Comparison of PFAS Fate and Transport Modeling Tools and Data Needs for Site-scale and Regional-scale Models

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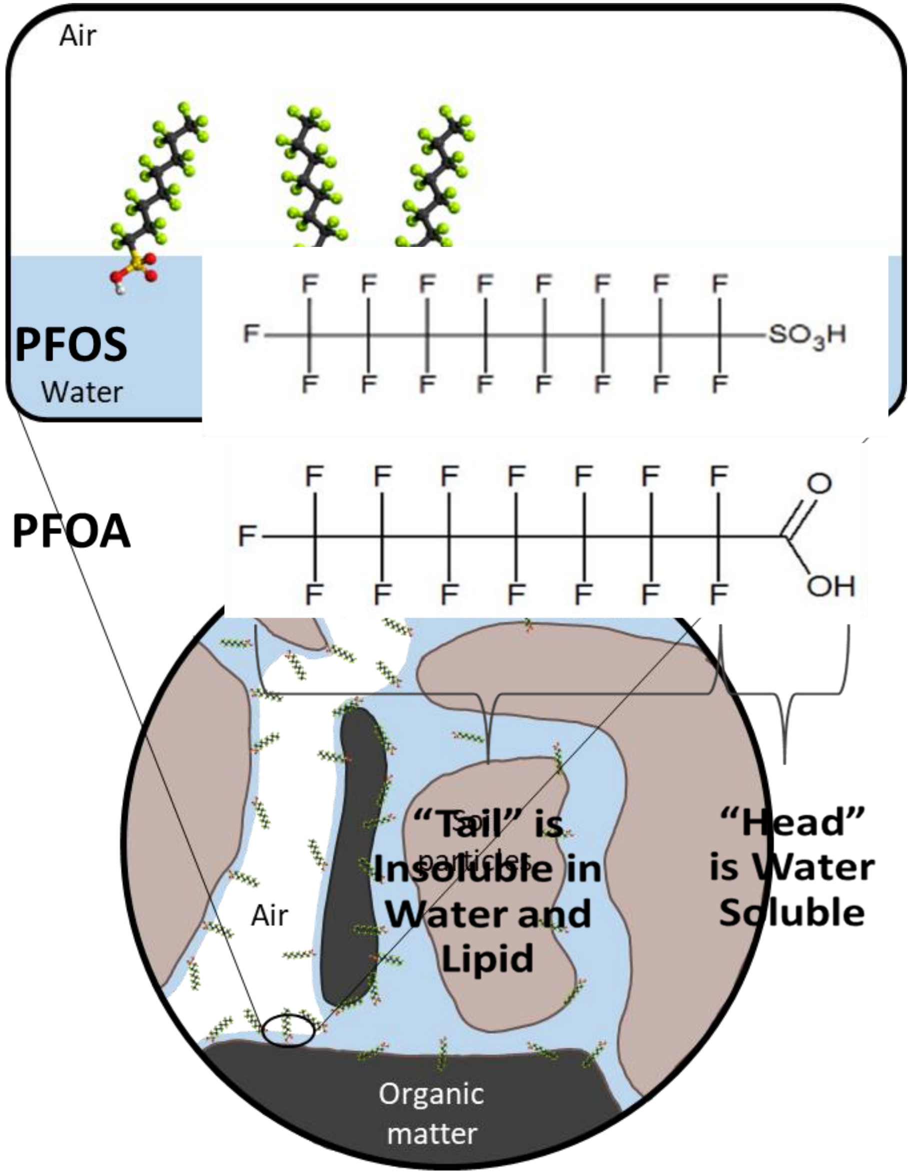
Outline

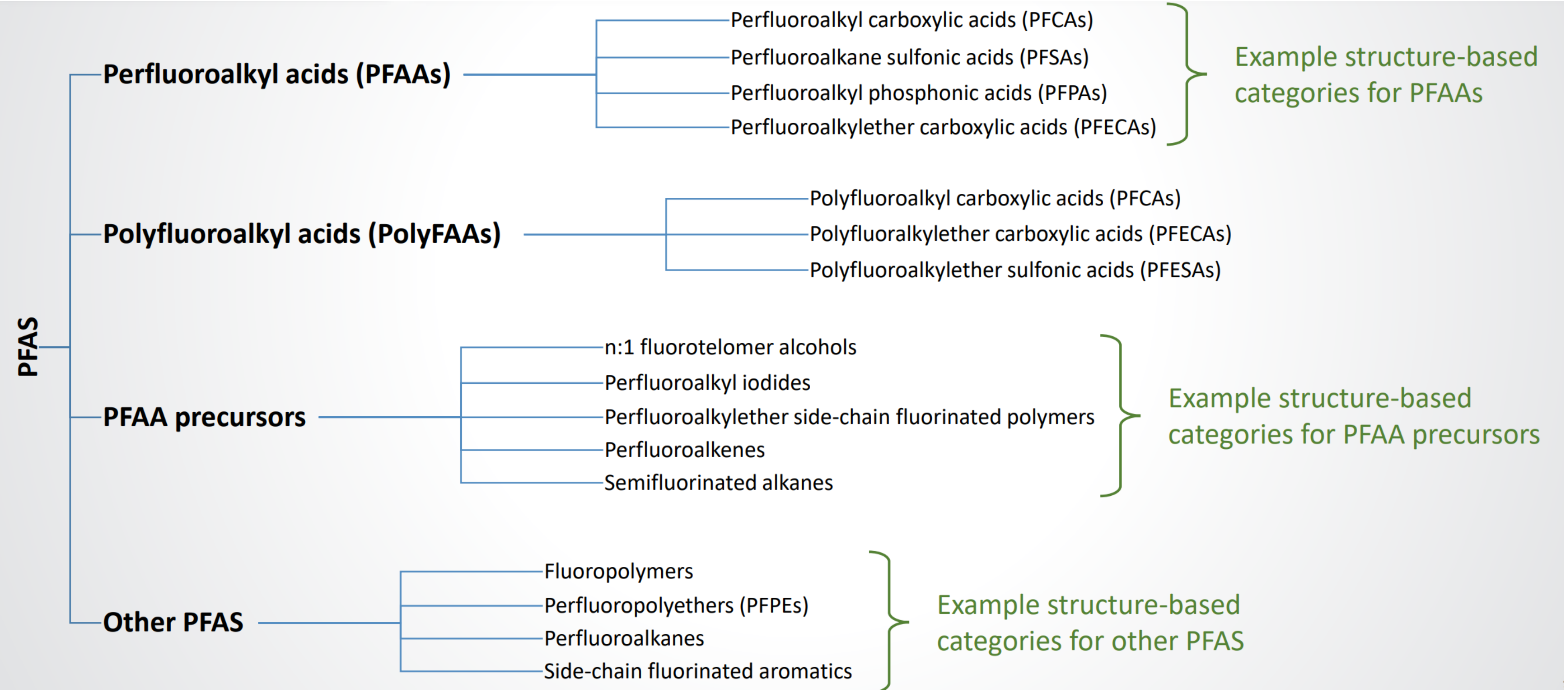
- PFAS Background & Regulations
- PFAS Fate & Transport
- Air-water interfacial sorption
- Modeling tools
- Modeling data requirements
- Knowledge gaps and ongoing research

What are PFAS?

- **P**er- and poly**f**luoro**a**lkyl **s**ubstances
  - Thousands of different compounds
  - Two compounds most persistent in environment
    - PFOA: Perfluoro octanoic acid (C-8)
    - PFOS: Perfluoro octane sulfonic acid (C-8)
- Unique physical-chemical properties
  - C-F bond is one of the strongest
  - Resistant to water, oil, and grease
  - Persistent, bioaccumulative
- Analytical methods can reliably measure ng/L or ppt levels
  - 1 ppt = 30 seconds in one million years
  - 1 ppt = one drop of water in 20 Olympic swimming pools



PFOA, PFOS and many more



PFAS

- **Perfluoroalkyl acids (PFAAs)**
  - Perfluoroalkyl carboxylic acids (PFCAs)
  - Perfluoroalkane sulfonic acids (PFSAs)
  - Perfluoroalkyl phosphonic acids (PFPAs)
  - Perfluoroalkylether carboxylic acids (PFECAs)

  Example structure-based categories for PFAAs
- **Polyfluoroalkyl acids (PolyFAAs)**
  - Polyfluoroalkyl carboxylic acids (PFCAs)
  - Polyfluoralkylether carboxylic acids (PFECAs)
  - Polyfluoroalkylether sulfonic acids (PFESAs)
- **PFAA precursors**
  - n:1 fluorotelomer alcohols
  - Perfluoroalkyl iodides
  - Perfluoroalkylether side-chain fluorinated polymers
  - Perfluoroalkenes
  - Semifluorinated alkanes

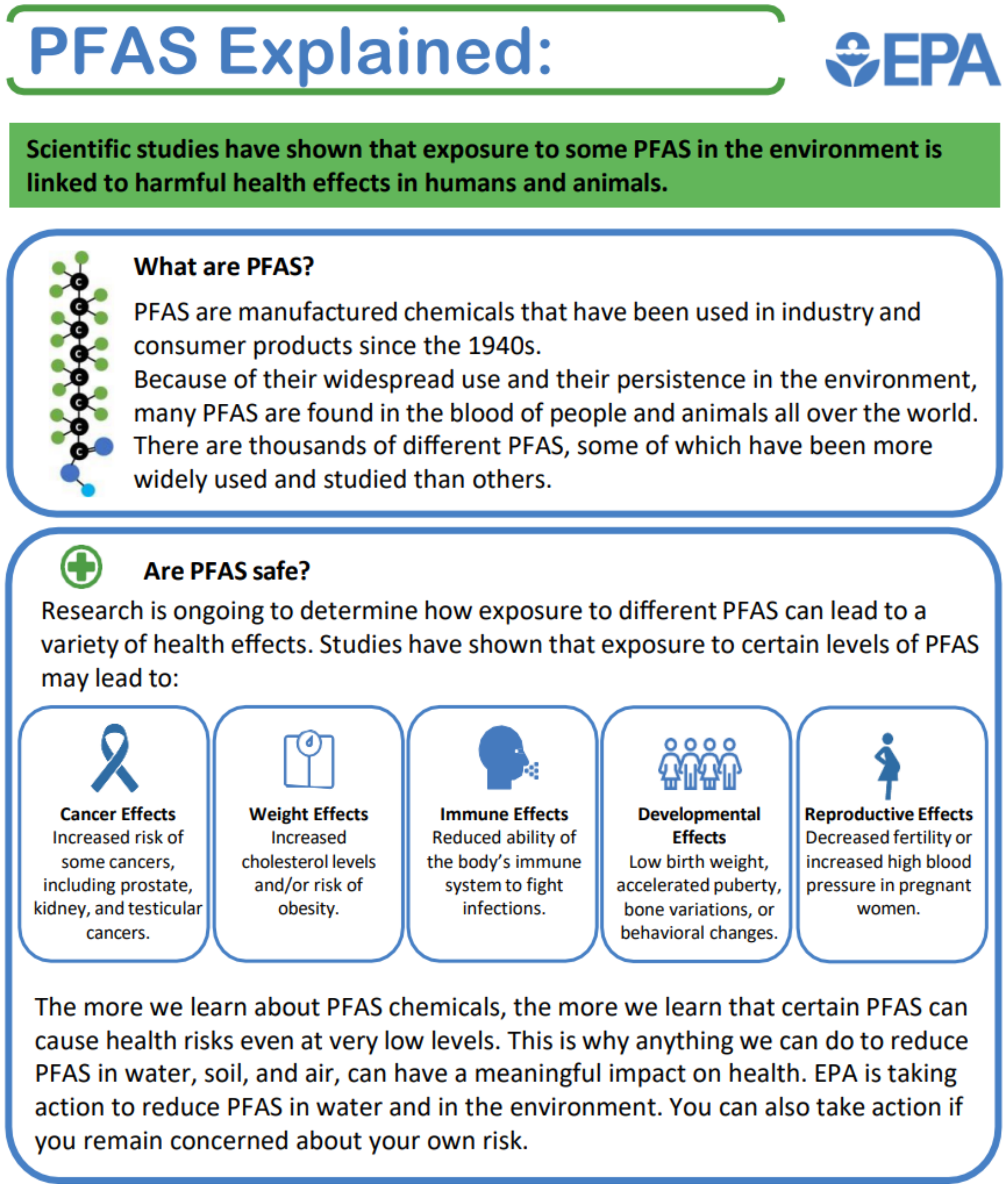
  Example structure-based categories for PFAA precursors
- **Other PFAS**
  - Fluoropolymers
  - Perfluoropolyethers (PFPEs)
  - Perfluoroalkanes
  - Side-chain fluorinated aromatics

  Example structure-based categories for other PFAS

Adapted from EPA 2021
www.epa.gov/pfas

Why are PFAS a big deal?

- Widely used in industry and consumer products
  - Multiple sources, not just aqueous film forming foams (AFFF)
- Leach from soil, migrate in groundwater, do not degrade
  - Groundwater, storm water, surface water are primary media of concern
- Reliably detectable at levels below 10 parts per trillion
  - Precautions needed when sampling environmental media
- Correlated with a range of health effects in humans
- Limited treatment options
- Heightened public and regulatory focus
  - 3M & Dupont settlements $12 Billion
  - In news and movies



PFAS Explained:

Scientific studies have shown that exposure to some PFAS in the environment is linked to harmful health effects in humans and animals.

What are PFAS?

PFAS are manufactured chemicals that have been used in industry and consumer products since the 1940s.
Because of their widespread use and their persistence in the environment, many PFAS are found in the blood of people and animals all over the world.
There are thousands of different PFAS, some of which have been more widely used and studied than others.

Are PFAS safe?

Research is ongoing to determine how exposure to different PFAS can lead to a variety of health effects. Studies have shown that exposure to certain levels of PFAS may lead to:

Cancer Effects Increased risk of some cancers, including prostate, kidney, and testicular cancers.

Weight Effects Increased cholesterol levels and/or risk of obesity.

Immune Effects Reduced ability of the body's immune system to fight infections.

Developmental Effects Low birth weight, accelerated puberty, bone variations, or behavioral changes.

Reproductive Effects Decreased fertility or increased high blood pressure in pregnant women.

The more we learn about PFAS chemicals, the more we learn that certain PFAS can cause health risks even at very low levels. This is why anything we can do to reduce PFAS in water, soil, and air, can have a meaningful impact on health. EPA is taking action to reduce PFAS in water and in the environment. You can also take action if you remain concerned about your own risk.

www.epa.gov/pfas

What are the sources of PFAS?

