ENGINEERING AND EXPEDITIONARY WARFARE CENTER

Per- and Polyfluoroalkyl Substances (PFASs) Site Characterization

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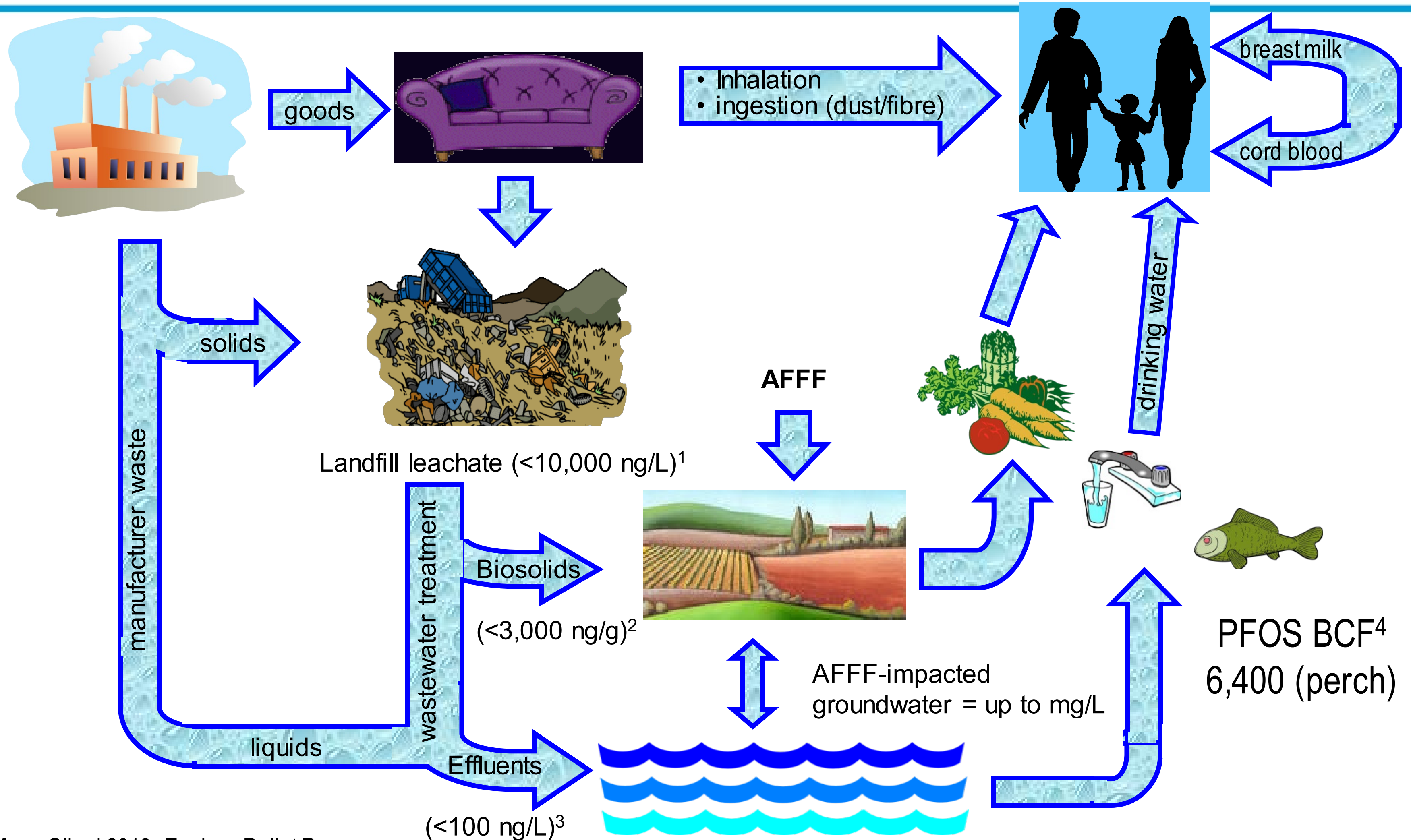
PFAS Site Characterization - General Considerations

- PFAS are a large group of compounds with widely varying structural and physical/chemical properties
  - Which ones to assess? PFAS with regulatory values? Precursors?
  - Should we, or can we, analyze all of them?
- Sources usually consist of PFAS mixtures
  - PFAS mixtures can be complex, and distributed over wide areas
- Multiple sources
  - Can they be differentiated?

PFAS Site Characterization General Considerations

- Regulatory values and laboratory detection levels are very low – this could mean assessing a very large area
  - Some PFAS transport readily, and are persistent
  - Background and multiple sources can complicate
  - Cross-contamination concern
- Development of an accurate Conceptual Site Model (CSM) is crucial
  - Historical use or presence of PFAS-containing materials, including off-site sources
  - Identify transport and exposure pathways, and potential receptors

Sources and Exposure Pathways



Adapted from Oliaei 2013, Environ Pollut Res

[1]Allred et al. 2014 J Chrom;[2] Schultz et al. 2006; Higgins ES&T 2005

[3]Schultz et al. 2006 a&b ES&T; [4]Ahrens et al. Chemosphere 2015

Understanding PFAS Fate & Transport

- Mixtures of PFAS require that a range of physical/chemical properties be considered

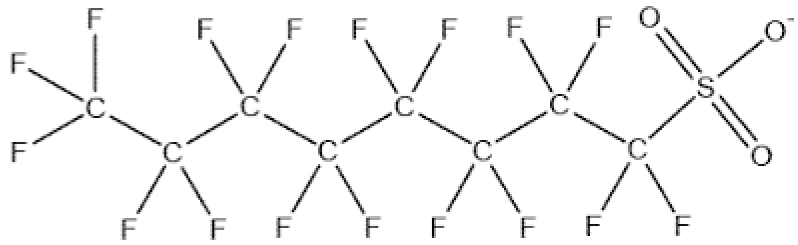
- PFAS compositions may change over time (e.g. PFAS in Aqueous Film-Forming Foam, or AFFF)

- Compounding the varied phys/chem properties of PFAS mixtures are varying site characteristics including soil types, geochemistry, and hydrology

….but, some generalizations can be made

Perfluoroalkyl Acids - PFAAs

- **Perfluoroalkyl Acids PFAAs**
  - PFSAs (sulfonates), PFCAs (carboxylates)
  - includes PFOS and PFOA, and most of the other analytes of EPA Method 537 and derivative methods



PFOS (Source: Environment Canada)

  - CF "tail": imparts hydrophobic character (longer is more hydrophobic, transports slower, linear slower)
  - Charged "head group" imparts water solubility; carboxylates transport faster than sulfonates for a given carbon chain length

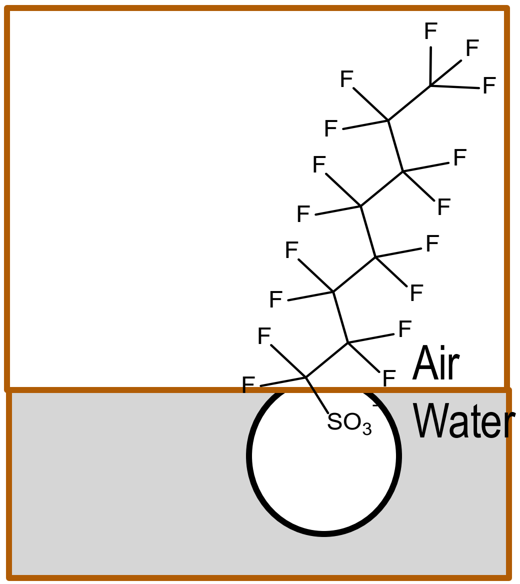
Environmentally-Relevant Properties: Anionic PFASs

- Anions at environmental & physiological pHs (4-10)
- Low vapor pressure and Henry's Law so cannot be air-stripped
- Water soluble so readily transported in soil/sediment

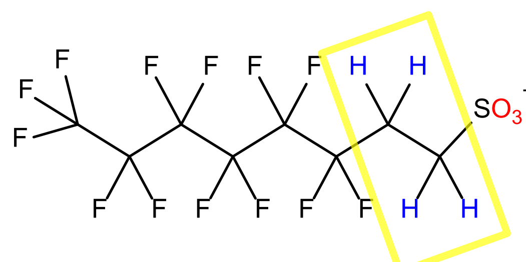
	Formula	MW	Aq Solubility (mg/L)	Boiling Point °C	Vapor Pressure	pKa	log Kow	Koc	BCF	LC50
PFOS	C8HF17SO3	500.13	570 at 24 deg C	249	2.0X10-3 mm Hg at 25 deg C	<1.0	4.49 (est)	480, 250-50,100	200-1,500 carp	7.8 mg/L bluegill sunfish 96 hr
PFOA	C8HF15O2	414.07	2,290-4,340 at 24 deg C	189	3.16X10-2 mm Hg at 25 deg C	-0.5 to 4.2	4.81 (est)	130	< 5.1-9.4 carp	15.5 mg/L Mysid neonate 96 hr
PFBS	C4F9SO3	300.01	510, temp not spec'd.	210-212	2.68X10-2 mm Hg at 25 deg C (est)	-3.31 (est)	1.82 (est)	180 est	0.71 rainbow trout	1,500 mg/L Zebra Danio embryo 4-cell, 144 hr

Two PFAS Groups: Per- and Polyfluorinated

- ***Perfluorinated*** (ECF synthesis) - *all* carbons in chain bonded only to F (e.g., PFOS and PFOA); linear and branched
  - Few engineered or environmental degradation processes degrade perfluorinated forms



- ***Poly*fluorinated** (Telomerization synthesis)
  - not all carbons in chain bonded to F, linear
  - CH_2 – spacer = 'weakness' in molecule, degradable/transformable



PFOS (***per***fluorooctane sulfonate)

6:2 FTSA (fluorotelomer sulfonate)

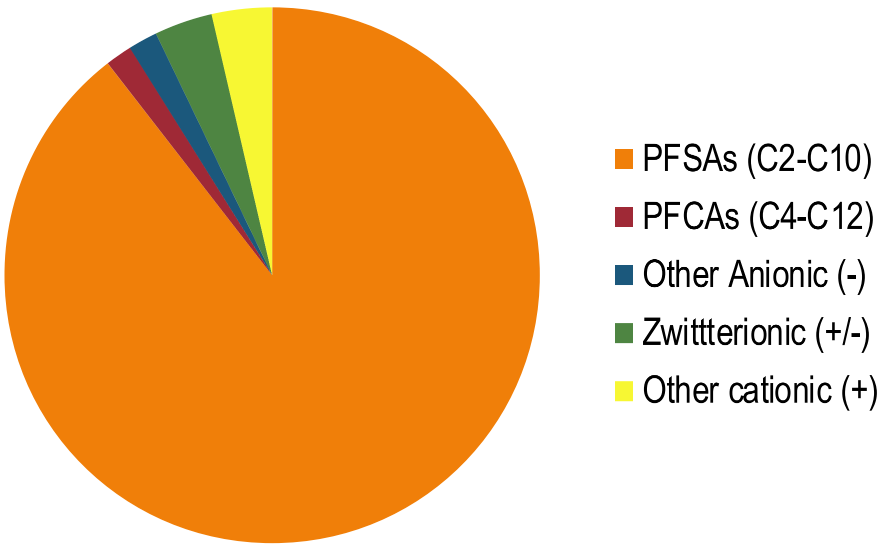
Site Characterization: AFFF-derived PFAS

- Aqueous film-forming foam
  - Complex, proprietary mixtures of fluorinated & hydrocarbon surfactants, water, corrosion inhibitors, solvent (e.g., butyl carbitol)
  - PFASs only comprise a few % by volume

