A Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Zones

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Battelle Chlorinated Conference 2022

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AGENDA / ACKNOWLEDGEMENTS

- Project Motivation and Objectives
- Site Description
- Mass Discharge/Mass Balance
- PFAS Transformation
- Modeling the Impact of Matrix Diffusion on Plume Extent
- Implications

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ESTCP ER-201633
Project Completed in 2022

Project Description

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ESTCP

Project ER-201633 *(final report will be posted soon)*

Motivation:

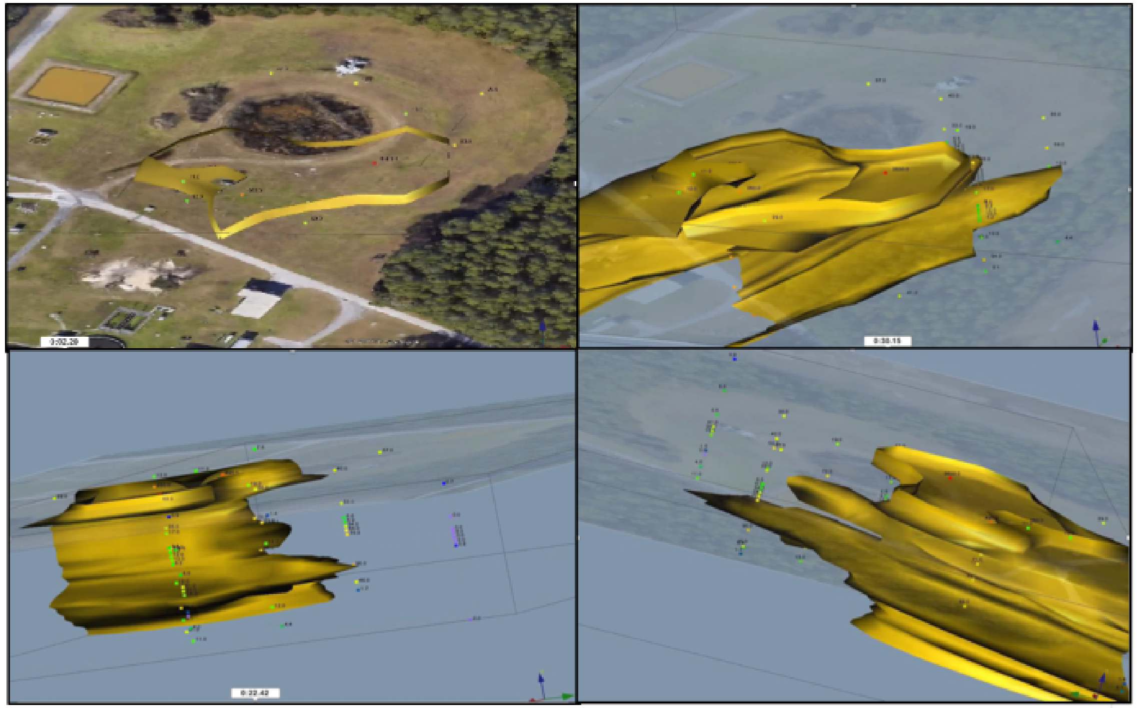
- Field-validate relevance of F&T processes that have primarily been studied at the lab scale
- Inform Conceptual Site Models for PFAS source areas

Detailed high-resolution sampling at 3 Sites:

- **Site 1:** Florida
- **Site 2:** California
- **Site 3:** Virginia

Project Objectives

- Use mass balance and modeling to improve ability to answer key questions:
    - How much PFAS mass is at the site?
    - How much of this mass has entered downgradient plume?
    - How much mass is retained in various soil types?
    - At what rate are precursors being converted to PFAAs?
- Use REMChlor-MD modeling to understand effect of matrix diffusion on plume development and remedy performance



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Environmental Science & Technology
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Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Areas

David T. Adamson,* Anastasia Nickerson, Poonam R. Kulkarni, Christopher P. Higgins, Jovan Popovic, Jennifer Field, Alix Rodowa, Charles Newell, Phil DeBlanc, and John J. Kornuc

Environmental Science & Technology
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Spatial Trends of Anionic, Zwitterionic, and Cationic PFASs at an AFFF-Impacted Site

Anastasia Nickerson, Alix E. Rodowa, David T. Adamson, Jennifer A. Field, Poonam R. Kulkarni, John J. Kornuc, and Christopher P. Higgins*

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ELSEVIER

Characterization of relevant site-specific PFAS fate and transport processes at multiple AFFF sites

David T. Adamson[a,*], Poonam R. Kulkarni[a], Anastasia Nickerson[b], Christopher P. Higgins[b], Jennifer Field[c], Trever Schwichtenberg[c], Charles Newell[a], John J. Kornuc[d]

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Journal of Contaminant Hydrology
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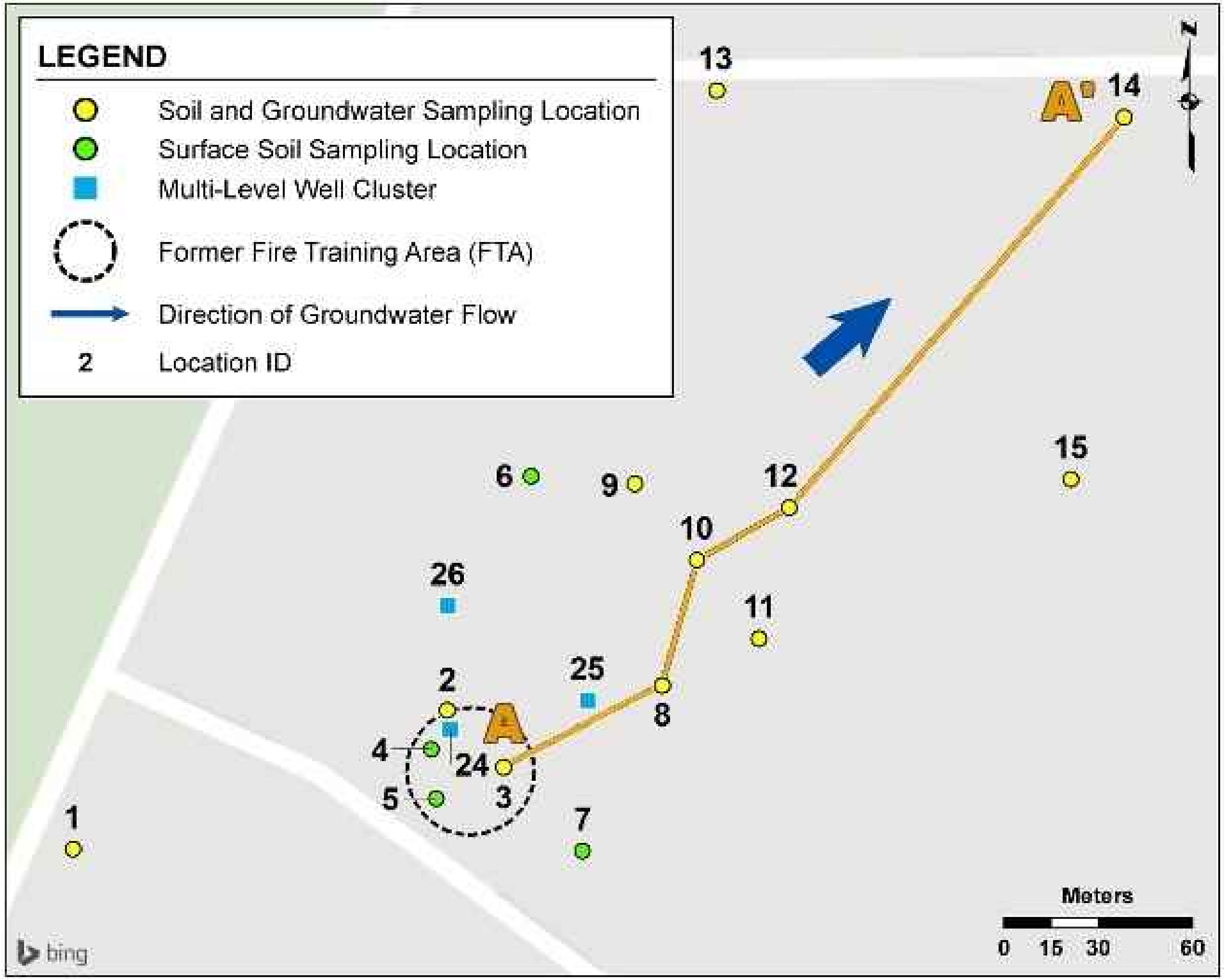
Modeling a well-characterized perfluorooctane sulfonate (PFOS) source and plume using the REMChlor-MD model to account for matrix diffusion