- More than 200 use categories and subcategories for more than 1400 PFAS
- Both industrial processes and consumer products
  - Non-stick cookware
  - Pizza box
  - Firefighting foams
  - Plating fume suppressant

http://smchd.org/pfas/

PFAS in consumer products
Implications: WWTPs and Landfills

- Paper and packaging (including pizza boxes, microwave popcorn bags)
- Clothing, sporting equipment
- Ski and snowboard waxes
- Non-stick cookware
- Polishes and waxes
- Hydraulic fluids
- Windshield wipers
- Adhesives
- Shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss
- Pesticides and herbicides

Source: https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf

Types of Sites with potential for PFAS

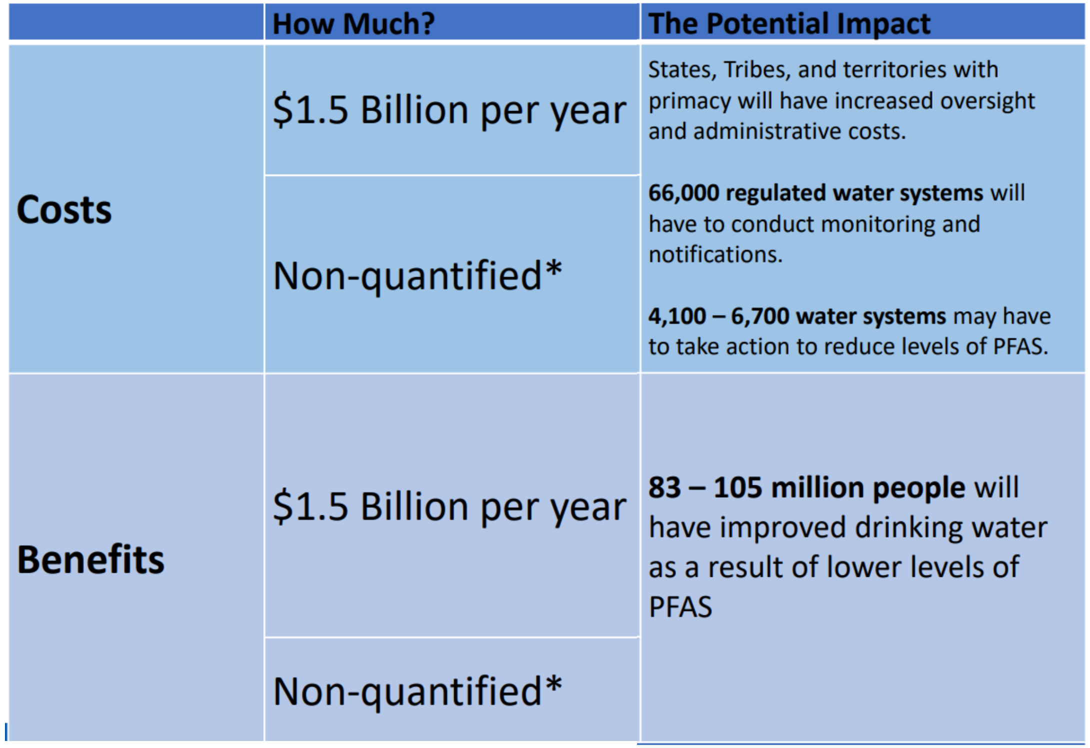
- Anywhere that AFFF fire suppression was used or **tested**
  - Airports, petroleum refineries/storage, manufacturing
- Manufacturing – use of PFAS-containing mixtures
  - Paints, waxes and varnishes; mold release compounds; etc
  - Electro-plating tank vapor suppressant
- Wastewater treatment plants (WWTP)
  - Discharge to surface water and biosolids/land applications
- Redevelopment – anywhere with PFAS-contaminated soil or groundwater
  - Disposal of soil and management of groundwater associated with capital projects
- Landfills – receiving consumer and industrial wastes
  - Leachate collection and treatment / migration to surface water
  - Migration to groundwater

* Non-point sources - Atmosphere, rainwater, sea spray aerosols

Safe Drinking Water Act: EPA’s New MCLs

- Very low values (parts per trillion)
- 5 chemicals with individual MCL
- Hazard index target of 1 for a combination of 2 or more of PFHxS, PFNA, HFPO-DA, and PFBS

Chemical	Maximum Contaminant Level Goal (MCLG)	Maximum Contaminant Level (MCL)
PFOA	0	4.0 ppt
PFOS	0	4.0 ppt
PFHxS	10 ppt	10 ppt
HFPO-DA (GenX chemicals)	10 ppt	10 ppt
PFNA	10 ppt	10 ppt
Mixture of two or more: PFHxS, PFNA, HFPO-DA, and PFBS	Hazard Index of 1	Hazard Index of 1

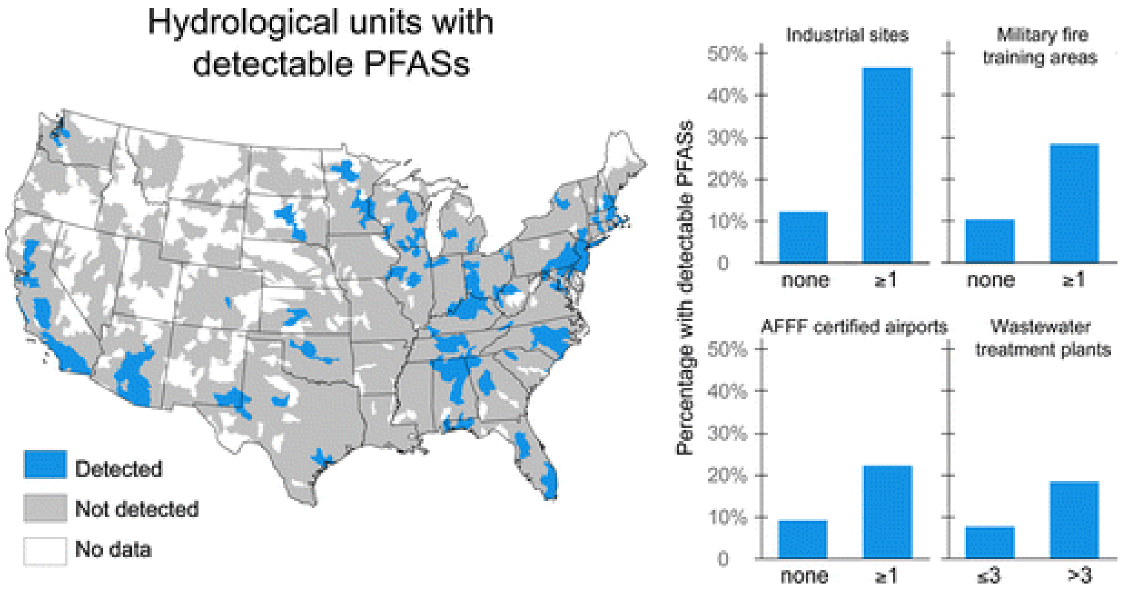


	How Much?	The Potential Impact
Costs	$1.5 Billion per year	States, Tribes, and territories with primacy will have increased oversight and administrative costs. **66,000 regulated water systems** will have to conduct monitoring and notifications. **4,100 – 6,700 water systems** may have to take action to reduce levels of PFAS.
	Non-quantified*	
Benefits	$1.5 Billion per year	**83 – 105 million people** will have improved drinking water as a result of lower levels of PFAS
	Non-quantified*	

MCLG is a <u>non-enforceable health-based goal of zero</u>. Per EPA, MCLG reflects the latest science showing that there is no level of exposure to these two PFAS without risk of health impacts

How prevalent are PFAS in drinking water?

- Unregulated Contaminant Monitoring Rule (UCMR3)
  - National monitoring 2013 – 2015
  - Large PWs (>10,000 people)
  - six PFAS compounds (70 ppt MRL)
- UCMR5
  - National monitoring 2023-2025
  - Small PWs (3,300-10,000 and some* < 3,300)
  - 29 PFAS (latest MCLs)




Environmental Science & Technology LETTERS
Letter
pubs.acs.org/journal/estlcu

Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

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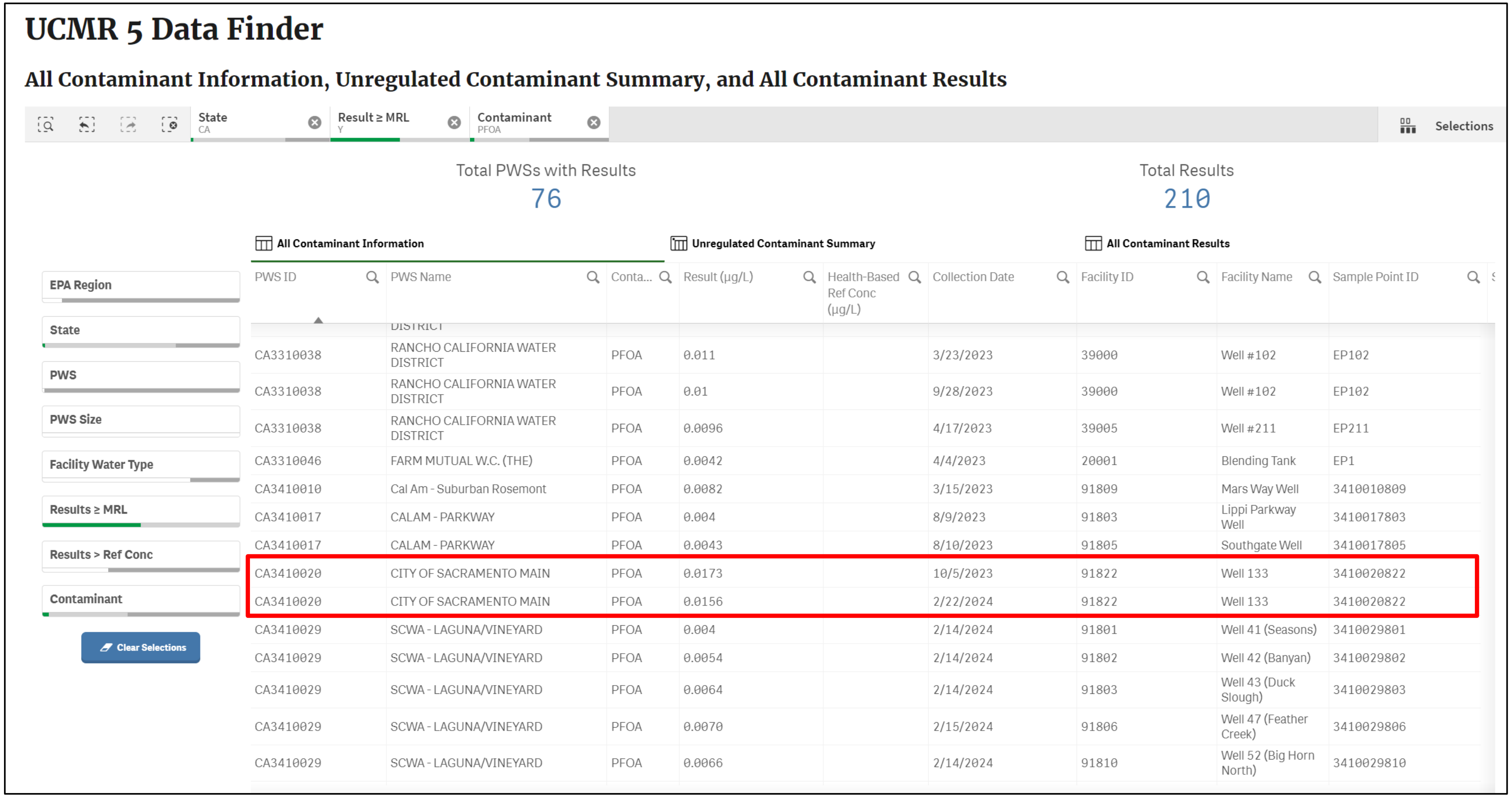
UCMR5 Data through July 2024



UCMR 5 Data Finder

All Contaminant Information, Unregulated Contaminant Summary, and All Contaminant Results

State: CA
Result ≥ MRL: Y
Contaminant: PFOA

Total PWSs with Results
76

Total Results
210

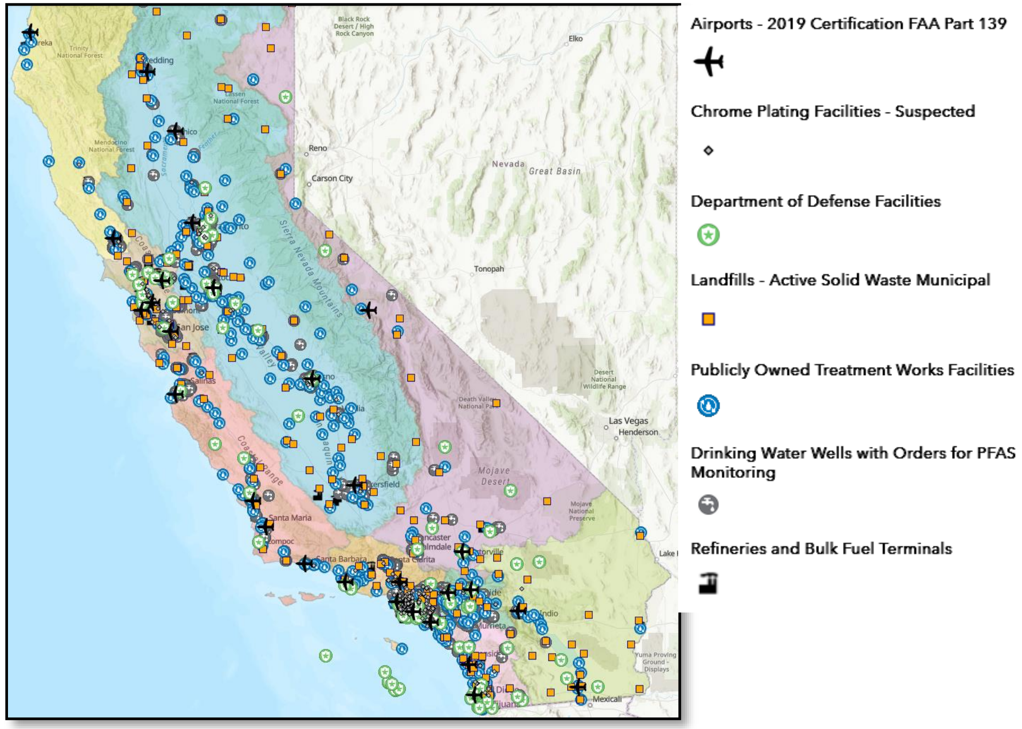
All Contaminant Information | **Unregulated Contaminant Summary** | **All Contaminant Results**

PWS ID	PWS Name	Conta...	Result (µg/L)	Health-Based Ref Conc (µg/L)	Collection Date	Facility ID	Facility Name	Sample Point ID
	DISTRICT							
CA3310038	RANCHO CALIFORNIA WATER DISTRICT	PFOA	0.011		3/23/2023	39000	Well #102	EP102
CA3310038	RANCHO CALIFORNIA WATER DISTRICT	PFOA	0.01		9/28/2023	39000	Well #102	EP102
CA3310038	RANCHO CALIFORNIA WATER DISTRICT	PFOA	0.0096		4/17/2023	39005	Well #211	EP211
CA3310046	FARM MUTUAL W.C. (THE)	PFOA	0.0042		4/4/2023	20001	Blending Tank	EP1
CA3410010	Cal Am - Suburban Rosemont	PFOA	0.0082		3/15/2023	91809	Mars Way Well	3410010809
CA3410017	CALAM - PARKWAY	PFOA	0.004		8/9/2023	91803	Lippi Parkway Well	3410017803
CA3410017	CALAM - PARKWAY	PFOA	0.0043		8/10/2023	91805	Southgate Well	3410017805
CA3410020	CITY OF SACRAMENTO MAIN	PFOA	0.0173		10/5/2023	91822	Well 133	3410020822
CA3410020	CITY OF SACRAMENTO MAIN	PFOA	0.0156		2/22/2024	91822	Well 133	3410020822
CA3410029	SCWA - LAGUNA/VINEYARD	PFOA	0.004		2/14/2024	91801	Well 41 (Seasons)	3410029801
CA3410029	SCWA - LAGUNA/VINEYARD	PFOA	0.0054		2/14/2024	91802	Well 42 (Banyan)	3410029802
CA3410029	SCWA - LAGUNA/VINEYARD	PFOA	0.0064		2/14/2024	91803	Well 43 (Duck Slough)	3410029803
CA3410029	SCWA - LAGUNA/VINEYARD	PFOA	0.0070		2/15/2024	91806	Well 47 (Feather Creek)	3410029806
CA3410029	SCWA - LAGUNA/VINEYARD	PFOA	0.0066		2/14/2024	91810	Well 52 (Big Horn North)	3410029810