- AFFFs on the Qualified Product List (QPL)
  - 1970-1976 Light Water (3M) and Ansulite (Ansul)
  - 1976 Aer-O-Water (National Foam)
  - 1994 Tridol (Angus)
  - After 2002 Chemguard (Chemguard), Fireaide (Fire Service Plus)
  - AFFFs currently on QPL (currently 11 products) http://qpldocs.dla.mil/search/parts.aspx?qpl=1910
- Multiple AFFFs used at most sites
  - Firefighter training areas and equipment test areas typically used repeatedly over years

3M AFFF: military-wide use began in 1970

- 89% PFSAs (e.g., PFOS) in 3M AFFF
- *Only* 1.6% of 3M AFFFs are PFCAs (e.g., PFOA)
- *All* contribute to total fluorine

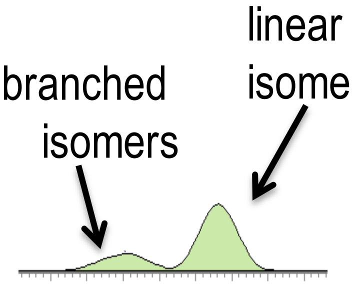


AFFF in use today

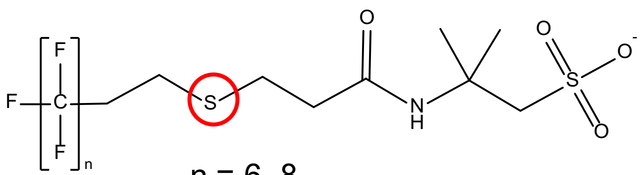
- PFOS production ceased in US in 2002; AFFF stockpiles removed from use over the past several years
- Continued use of fluorotelomer-based AFFF
  - Does not contain PFOS and precursors do not degrade to PFOS
  - Precursors degrade to PFCAs (including PFOA) and FTSAs
  - Reformulations generally contain smaller carbon chain lengths (<C6)
- Residuals in equipment possible (PFOS)
- Fluorine-free foams being developed/tested

PFSAs & PFCAs in 3M AFFF

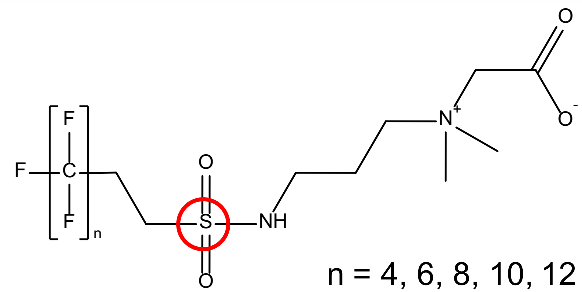
- **When produced by 3M's electrofluorination (ECF) process[5]**
  - 'crude' synthesis, many side products
  - odd & even[1,2] chain lengths (C2-C14)[3,4]
  - **C2 & C3 sulfonates recently found in AFFF and groundwater**
  - branched & linear isomers (30:70)[1,5,6]
    - **if branched isomers are excluded by the lab, concentrations are underestimated (biased low) by ~25%**

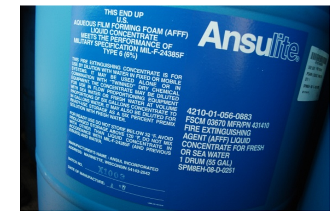


Fluorotelomer-Based AFFFs



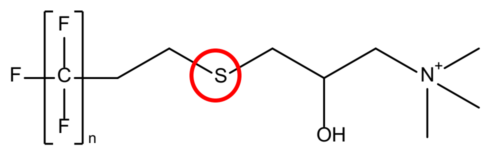
n = 6, 8
Ansul (1970), Angus (1994), Chemguard (2002)



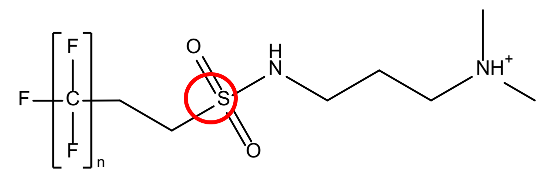


n = 4, 6, 8, 10, 12 **note: long chain lengths**
National Foam (1976), Fire Service Plus (2002)

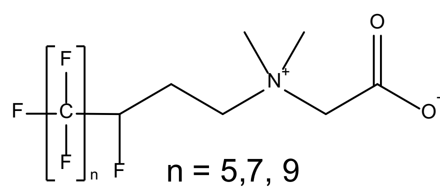
- add to total mass of F
- none on UMCR3 & Method 537 lists
- potential to degrade to 6:2 & 8:2 fluorotelomer sulfonates & PFCAs
- 6:2 & 8:2 fluorotelomer sulfonates not major components in AFFF



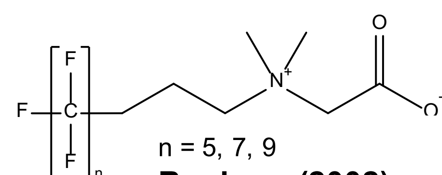
n = 6, 8
Angus (1994)



n = 6, 8
National Foam (1976), Fire Service Plus (2002)



n = 5,7, 9
Buckeye (2002)



n = 5, 7, 9
Buckeye (2002)

Transport

- Anions > zwitterions > cations
- Anions: shorter chain lengths generally migrate faster (less retardation)
- Weak acids/bases: transport will depend on pH and molecule's charged state (ionic or neutral)

Transport – PFAS Chemical Properties

- Transport determined in part by chemical structure
  - Anions > zwitterions > cations
  - Shorter chain lengths generally migrate faster (less retardation, lower Koc)
    - Carboxylates migrate faster than sulfonates (same carbon chain length)
    - likely to impact surface waters – more common to impact fresh than saltwater
    - challenging to remove by GAC
  - For many precursors, transport will depend on pH and molecule's charged state
- Cationic & zwitterionic PFASs may be cation exchanged onto source-zone sediments

Media - Solution Chemistry & Transport

- Decreasing pH (more acidic), increases retardation
- Organic carbon increases retardation
- Ca++ increases retardation (saltwater wedge retardation)
- Iron oxides increase retardation
- Increasing ionic strength increases retardation – may be relevant for sites near estuaries/ocean
- Remedial approaches that change pH or introduce polyvalent cations (i.e., ISCO) potentially impact anionic PFAS transport
- Sorption *generally* increases in the presence NAPLs

Some PFAS Plumes are Large

- Sweden: Military airport origin of km-long plume
  - Spatial distribution related to drinking water delivery, occurring in or before 1990s
  - PFBS in blood even though short chain
- Oakey Aviation Base (military) in SW Queensland, Australia extends over 4 km
- Leaky landfill, military, and civilian airports sources of human exposure to PFASs through drinking water

Other Widespread Sources: Landfills

Landfill Leachate

- 2nd most concentrated (tens of μg/L)[1-3] point source of many PFAS classes after AFFF-impacted groundwater
- most abundant short-chain PFCAs & fluorotelomer acids (unique signature to landfill leachate)[3]

Other Widespread Sources: Wastewater Treatment

- **Municipal and industrial wastewater treatment plant (WWTP) effluent**
  - 3rd highest source (< 0.1 μg/L levels) after landfill leachates and AFFF-impacted sites
  - No significant removal of PFOA & 6:2 fluorotelomer sulfonate
  - *Net increase* in PFOS mass flow during WWTP
- **Land application of WWTP biosolids leaches to soil and groundwater where biosolids applied**

Other Sources: Electroplating and Plastics/Polymer Manufacturing

- Chromium electroplating – PFASs used for mist suppression
  - PFCAs and PFSAs (µg/L) in discharge water
  - 6:2 FTSA 'alternative' mist suppression agent
- Industrial (plastics/polymer) manufacturing sources
  - PFNA: West Deptford, NJ Solvay Specialty Polymers
  - PFOA: Saint Gobain Performance Plastics and Honeywell polymer manufacturing in Hoosick Falls, NY
- Limited public data: municipal airports, AFFF production/formulation sites, oil refineries

What/Where to Sample (Navy Sites)

Investigation Considerations

CSM Substantiates Investigation; Generally 2 Categories in DoN:

Historical Release and/or Use of AFFF; examples:

- Fire Training Areas (FTAs) using AFFF
- Equipment Test Areas
- Crash or Fire Sites where AFFF was used
- Fuel Spills Treated with AFFF
- Hangars, Runways & Flight line areas
- Storage areas, piping systems, and equipment cleanout areas
- Runoff collection areas

Historical activities that may have released PFAS, examples:

- Mist suppression in plating facilities
- Oil-water separators
- Other piping systems
- Wastewater Treatment Plant effluent and biosolids

Sampling for PFAS

- Many common materials and sampling equipment contain PFAS
- Dealing with ultra-low detection levels

AVOID:

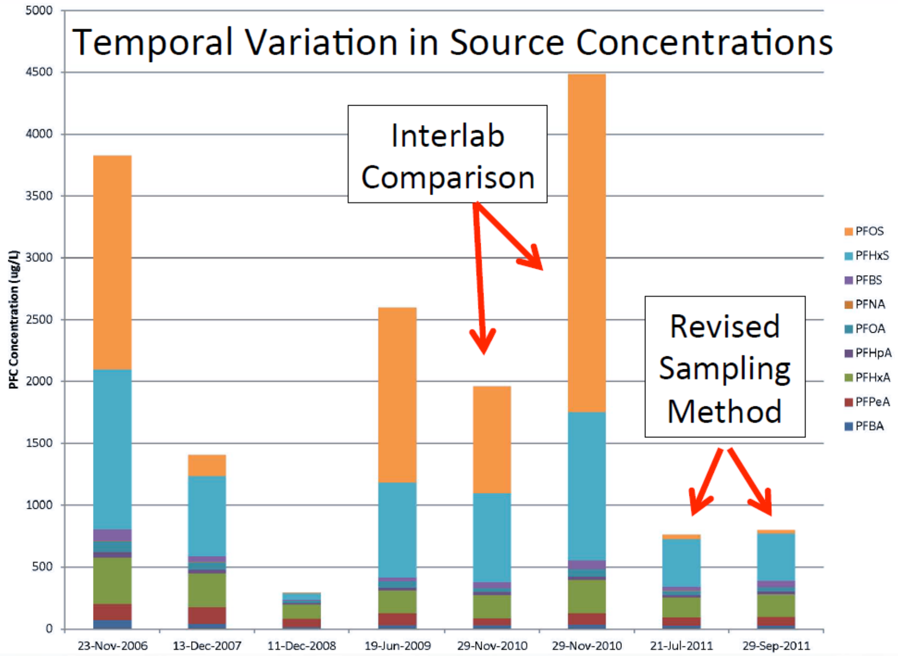
- Tyvek
- Teflon
- Water-proof clothing
- New clothing
- Blue Ice
- Handling food packaging
- Non-stick or water/grease/stain-resistant
- Glass containers

OK:

- Plastic containers (HDPE or polypropylene, no lined caps)
- Nitrile gloves (change often)
- HDPE tubing and bailers
- Alconox or Liquinox soaps
- PFC-free laboratory certified water

Sampling for PFAS - Stratification

- PFAS accumulate on water surface (varies with site)
- Do not collect water at the very surface
- Bailers work well



Source: Transport Canada, SLR Consulting Ltd.