Poonam R. Kulkarni[a], David T. Adamson[a], Jovan Popovic[b], Charles J. Newell[a]

Overview of Sampling and Analysis Program



- Former Fire Training Area (1968-1991)
- Previously remediated under state petroleum program
  - Excavation of shallow soils, low-temp thermal desorption of excavated soils, then refill of excavation
- Shallow water table (~ 5 ft bgs)
- Sandy soils with distinct lower-permeability lenses within 15 ft

Overview of Sampling and Analysis Program

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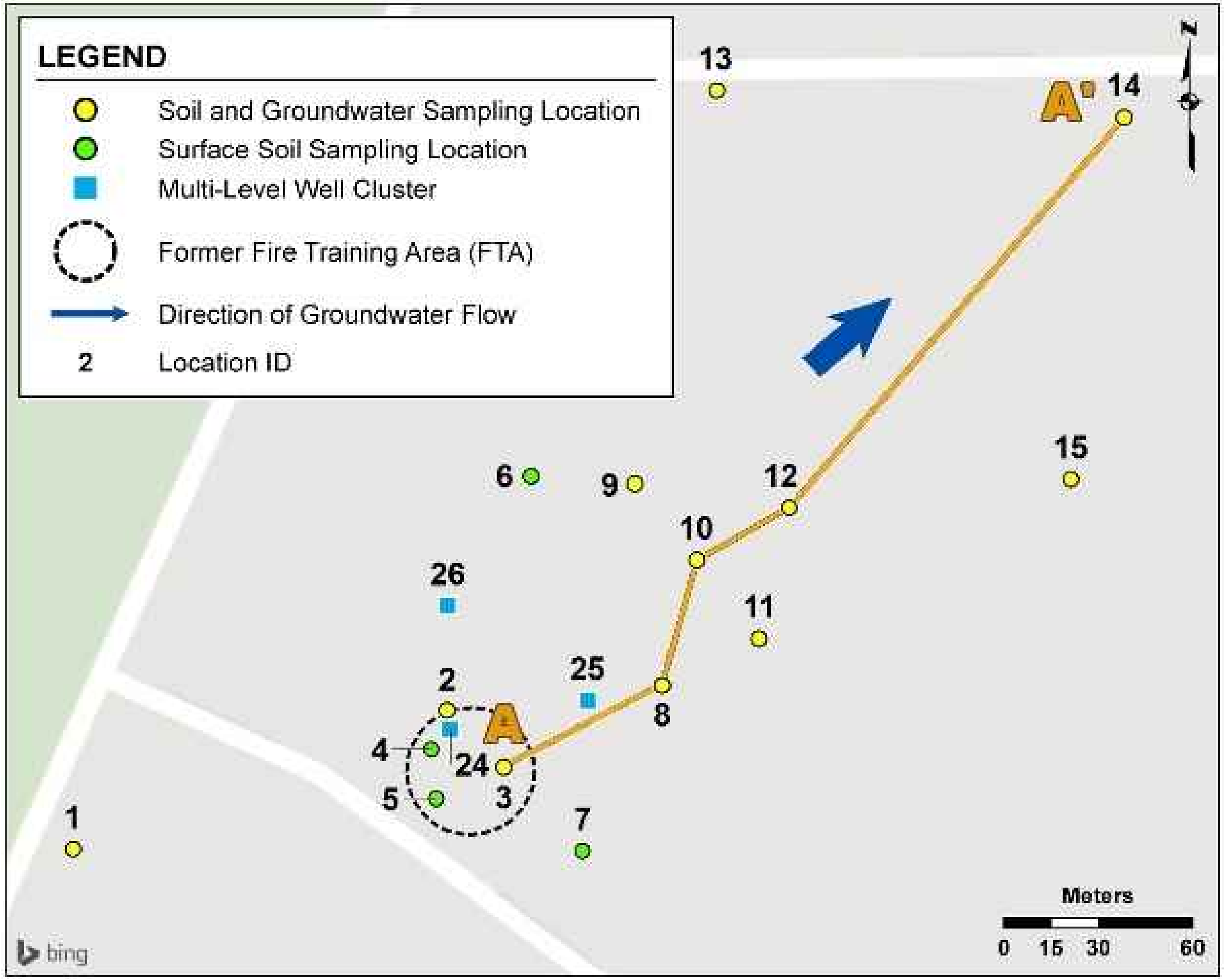

- Multiple groundwater and soil samples from each location to show vertical distribution
  - Total GW = 58 samples
  - Total Soil = 105 samples
- High-resolution mass spectrometry w/ QToF
  - Quantifies and/or semi-quantifies hundreds of individual PFAS
- Stratigraphic data:
  - HPT logging at multiple locations