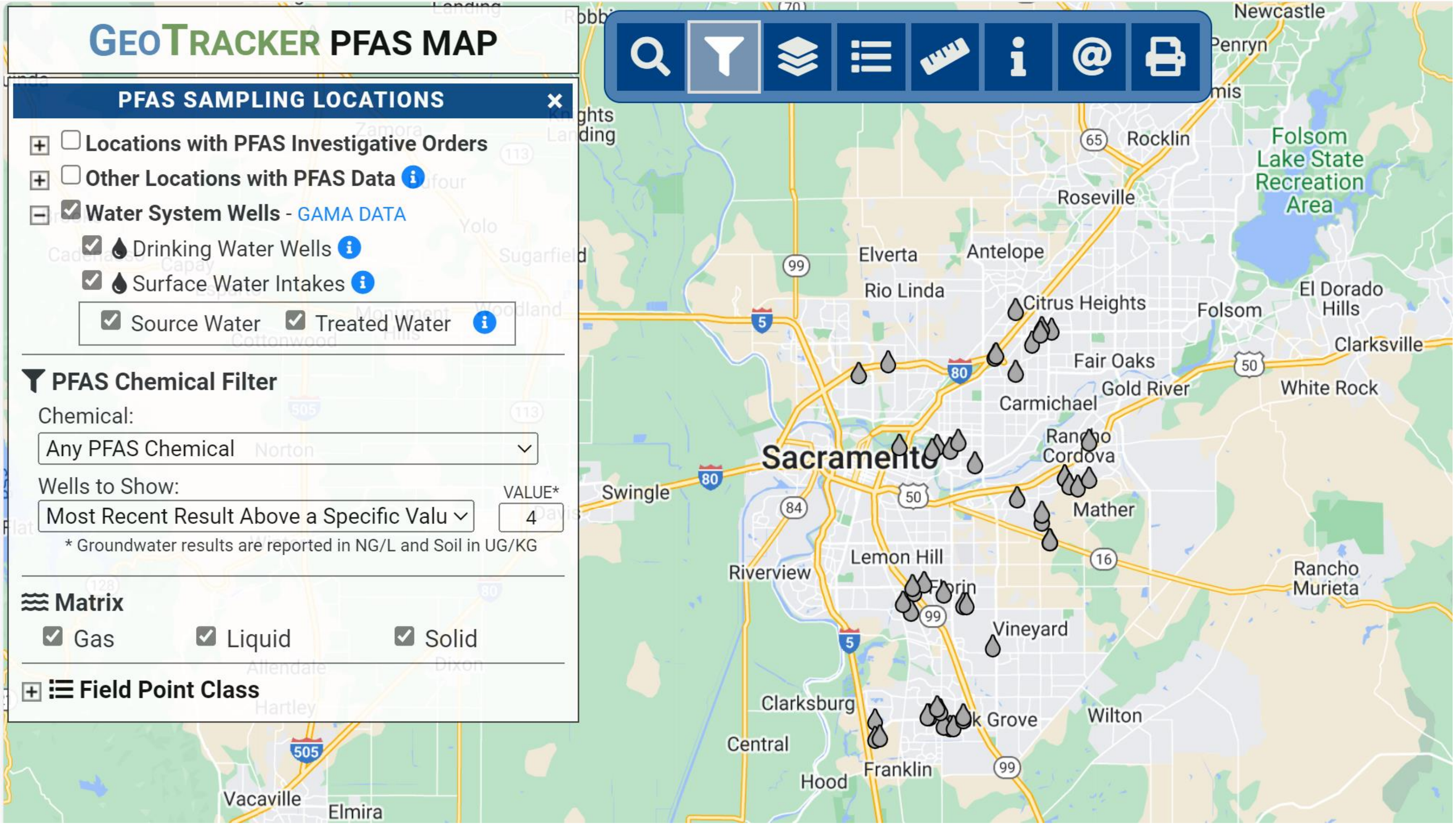
*Total number of unique PWSs with one or more averages greater than respective PFAS MCL = 393 of 3,463 (11%)

State Water Resources Control Board Investigative Orders

- As part of statewide effort, SWRCB implemented phased investigation to obtain preliminary understanding of PFAS concentrations at certain facilities
  - data to inform decisions on regulatory action in anticipation of regulatory standards
- Phase I:
  - 31 airports
  - 252 municipal solid waste landfills
  - >1,000 drinking water wells/sources
- Phase II and III
  - plating facilities
  - refineries, bulk terminals, and non-airport fire training areas
  - wastewater treatment & pre-treatment plants
  - domestic wells



https://www.waterboards.ca.gov/pfas/



GEOTRACKER PFAS MAP

PFAS SAMPLING LOCATIONS ×

- ⊞ ☐ Locations with PFAS Investigative Orders
- ⊞ ☐ Other Locations with PFAS Data
- ⊟ ☑ Water System Wells - GAMA DATA
  - ☑ Drinking Water Wells
  - ☑ Surface Water Intakes
    - ☑ Source Water ☑ Treated Water

PFAS Chemical Filter

Chemical: Any PFAS Chemical

Wells to Show: Most Recent Result Above a Specific Valu

VALUE* 4

* Groundwater results are reported in NG/L and Soil in UG/KG

Matrix

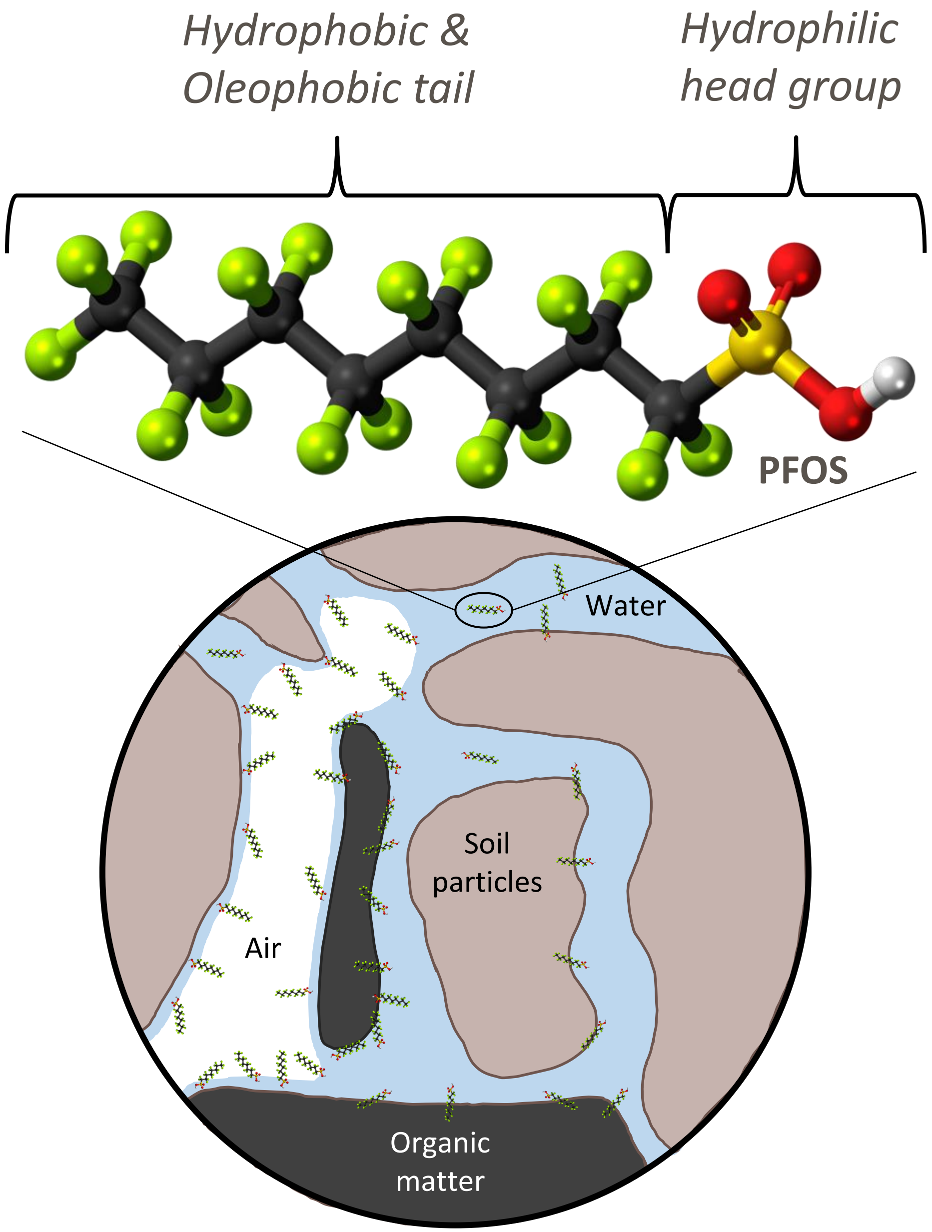
☑ Gas ☑ Liquid ☑ Solid

⊞ **Field Point Class**

PFAS Fate & Transport

PFAS Fate & Transport

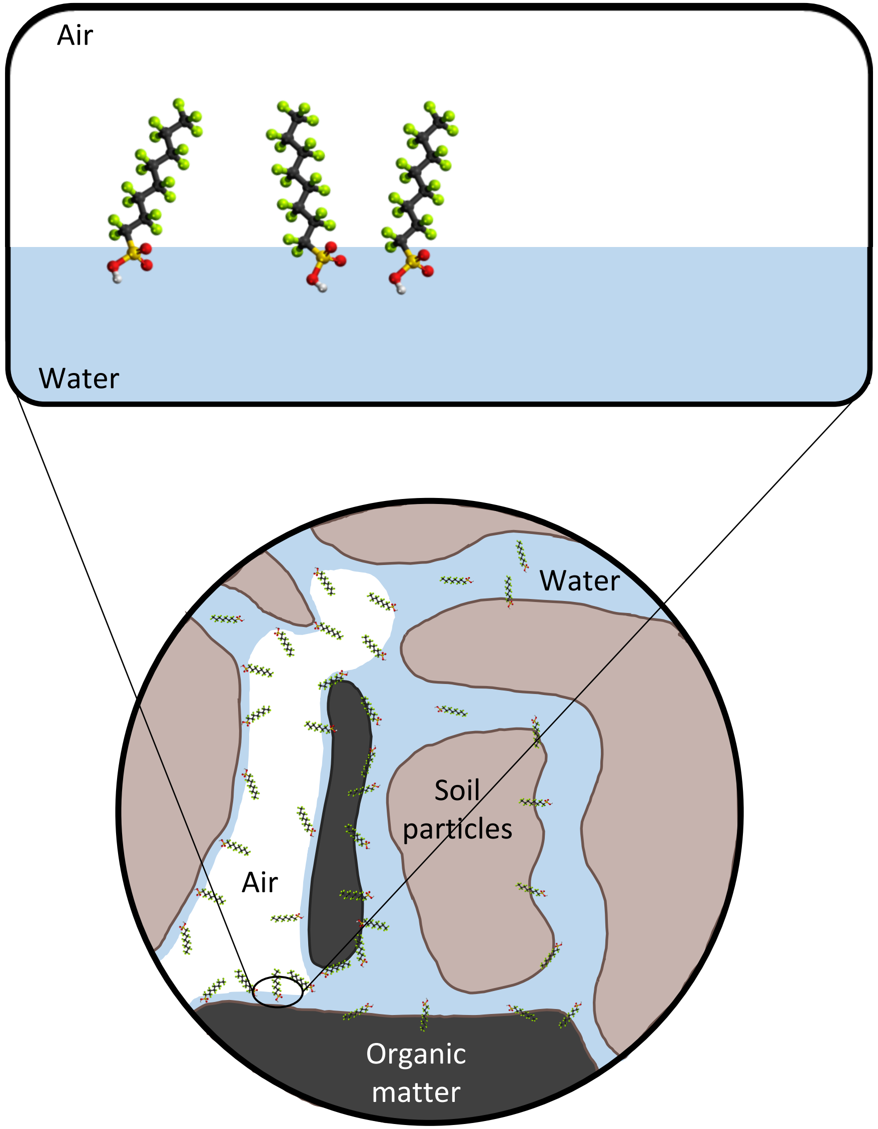
- PFAS have unique, surface-active properties that impact their fate & transport in the vadose zone.
- These surface-active properties cause PFAS to be retained at solid –water and air–water interfaces.
- Evidence suggests that due to increased retention, vadose zones can potentially serve as long-term sources of contamination to groundwater.



