Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

PFAS Site Characterization

Jovan Popovic, Ph.D.
Naval Facilities Engineering Command (NAVFAC)
Engineering and Expeditionary Warfare Center (EXWC)

FRTR, Arlington, VA, September 26, 2019

Presentation Overview

- Introduction
- PFAS Sources
- Characteristics of PFAS Plumes
- Analytical Methods
- Case Studies
- Wrap-Up

PFAS Sources

AFFF Impacted Sites (FTA, runways, storage tanks, leaky pipes, crash sites, hangars, fuel farm)

- Most concentrated source, typically from ECF PFSA and PFCA
- Example of PFOS and PFOA concentrations 1,000 and 6,000 µg/L up to mg/L concentrations

Chrome Metal Plating Shops

- PFASs used for mist suppression
- PFCAs and PFSAs (µg/L) in discharge water
- Leads to high concentration in wastewater, biosolids, landfill leachate, effluent water and therefore SW and fish

Landfill Leachate

- 2nd most concentrated (tens of µg/L (<10,000 ng/L)) point source of many PFAS classes
- Most abundant short-chain PFCAs & fluorotelomer acids

WWTP Effluent

- Municipal and industrial 3rd highest source (<0.1 µg/L levels, < 100 ng/L)
- No significant removal of PFOA & 6:2 fluorotelomer sulfonate
- *Net increase* in PFOS mass flow during WWTP
- Land application of WWTP biosolids (<3,000 ng/g) leaches to soil and groundwater where biosolids applied

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PFAS Characteristics – AFFF

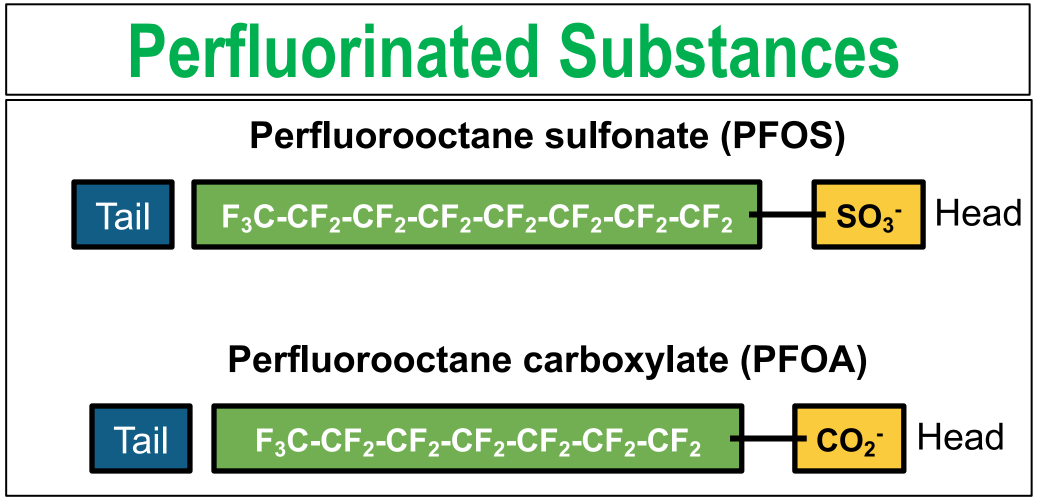
- PFAS containing AFFF used by military
- Electrochemical fluorination (ECF) process (original formulation); phased out in early 2000s.
  - Domestic production of ECF derived AFFF ceased in late 1990’s; existing stockpiles used until early 2000s
- odd & even chain lengths (C2-C14)
- C2 & C3 sulfonates recently found in AFFF and groundwater
- branched & linear isomers (30:70)
- 89% PF**S**As (e.g., PFOS) in original AFFF formulation
- *Only* 1.6% of original PFAS containing AFFFs are PFCAs (e.g., PFOA)

PFAS Characteristics – Fluorotelomer Based AFFF

- Currently in use
- Multiple manufacturers with varying formulations
- Formulations contains little to no PFOS
- Precursors more commonly degrade to PF**C**As (including PFOA) and FTSAs; some degradation to PFOS, but uncommon
- Recent formulations generally contain smaller carbon chain lengths (C6 and below)

PFAS Characteristics that Affect Partitioning and Transport

- CF “tail”: imparts hydrophobic character (longer is more hydrophobic, transports slower) – dominated by hydrophobic interactions
- Charged “head group” imparts water solubility;
- Carboxylates transport faster than sulfonates for a given carbon chain length



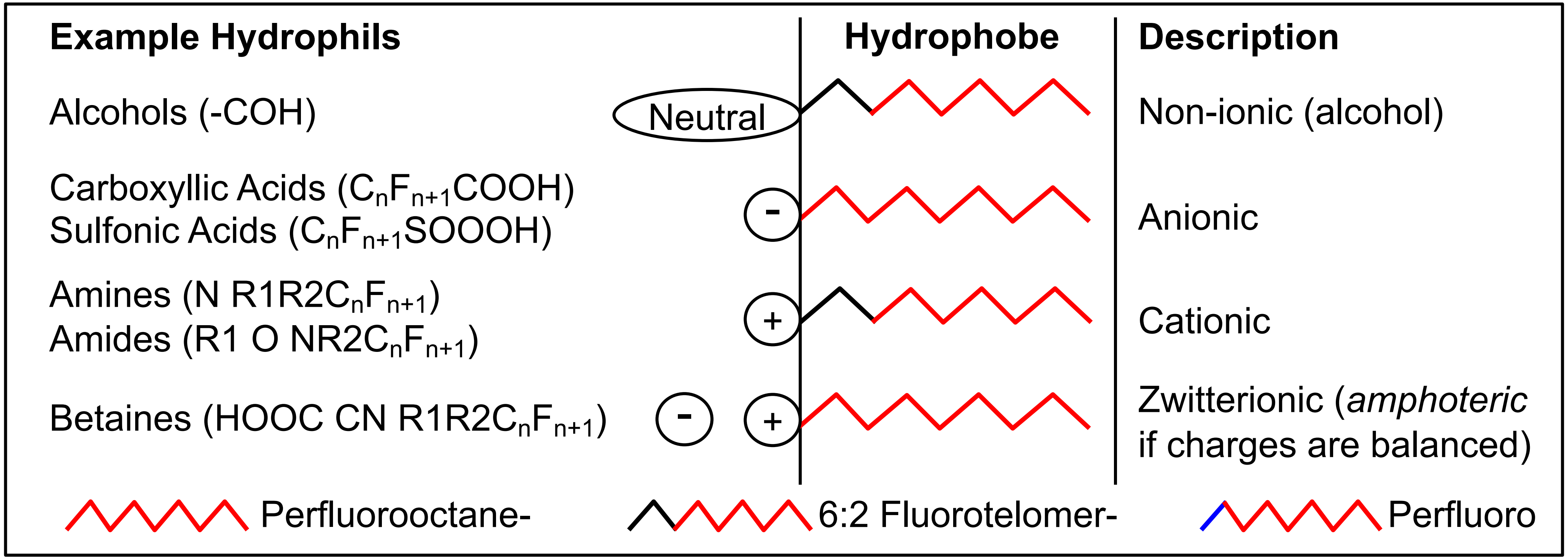
Perfluorinated Substances

Perfluorooctane sulfonate (PFOS)

Perfluorooctane carboxylate (PFOA)

PFAS Characteristics that Affect Partitioning and Transport

- PFOS and PFOA exist as anions at environmentally relevant pH (4 to 6)
- Transport Anions > zwitterions > cations
- Greater CF chain length increases sorption, decreases transport
- Cationic and zwitterionic PFASs may be cation exchanged onto source-zone sediments



Example Hydrophils		**Hydrophobe**	**Description**
Alcohols (-COH)	Neutral		Non-ionic (alcohol)
Carboxyllic Acids ($C_nF_{n+1}COOH$) Sulfonic Acids ($C_nF_{n+1}SOOOH$)	-		Anionic
Amines (N $R1R2C_nF_{n+1}$) Amides (R1 O $NR2C_nF_{n+1}$)	+		Cationic
Betaines (HOOC CN $R1R2C_nF_{n+1}$)	- +		Zwitterionic (*amphoteric* if charges are balanced)

PFAS Characteristics that Affect Partitioning and Transport

- Low vapor pressure and Henry's constant due to surfactant nature
- Branched-chain isomers sorb less than linear-chain isomers

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility (mg/L)	0.0027 @ 24°C	**3,400-9,500 @ 25°C**	**519 @ 20°C**	1,100 @ 20°C	1,780 @ 20°C
Vapor Pressure @ 25°C (mmHg)	$4.05x10^{-5}$	**0.5-10**	**$2.48x10^{6}$**	77.5	97
Henry's Constant (atm-m^3/mol)	$4.6x10^{-3}$	0.0908	**$3.05x10^{6}$**	0.0103	0.0056
Organic Carbon Part. Coeff. (Log K_{OC})	4.8-6.8	2.06	**2.57**	2.42	2.15

Soil Chemistry Characteristics that Affect Partitioning, and Transport

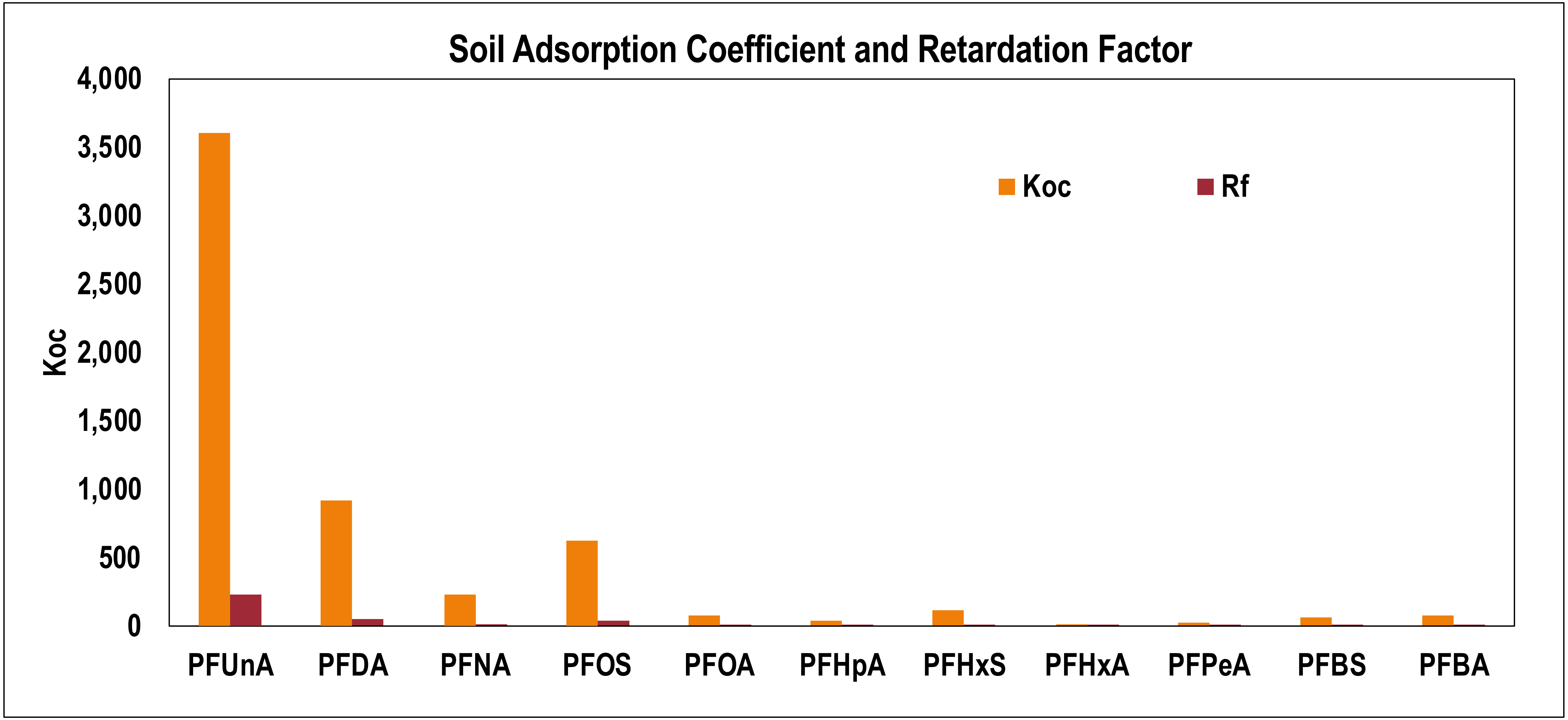
- Organic rich soils, oils, and other organics increase sorption
- Cation exchange onto source-zone sediments
- Sorption generally increases in the presence NAPLs
- Sorption by metal oxides and clay mineralogy
- The net charge on aquifer materials like clays is anionic, mineral like iron and aluminum are cationic