Overview of PFAS Distribution

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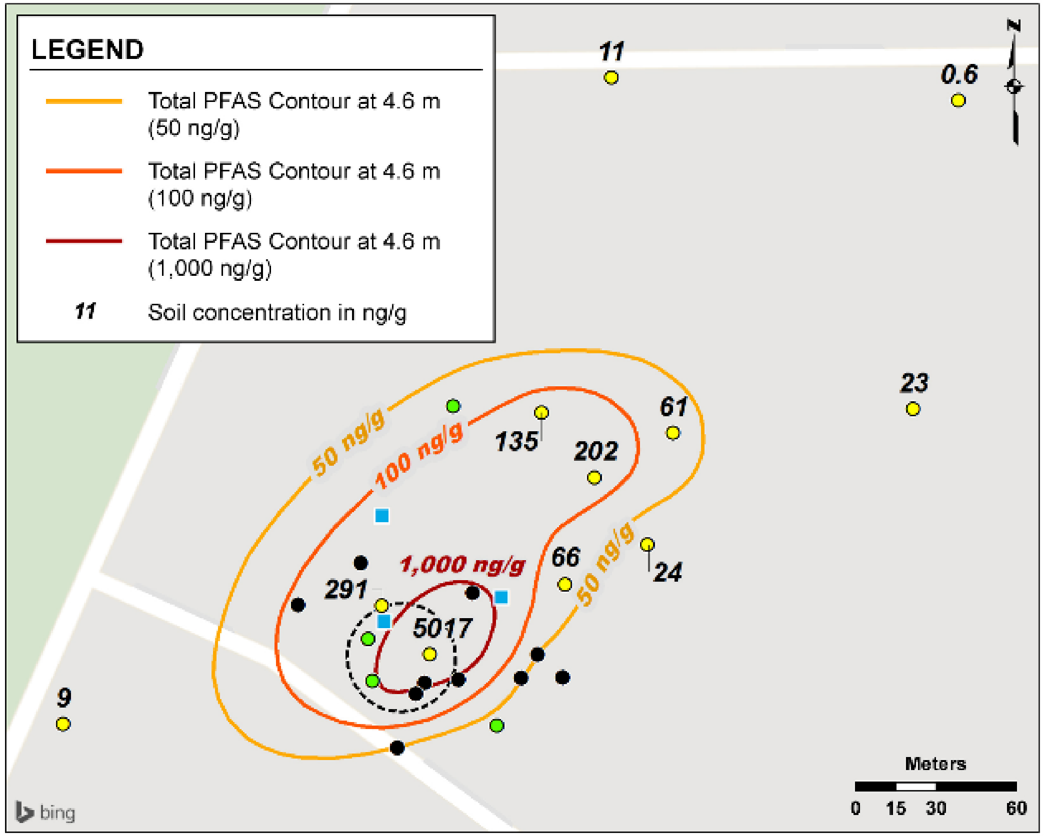
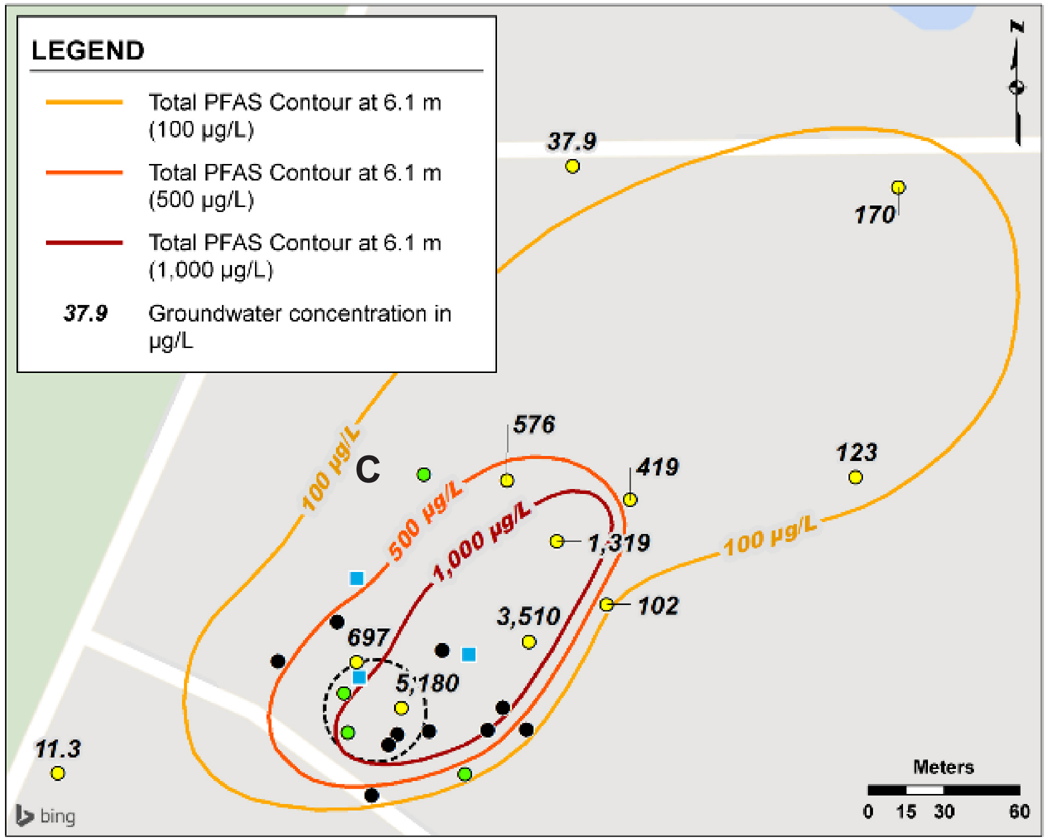
SOIL