Pore-scale view of the vadose zone

Air-water Interfacial Adsorption

- Retention at these air–water interfaces is largely dependent on the amount of interfacial area available for sorption, and PFAS concentrations
- Hydrophobicity and PFAS chain-length are directly correlated to retention at these interfaces
- Sorption at these interfaces can significantly impact PFAS leaching into groundwater
- Sandy soils at lower saturation may retain higher amount of PFAS than clays at higher saturation



Pore-scale view of the vadose zone

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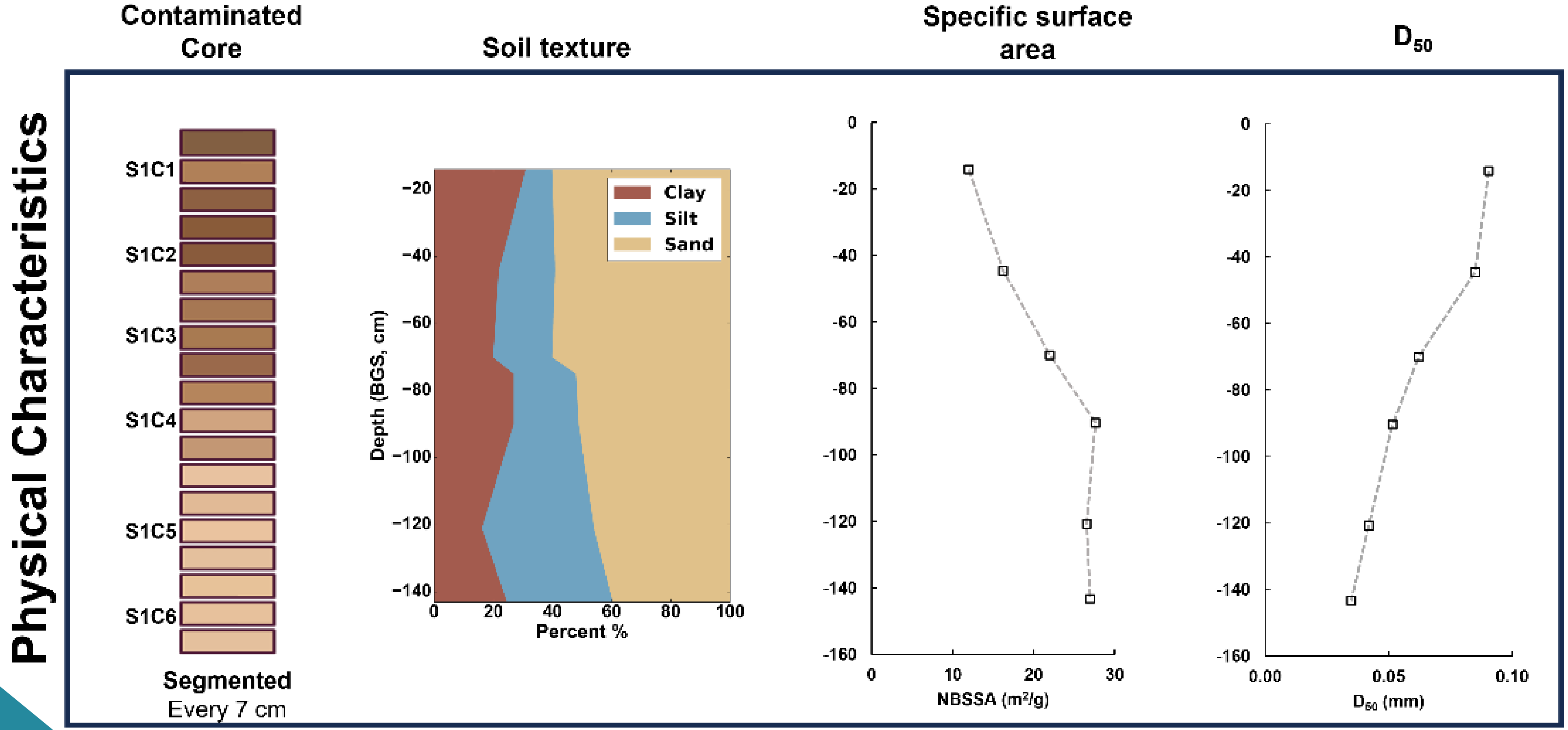
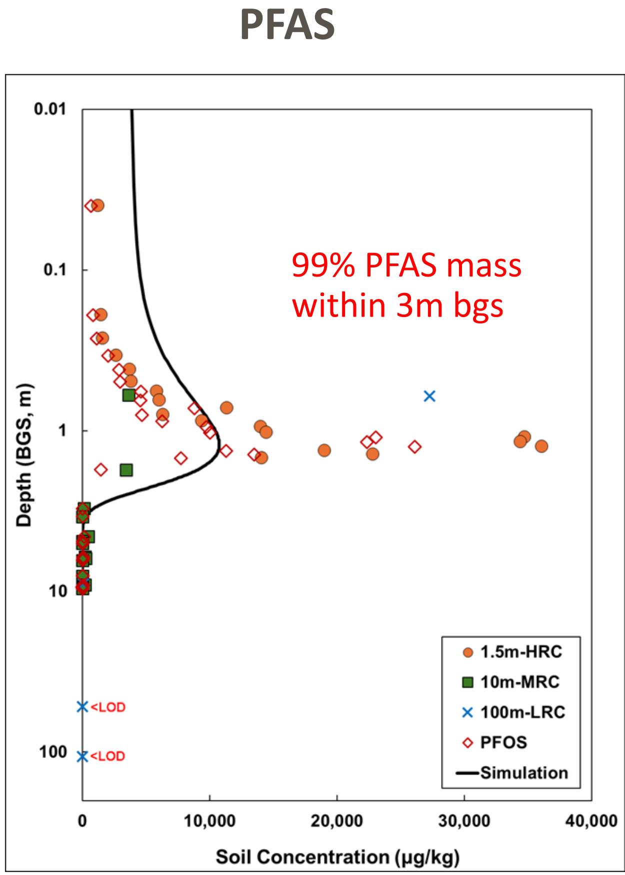
Sorption to Air-Water Interface

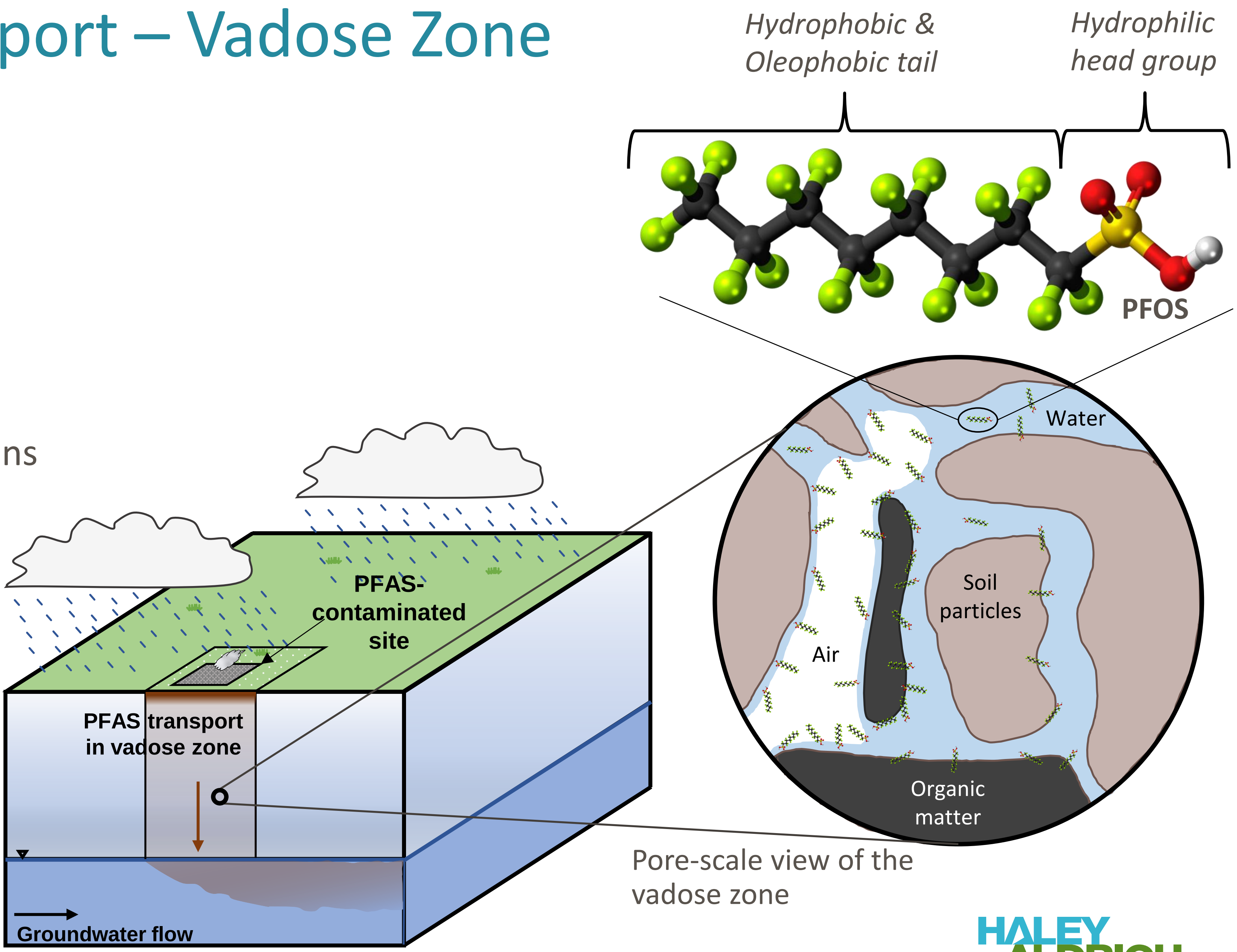




Measurements of soils parameters, surface area, PFAS at Davis Monthan Air Force Base from Brusseau (pers. comm., 2024)

PFAS Fate & Transport – Vadose Zone

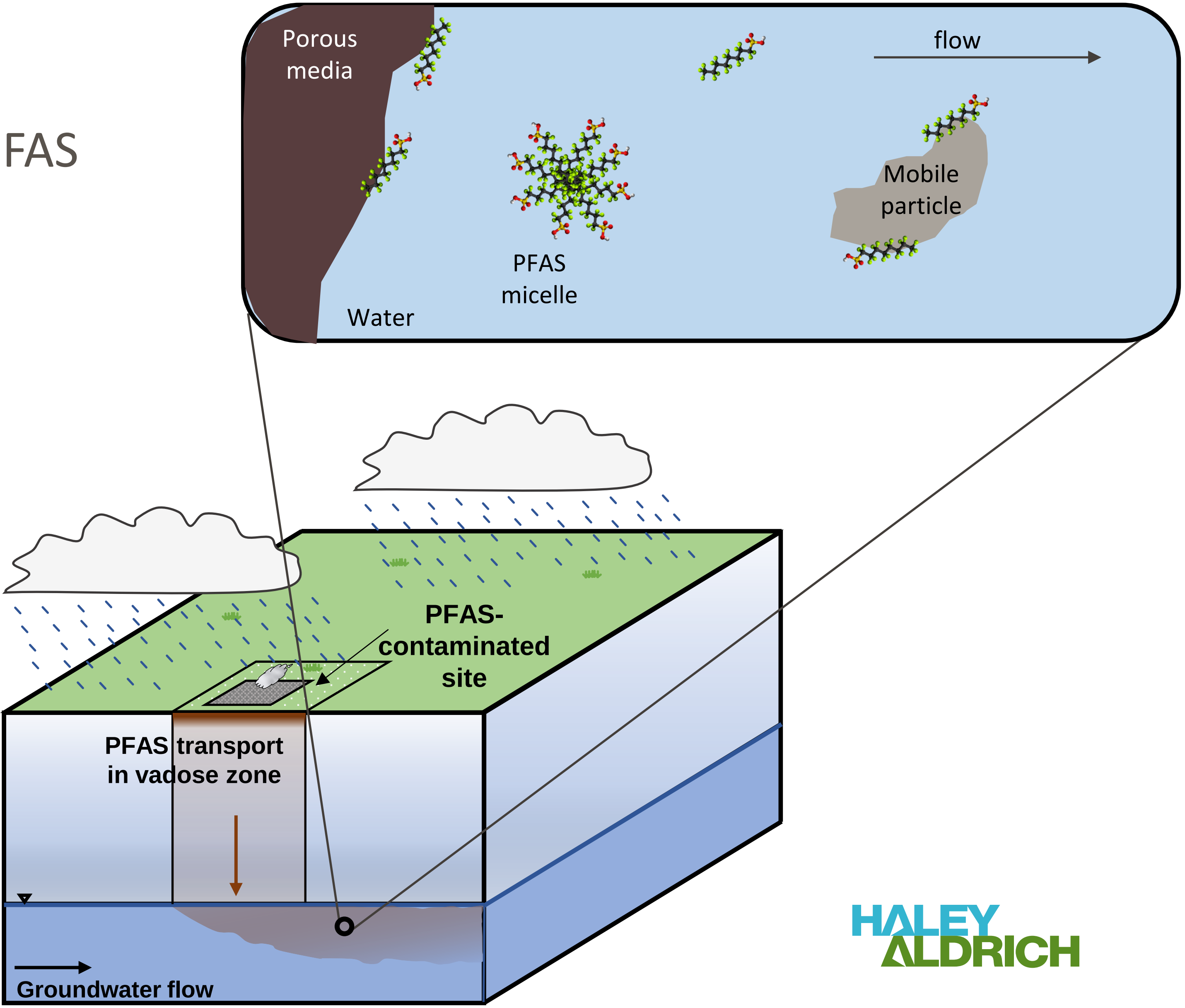
- Retention at air–water interfaces
  - Surfactant properties of PFAS
  - Variable water content
  - Degree of hydrophobicity
  - Composition and concentrations of PFAS in solution
  - Properties of porous media
  - Uptake via biota/plants
- Retention at solid–water interfaces
  - Amount of organic carbon
  - Competitive sorption



Pore-scale view of the vadose zone

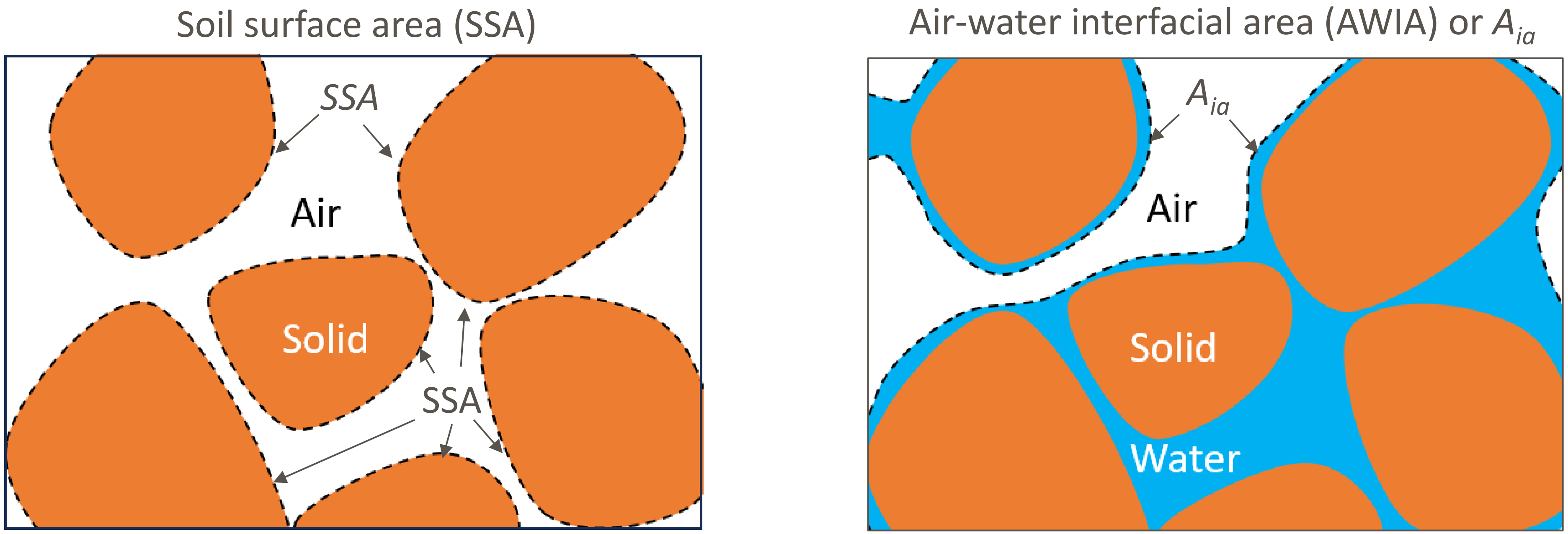
PFAS Fate & Transport – Groundwater

- Advection and dispersion
- Degradation of precursors to terminal PFAS
- Molecular diffusion processes
- Facilitated transport mechanisms
  - Colloidal transport
  - Formation of micelles
  - Presence of co-contaminants
- Sorption to solid surfaces and organics



