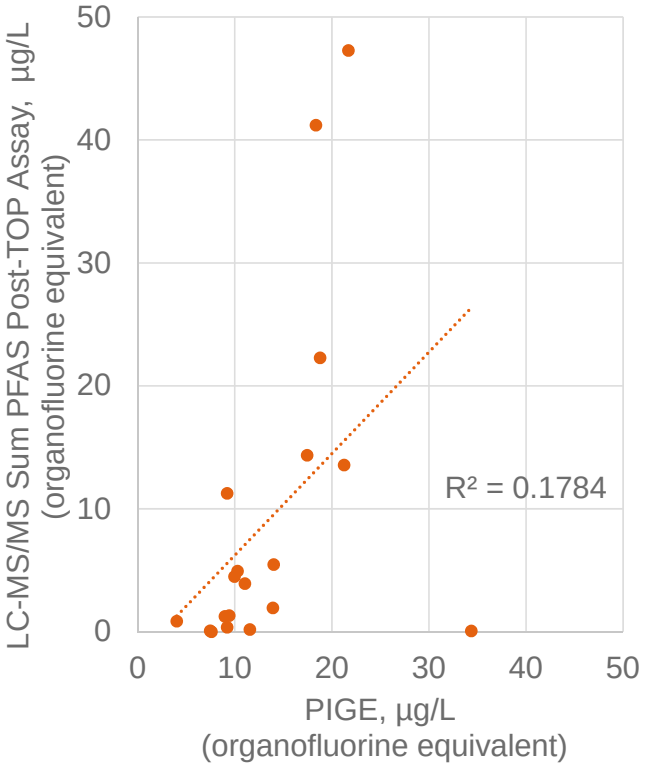
Sample 3: TOP Assay provides additional information on PFAS contamination scale

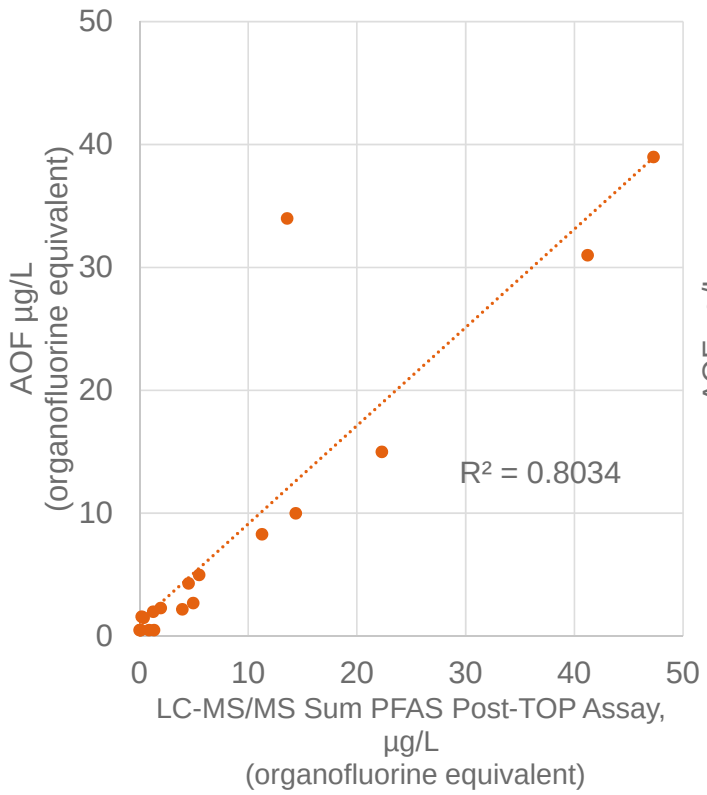
Sample 4: TOP Assay Confirms no Additional PFAS