Source: Nickerson et al., 2020, *ES&T*

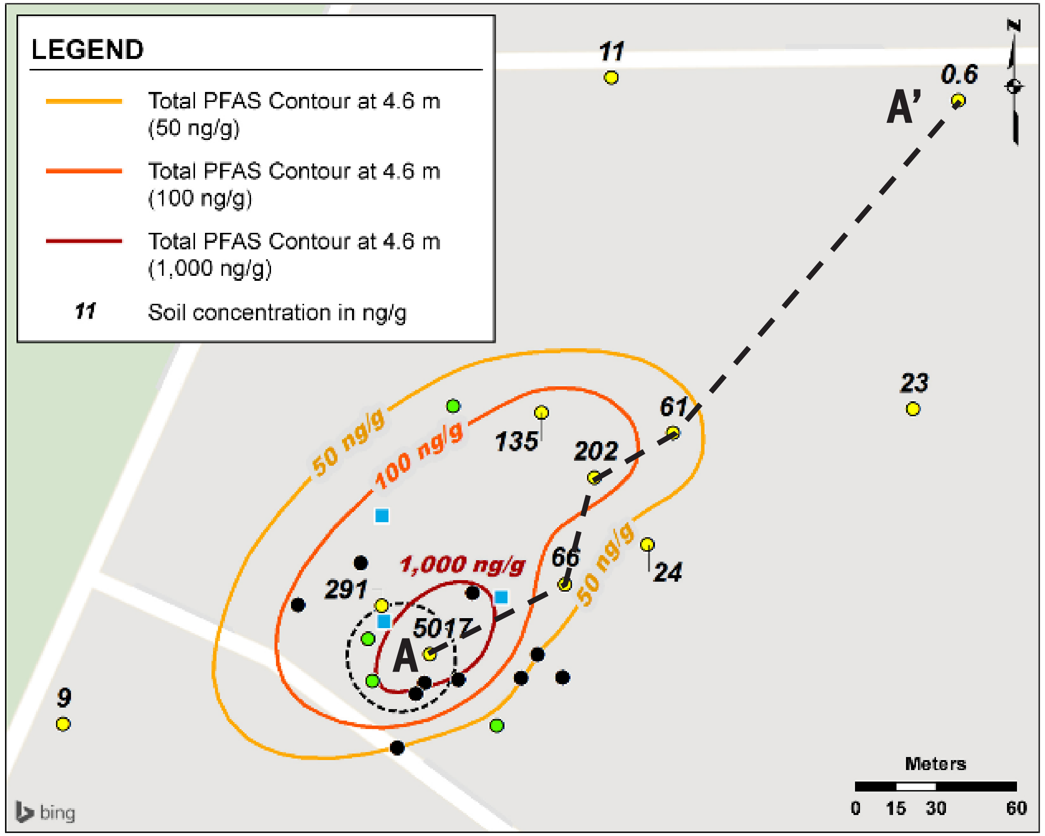
GROUNDWATER

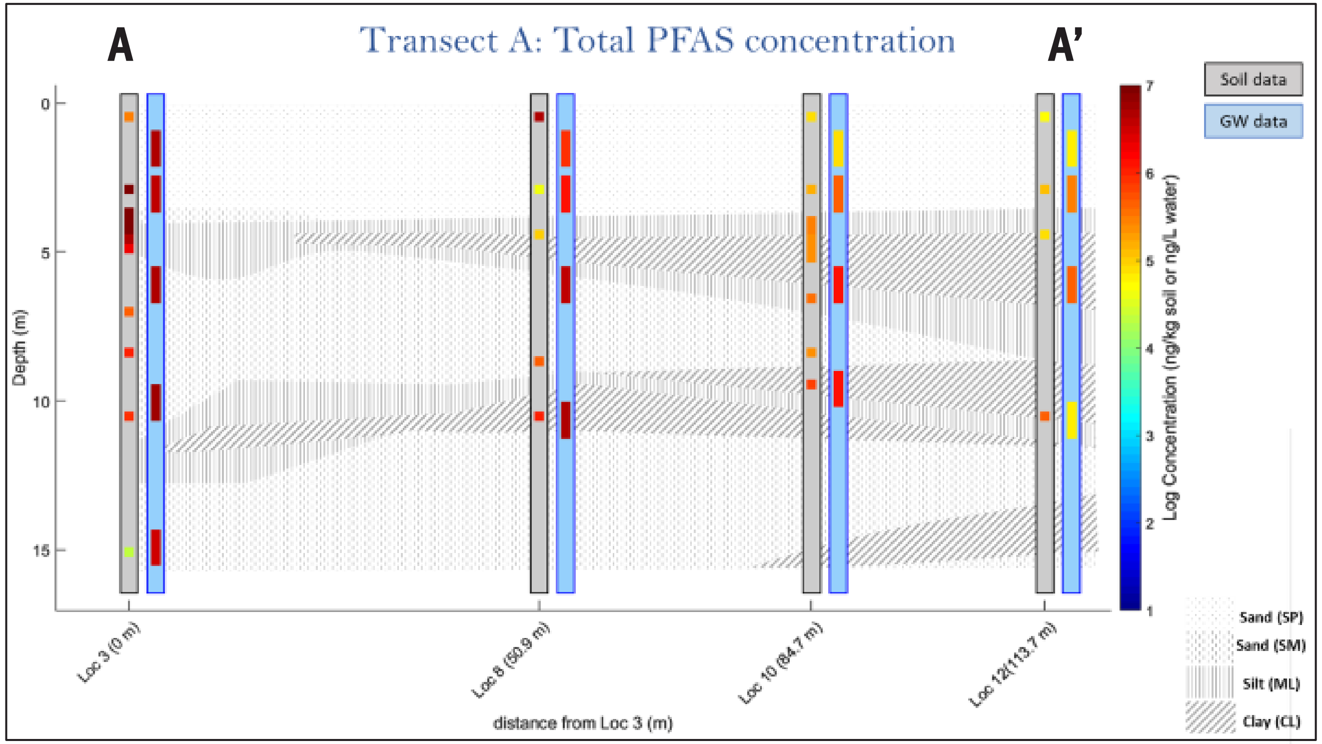


Contour is approximate, and some locations are not included in contouring.

Overview of PFAS Distribution

SOIL

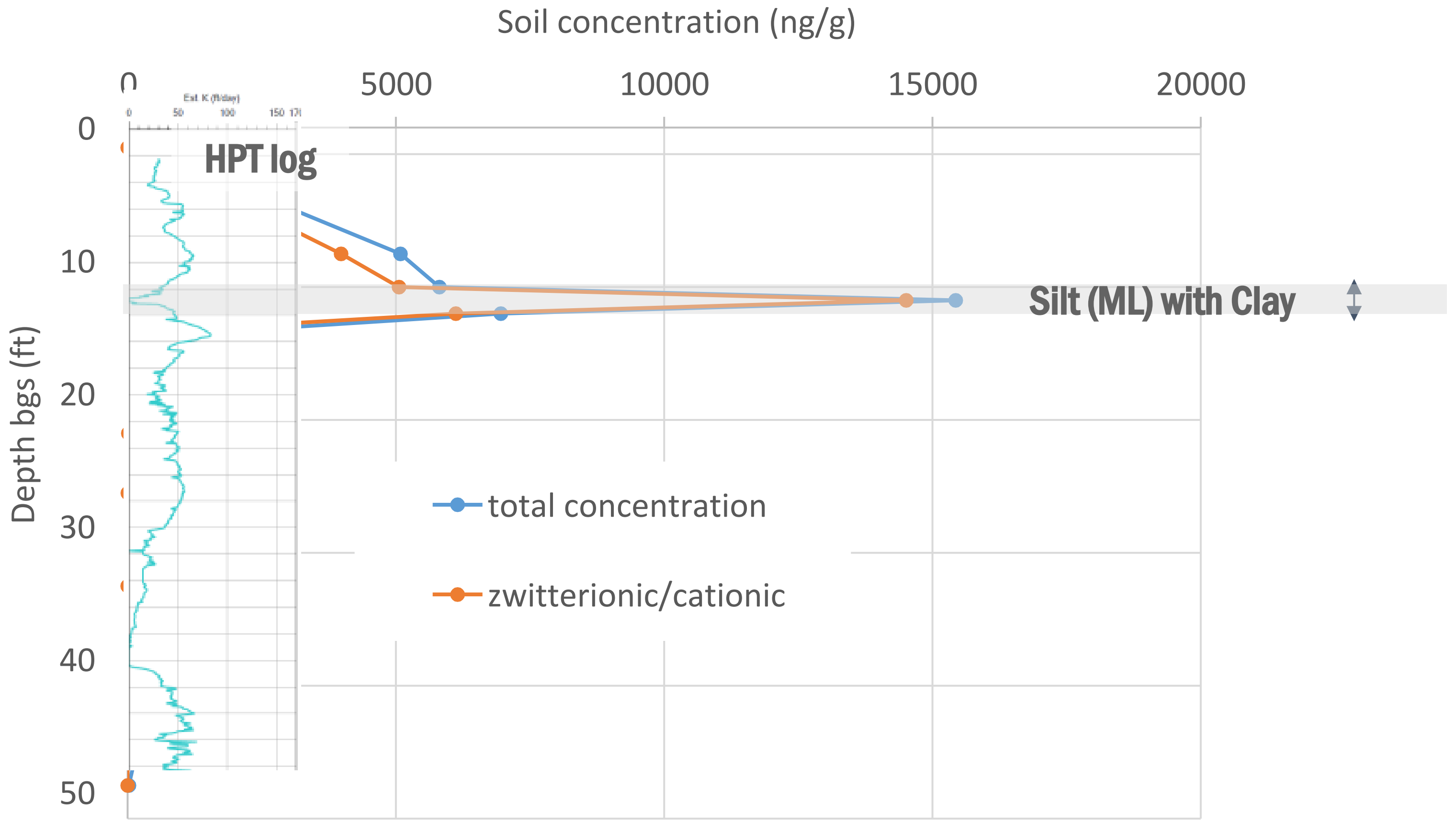




Source: Nickerson et al., 2020, *ES&T*

Influence of Source Composition and Site Stratigraphy on Vertical Distribution

Location 3 (Source Area Location)



Source: Modified from Nickerson et al., 2020, *ES&T*

- Significant portion of soil PFAS in the source zone is from zwitterionic and cationic compounds
- Highly associated with lower-permeability soil intervals