PFAS Analytica Methods - EPA Method 537

- Determines 14* PFASs, for the drinking water matrix only
- Uses liquid chromatography/tandem mass spectrometry (LC/MS/MS):
  - 9 perfluoroalkyl carboxylates: C6-C14 (where C8 = PFOA)
  - 3 perfluoroalkyl sulfonates (C4, C6, C8 where c8 = PFOS)
  - 2 sulfonamidoacetic acids (N-MeFOSAA, N-EtFOSAA)

*Many labs now offer a 24 compound list, including 3 fluorotelomer sulfonates

Non-Drinking Water PFAS Methods

- Each lab develops its own method for various matrices other than drinking water
- No EPA guidance on hold times, thermal preservation requirements
- EPA published methods are being developed
- In the meantime, DoD ELAP addressing these issues through modification to DoD QSM requirements
- DoD uses laboratories that have ELAP-accredited methods (matrix-specific) for non-drinking water PFAS determination; methods are compliant with QSM 5.1, Table B-15 (LC-MS/MS)

What About "the Other" PFASs?

- Over 300 PFAS have been identified in AFFF formulations & groundwater
- 6:2 Fluorotelomer Sulfonate found at high levels in DoD GW at FTA
- Some compounds at levels greater than PFOS/PFOA (which can be in ppm range)
- QTOF is used to identify and quantify other PFAS but lack of standards for many PFAS means results are semi-quantitative
- Few labs are currently equipped to determine large list

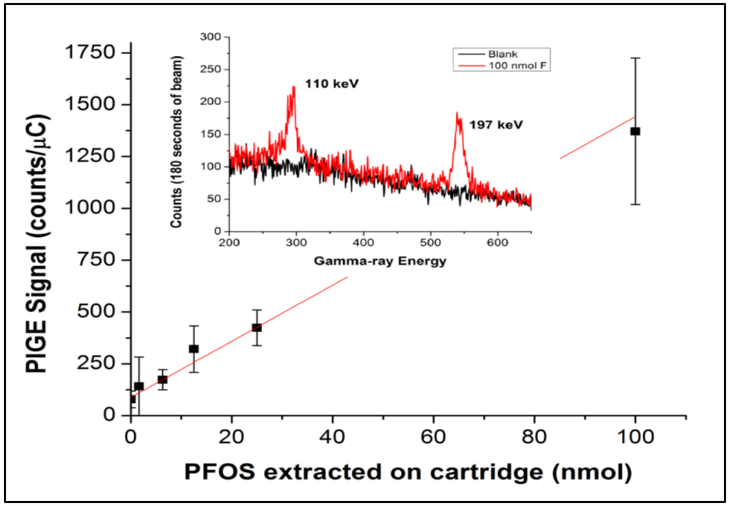
Other PFASs Beyond Method 537 Analytes

Useful when:

- Additional toxicity data or regulatory values become available
- States require other PFASs (if promulgated)
- For delineation (shorter compounds C4 & C2 move faster)
- Treatment feasibility (e.g. GAC may not adsorb short chain compounds)
- Biotic and abiotic transformation / mass balance
- Tracing sources in mixed plumes
- Source zones may contain cations & zwitterions not normally analyzed; these may be mobilized by being transformed by ISCO, for example
- Fluorotelomer AFFF formulations are being delineated

Precursors and Total Fluorine: Alternative Methods

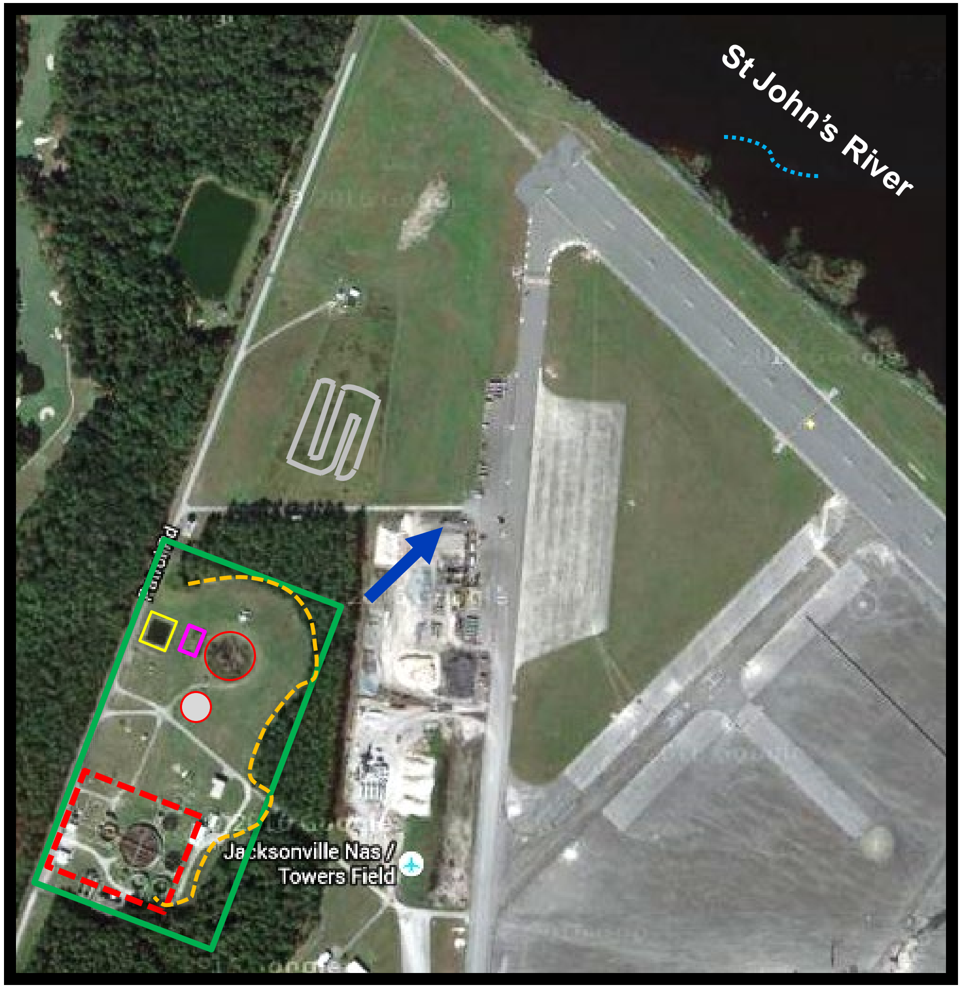
- Total oxidizable precursor (TOP) assay[1]
  - Polyfluorinated chemicals react with hydroxyl radicals but *perfluorinated* do not (e.g., PFOS and PFOA)
  - Net increase in PFCAs after oxidation of sample = precursors
- Total fluorine by PIGE[2]
  - PFAS sorbed onto media to create 'target'
  - 10 nA of 3.4 MeV protons for 180 s
  - Quantitative, high-throughput, inexpensive



- AOF – Adsorbable Organic Fluorine
  - Total F by IC after combustion of organofluorine; limited availability

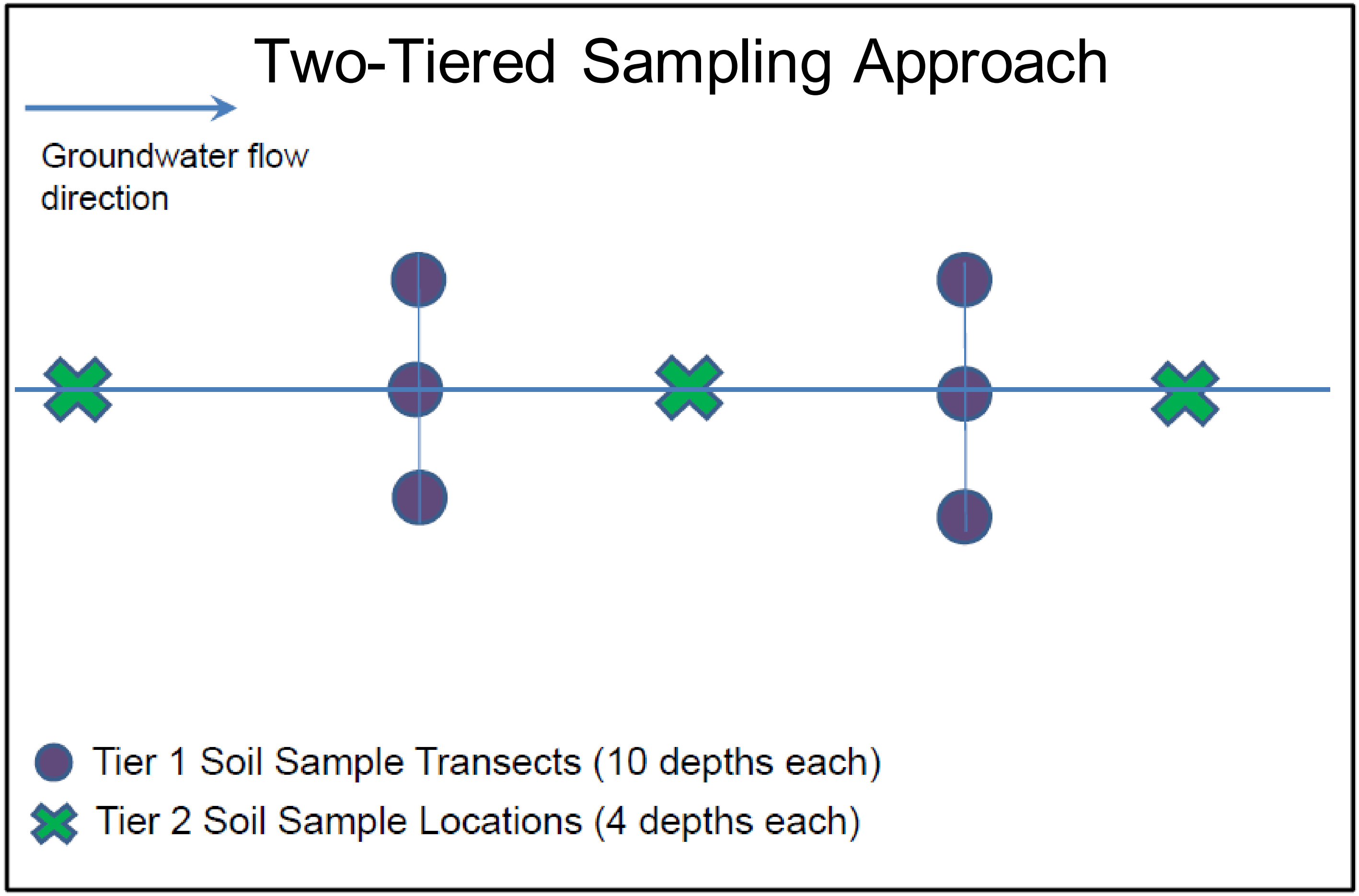
Case Study – NAS Jacksonville Firefighter Training Area and WWTP