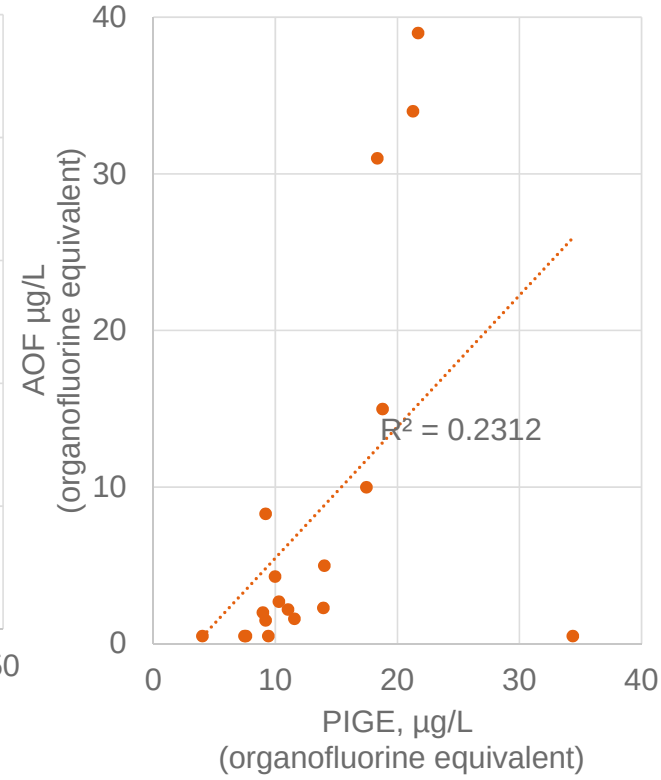
Sample 5: **Key use of TOP Assay –** confirms no PFAS present



Comparison of PIGE, AOF, and TOP Assay on AFFF-Impacted Groundwater







What approaches do you use when sampling for PFAS?

- Programmatic/Portfolio approach
  - Developed comprehensive SOPs for all anticipated media
    - Including “Do Not Use/Wear” list and list of “Acceptable Alternatives”
    - Extraordinary media protocols (livestock, crops, blood, fish, etc.)
  - Developed a 3 part training series and made training mandatory
  - Established our own source of PFAS-free rinsate water (IX treated)
  - Established a robust lab prequalification and chemistry data quality assurance program
- Collect very robust set of Field, Rinsate, and Trip Blanks

What issues have you encountered?

- Specialized equipment required (e.g. No Teflon seals)
- Removing and evaluating dedicated sampling pumps
- Blank contamination - contributions from background?

What do you request from labs?

- Participate in Performance Testing
- Show us your SOPs
- Requested onsite lab audits
- Requested that they manage, notify, and document changes
- Follow QSM 5.1 ASAP
- Partner with us for a good/acceptable outcome

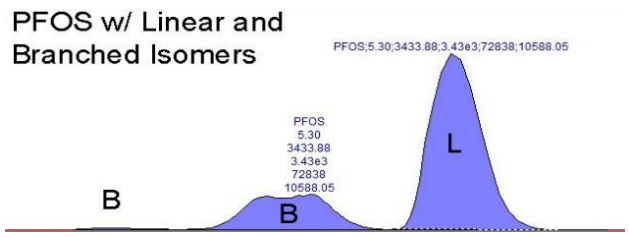
What lab strengths and weaknesses have you observed?

Strengths

- Working hard to improve in rapidly changing field
- Rapidly adding additional capabilities
- Cooperating with round robin sampling studies and resolving issues

Weaknesses

- SOP differences, new employees not following SOPs
- Capacity? - 27 instruments at DOD ELAP certified labs, Slower TATs, SPE Cartridge shortage
- Accuracy – Reference standard differences?
- Precision 3rd party QC differences, although getting much better
- Branched and linear isomers
  - More compounds have them
  - Response factor differences



What questions should site managers ask labs?

- Be prepared for changing target analyte lists, decreasing screening levels and lower detection limit requirements
  - SW, GW, and Sediment samples can be quickly and easily re-collected
  - Subsurface Soil samples more time consuming and costly to recollect
    - Collect extra sample for future reanalysis? Freeze samples?
- Focus target analyte lists on those PFAS compounds associated with facility processes where possible
- Integrate 3rd party QC Sample or SRM testing until routine round robin proficiency testing is commonplace
- Most importantly
  - use a lab with proven PFAS experience
  - establish a backup lab
  - continue to evaluate them on ongoing basis!