Groundwater Chemistry Characteristics that Affect Partitioning and Transport

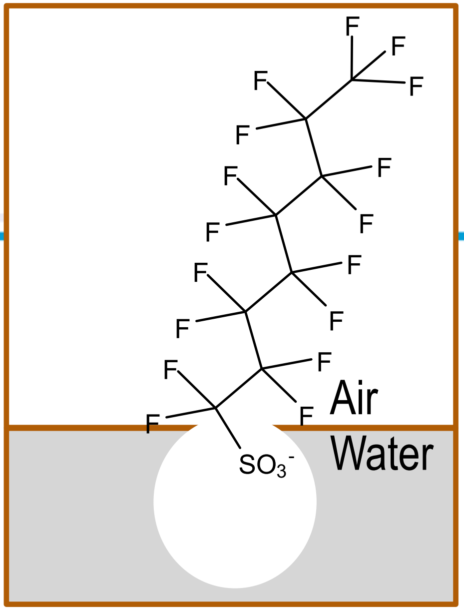
PFAS are surfactants therefore sensitive to water chemistry

- Increasing ionic strength increases retardation–may be relevant for sites near estuaries/ocean
- Low pH (changes protonation of sorption sites) and increased polyvalent cations increase sorption and retardation
- Competition by co-contaminants

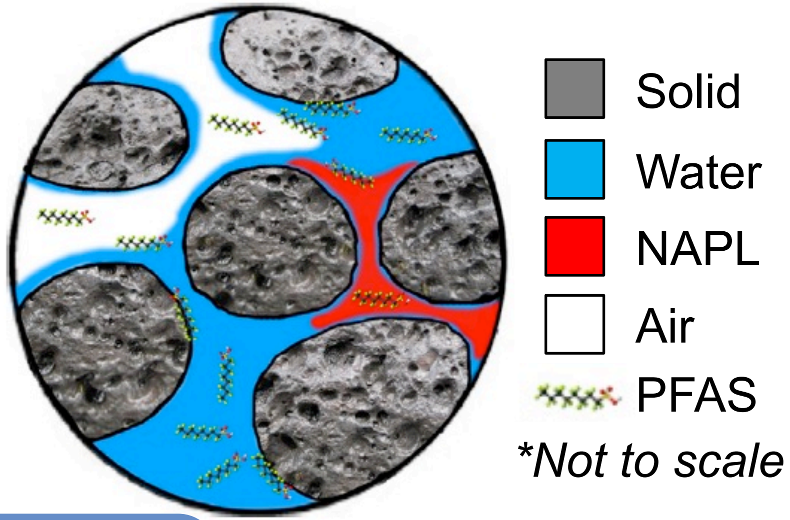
Typical Sorption Behavior of PFAS



PFAS Transport Characteristics in Source Zone



- Air/water partition coefficients (primary source of retention in vadose zone ~ 50% of total retention (surfactant) but vary greatly among different PFAS
- Adsorption at air/water interface – bubbles on surface important in waste water treatment
- Adsorption at NAPL/water interface
- Partitioning to NAPL in both vadose and saturated zone
- Partitioning to soil in vadose zone



**Not to scale*

Key Point

Significant for understanding migration potential and mass flux to GW therefore critical for human health risk assessments

Effect of Prior Remediation of Co-Contaminants on PFAS Transport

- Permanganate and peroxide oxidizers increase mobility due to liberation of organic matter
- Persulfate reduces mobility due to lowered pH and increased iron
- Amending with emulsified oil may have increased retention

How Characterizing PFAS Sites is Different from other Contaminated Sites

- State of knowledge is changing rapidly
- Analytical methods including reporting limits and parameter lists continue to evolve
- Cross contamination during sampling is still a concern
- Regulatory environment keeps changing
- Fate and transport cannot be fully evaluated due to the lack standardized and validated leaching method to derive a soil to groundwater protection values

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Analytical Method Selection – Drinking water

EPA Method 537.1

- Drinking water only
- Recently updated to include 4 PFOA and PFOS replacements for a total method analyte list of 18 PFAS
- Modifications to this method are not permitted, therefore lab must be accredited for EPA 537.1
- DoD ELAP labs accredited for EPA 537.1 can be found at http://www.denix.osd.mil/edqw/home/ by identifying the method searched as EPA 537.1
- Verify analyte list that lab is accredited for through review of lab's DoD ELAP Scope of Accreditation Certificate on the Accreditation Body's Website

Analytical Method Selection – All Other Media

DoD currently uses laboratories accredited for:

“PFAS by LCMSMS Compliant with Table B-15 of QSM 5.1 or Latest Version” Method:

- In-house lab methods, not an EPA method
- Larger method analyte list than EPA 537, typically includes some PFAS found at high levels in DoD groundwater quantity (e.g., 6:2 FTS) at FTAs; currently up to 24 compounds
- Must meet all requirements found in DoD QSM Version 5.1 or later (current version, 5.2) Table B-15

What About “the Other” PFASs?

- Some PFAS found at concentrations greater than PFOS/PFOA in DoD groundwater at FTA(which can be in ppm range) are not included in EPA Method 537.1
- DoD ELAP labs have been accredited to Table B-15 for many of these PFAS (e.g., 6:2 Fluorotelomer Sulfonate)
- Well over 300 PFAS have been identified in AFFF formulations & groundwater using other instrumentation such as QTOF
- QTOF is used to identify other PFAS but lack of standards, therefore results for many PFAS are not quantitative
- DoD ELAP does not accredit QTOF analysis for PFAS due to its qualitative nature

QTOF = quadrupole time of flight mass spectrometry

Other PFASs Beyond Method 537 Analytes – WHY?

- Additional toxicity data or regulatory values become available
- States may 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

Method Development Efforts

EPA OW Method

- Drinking Water
- 25 compounds, with a focus on short chain PFAS

EPA SW-846 Method 8327

- Non-potable water
- 24 compounds
- Not compatible with DoD QSM 5.1 or later Table B-15

EPA SW-846 Method 8328

- Non-potable water and Soil and Sediment
- Includes 25 compounds
- Compatible with DoD QSM 5.1 or later Table B-15

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Introduction to NAS Jacksonville Case Study

NAS Jacksonville

- ESTCP project & NAVFAC HQ funded investigation
- Detailed evaluation of fate and transport of PFAS
- Additional analysis conducted beyond Navy guidance

Jacksonville Case Study

- Use high-resolution sampling and advanced analytical techniques to identify PFAS source areas and differentiate sources
- Determine site-specific factors that affect PFAS transport, for example:
  - Organic carbon (carbon chain length/hydrophobicity)
  - pH
  - Ionic strength
  - Redox, dissolved oxygen
  - Field conditions (e.g., comparison with laboratory-derived Kd’s)

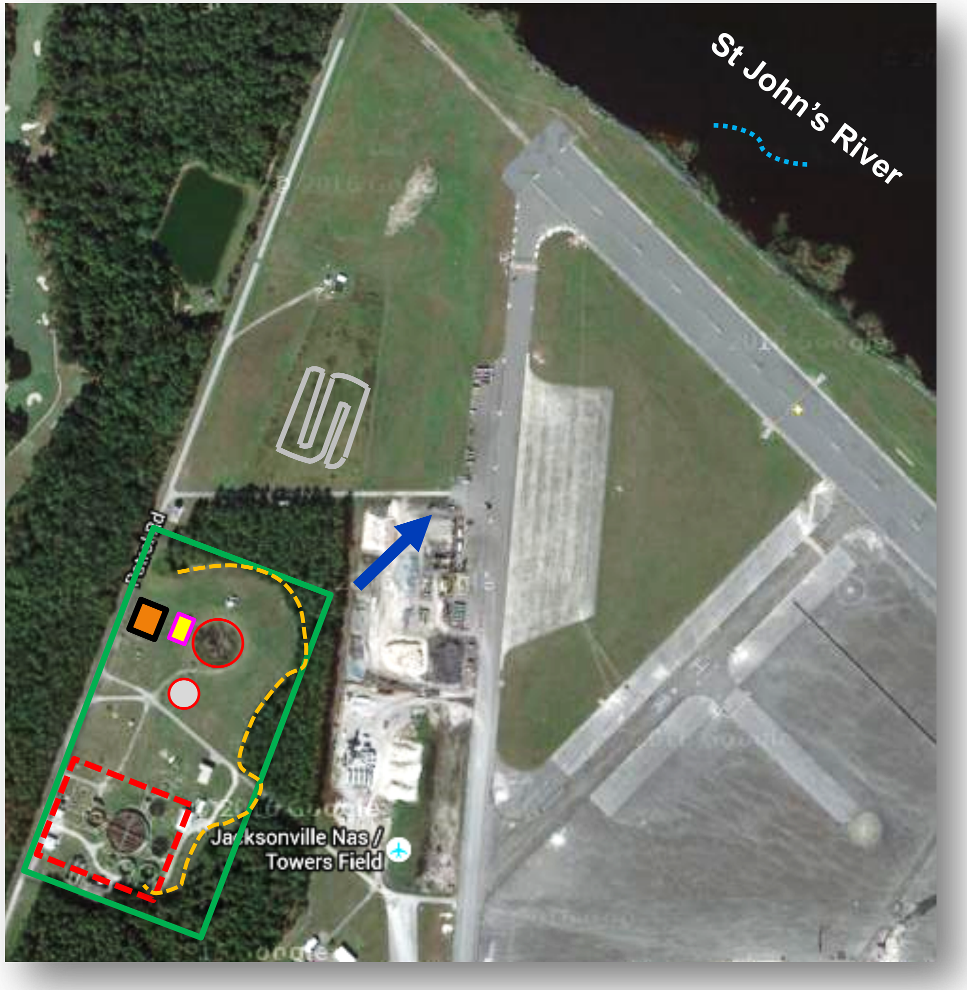
Jacksonville Case Study (cont.)

- Characterize PFAS composition in various media
  - Differential transport of PFAS
  - Mass storage in low permeability zones, sorbed species
  - Identify precursors, transformation and dead-end products
  - Estimate flux from source areas
  - PIGE, Top Assay and LC MS/MS result comparisons

PIGE = Particle Induced Gamma Ray Emission
LC MS/MS = Liquid Chromatography Mass Spectroscopy