PFAS Sorption at Air-Water Interface

Air-Water Interfacial Area

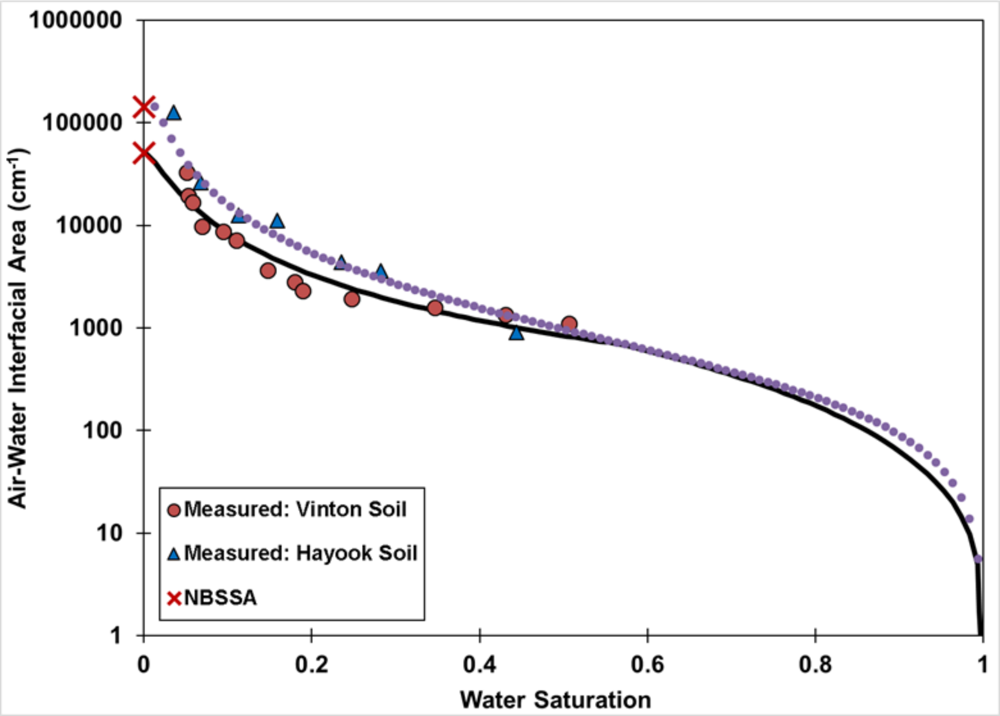


Soil Surface Area (SSA) is an intrinsic property similar to porosity

AWIA depends on SSA and saturation, drainage & imbibition history

Air-Water Interfacial Area, Specific Surface Area and Saturation

Experimental



Brusseau (pers. comm., 2024)

Empirical

$$(1 - S_w)A_{max}$$

$$3.9\,(1 - S_w)\,d_{50}^{-1.2}$$

$$\rho_w g \phi / \sigma_0 (1 - S_w)$$

$$x_2 S_w^2 + x_1 S_w + x_0$$

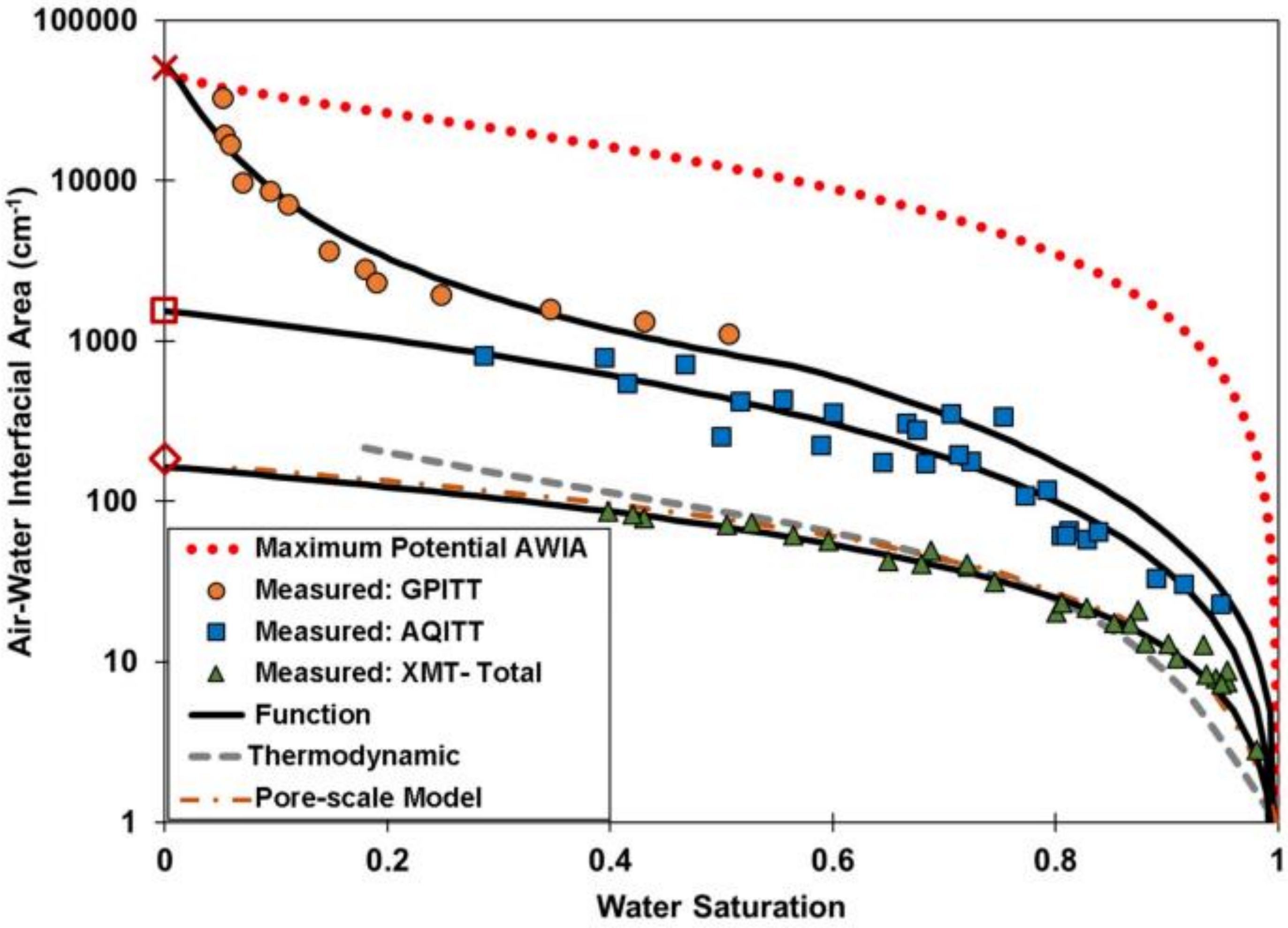
$$[0.83(1 - S_w)^2 + 0.16(1 - S_w)] * [761\,logNBSSA - 2025]$$

$$\text{SSA}\left[1 + (\alpha S_w)^a\right]^{-\left(2 - \frac{1}{a}\right)}$$

- Most relationships cannot capture AWIA at very low saturations
- Likely conservative due to less AWIA sorption, especially for heavier PFAS

AWIA Laboratory Measurement Methods

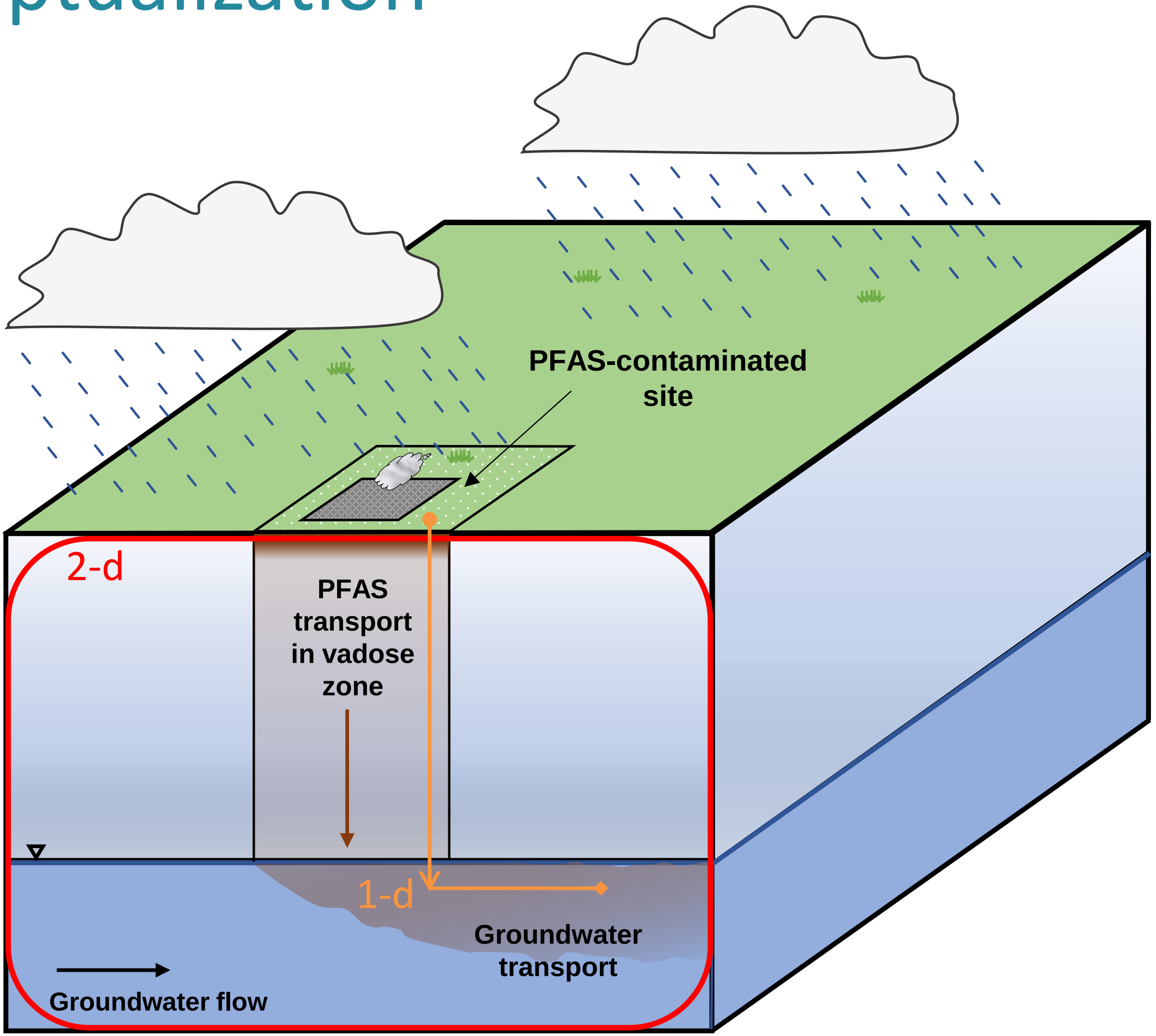
- Gas-phase interfacial tracer test – most representative
- Aqueous interfacial tracer test – not accurate at lower water saturations
- X-ray microtomography – does not capture surface roughness



Brusseau (pers. comm., 2024)

PFAS Fate & Transport - Conceptualization

- PFAS present within surface soils enters the unsaturated zone via a flux of infiltrating water
- PFAS is attenuated as it travels through the vadose zone and enters groundwater
- Leaching occurs from the vadose zone into groundwater
- PFAS is then transported through groundwater to downgradient receptor points



3-d conceptual site model

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Governing Equations – what’s new with PFAS

$$\frac{\partial(\theta C)}{\partial t} + \rho_b \frac{\partial C_s}{\partial t} + \boxed{\frac{\partial C_{aw}}{\partial t}} + \frac{\partial}{\partial z}(\theta v C) - \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) = 0$$

Solid-phase sorption

$$C_s = K_f C^N$$

Air-water interfacial sorption

$$C_{aw} = \frac{1}{R_g T} \frac{\sigma_0 b}{a + C} \boxed{A_{aw}} C = K_{aw} A_{aw} C$$

PFAS* retardation coefficient

$$R_{PFAS} = 1 + K_d \frac{\rho_b}{\theta} + \boxed{K_{aw} \frac{A_{aw}}{\theta}}$$

*Surfactant-induced flow

*Rate-limited sorption

*precursor transformation

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How does PFAS compare to other “legacy” pollutants?

- Migration in groundwater largely controlled by sorption to organic carbon, similar to other common organic contaminants
- Longer-chain PFAS tend to exhibit greater sorption and thus slower migration
- BUT, other factors are also important:
  - Slower migration/flushing above water table due to accumulation at air-water interface
  - Precursor transformation affects fate & transport
  - Low pH and presence of cations slows migration
  - Absorption into NAPL (e.g., fuel, solvents)

Organic carbon sorption affinity

Reduction in groundwater migration rate due to sorption

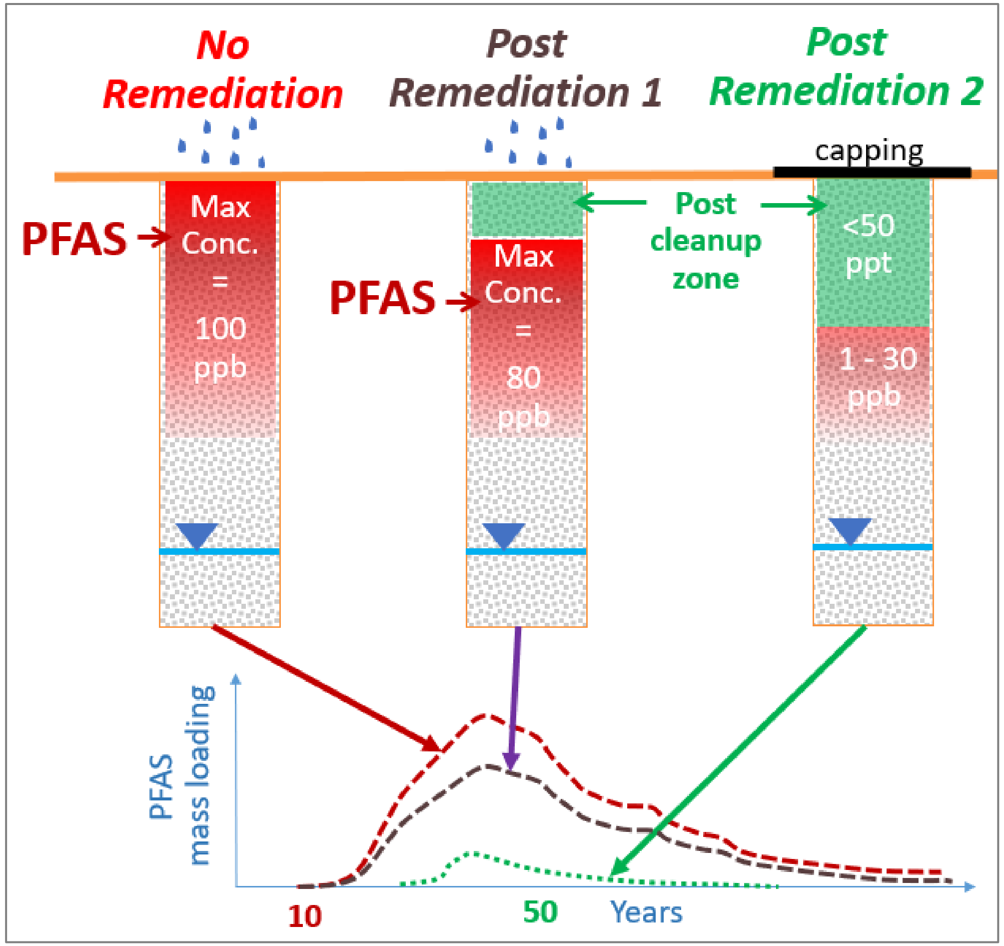
	K_{oc}	Retardation
benzene	66	5.1
PFOA	78	5.8
TCE	126	8.8
PFOS	631	40.1