Fire Training Area (FT-02) General Site Characteristics



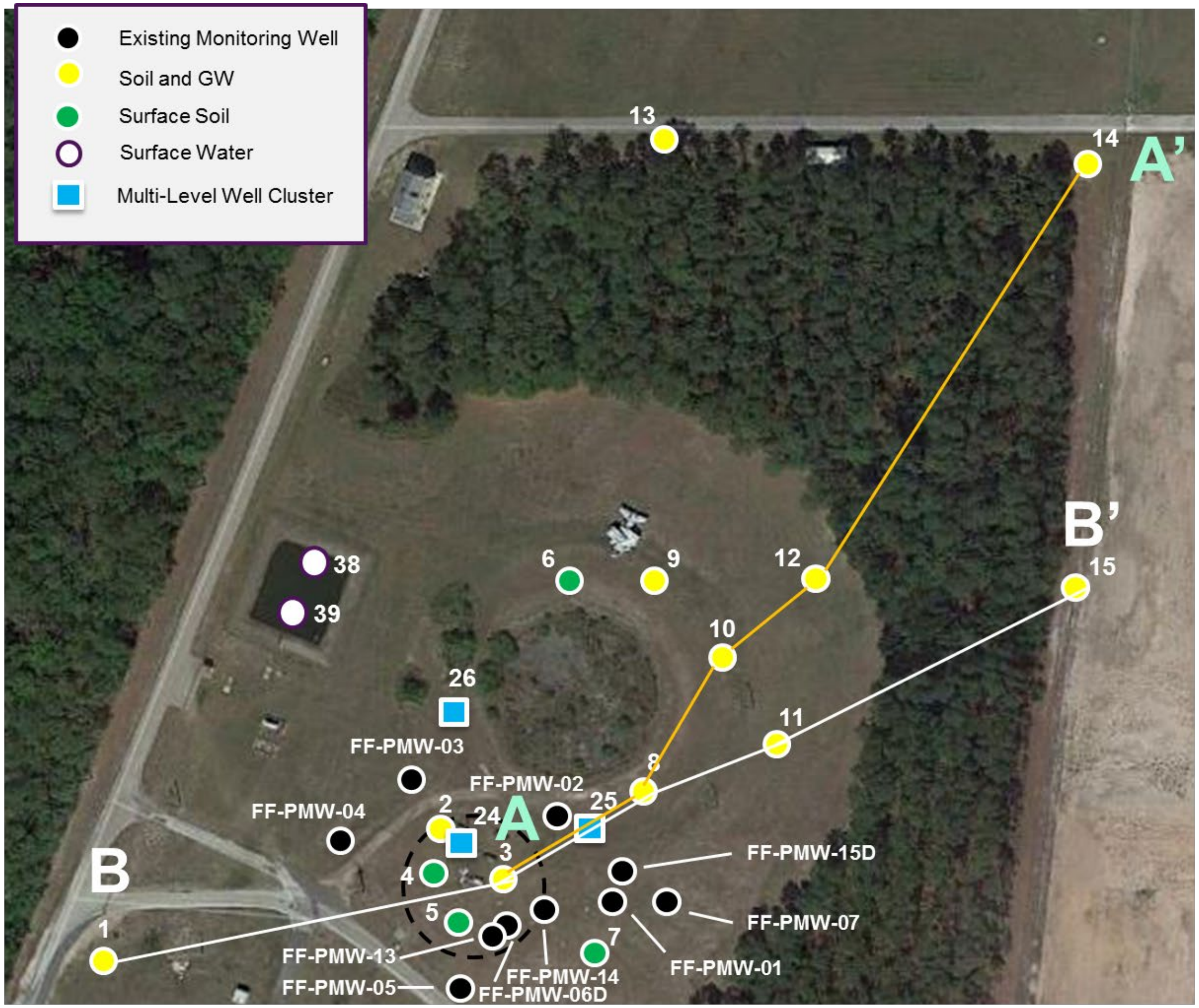
(grey filled circle)	Former Training Area – In use 1968-91
(red circle)	Current Fire Training Area
(yellow square)	Pond/Pump Station
(red dashed square)	Waste Water Treatment Plant
(grey outline)	Unlined Polishing Pond
(magenta rectangle)	OW Separator
(blue dotted line)	St. John's River
(yellow dotted line)	Tree Line
(blue arrow)	GW Flow Direction: Primarily N/NE

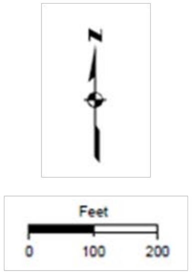
Case Study – NAS Jacksonville Firefighter Training Area and WWTP



Groundwater sampling co-located, but 4 samples per location

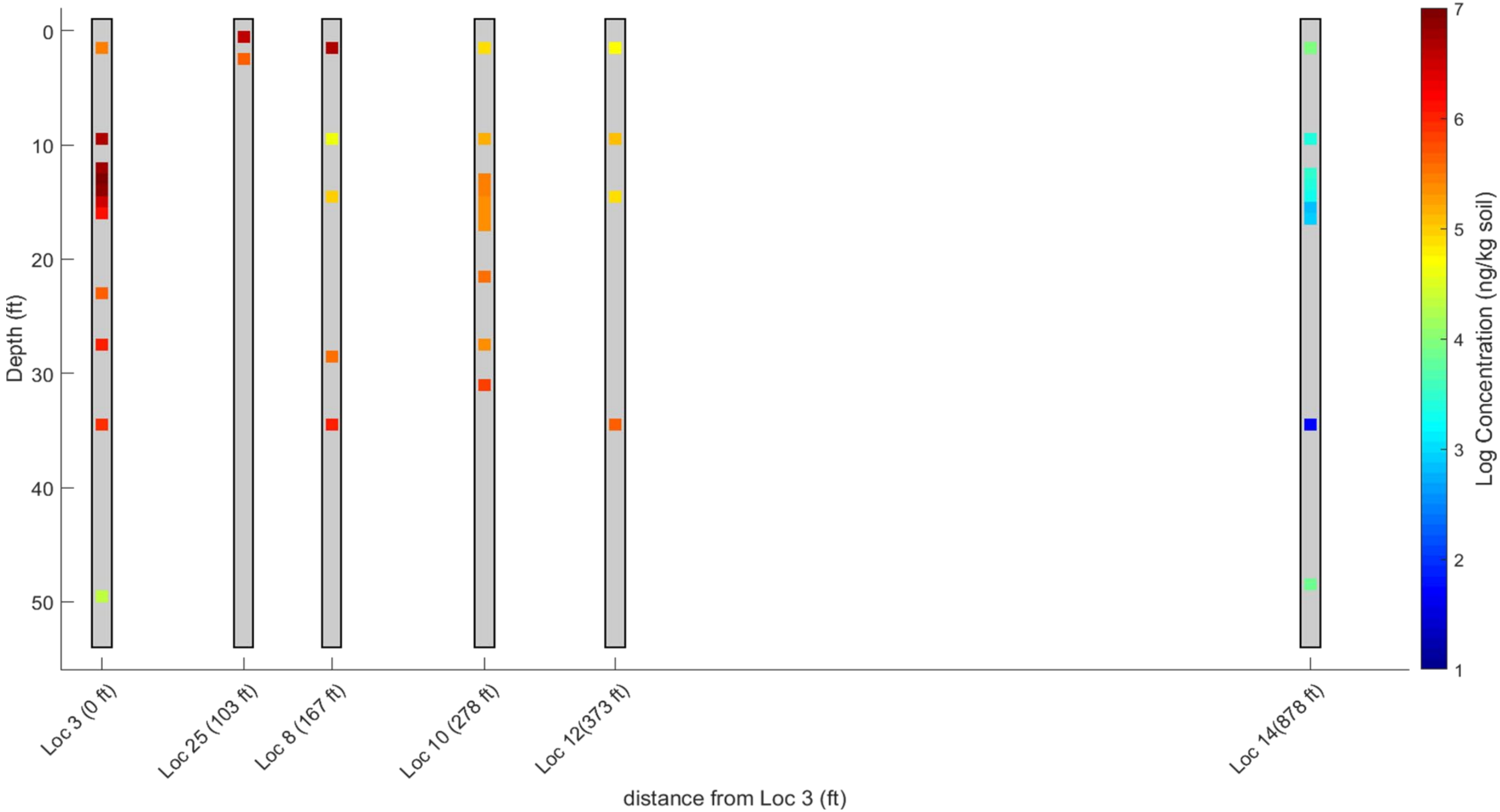
Case Study – NAS Jacksonville Firefighter Training Area and WWTP



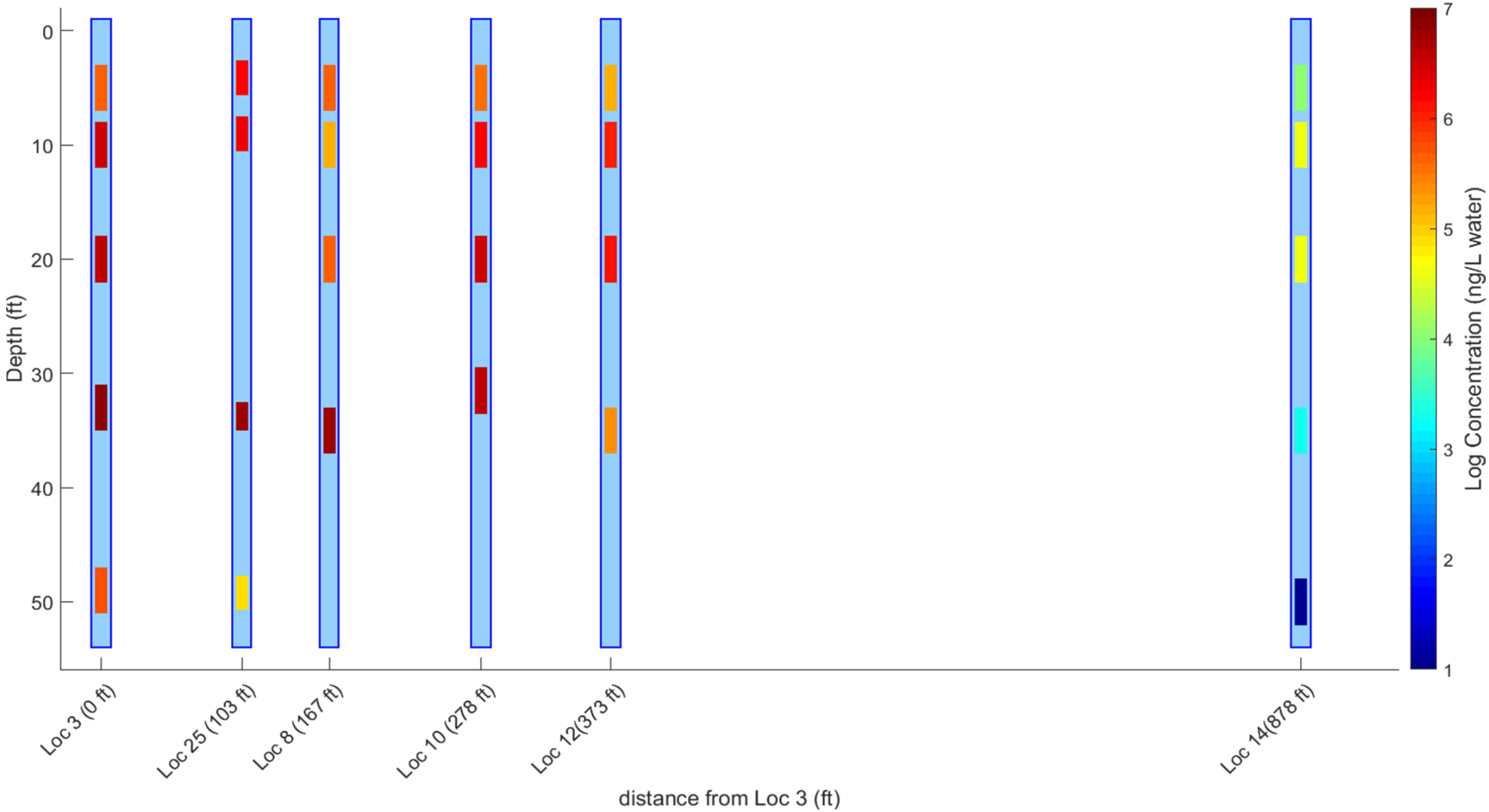


The former fire training area (FTA) is marked by the dashed circle. We will consider this the source zone, with peak concentrations around Location 3.