Site Description: NAS Jacksonville

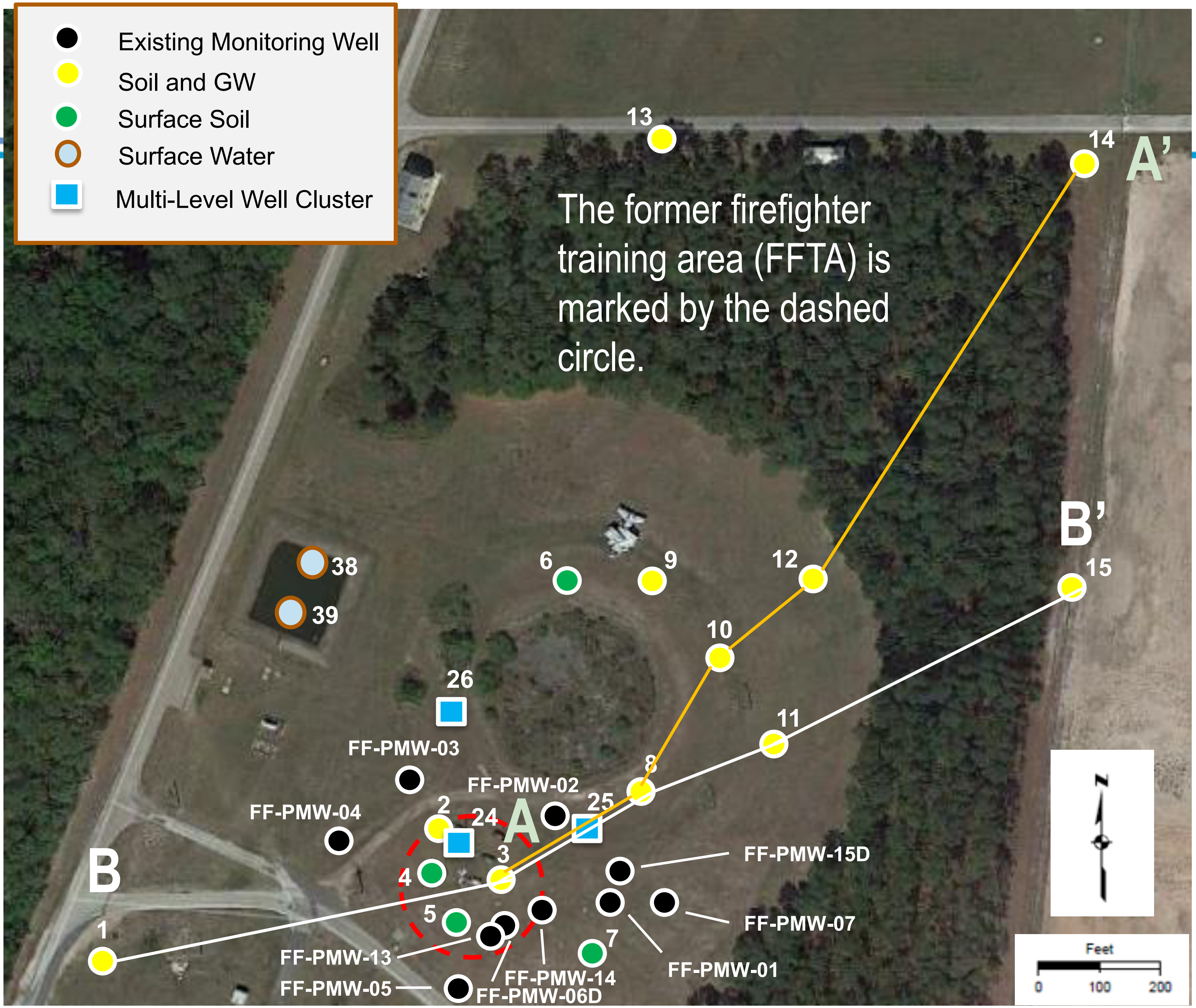
Firefighter Training Area (FT-02) General Site Characteristics



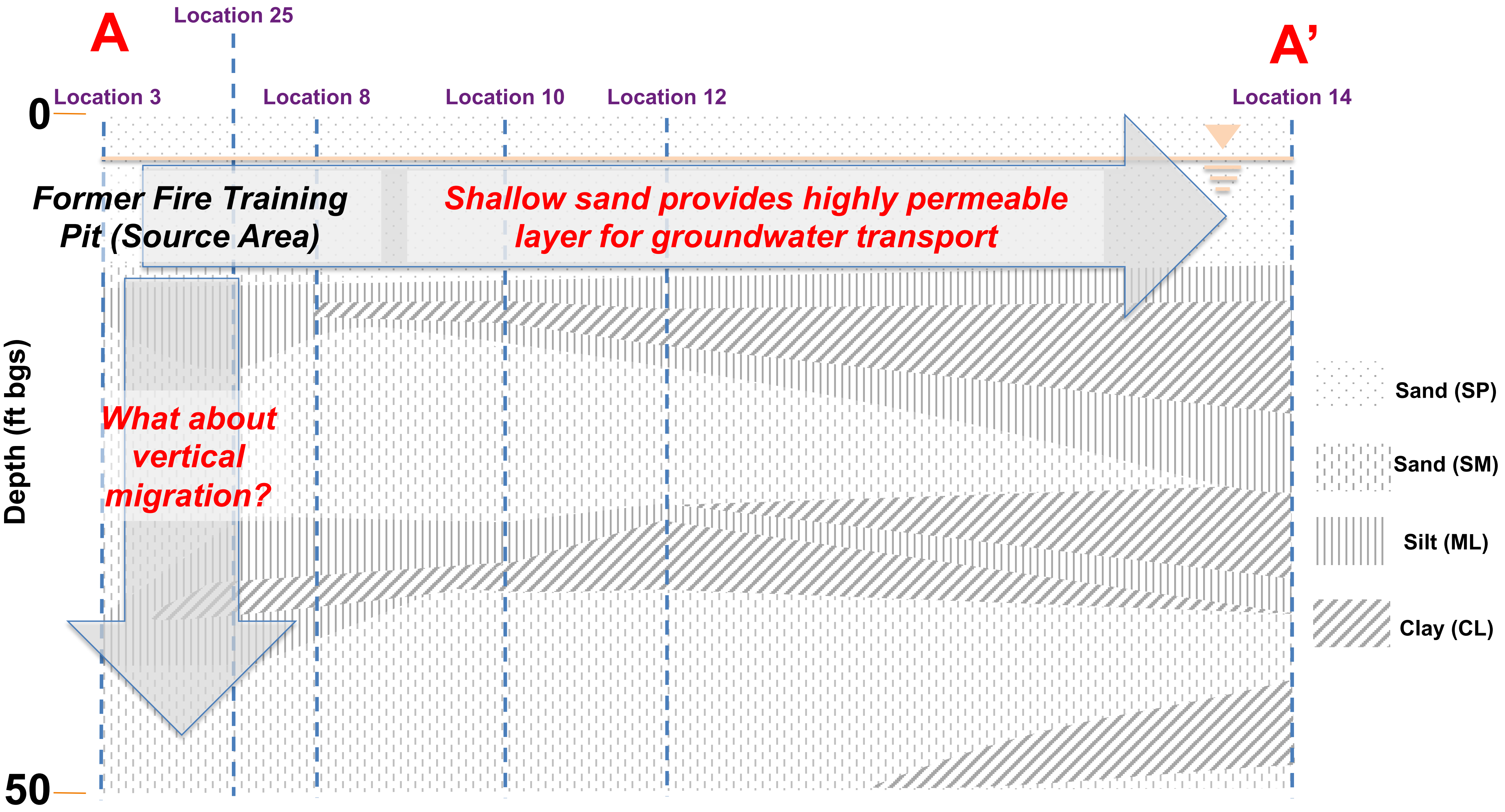
●	Former Training Area – In use 1968-91
○	Current Fire Training Area
🟧	Pond/Pump Station
⬚	Wastewater Treatment Plant
▱	Unlined Polishing Pond
▮	Oil/Water Separator
⋰	St. John's River
⋯	Tree Line
↗	Groundwater Flow: Primarily N/NE

Jacksonville Site Map

- 3 Sampling Rounds
  - Sep 2017: Primary
  - Jul 2018: Vertical gradient, Background, ELAP Lab comparison (3 multi-level well clusters 4 depths each, MW sampling, soil sampling)
  - Oct 2018: Background



The former firefighter training area (FFTA) is marked by the dashed circle.



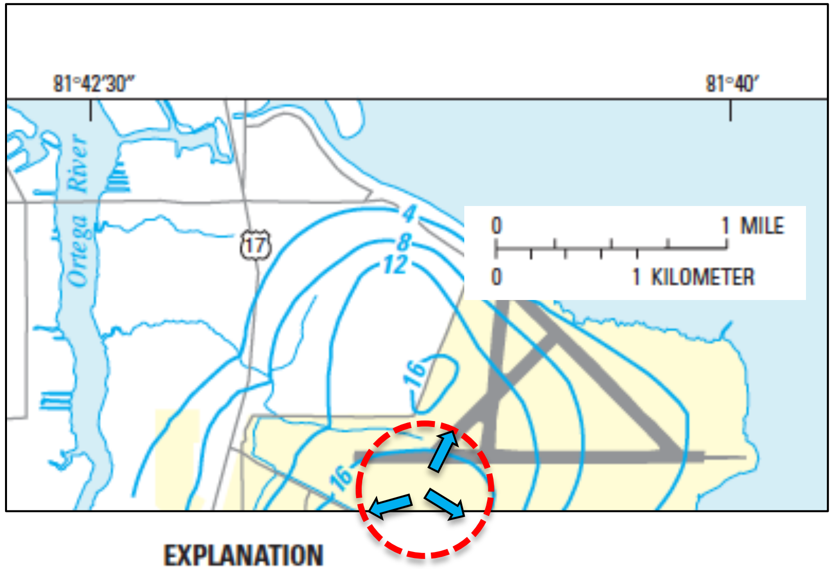
Former Fire Training Pit (Source Area)

Shallow sand provides highly permeable layer for groundwater transport

What about vertical migration?

Relevant Hydrogeologic Characteristics (cont.)

Fire Training Area is in a high regional recharge area that results in radial flow with potential for downward groundwater gradients



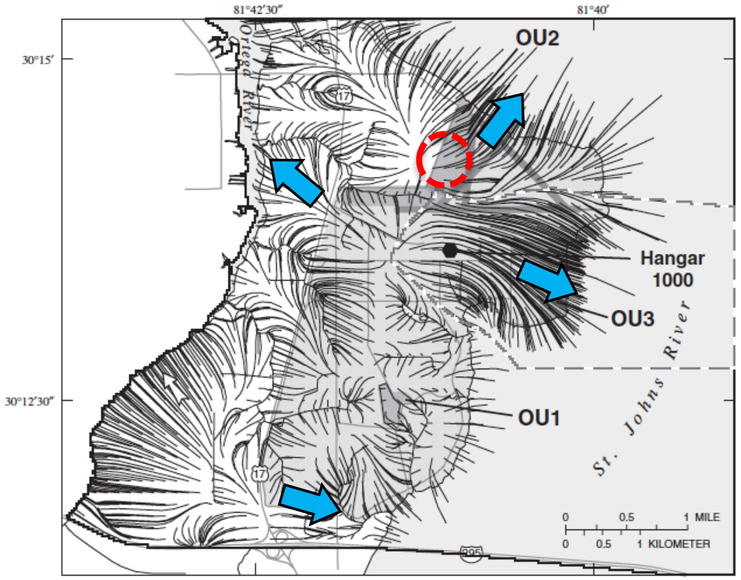
EXPLANATION

—20— LINE OF EQUAL ELEVATION OF THE WATER TABLE—In feet above NGVD 1929. Contour interval 4 feet.

🟨 JACKSONVILLE NAVAL AIR STATION

▨ OPERABLE UNIT 1

Regional Flow Arrows Interpreted by GSI



EXPLANATION

▭ NAVAL AIR STATION, JACKSONVILLE

▨ OPERABLE UNITS

—— CREEKS AND DITCHES

—— PARTICLE PATHLINES–Shows simulated ground-water flow paths

– – SUBREGIONAL STUDY AREA AND SUBREGIONAL MODEL BOUNDARY

⬅ GROUND-WATER FLOW ARROW–Shows direction of ground-water flow along pathlines

—— REGIONAL STUDY AREA AND REGIONAL MODEL BOUNDARY

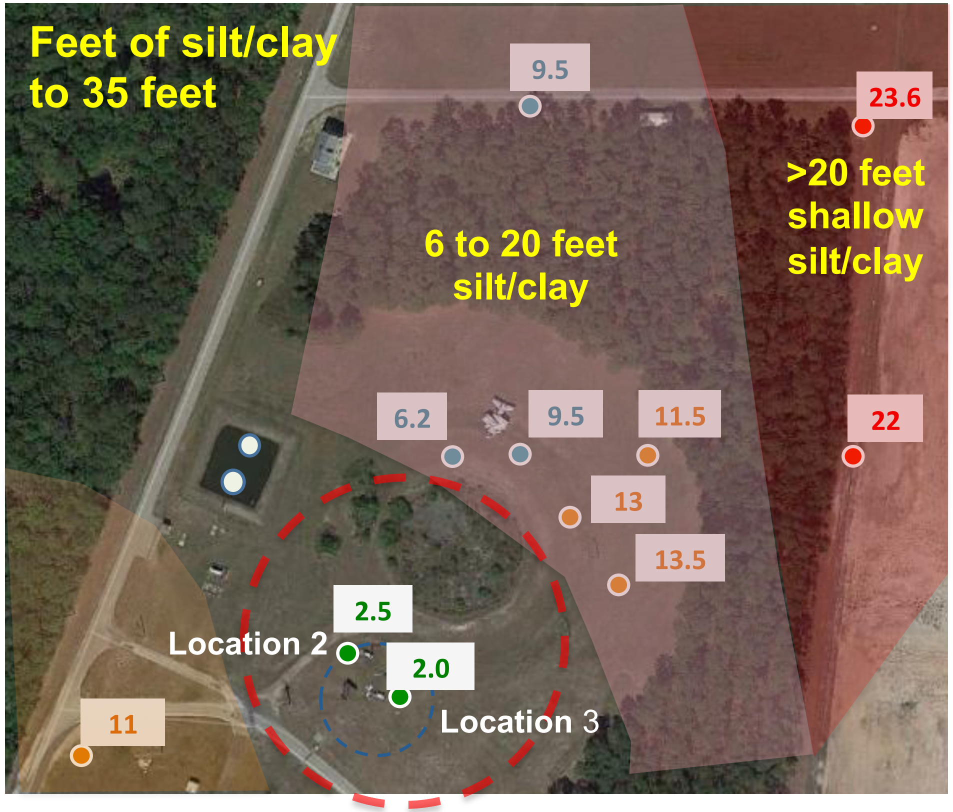
This USGS potentiometric surface map shows groundwater mound near FT-02, indicating a high recharge area

USGS modeling study map shows groundwater streamlines originating near FT-02, indicating a high recharge area

Relevant Hydrogeologic Characteristics (cont.)