Retardation values predicted for sandy soil with organic carbon content of 1% by weight

Modeling Tools

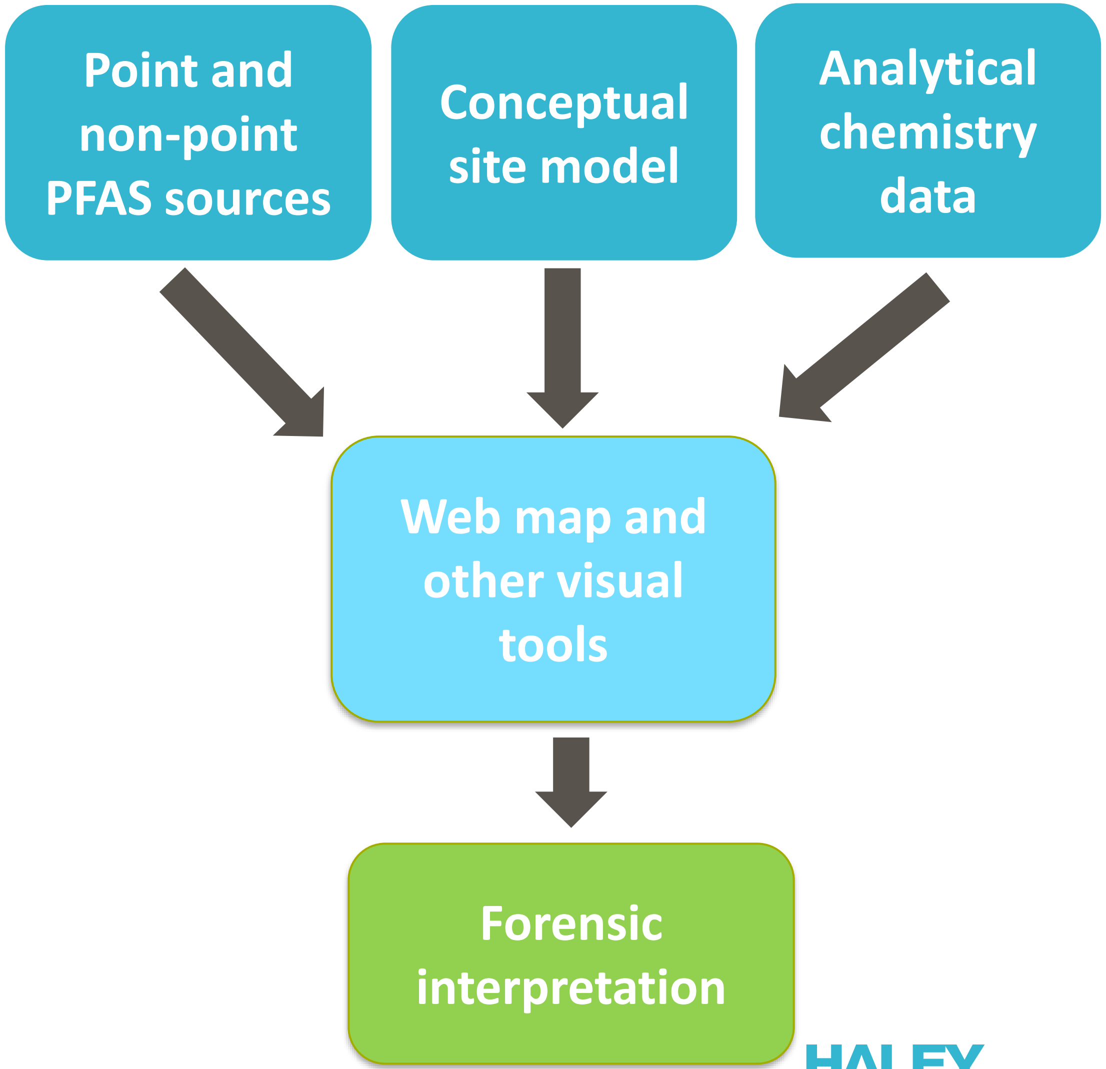
Modeling Objectives

- Characterization
- Vadose zone source remediation
  - soil-screening levels
  - leachate mass flux
- Groundwater plume management
  - saturated zone mass flux
  - concentration at compliance well
  - wellhead treatment
- Source identification & forensic analyses



Multiple lines of evidence are needed for PFAS source differentiation

- Several PFAS-impacted sites in proximity to point sources
- The same compounds have been used in many different products
- "Fingerprints" associated with specific industries (airport, wastewater treatment, landfills, industrial sources) have not been established
- PFAS source attribution cannot rely on chemistry data alone


Point and non-point PFAS sources

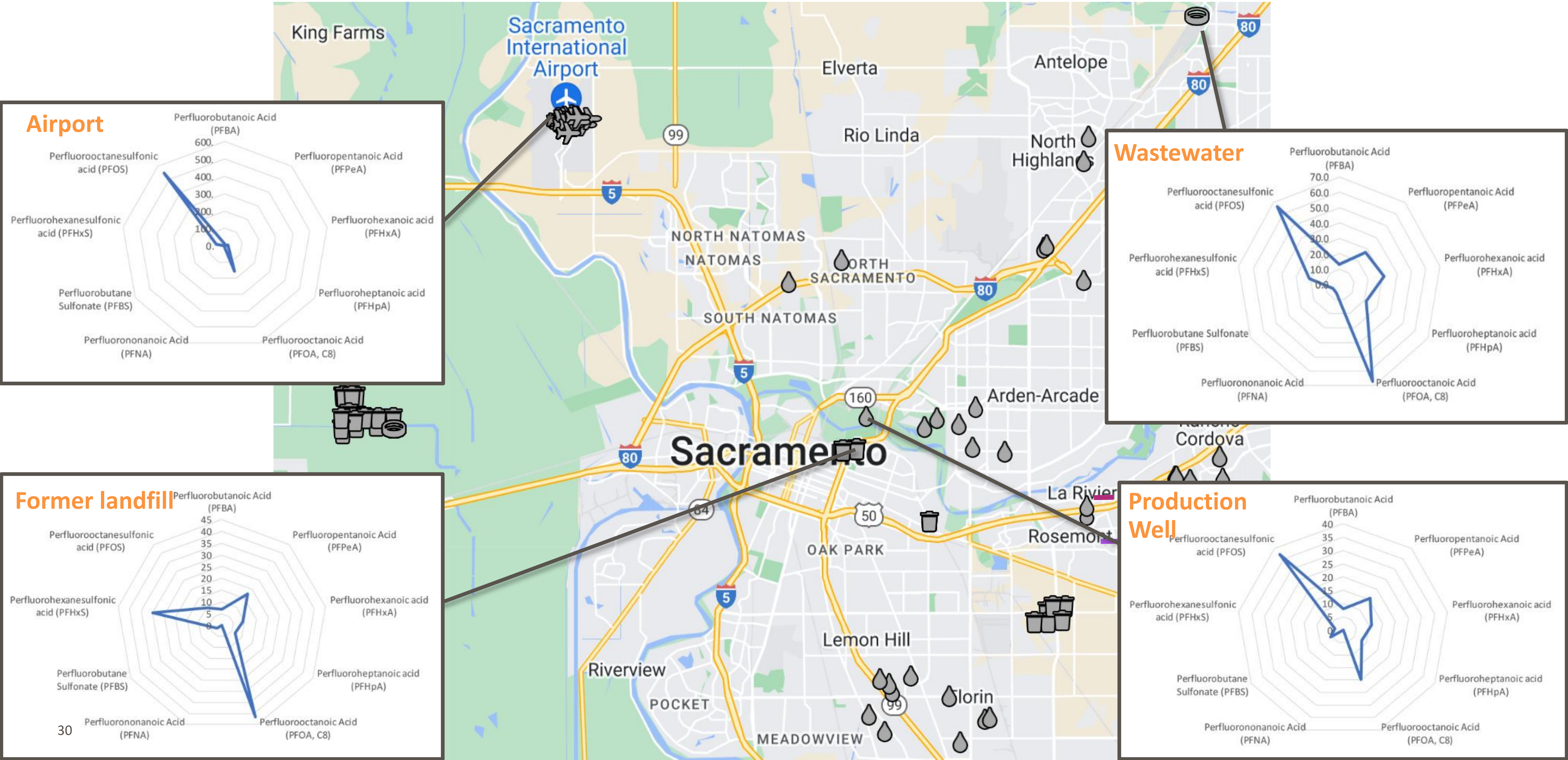
Conceptual site model

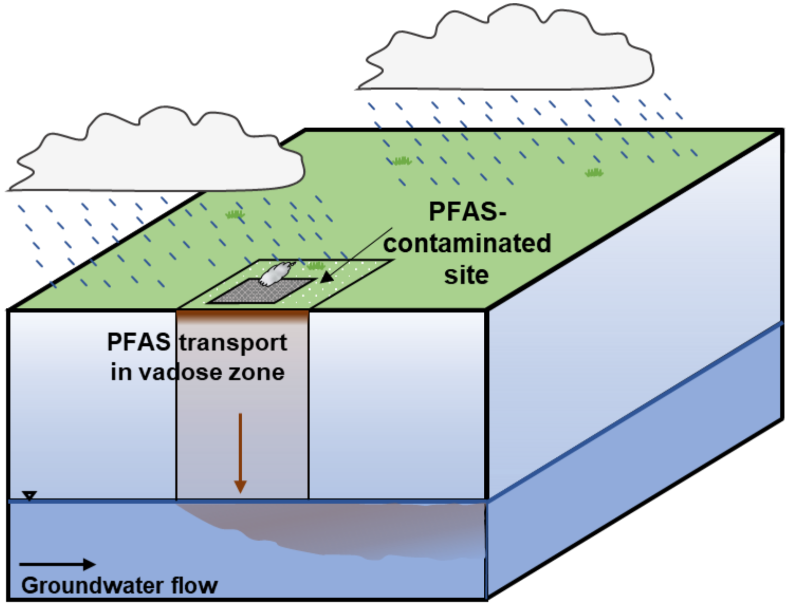
Analytical chemistry data

Web map and other visual tools

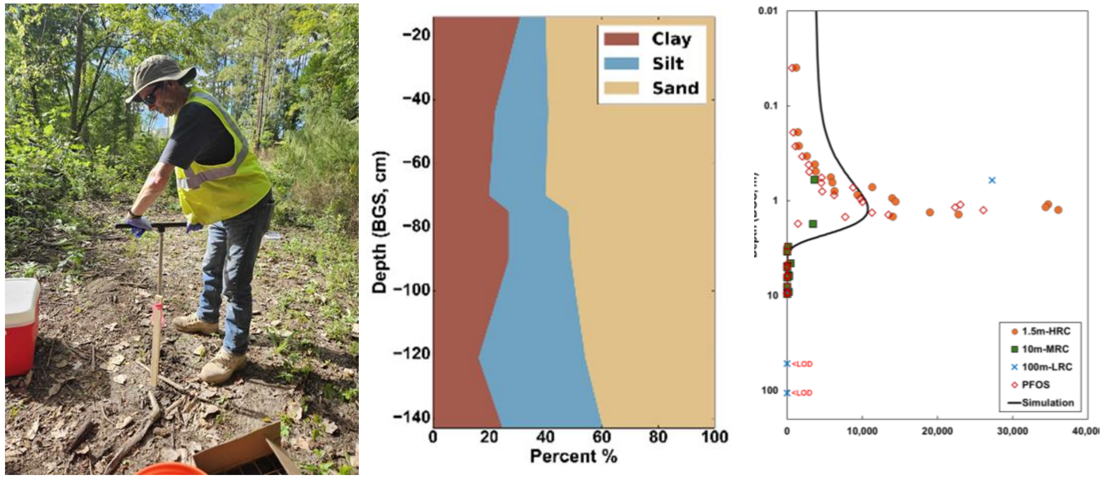
Forensic interpretation

Source identification (For illustration purposes only)