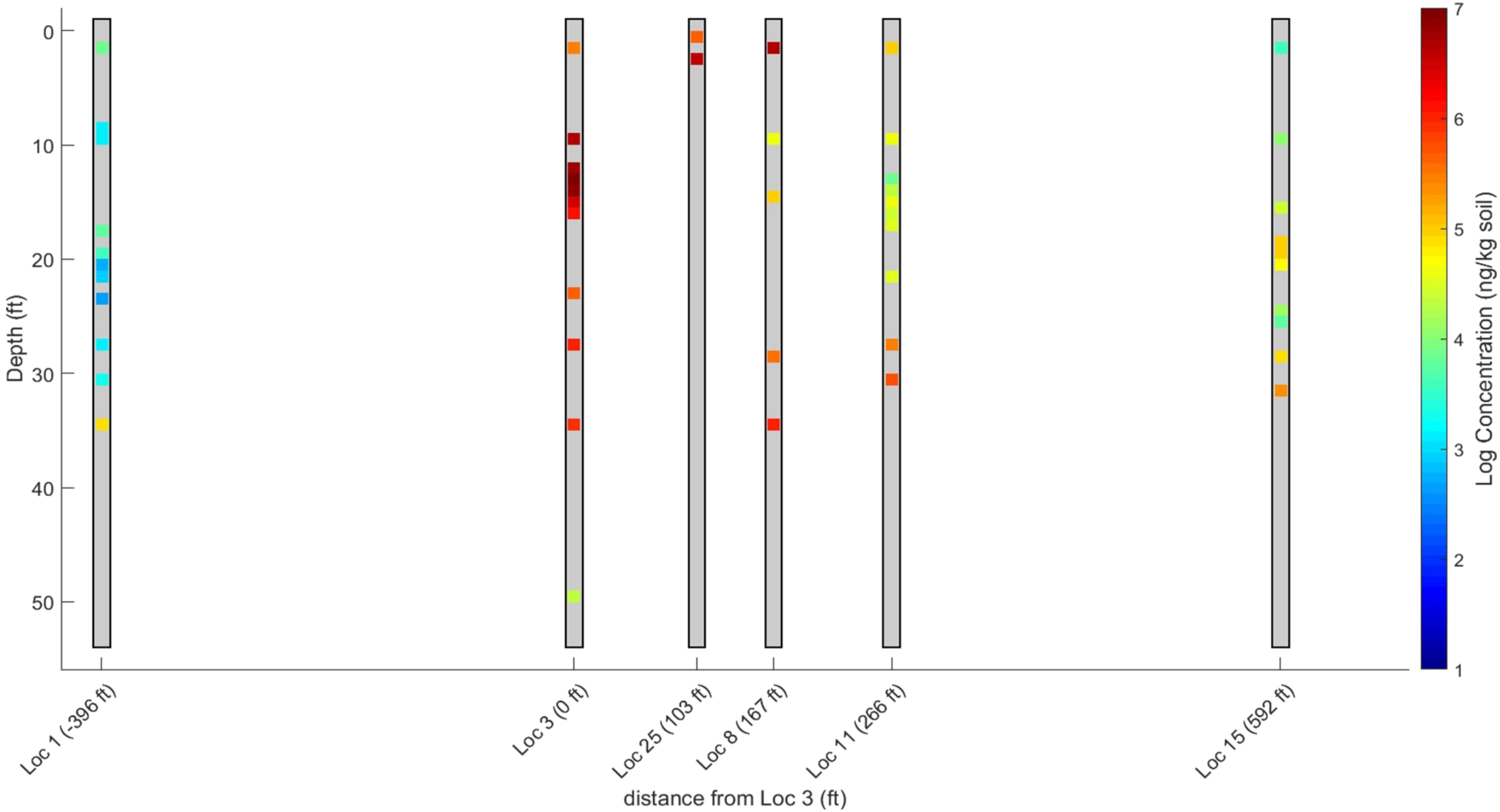
Transect A: sum soil PFAS (ng/kg)



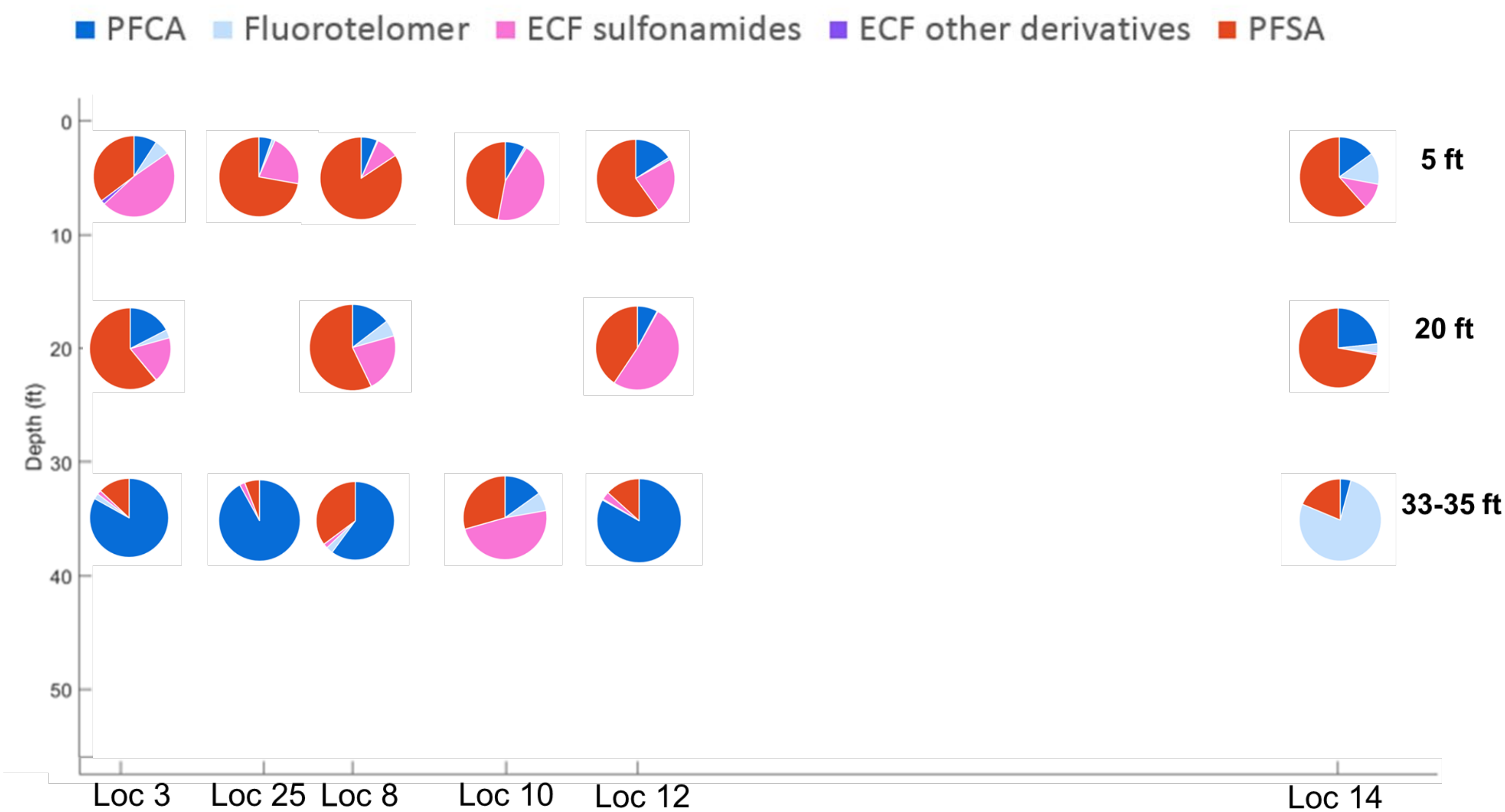
Transect A: sum water PFAS (ng/L)



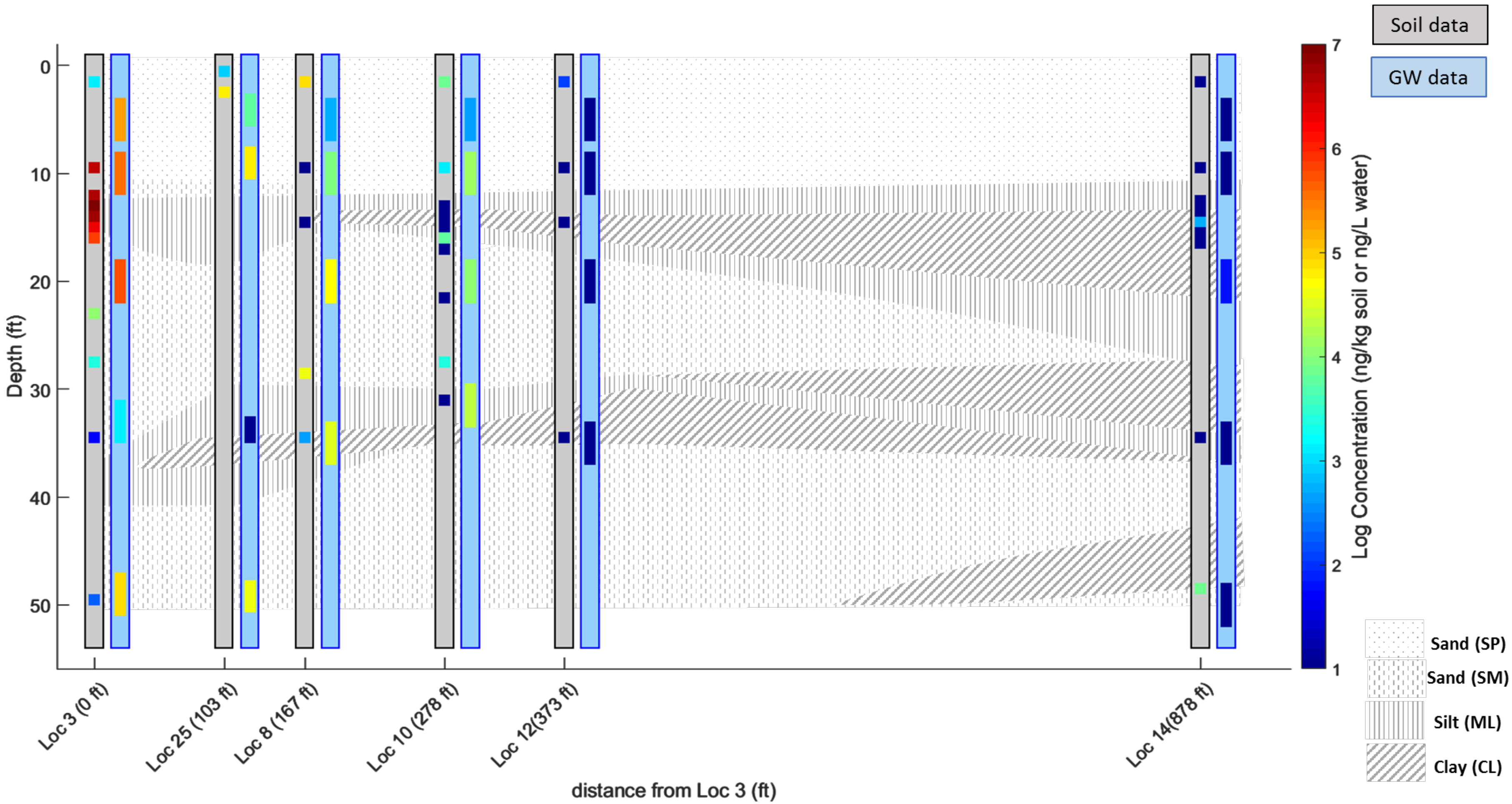
Transect B: sum soil PFAS (ng/kg)