Evidence for Vertical Migration Pathways

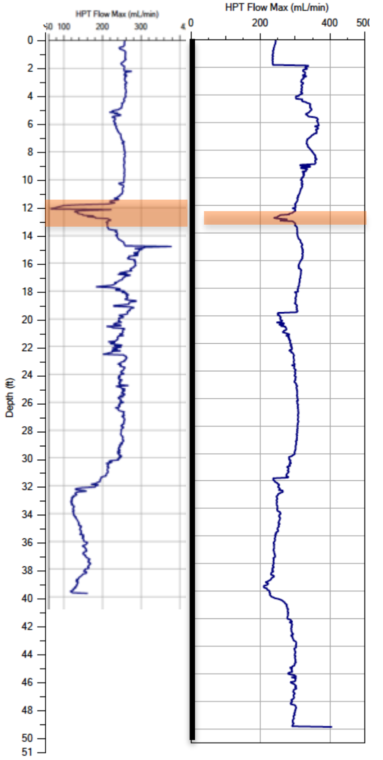
1



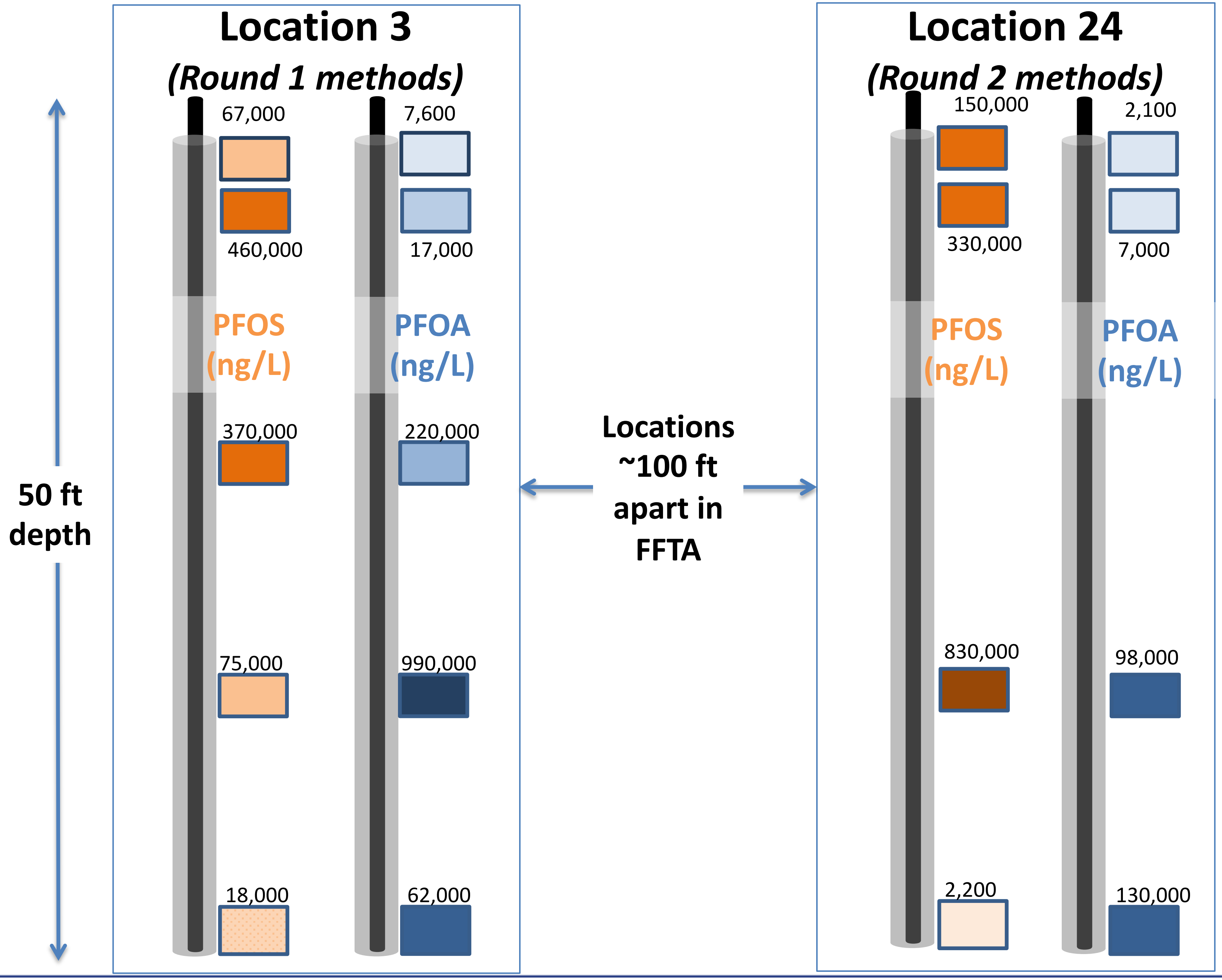
Geologic borings from this project show that areas outside of the former pit are surrounded by much more silt/clay, helping drive groundwater vertically downward through pit area.

2

LOCATION 2 (flow ml/min) **LOCATION 3** (flow ml/min)



HPT results from this project show the silt unit in pit area is very thin in places and provides little resistance to downward flow (e.g., see Location 3)



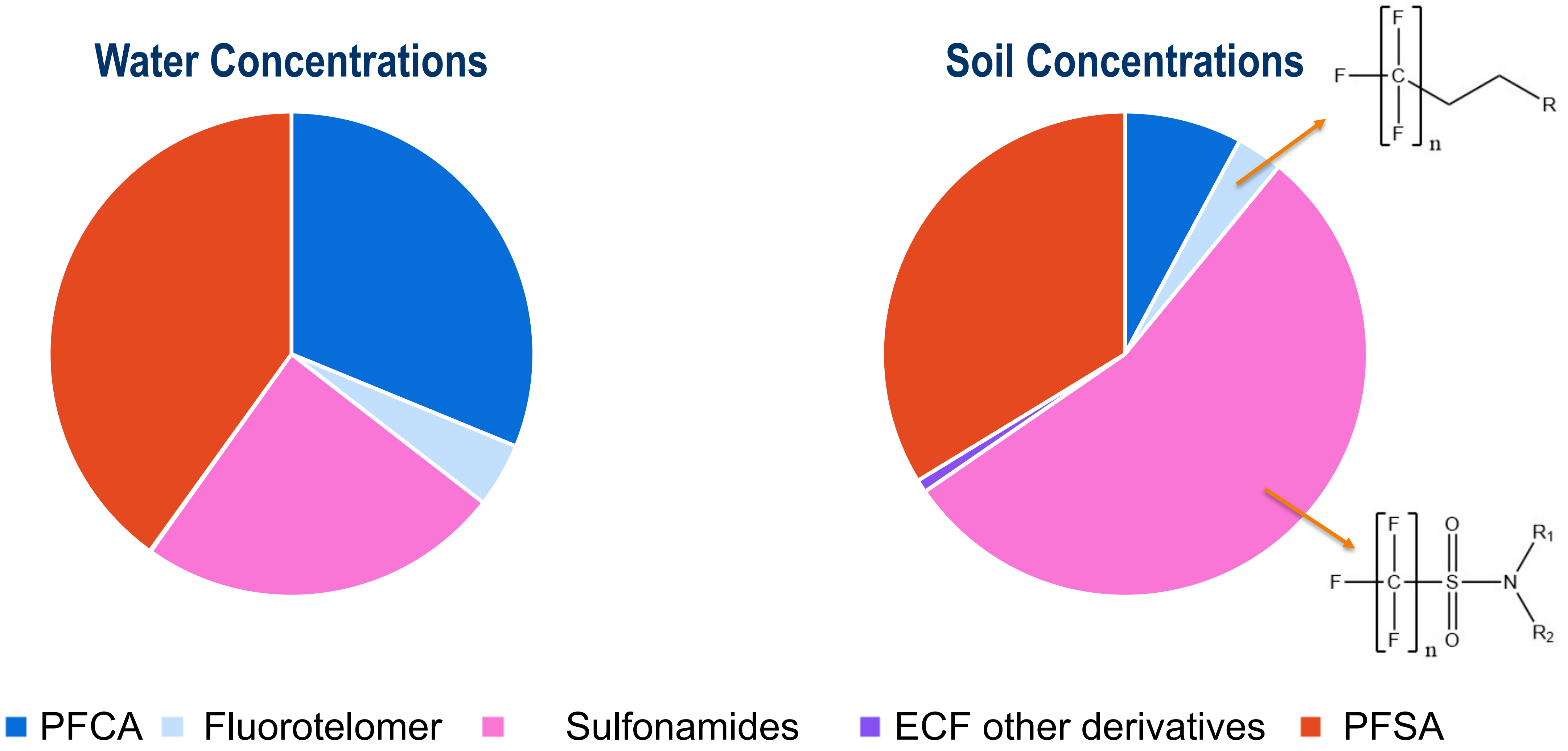
Locations ~100 ft apart in FFTA

RESULT: **Similar patterns of increasing PFAS conc. w/depth for GW grab samples *(Round 1)* and well samples *(Round 2)***

IMPLICATION:

Vertical flow helps explain elevated concentrations at depth *(not a sampling artifact)*