Mass Balance Model: *Approach*

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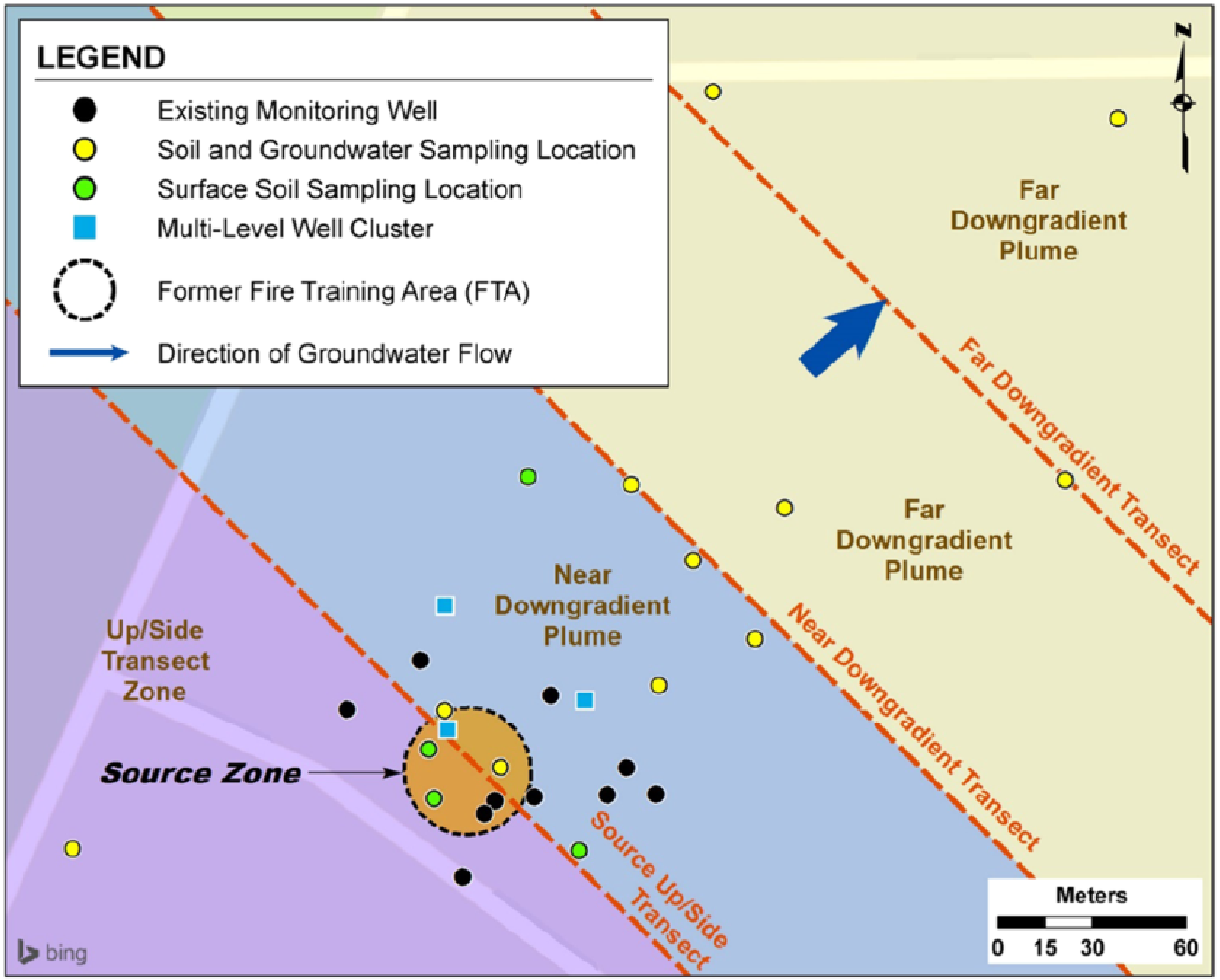
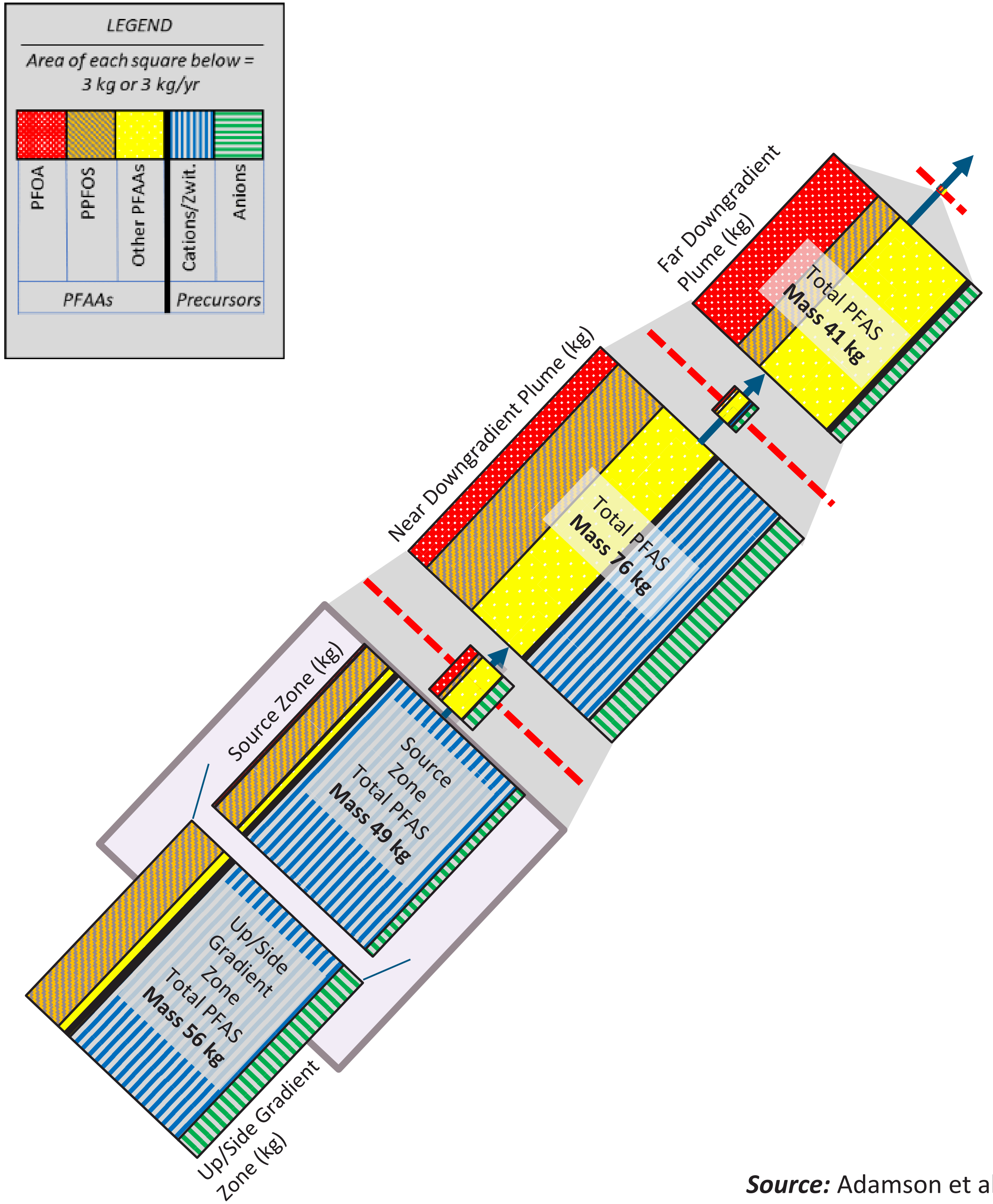


- Create 3-D grid of PFAS soil data and soil type across site
- Divide model domain into 4 different spatial zones
- Use PFAS distribution as basis for interpolating mass of key PFAS classes within each zone
- Sum the mass within each class/zone to get site-wide estimate of total PFAS mass
- Use similar approach for PFAS mass discharge at 3 key transect locations

Source: Adamson et al., 2020, *ES&T*



Source: Adamson et al., 2020, *ES&T*

Mass Balance Model: *Results*

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- **Estimated total PFAS = 252 kg**
- 47% of remaining mass is in source/near-source areas
- 52% of remaining mass is in the form of polyfluorinated “precursors”
  - 83% of precursor mass is zwitterionic/cationic