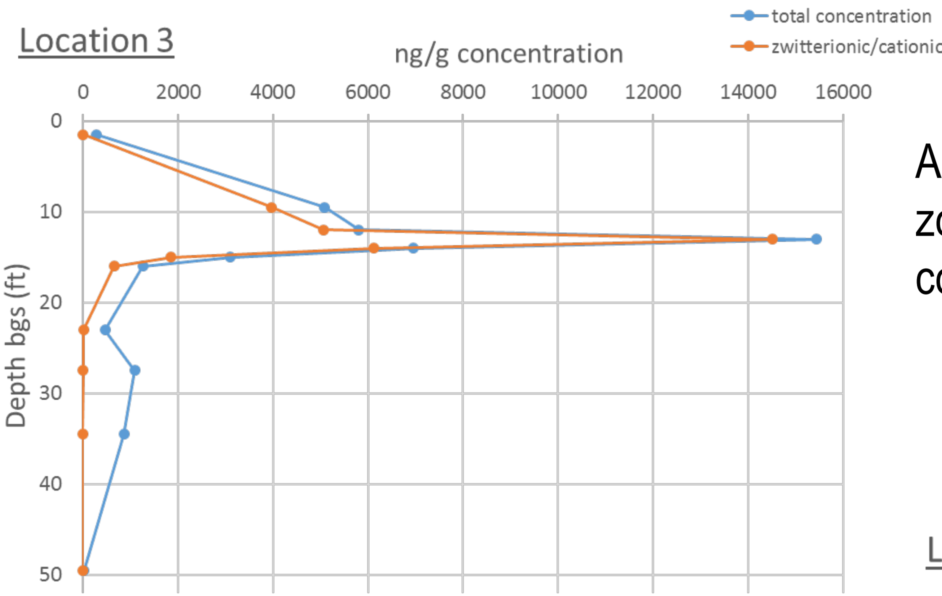
PFAS Composition Distribution Transect A: Groundwater



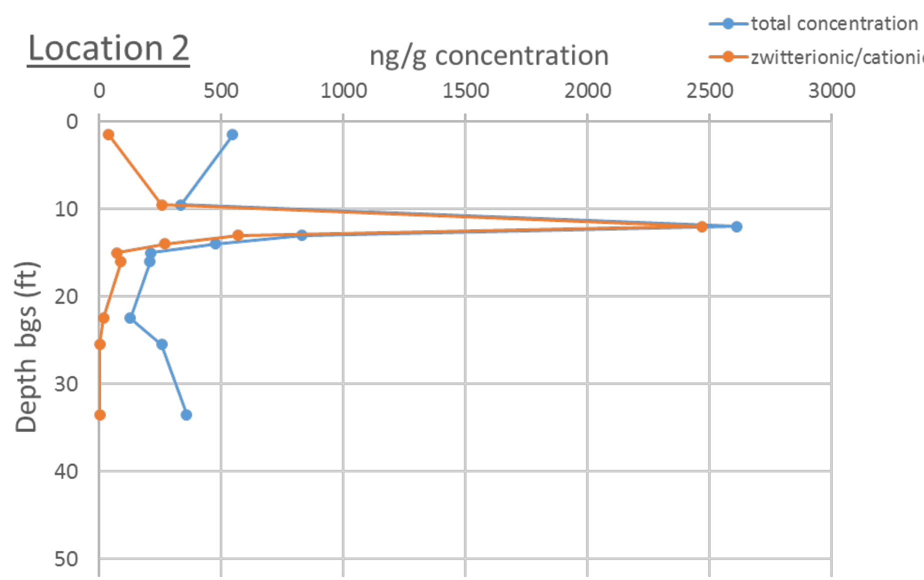
Sum of Zwitterionic and Cationic PFAS: Transect A



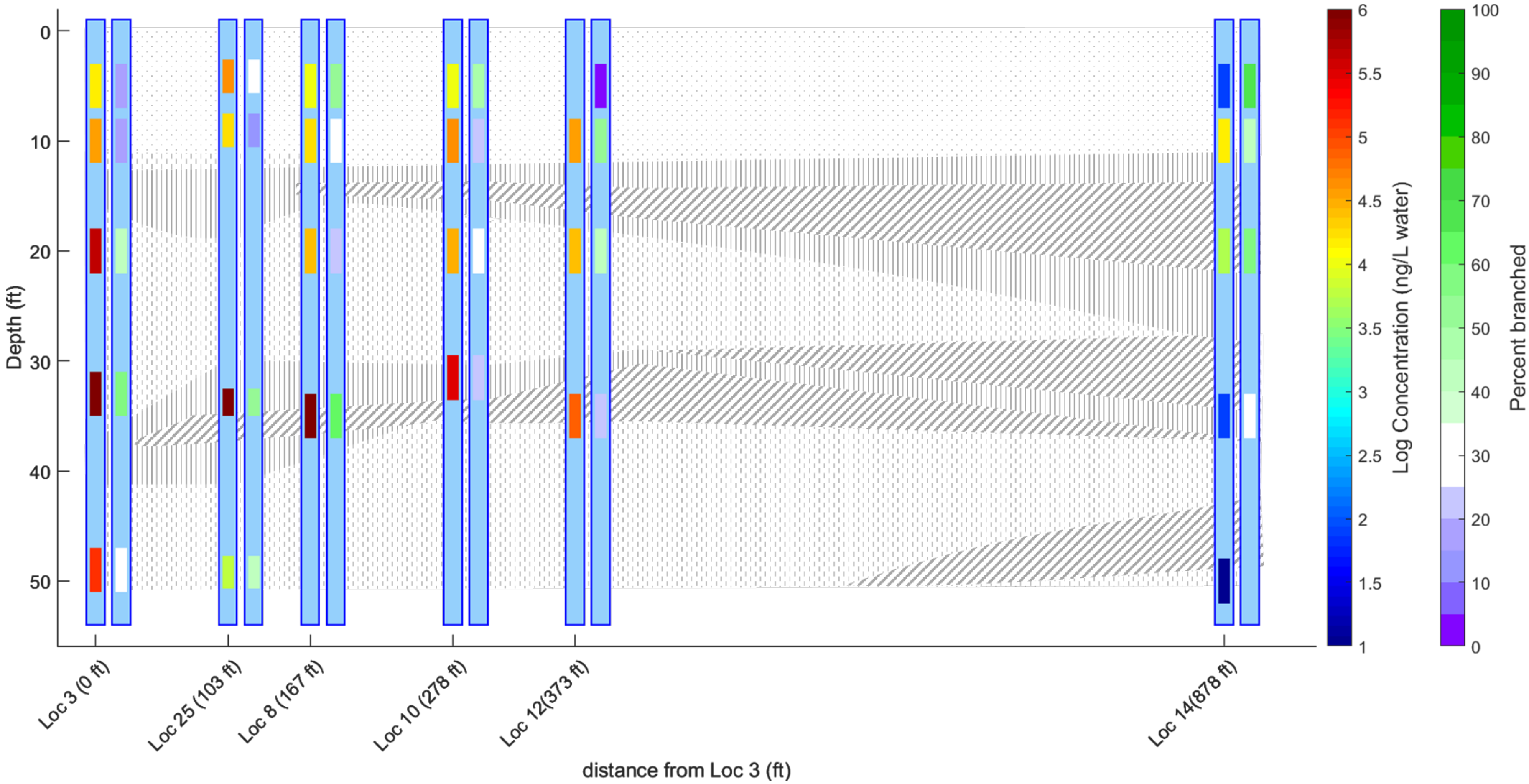
Source Zone Soils are Dominated by Cationic and Zwitterionic PFAS



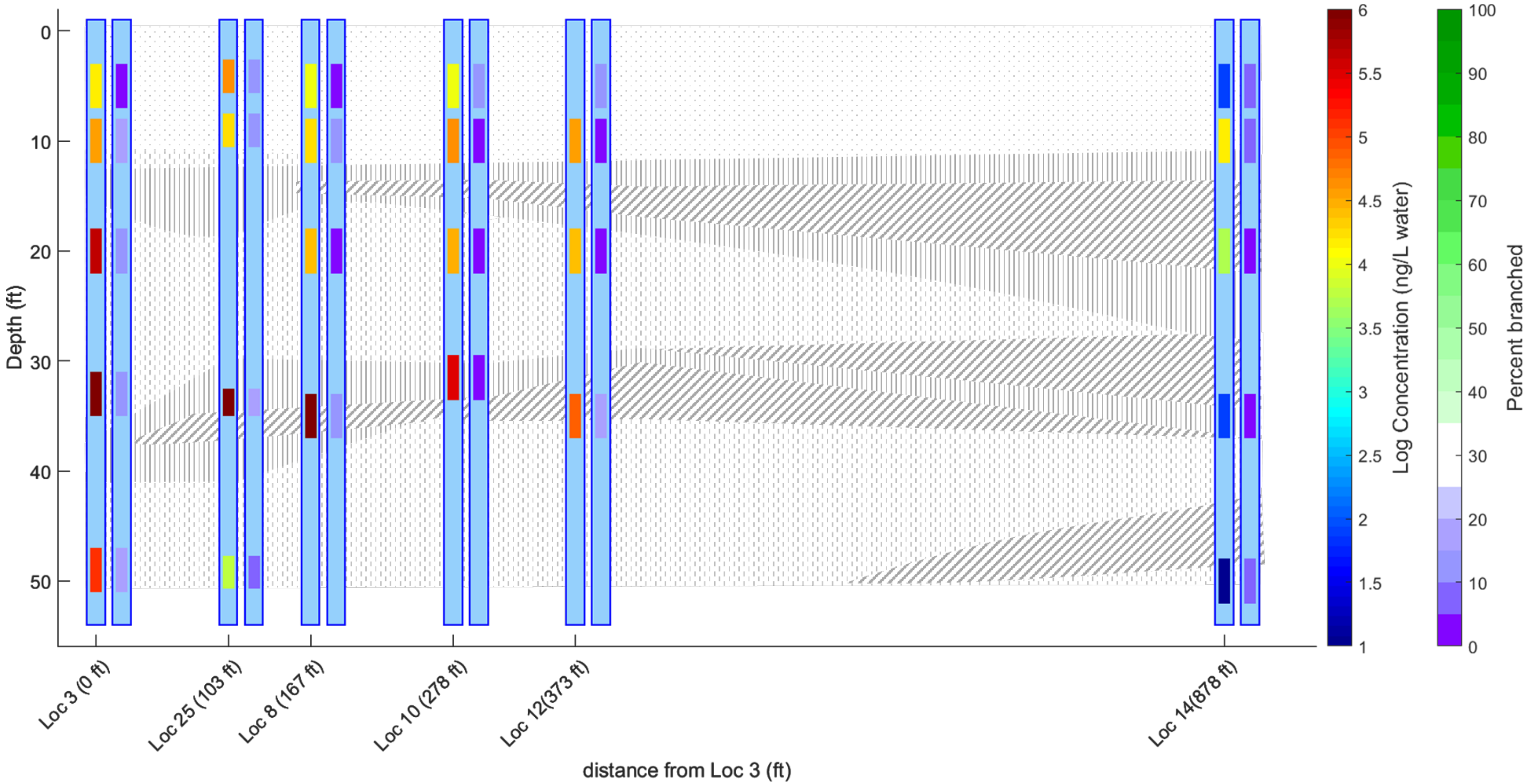
A high percentage of the soil PFAS mass at the source zone (Locations 2 & 3) is from zwitterionic and cationic compounds.