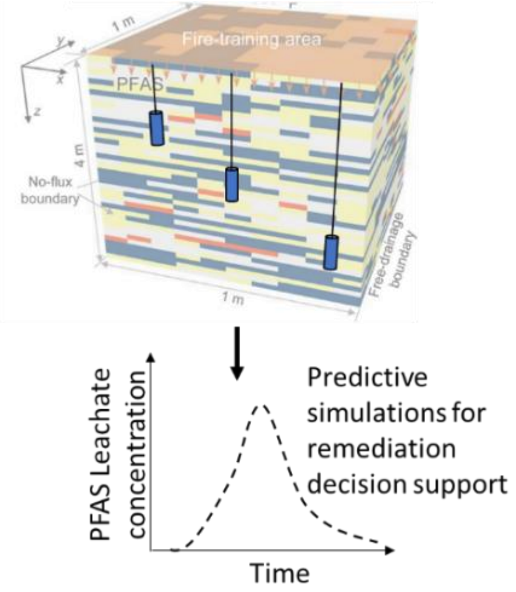




Conceptual Site Model



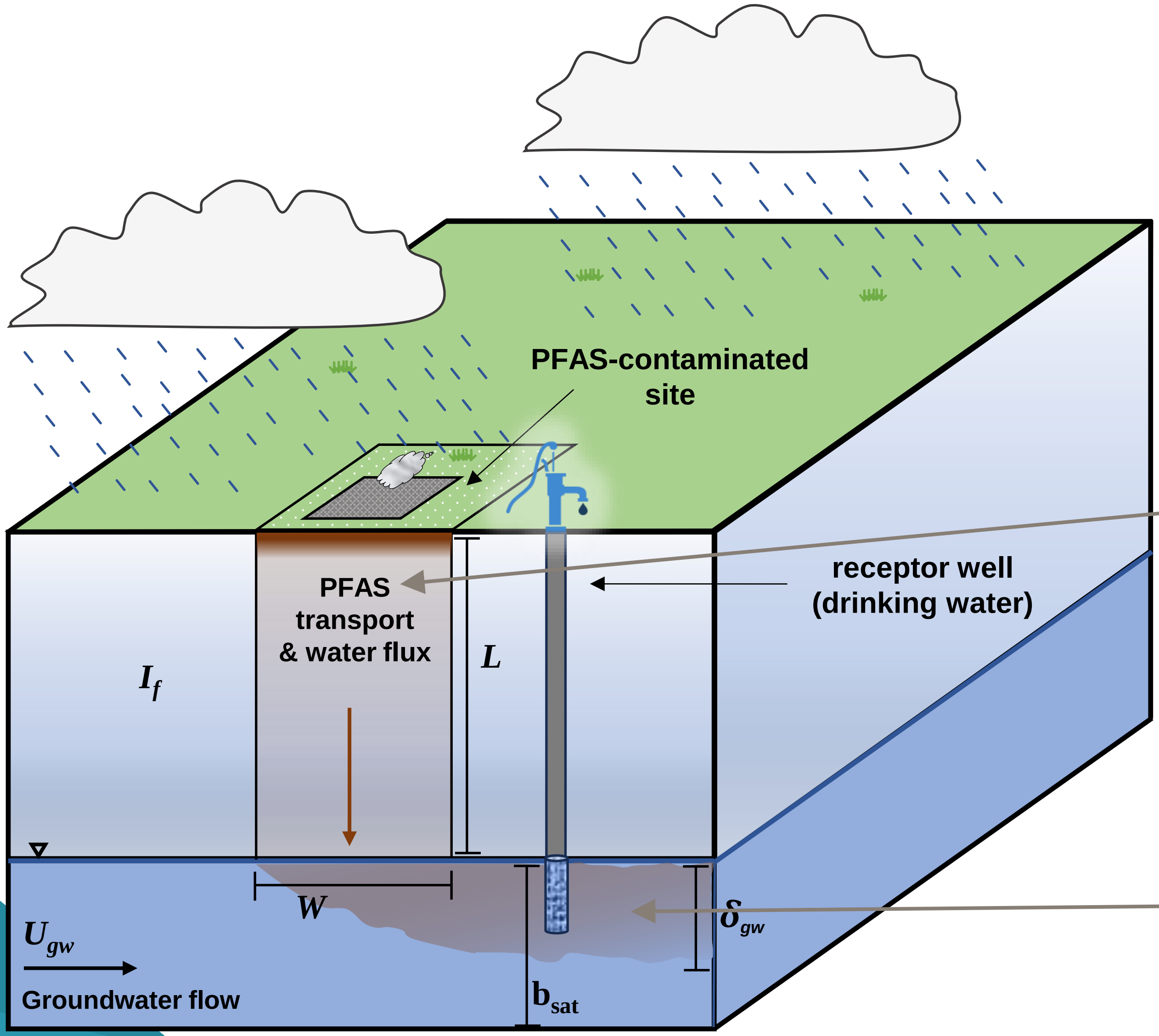
Characterization

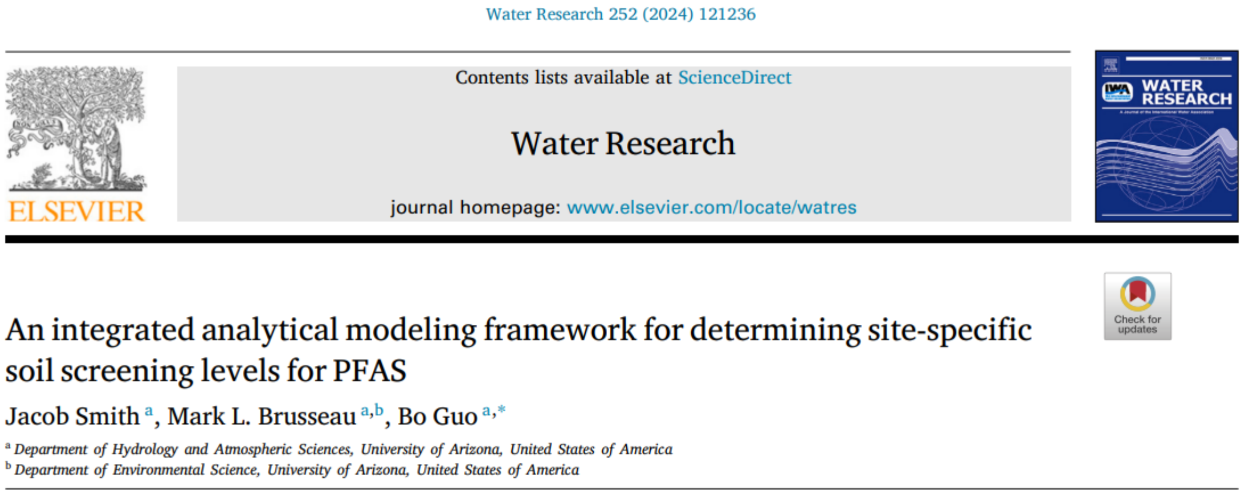


Predictive simulations for remediation decision support

Numerical Modeling

1-D Analytical Modeling Tool

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journal homepage: www.elsevier.com/locate/watres

ELSEVIER

An integrated analytical modeling framework for determining site-specific soil screening levels for PFAS

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[b] Department of Environmental Science, University of Arizona, United States of America

- **Vadose-zone –** simplified analytical model developed by Guo et al., 2022
  - Attenuates PFAS in the vadose zone
  - PFAS transport driven by infiltration
  - Derives PFAS leachate concentrations
- **Groundwater –** simple mixing, box-model
  - Dilutes PFAS leachate concentrations

Vadose Zone Mathematical Model

- Analytical solution to a PFAS-specific, advection-dispersion equation (Guo et al.,2022)
  - Transport driven by 1-D, steady-state water flow
  - Homogenous, uniformly unsaturated vadose zone

$$\boxed{\beta(1+R_s+R_{aw})}\frac{\partial C}{\partial t}+\boxed{\frac{\rho_b\alpha_s}{\theta}\left[(1-F_s)\,K_dC-C_{s,2}\right]}+\frac{\partial}{\partial z}(vC)-\frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right)=0$$

$$R_s=\frac{\rho_b K_d}{\theta} \qquad R_{aw}=\frac{K_{aw}A_{aw}}{\theta}$$

(Retardation)

$$\boxed{\frac{\mathrm{d}C_{s,2}}{\mathrm{d}t}}=\alpha_s\left[(1-F_s)\,K_dC-C_{s,2}\right]$$

(PFAS concentration in kinetic solid-phase domain)

$\beta=(1+F_sR_s+R_{aw})/R$
R = Retardation Factor (-)
C = Aqueous conc. (μmol/cm^3)
t = Temporal resolution (s)
ρ_b = Bulk density (g/cm^3)
α_s = First order rate const. kinetic (-)
θ = Water content (-)
F_s = Fraction of instant sorption (-)
K_d = Solid adsorption coefficient (cm^3/g)
$C_{s,2}$ = Conc. in kinetic ads. domain (μmol/cm^3)
z = Vertical resolution (cm)
v = Interstitial porewater velocity (cm/s)
D = Dispersion coefficient (cm^2/s)

- Two-domain model, in which solid-phase adsorption has both **equilibrium** and **kinetic** sorption
- Linear adsorption at solid –water and air–water interfaces

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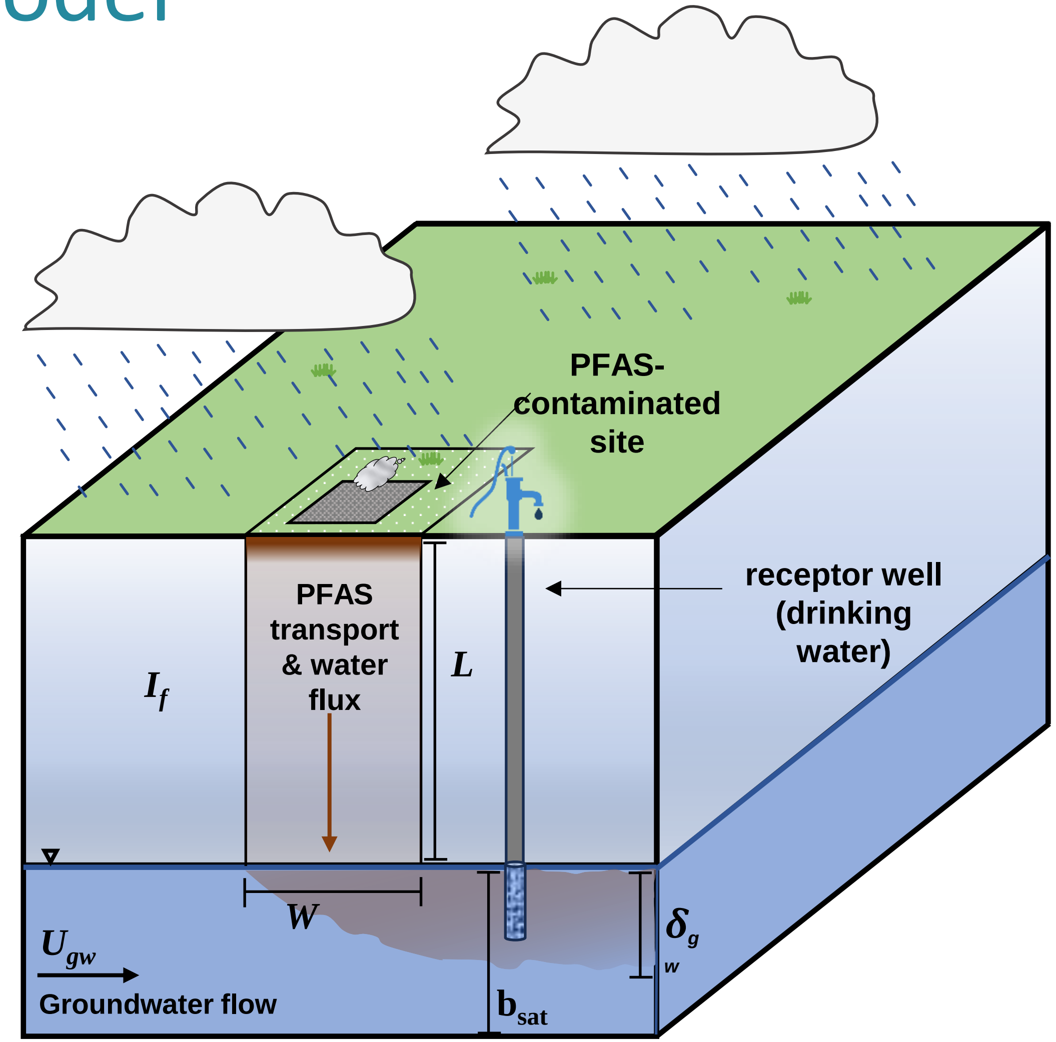
Key Assumptions: 1-d Analytical Model

1. One-dimensional, steady-state water infiltration;
2. Homogenous, uniformly unsaturated vadose zone;
3. Linear sorption at solid–water and air–water interfaces;
    - two-domain approach to represent kinetic solid-phase adsorption
    - air–water interfacial adsorption is considered instantaneous
4. Partitioning to vapor/air phase neglected;
5. Production of PFAS due to precursor transformation not considered

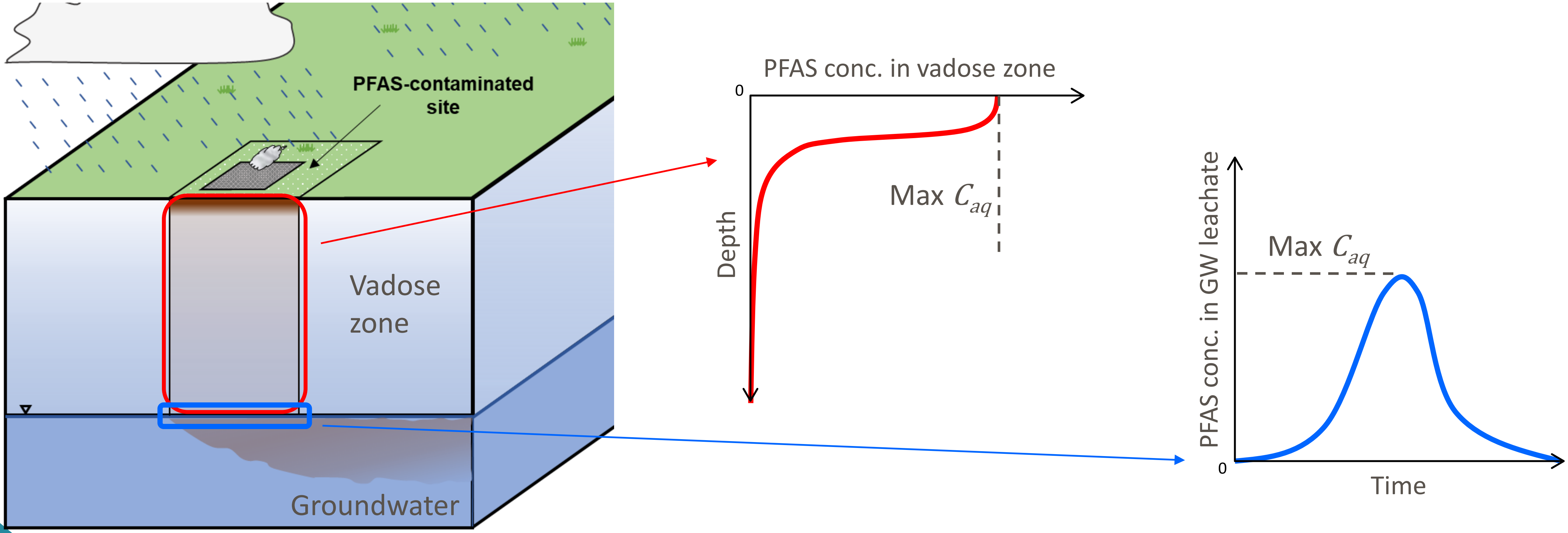


Key Inputs: 1-d Model

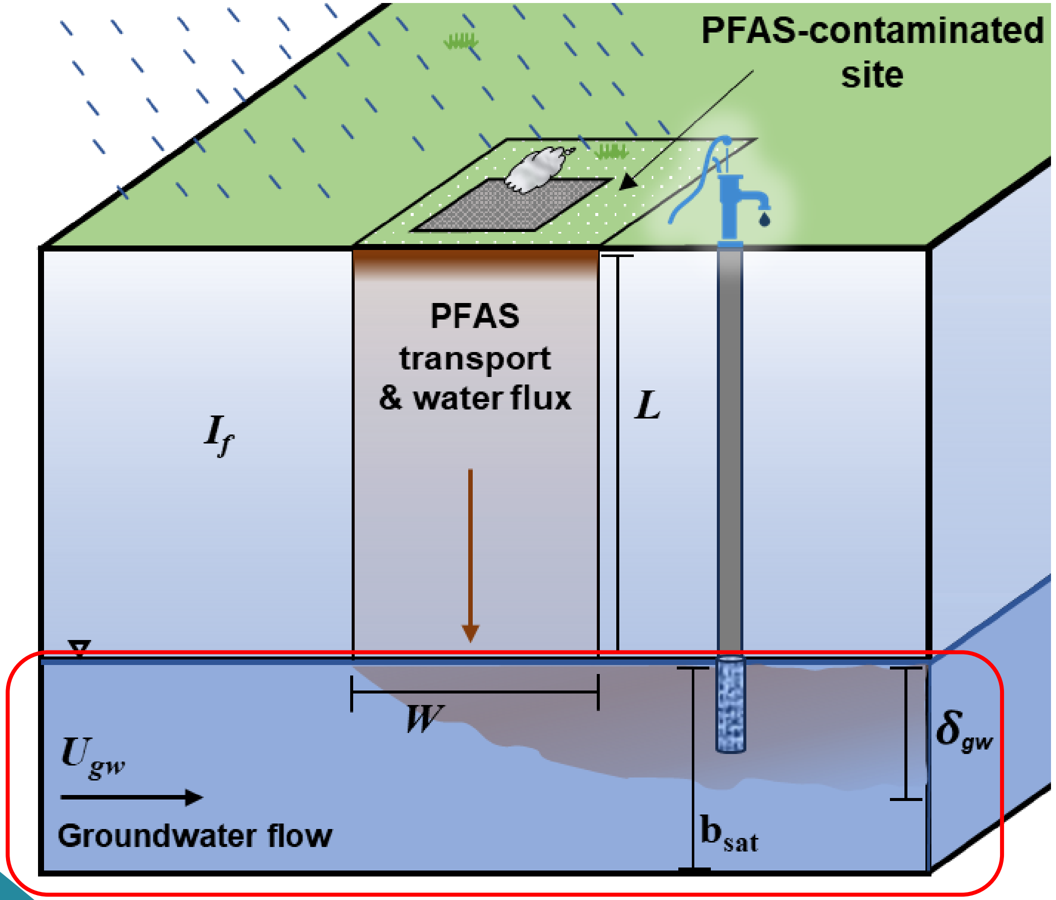
- Site-specific soil and hydraulic properties
  - Soil moisture, soil characteristic parameters, infiltration, conductivity, air-water interfacial area
- PFAS specific properties
  - Molecular weight, sorption coefficients at air-water and solid-water interfaces, surface tension parameters
- Initial soil or aqueous PFAS conditions
- Any number of depth-discrete data points can be used
  - Single point at surface;
  - Multiple concentrations at depth forming a complete soil profile
  - Model can interpolate incomplete soil concentration profiles between discrete data points