Mass Balance Model: *Results*

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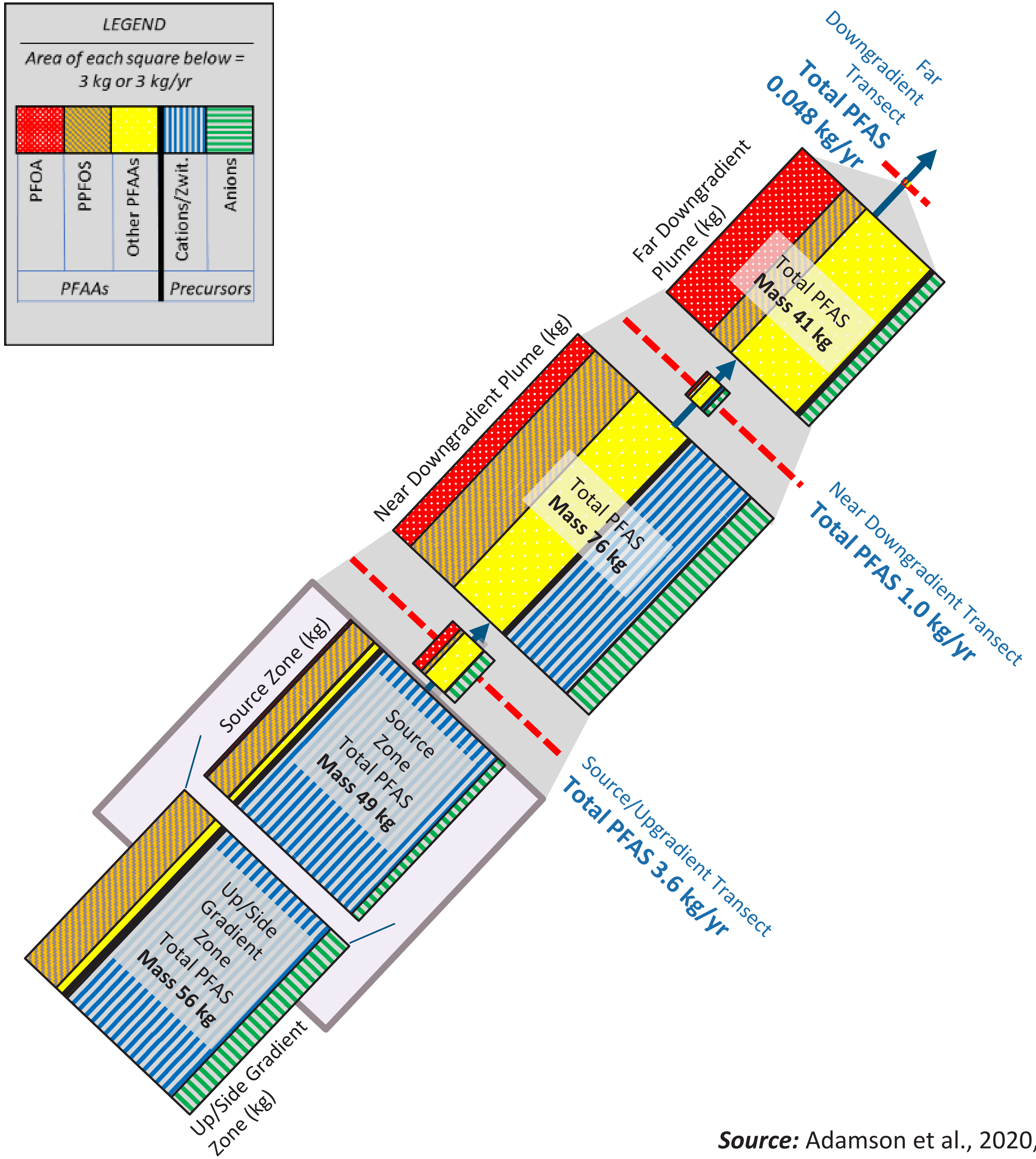


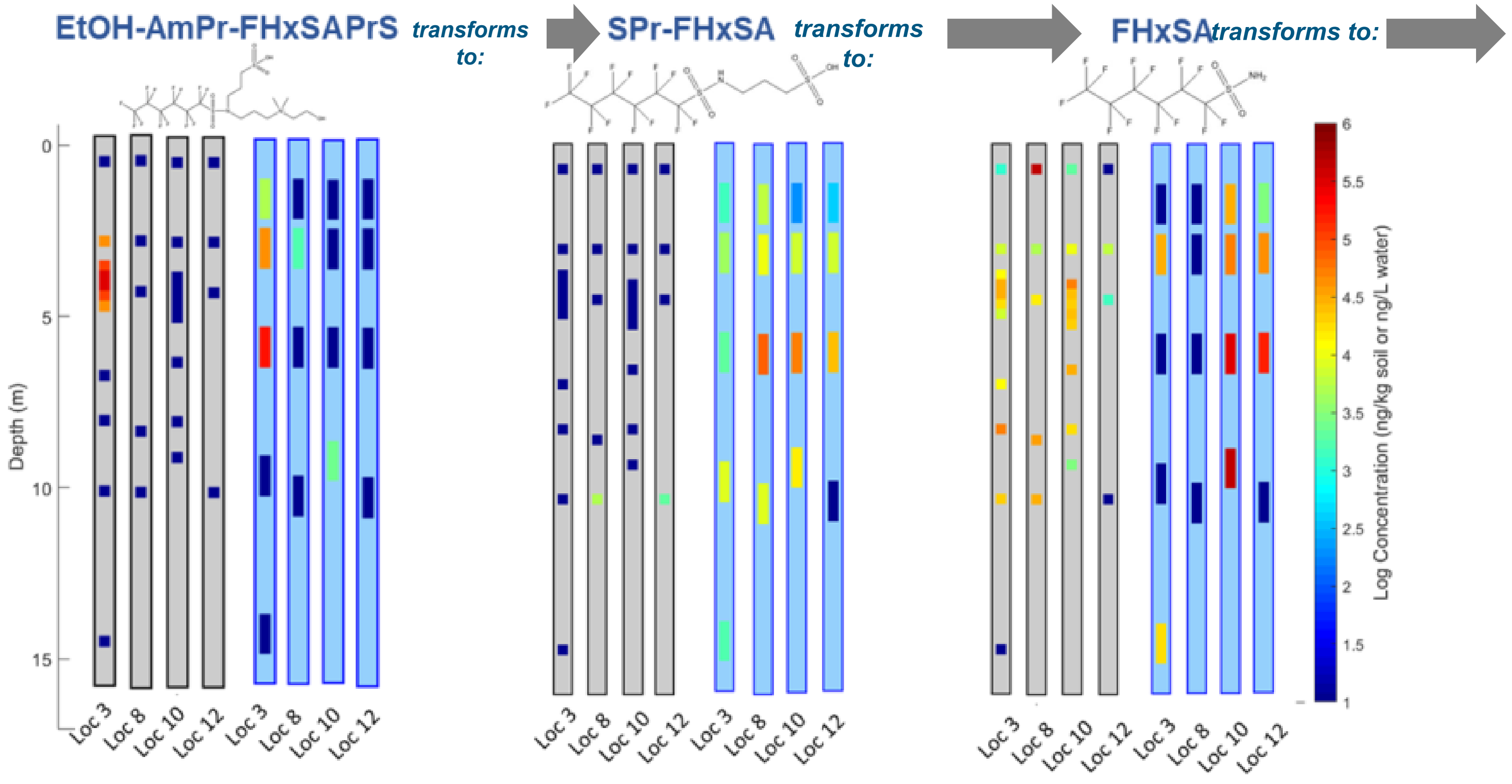
Source: Adamson et al., 2020, *ES&T*

- Mass discharge decreases by 99% between the source and the far downgradient transect
- 82% of remaining mass is associated with lower-k soils
  - Includes 94% of zwitterionic/cationic mass

KEY POINTS

- Confirms strong retention of zwitterionic/cationic PFAS due to preferential sorption characteristics
- Confirms influence of matrix diffusion processes

Precursor Transformation



- ↓ in concentration of "parent" precursor moving away from source area
- Corresponding ↑ in concentration of presumptive transformation by-products moving away from source area

Concentration profiles of possible transformation products in soil and groundwater are shown along transect A (soil data in gray bars, groundwater data in blue bars).