% Branching PFOS; Transect A (groundwater)



% Branching PFOA; Transect A (groundwater)



Case Study – NAS Jacksonville Firefighter Training Area Results Summary

NAVFAC

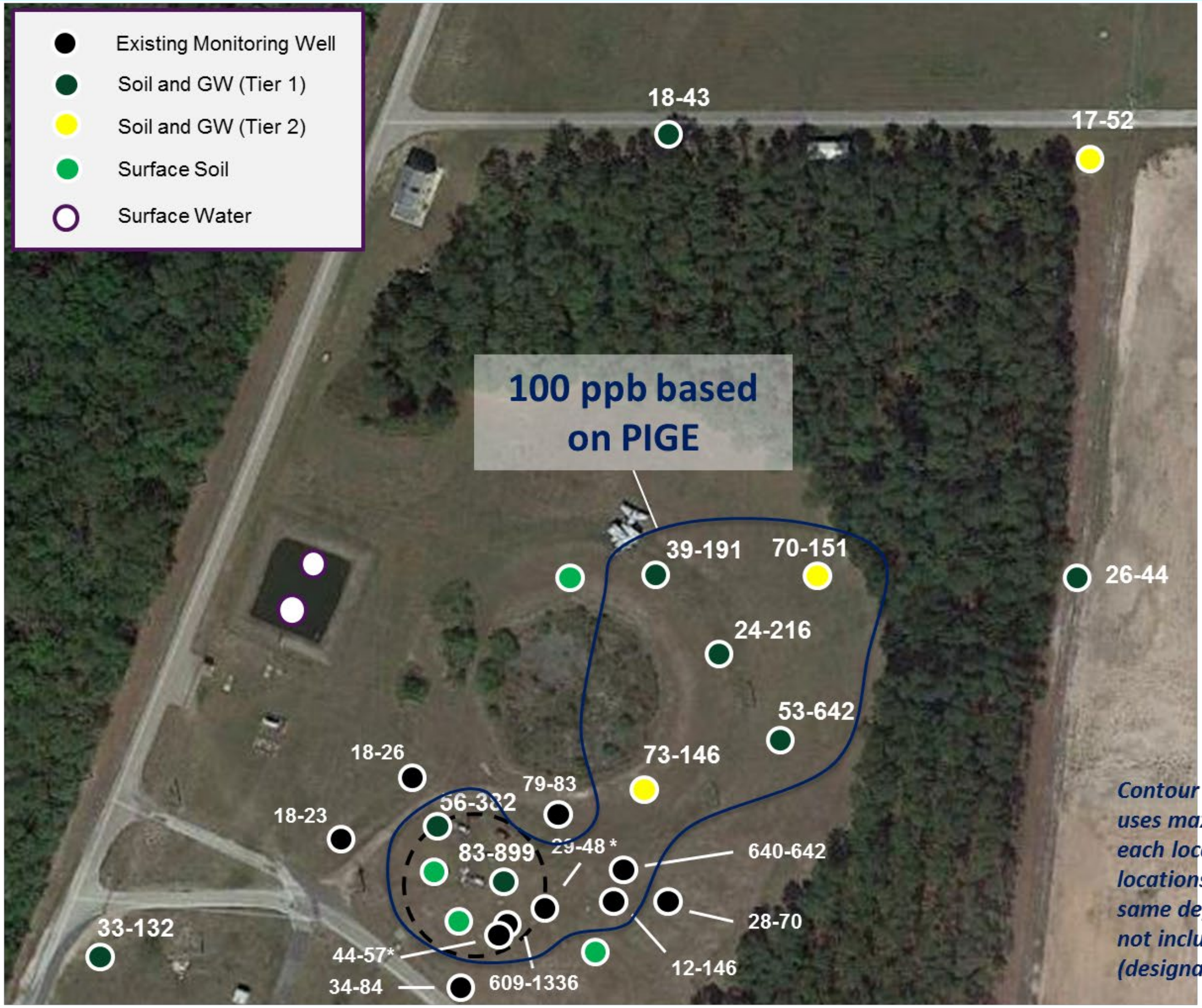
- Significant penetration with depth at source zone (location 3), and often elevated concentrations at depth in downgradient locations
- Compositional changes with depth and distance from the source
  - Increasing PFCA concentrations with depth (especially in groundwater)
  - Cations/zwitterions mainly in source zone for soil, some transport observed for groundwater but more limited than anion transport
  - Some presumed transformation products have peak concentrations at intermediate locations from source
- Linear vs branched PFOS patterns different from PFOA patterns
  - PFOA may be formed from transformation of fluorotelomer precursors
  - Differential transport of PFOS isomers evident

PFAS Site Characterization Summary

- Process is basically the same as other contaminants such as BTEX
- Develop a CSM which includes the PFASs of concern
- Incorporate Fate & Transport information for the population of PFAS of concern
- Determination of all PFAS species at a site may not be possible using currently available analytical methodology from all but a few (academic) laboratories
- Use proper containers (HDPE, PP) for sample collection and avoid PFAS-containing materials during sampling
- "Chromatographic effect" on PFAS distribution in site soil/groundwater evident vertically and horizontally
- Mass storage in low permeability zones and persistence and transformation of PFAS supplies groundwater plumes for extended periods

Questions

Case Study – NAS Jacksonville Firefighter Training Area and WWTP



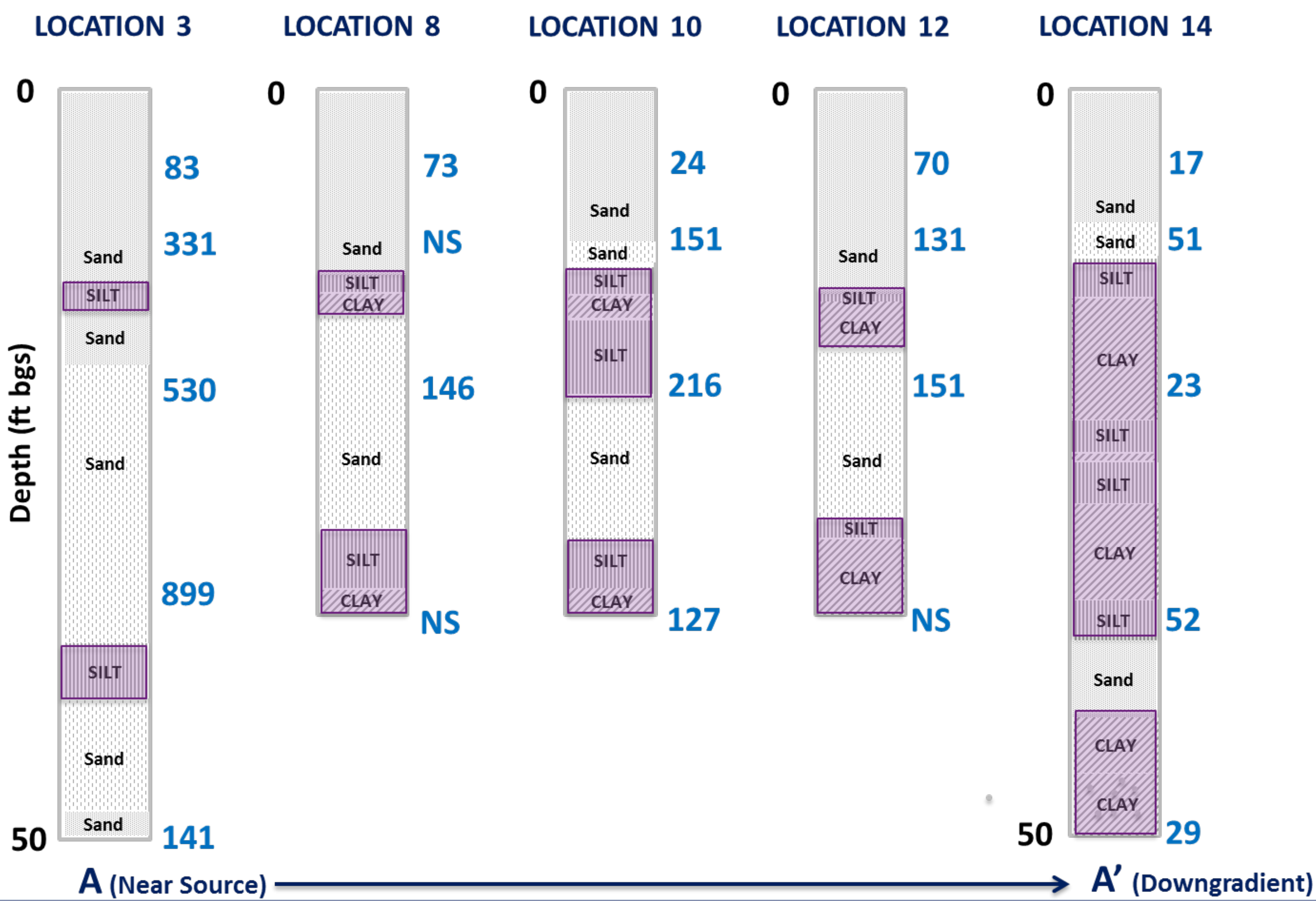
PIGE Screening Data:

Groundwater (range of ppb Fl from multiple sample depths)

*Contour is approximate and uses max concentration at each locations. Not all locations sampled across the same depths. Some locations not included in contouring (designated with *).*

Case Study – NAS Jacksonville Firefighter Training Area and WWTP

Results: Jacksonville PCA 15 FFTF – PIGE Screening Data (ppb Fl)