PFAS Concentrations Over Entire Site

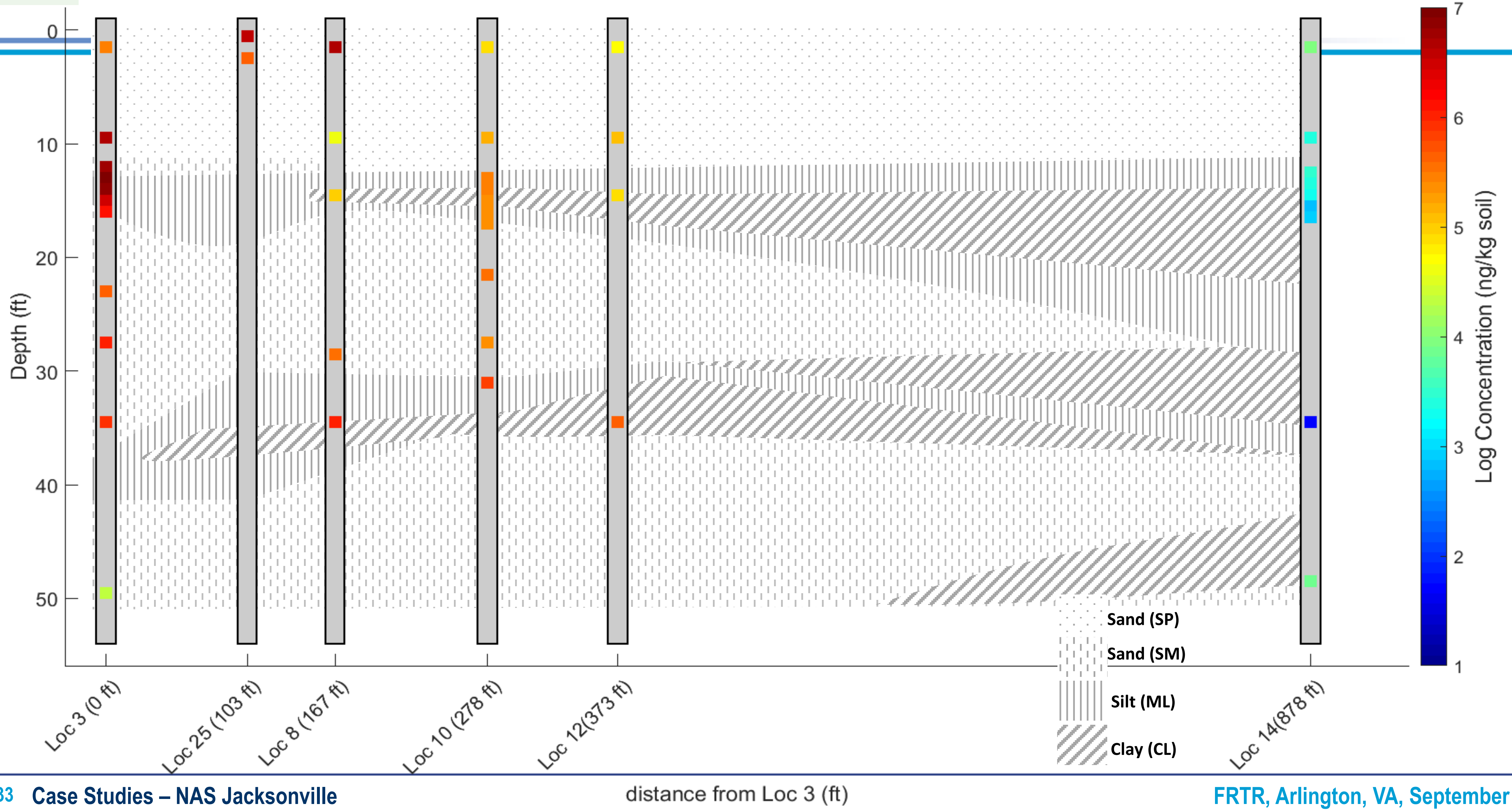


Water Concentrations

Soil Concentrations

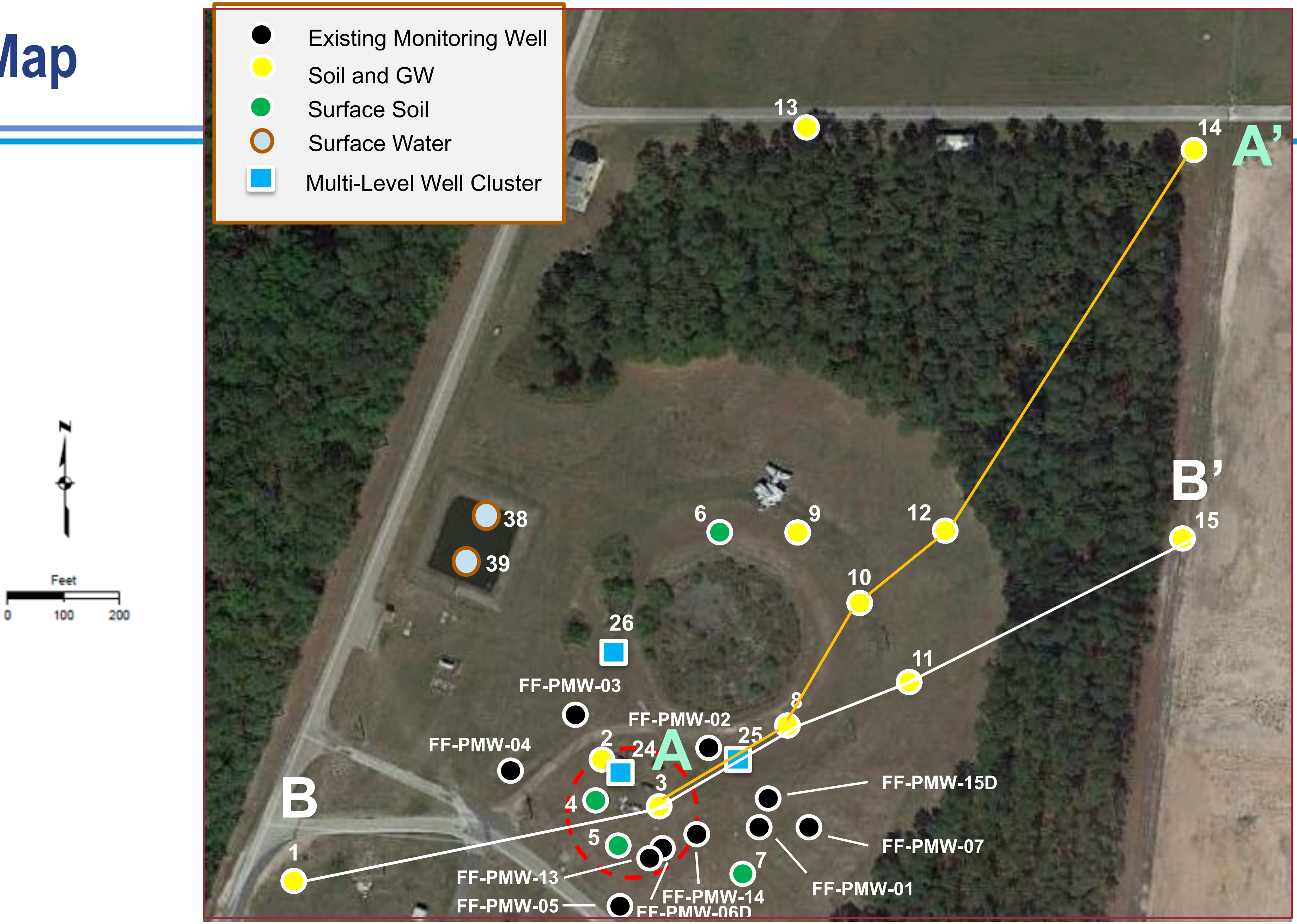
*SQ

Transect A: sum soil PFAS (ng/kg)



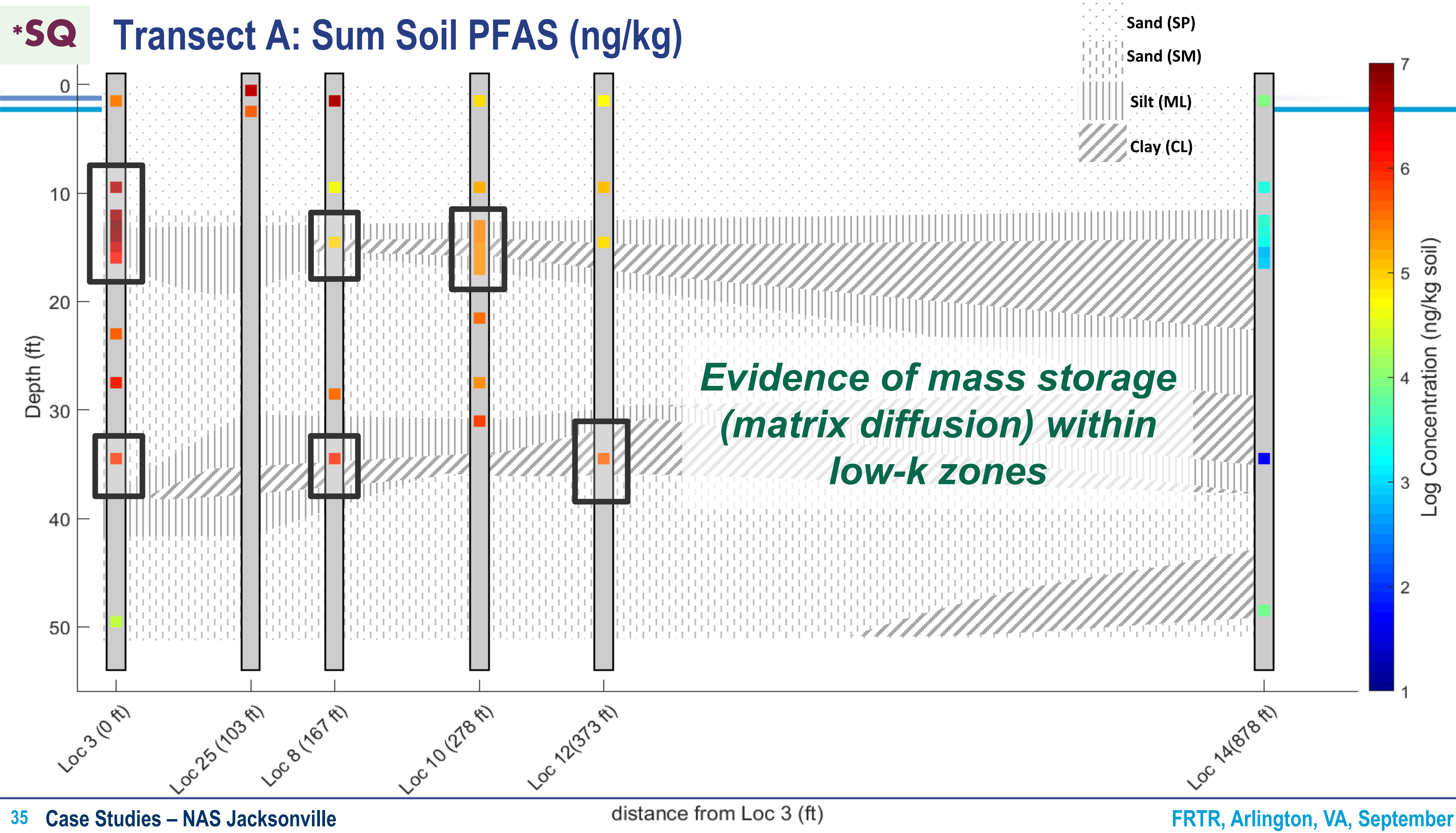
Jacksonville Site Map

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.



***SQ**

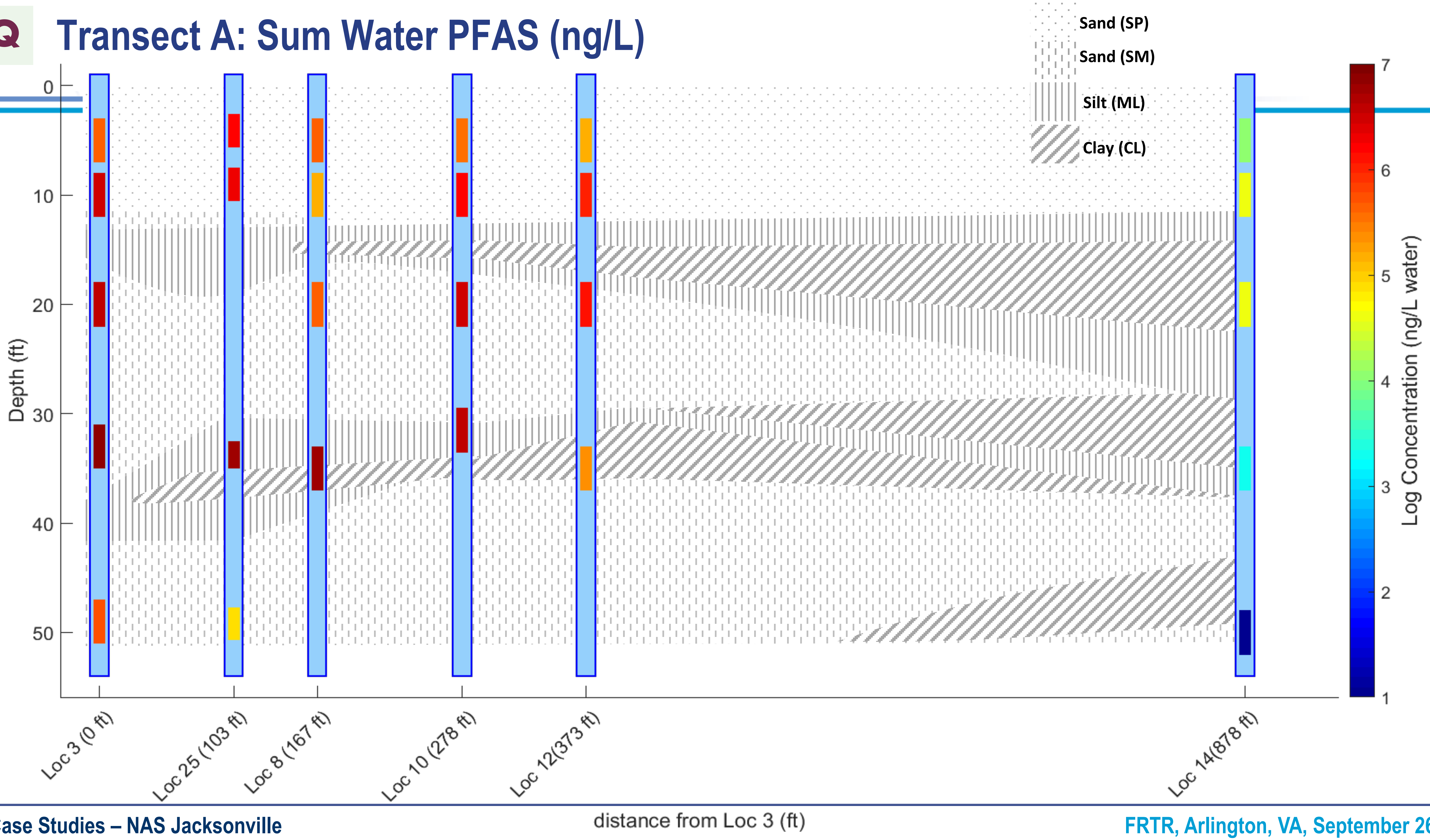
Transect A: Sum Soil PFAS (ng/kg)