Source: Nickerson et al., 2020, *ES&T*

Mass Balance Model: *Results*

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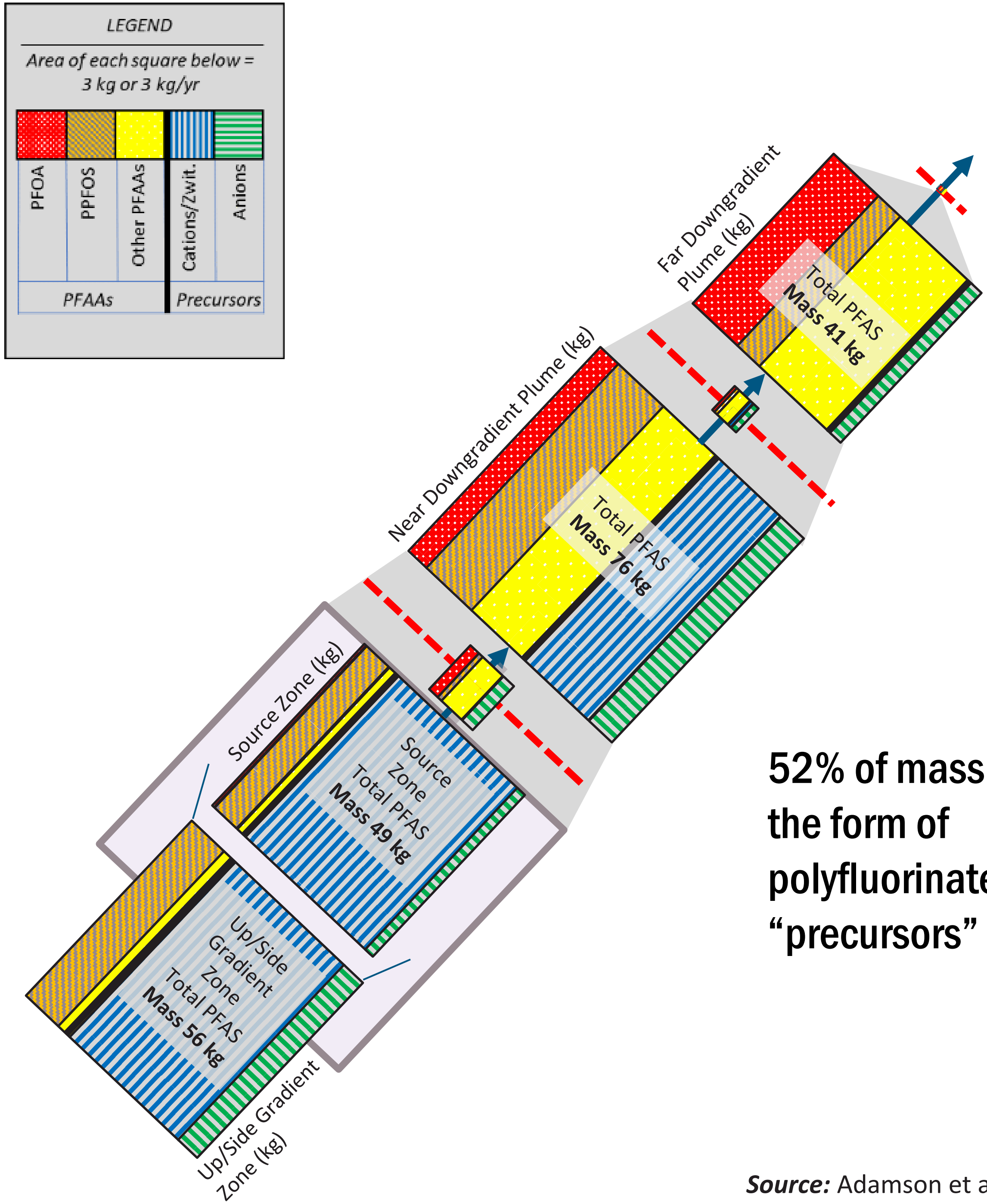

52% of mass is in the form of polyfluorinated "precursors"

Source: Adamson et al., 2020, *ES&T*

- Conversion of precursor mass to dead-end products (PFAAs) is slow **(< 2% per year)**
    - Based on site history and assumptions about composition of released products
- May reflect site-specific characteristics (e.g., bioavailability) that limit transformation rates
- Not necessarily the same at all sites!

Fate and Transport Modeling: *Approach*

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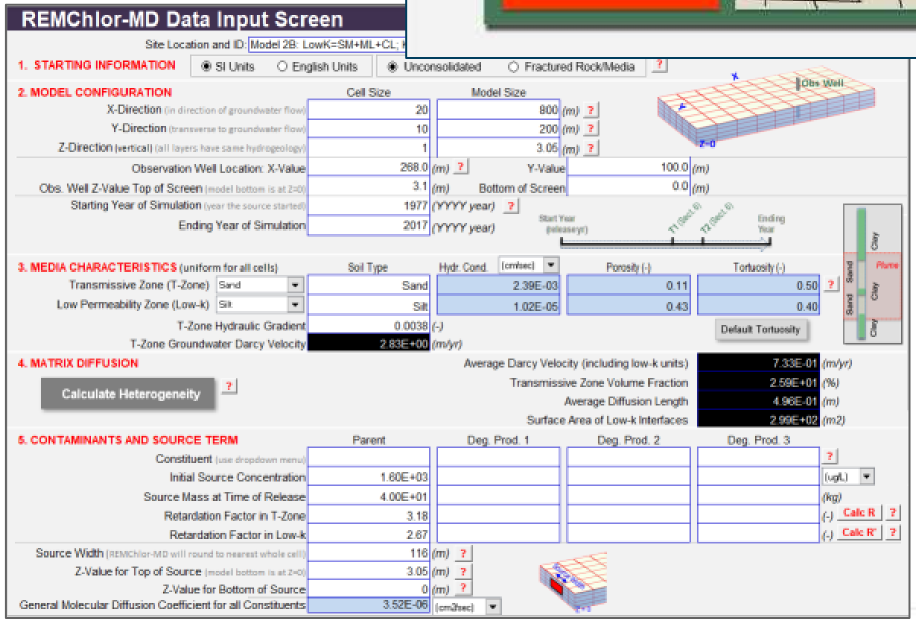
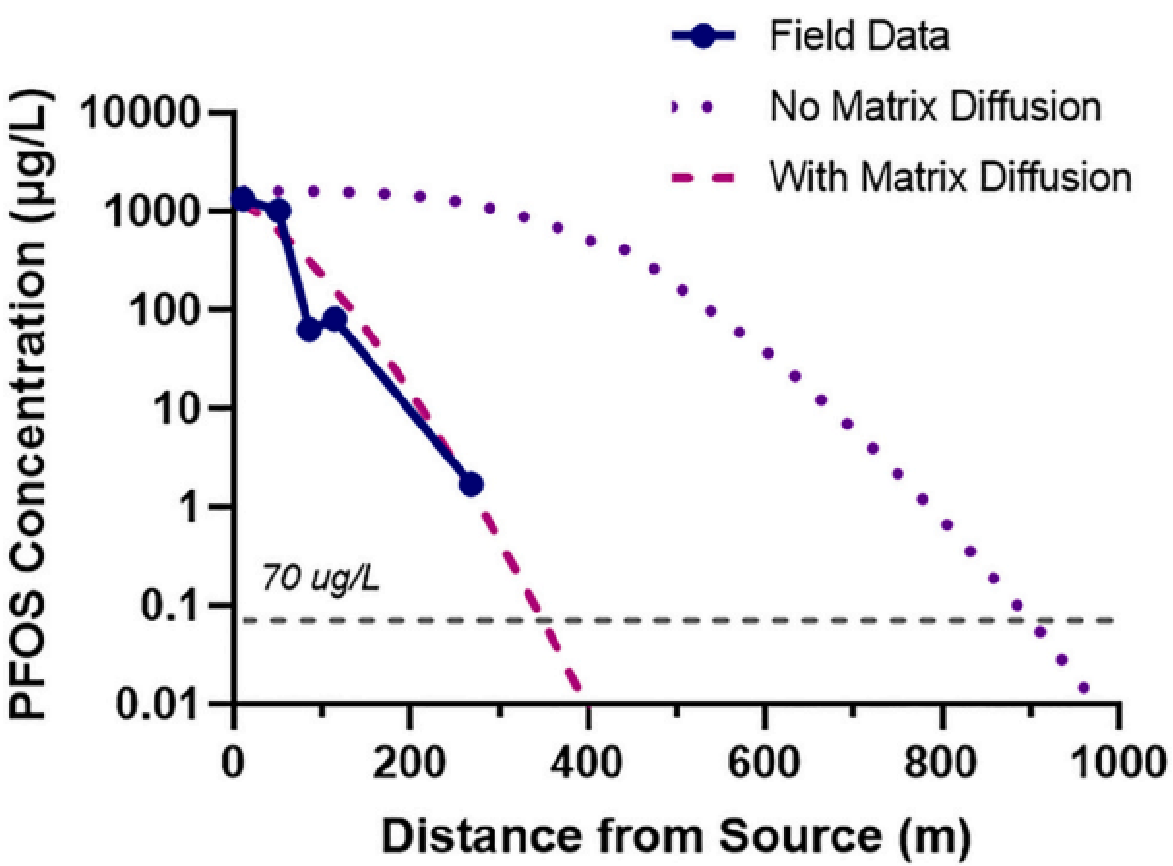
- Use REMCHLOR-MD as screening tool for understanding influence of matrix diffusion processes on PFOS plume extent