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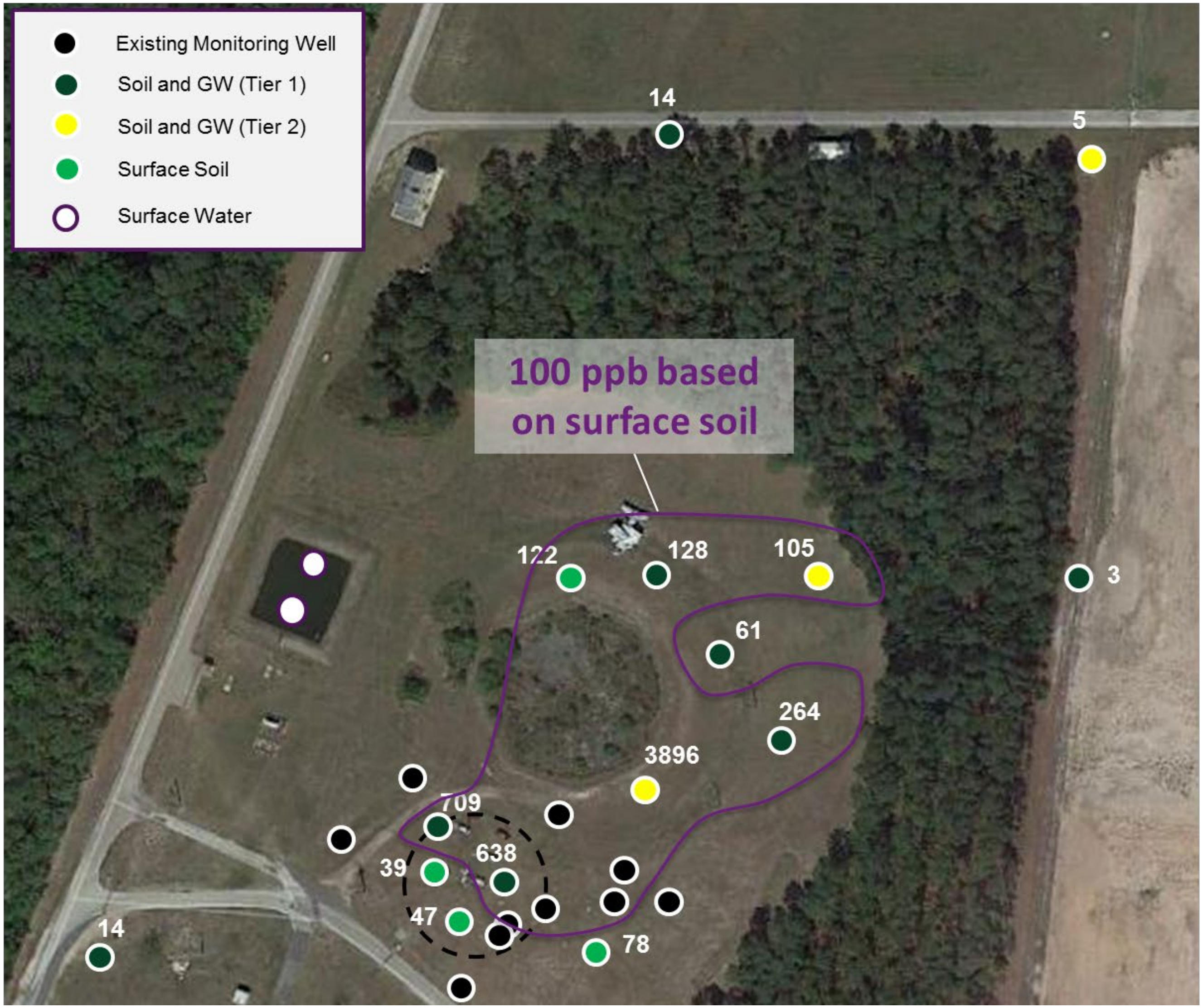
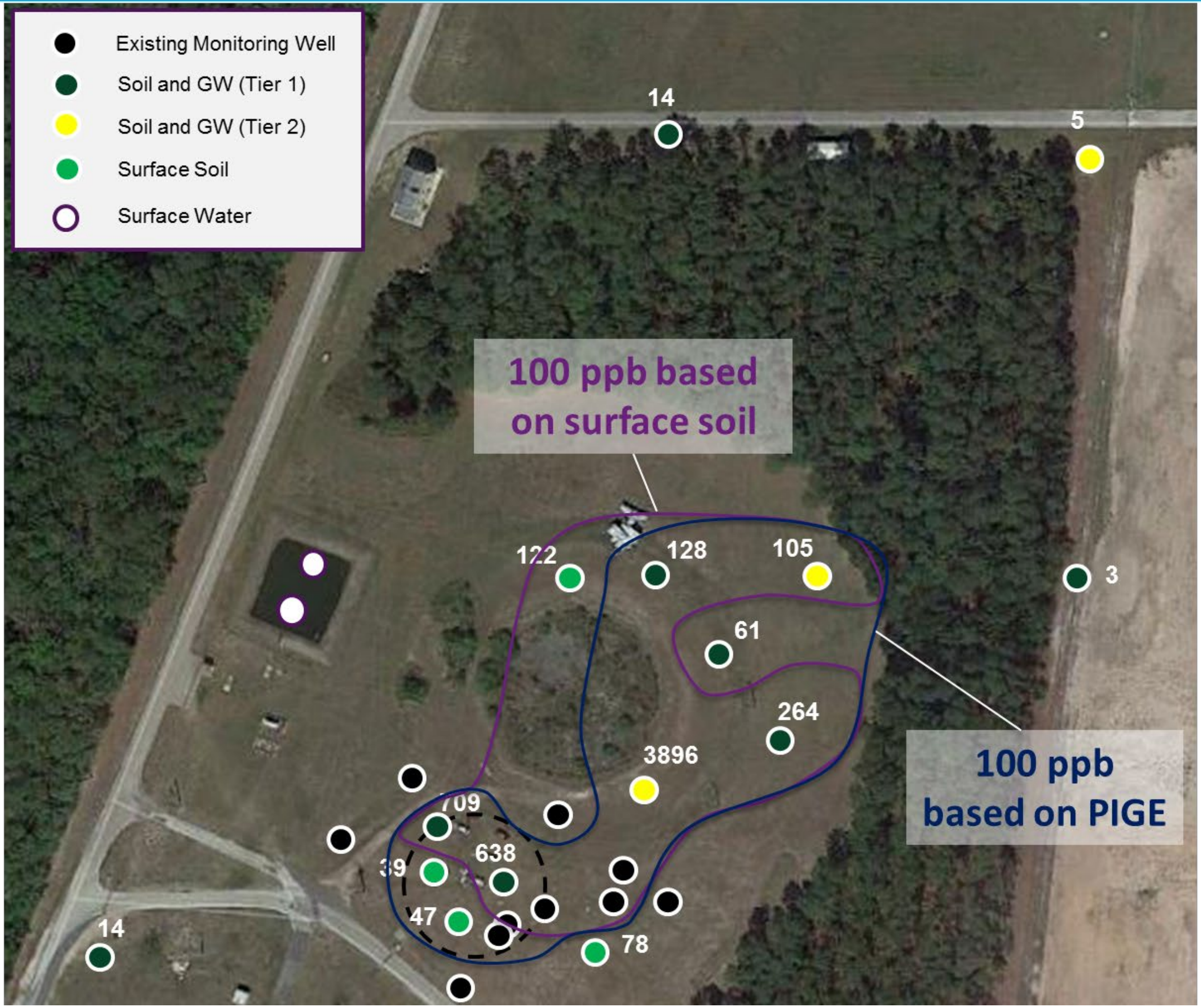


Total PFAS:

Surface Soil (ng/g)

Case Study – NAS Jacksonville Firefighter Training Area and WWTP

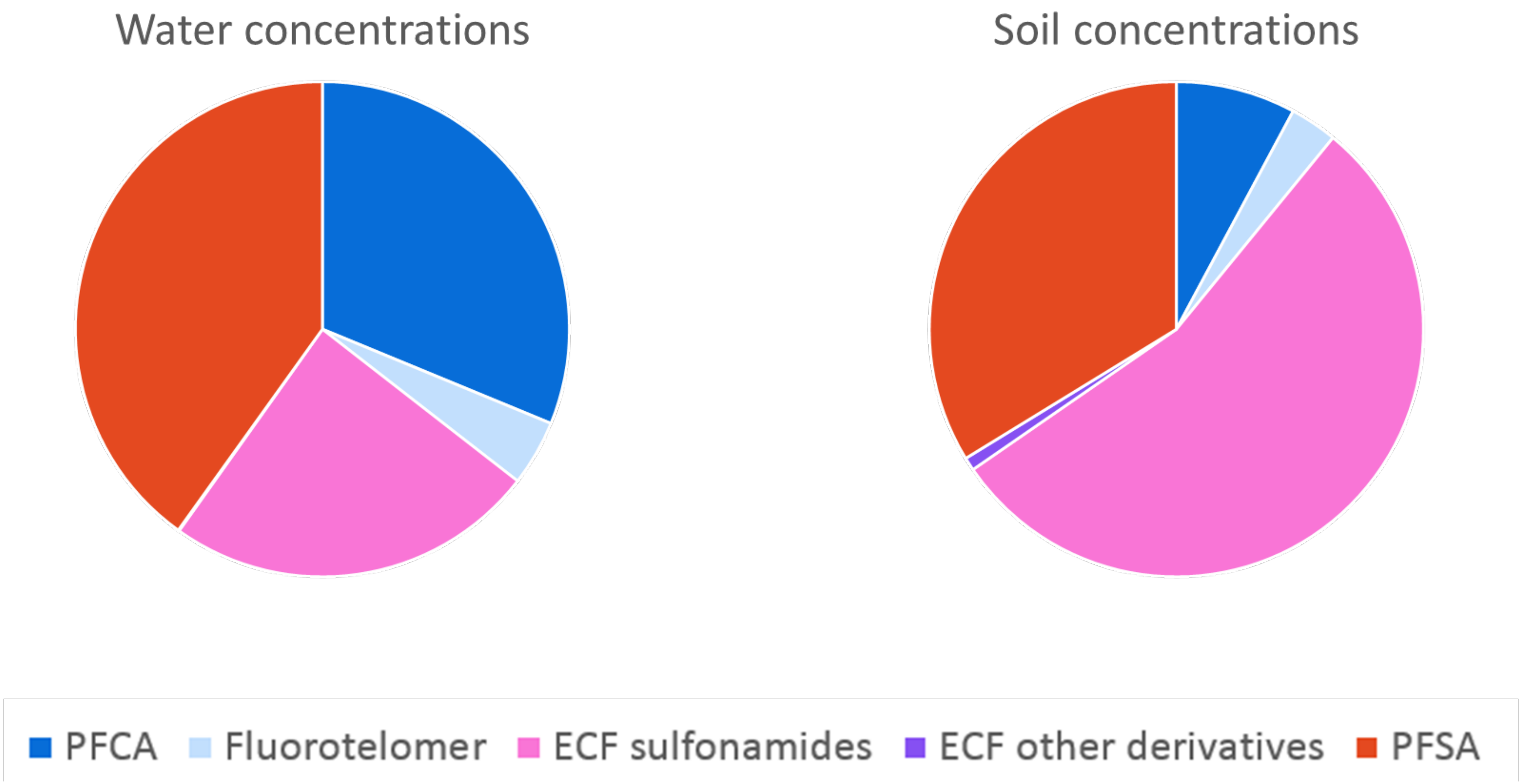


Total PFAS:

Surface Soil (ng/g) – Comparison with PIGE data

Note: data are preliminary and may change slightly following lab corrections

Relative PFAS Concentrations at NAS JAX, FFTA



PFAS Projects at EXWC

- NESDI 527 “Structure-Function Relationship and Environmental Behavior of Per- and Polyfluorochemicals from Aqueous Film-forming Foams“
  - Determination of PFAS in various media across Navy using expanded library of compounds and structure-activity relationships.
- NESDI 534 “Technology Evaluation and Sampling for Treatment of Perfluorochemicals”
  - Assess effects of prior treatment of co-contaminants (e.g. treatment of TPH at firefighter training areas) on PFAS nature and extent.
- NESDI 555 “Demonstrating the Effectiveness of Novel Treatment Technologies for the Removal of Poly and Perfluoroalkyl Substances (PFASs) from Groundwater”
  - Determine effectiveness of new sorbents, including amendments, as well as degradative methods on PFASs in water and soil.

PFAS Projects at EXWC (cont'd)

- ESTCP ER-201633 "Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substance (PFASs) in Environmental Media at DoD Sites for Informed Decision-Making"
  - High resolution sampling and analysis for detailed site characterization of PFAS source areas and plume to understand transport and transformation of the 300+ PFAS compounds known to be associated with AFFF.
- ESTCP ER-201729 "Field Demonstration to Enhance PFAS Degradation and Mass Removal Using Thermally-Enhanced Persulfate Oxidation Followed by Pump-and-Treat"
  - Demonstrate the treatment of PFASs in situ using persulfate and peroxide under acidic conditions followed by pump-and-treat.

PFAS Projects at EXWC (cont'd)

- ESTCP (Wood lead) "Removal and Destruction of PFAS and Co-contamination from Groundwater"
  - Treatment train approach using a four-step process to remove, concentrate, and destroy PFASs: (1) ion exchange (IX) media (2) IX media regeneration and reuse; (3) regenerant solution distillation and reuse; and (4) onsite destruction of concentrated PFASs in concentrates by plasma.