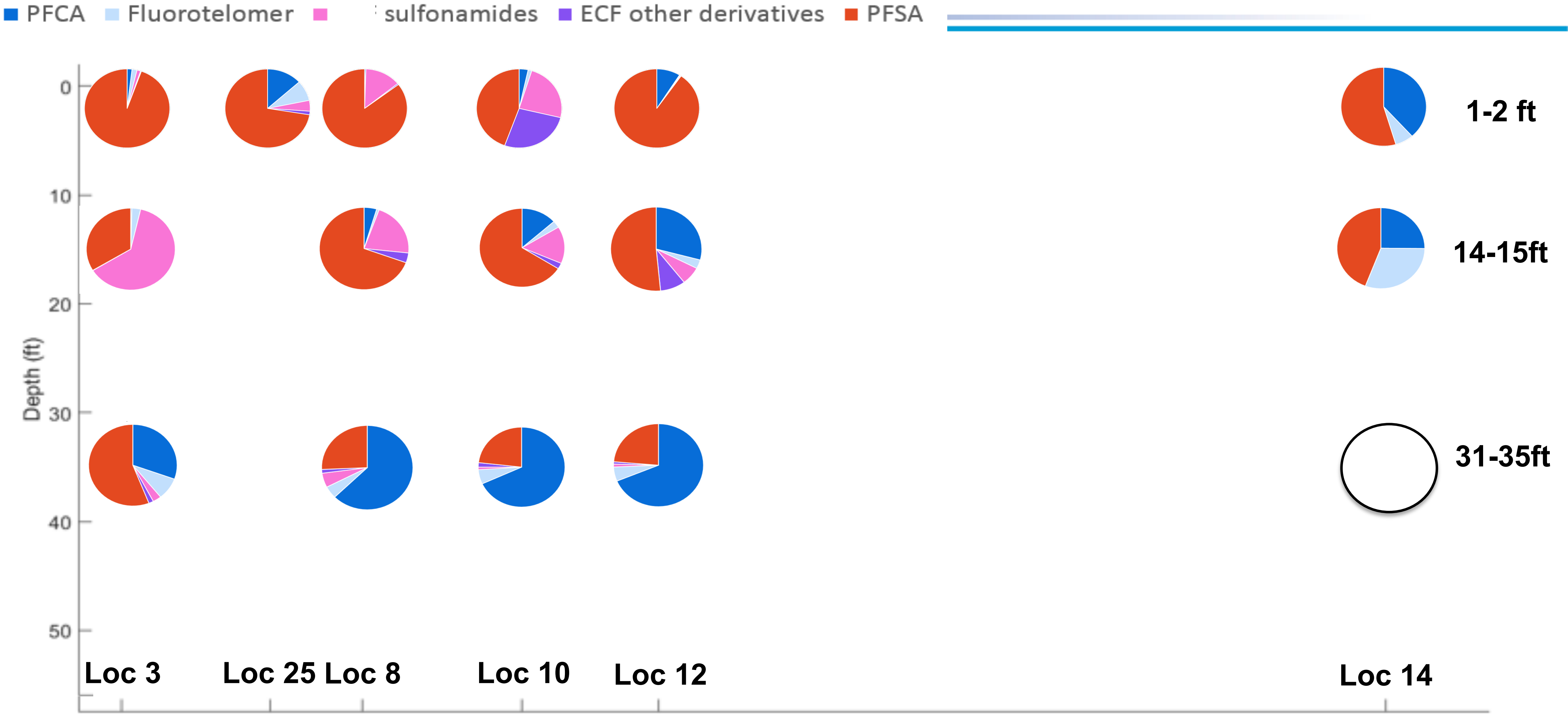
Evidence of mass storage (matrix diffusion) within low-k zones

*SQ

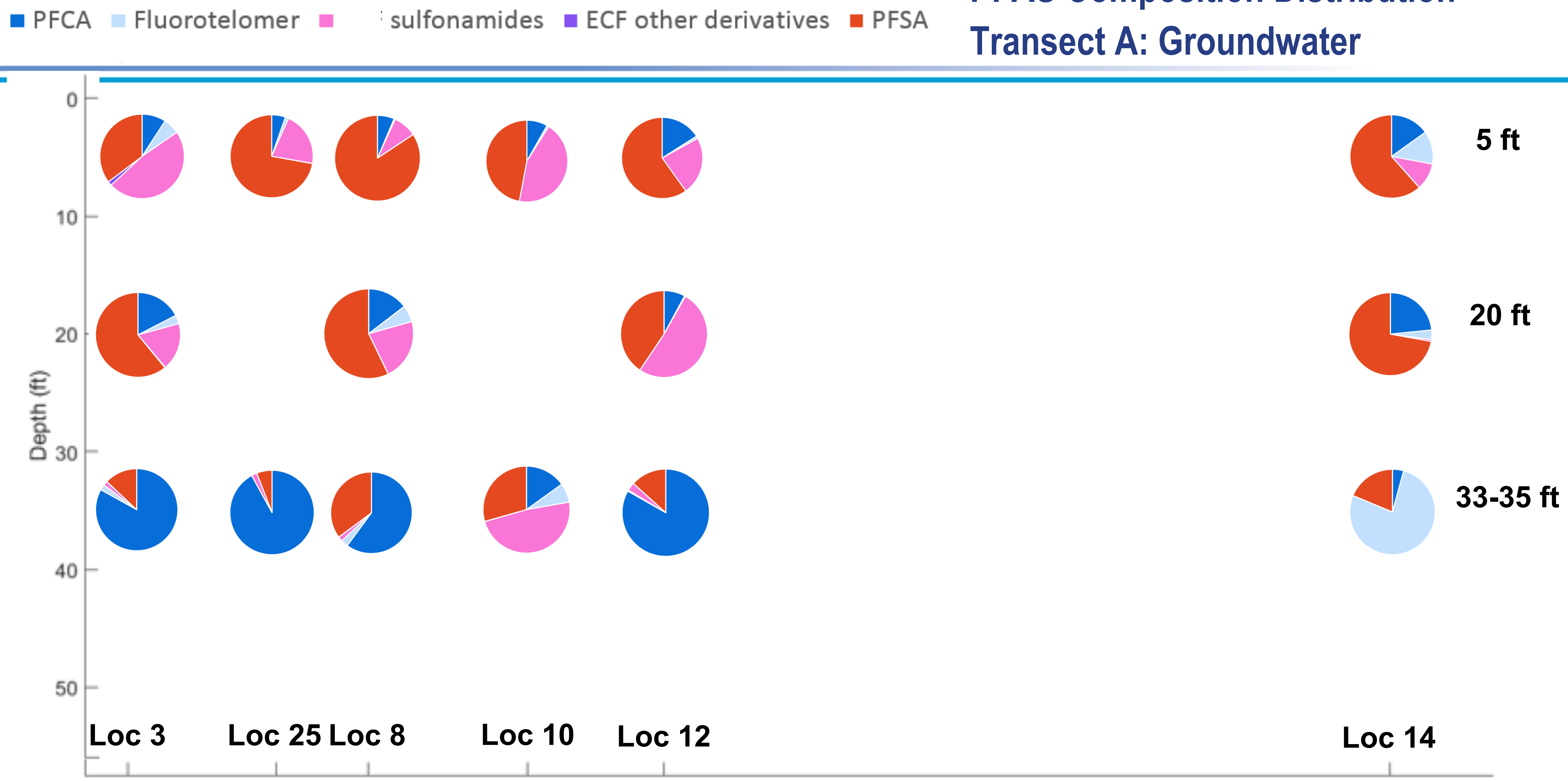
Transect A: Sum Water PFAS (ng/L)