- Model predictions in the presence and absence of matrix diffusion (MD) can be calibrated to field data



Impacts of Matrix Diffusion on Plume Length

- How well do model data align with PFOS field data in the presence and absence of matrix diffusion?
  - **Poor fitting with field data if matrix diffusion process was not included in model**
- Data indicate much current PFOS plume length is much shorter due to influence of matrix diffusion



Source: Kulkarni et al., 2022, *JCH*

Implications of Matrix Diffusion on Source Remediation Performance

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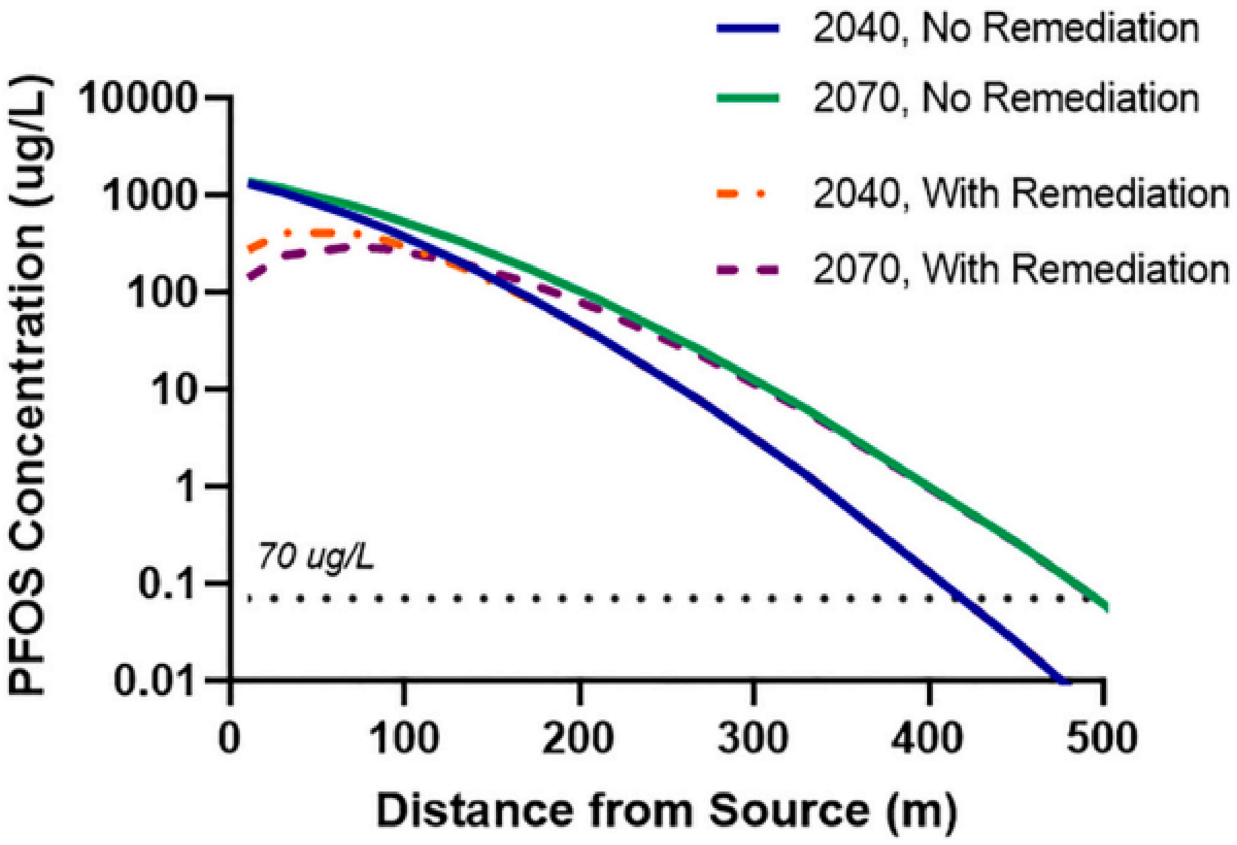
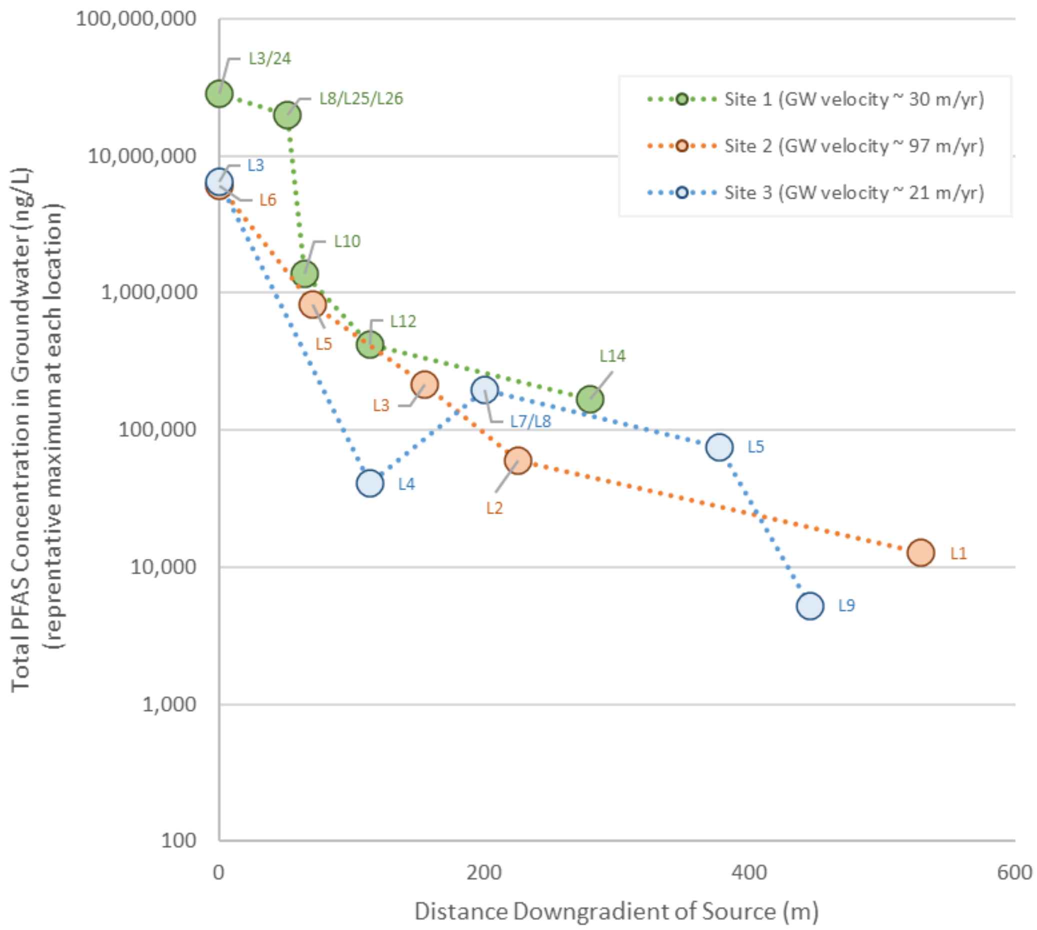
- Predicted effects of source remediation on plume migration
  - **Source remediation would reduce concentrations only in the first ~100 m downgradient from source**
- Will other site management strategies be better suited for *this site*?



Source: Kulkarni et al., 2022, *JCH*

Key Take-Aways

- **High-resolution characterization data** can help build quantitative estimates of mass distribution and plume predictions
- **F&T processes for PFAS are relatively unique** and influence the extent of retention vs. migration
- **Relevance of these processes may vary by site**
- At this site, retention of PFAS (especially precursors) within source area and lower-k soils was observed, resulting in **slow transformation** and **less migration** than expected



Source: Adamson et al., 2022, *Environmental Advances*

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