PFAS Composition Distribution Transect A: Soil

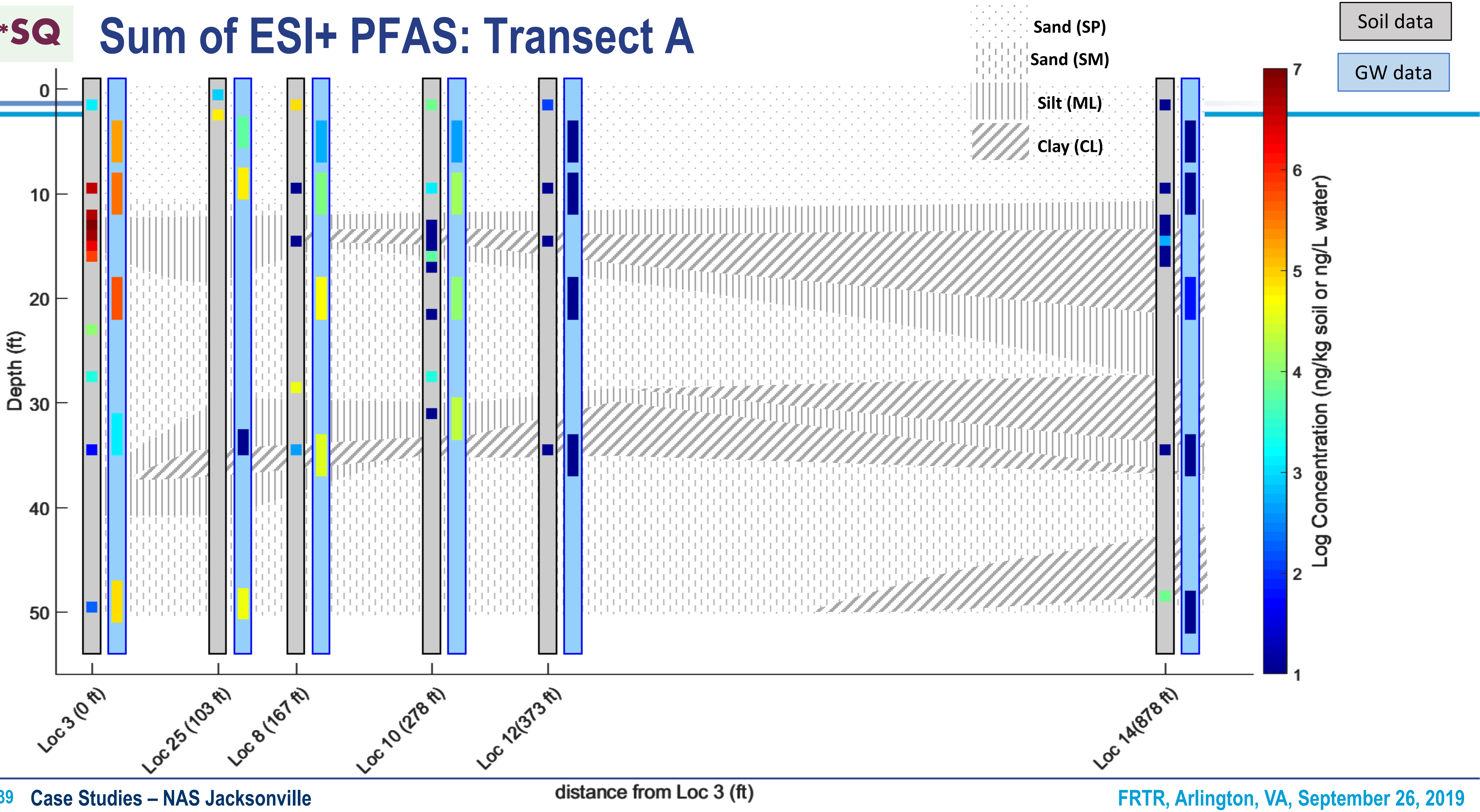


PFAS Composition Distribution
Transect A: Groundwater



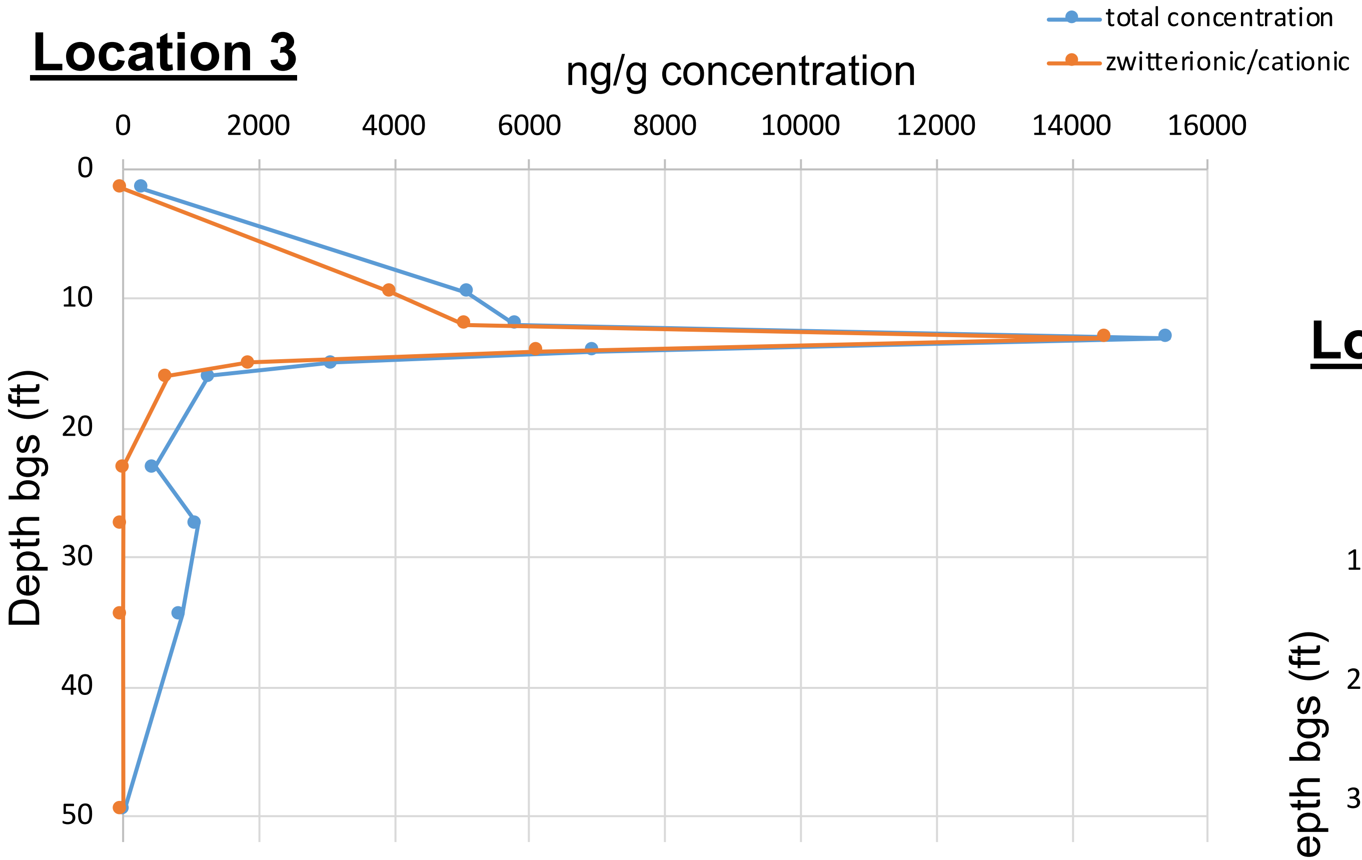
*SQ

Sum of ESI+ PFAS: Transect A

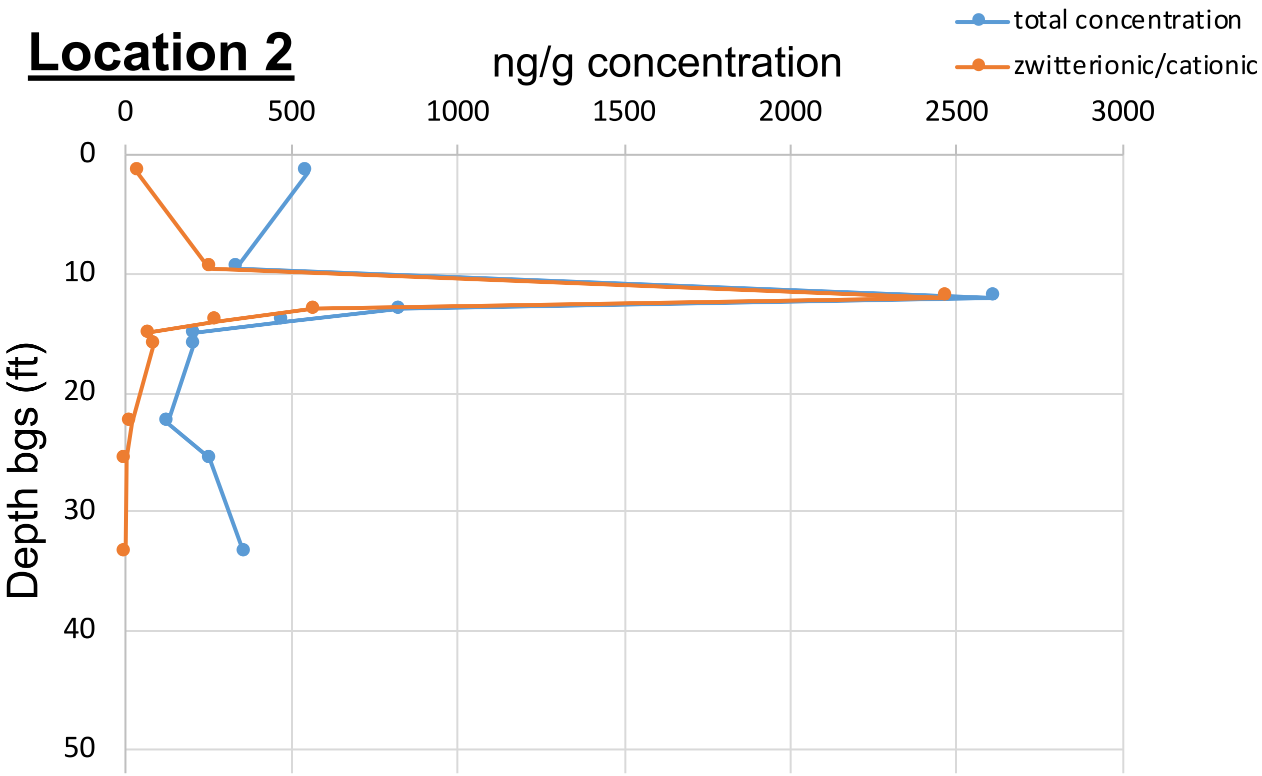


A high percentage of the soil PFAS mass at the source zone (Locations 2 & 3) is from zwitterionic and cationic compounds

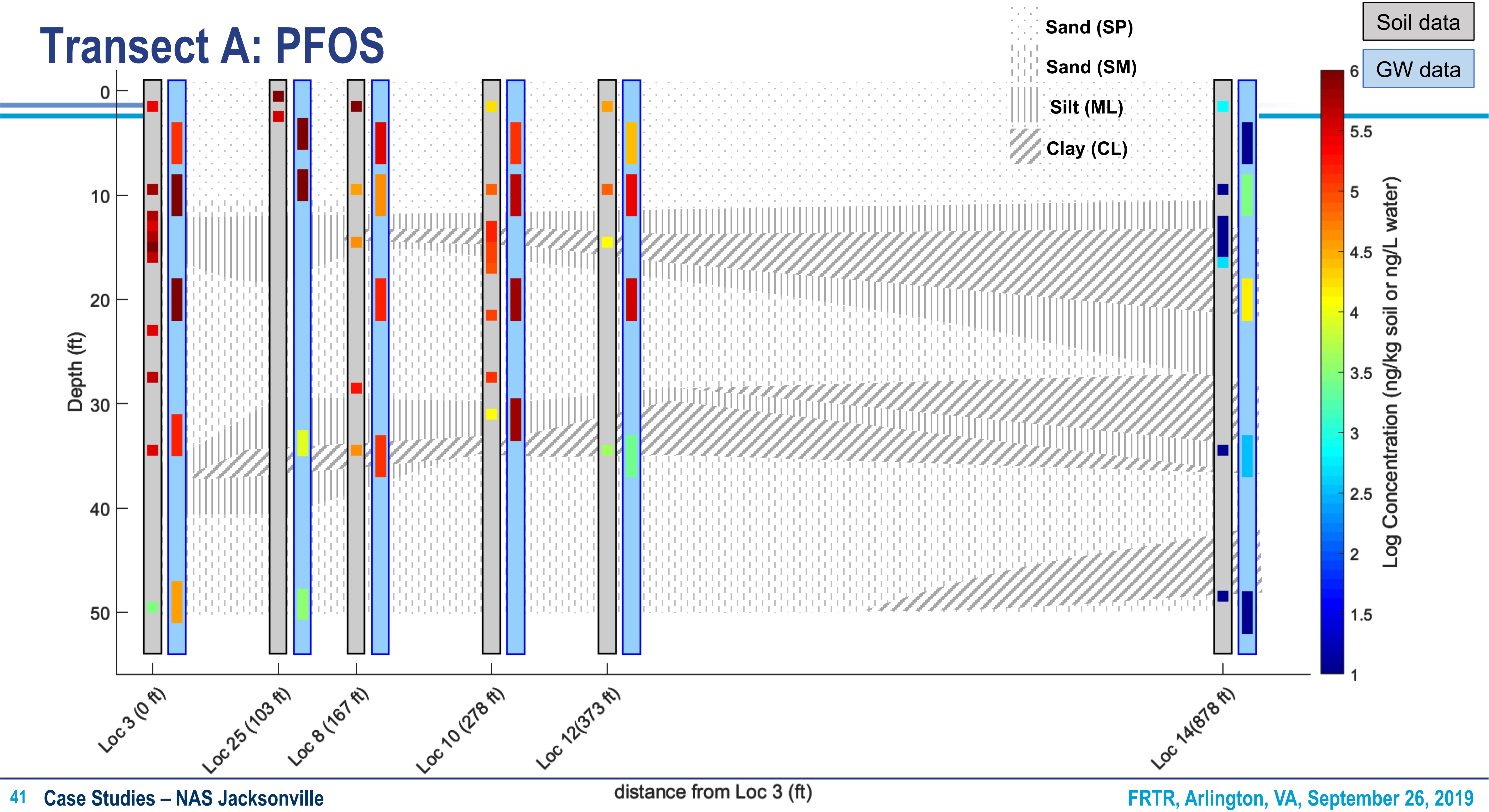
Location 3



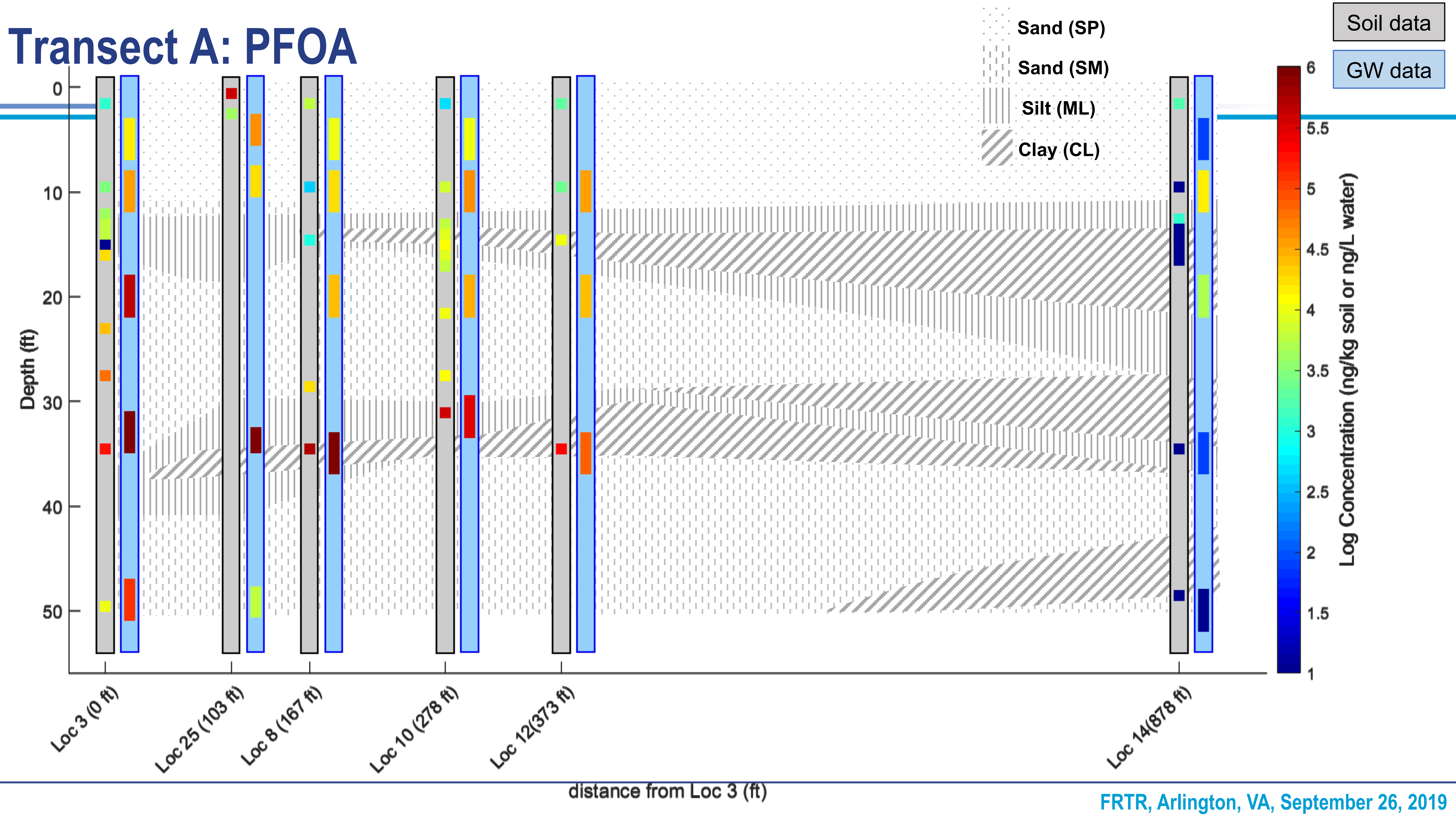
Location 2



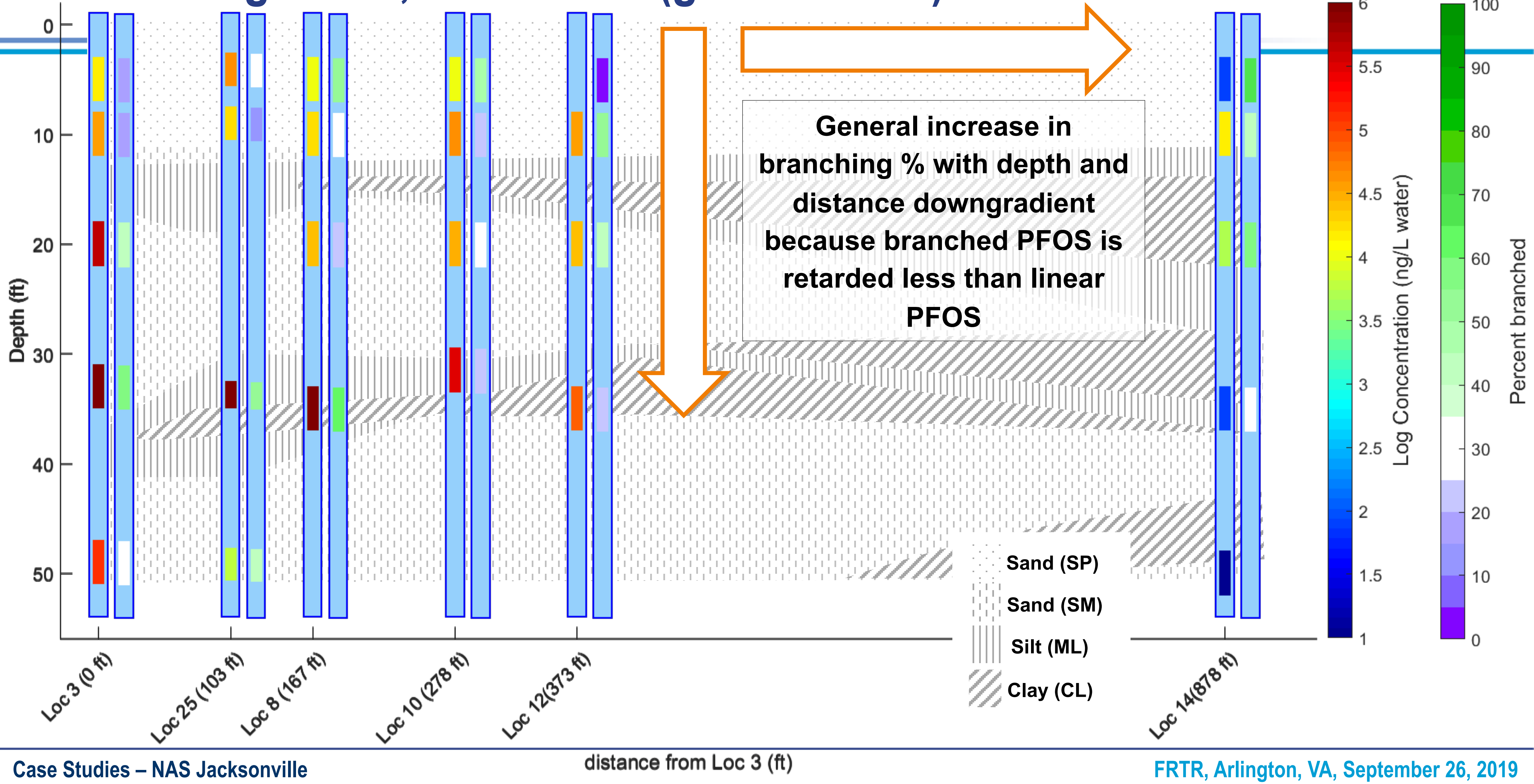
Transect A: PFOS



Transect A: PFOA

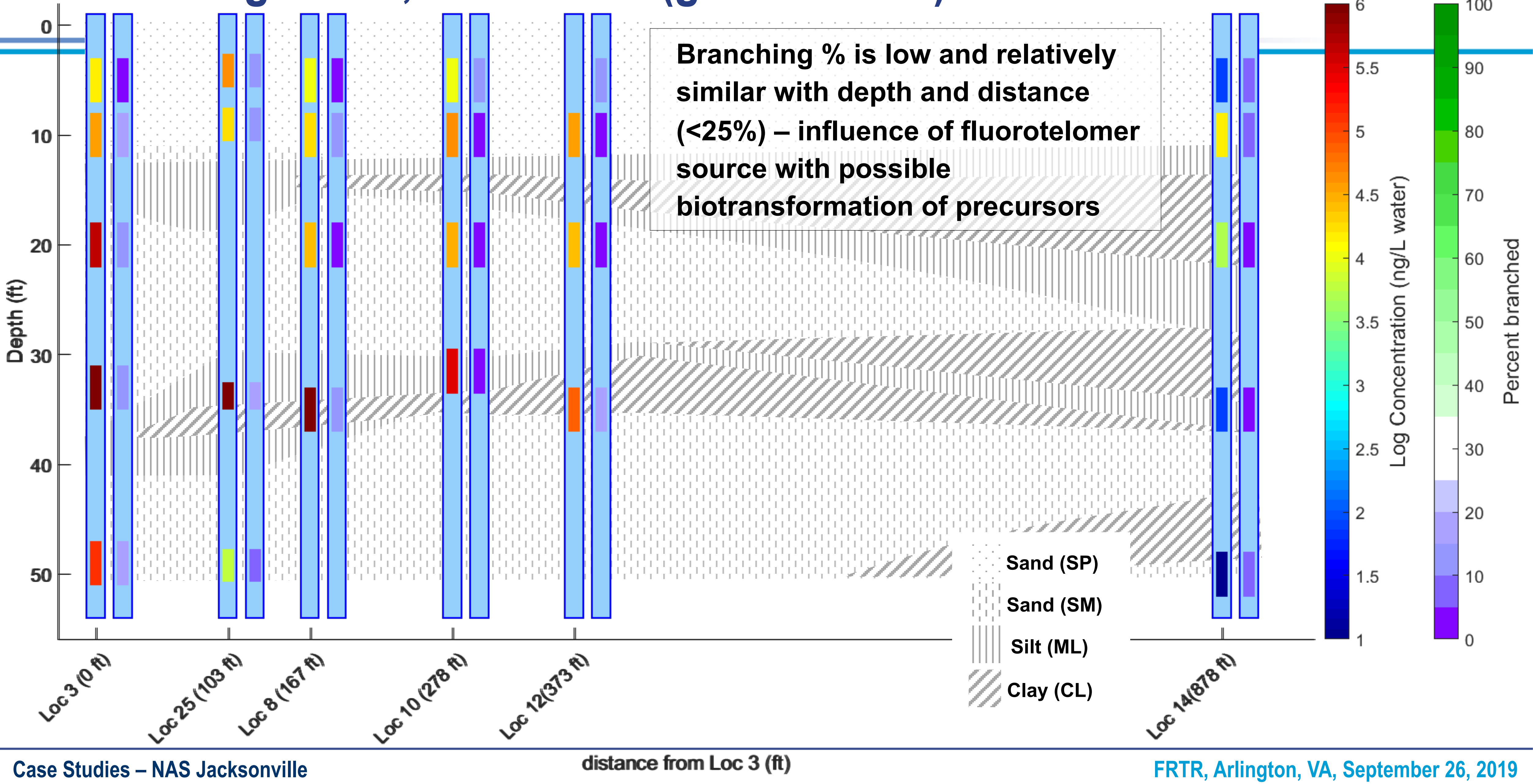


% Branching PFOS; Transect A (groundwater)



General increase in branching % with depth and distance downgradient because branched PFOS is retarded less than linear PFOS

% Branching PFOA; Transect A (groundwater)



Branching % is low and relatively similar with depth and distance (<25%) – influence of fluorotelomer source with possible biotransformation of precursors

Summary of Jacksonville Case Study

- 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
    - Soil cation/zwitterion concentrations peak between 9 and 17 ft bgs
- Linear vs branched PFOS patterns different from PFOA patterns
  - PFOA may be formed from transformation of fluorotelomer precursors
  - Differential transport of PFOS isomers evident

Ongoing and Upcoming PFAS Research Topics at EXWC

HQ-Funded

- Sonic Treatment for PFAS in IDW water and regenerant
- Improved sorbents for PFAS in groundwater
- Retardation of PFAS plumes in groundwater
- On-site thermal treatment of PFAS in IDW soil

NESDI

- New sorbents for removing PFAS from groundwater
- Characterization of PFAS in source zones previously treated for co-contaminants
- Fate and transport of PFAS from release to receptor
- In situ PFAS stabilization using cationic polymers (polyDADMAC)

NAVFAC Points of Contact

- Jovan Popovic (NAVFAC EXWC)
  - (805) 982-6081
  - Jovan.Popovic@navy.mil

NAVFAC
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Questions and Answers