Vadose Zone Mathematical Model

Derives a **Vadose-Zone Attenuation Factor** $(AF_{vz}) = \dfrac{\text{Max } C_{aqueous} \text{ of } \boxed{\text{PFAS in vadose zone}}}{\text{Max } C_{aqueous} \text{ of } \boxed{\text{PFAS discharged to GW}}}$



Groundwater Dilution Model



USEPA standard Dilution Factor (*DF*) model (1996)

- Dilutes PFAS leachate passed on from vadose-zone model
- Homogenous, isotropic, unconfined aquifer
- Facilitated transport not considered
- Receptor point is adjacent to source zone

$$DF = 1 + \frac{U_{gw}\delta_{gw}}{I_f W}$$

$$\delta_{gw} = \sqrt{2\alpha_v W} + b_{sat}\left[1 - \exp\left(\frac{-I_f W}{U_{gw} b_{sat}}\right)\right]$$

δ_{gw} = Mixing zone depth (cm)
α_v = Vert. dispersivity (cm)
W = Lateral width of site (cm)
b_{sat} = Saturated thickness (cm)
I_f = Net infiltration (cm/yr)
U_{gw} = GW Darcy velocity (cm/yr)

Integrated Framework

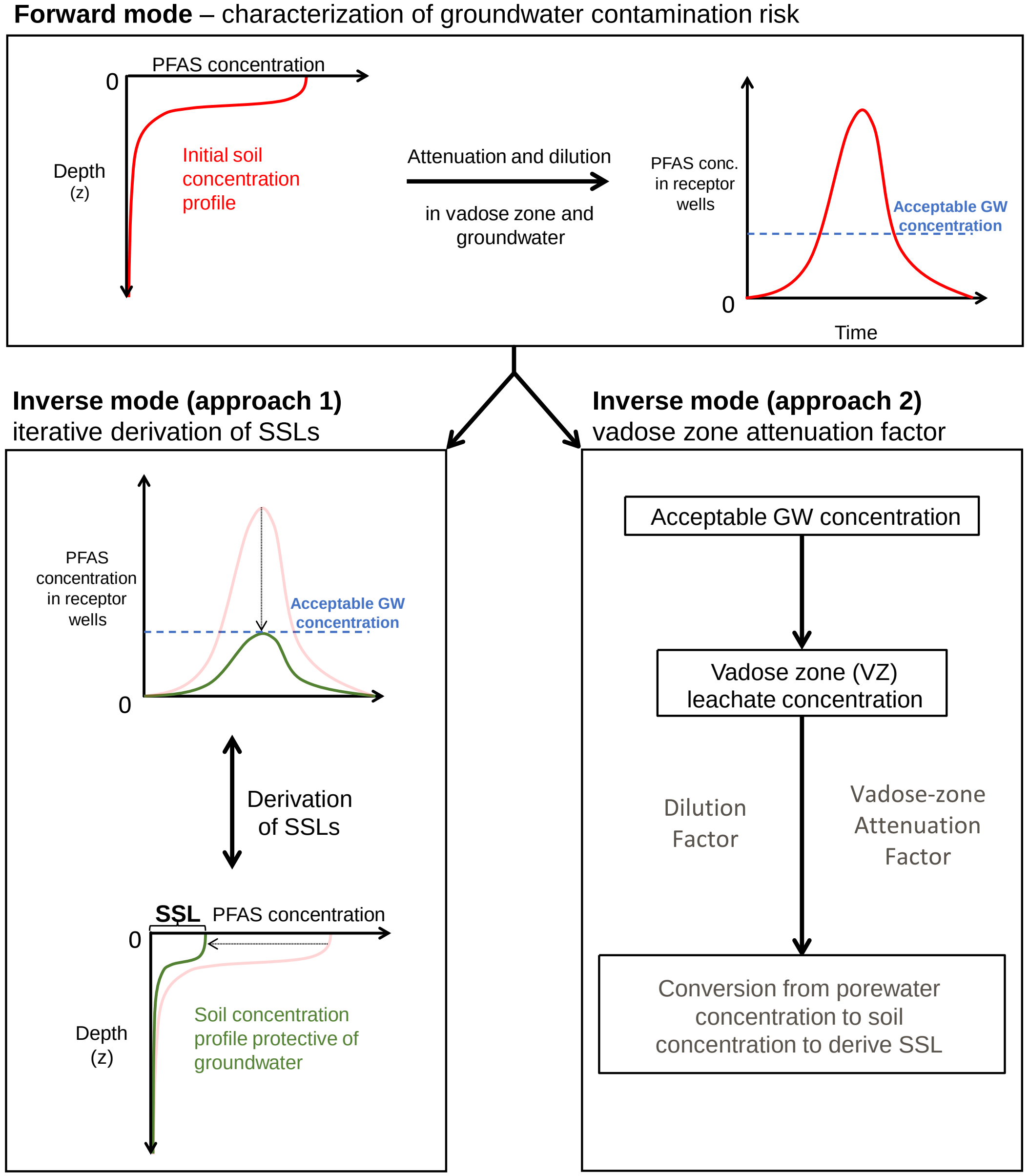
Forward Mode

- Determines groundwater PFAS concentrations in time
- Derives site-specific Vadose-Zone Attenuation Factor

Inverse Modes

- Derive site-specific SSLs

Extracting the AF_{VZ} from the forward mode allows for further simplification of the solution.



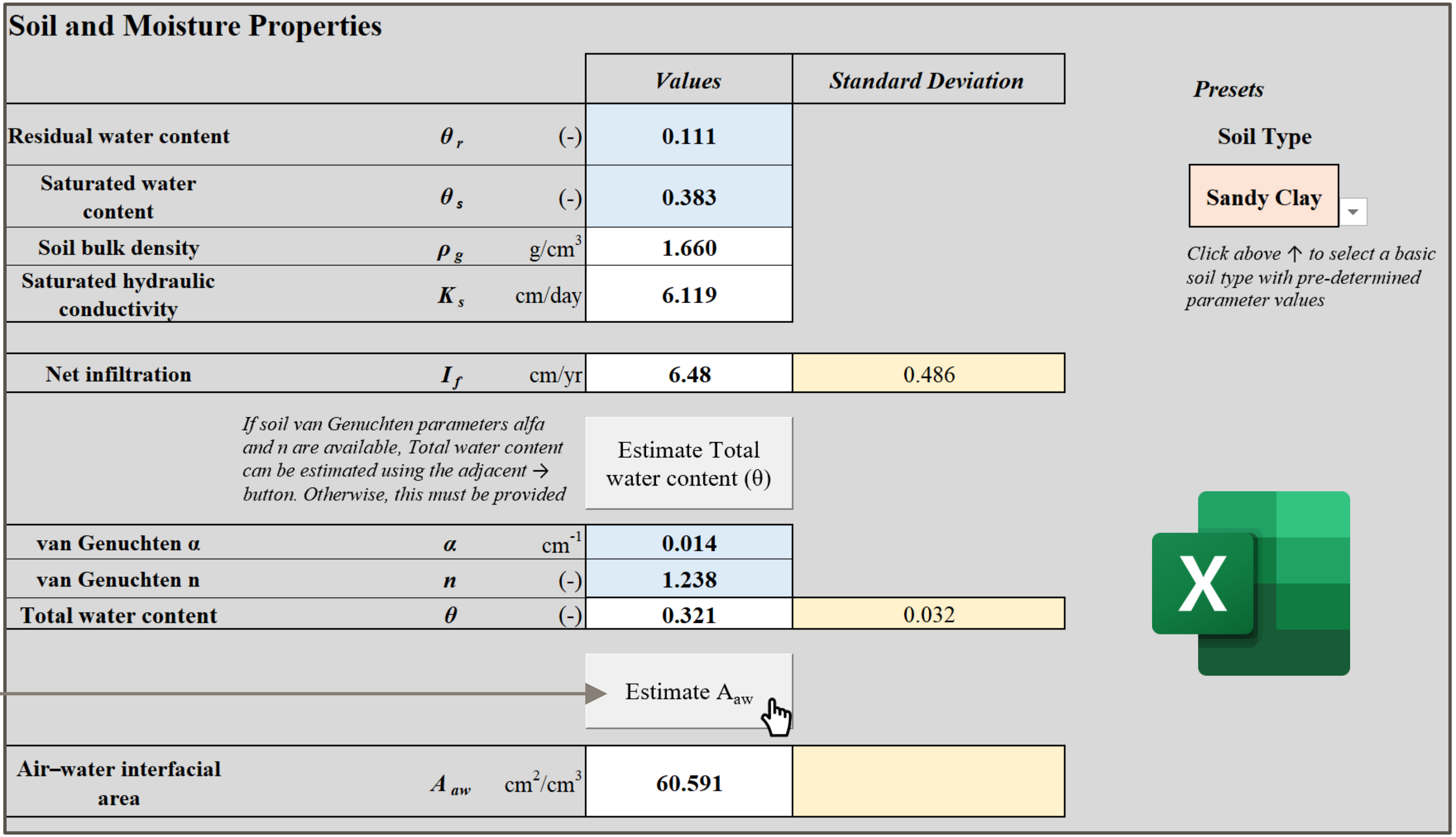
Forward mode – characterization of groundwater contamination risk

Inverse mode (approach 1)
iterative derivation of SSLs

Inverse mode (approach 2)
vadose zone attenuation factor

Excel-based Modeling Framework

- Excel tool has a **clear, and simple user-interface.**
- Users input data or can extract soil characteristics from Hydrus soil database
- Tool has assistive **estimation ability** for certain parameters.



Soil and Moisture Properties

			Values	*Standard Deviation*
Residual water content	θ_r	(-)	**0.111**	
Saturated water content	θ_s	(-)	**0.383**	
Soil bulk density	ρ_g	g/cm^3	**1.660**	
Saturated hydraulic conductivity	K_s	cm/day	**6.119**	
Net infiltration	I_f	cm/yr	**6.48**	0.486
van Genuchten α	α	cm^{-1}	**0.014**	
van Genuchten n	n	(-)	**1.238**	
Total water content	θ	(-)	**0.321**	0.032
Air–water interfacial area	A_{aw}	cm^2/cm^3	**60.591**	

If soil van Genuchten parameters alfa and n are available, Total water content can be estimated using the adjacent → button. Otherwise, this must be provided

Presets

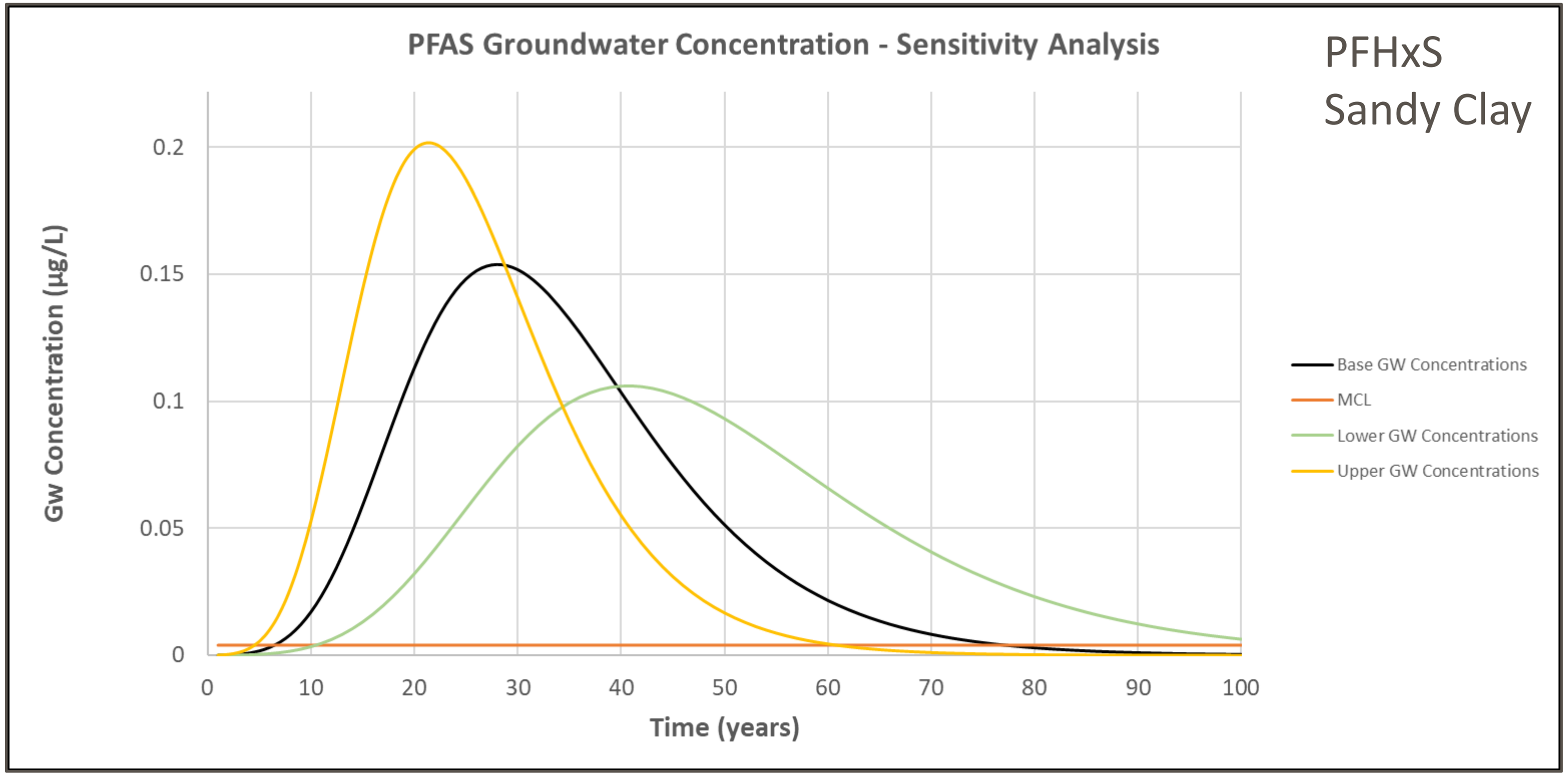
Soil Type

Sandy Clay

Click above ↑ to select a basic soil type with pre-determined parameter values

Module 1 – Sensitivity Analysis

- This module allows users to perturb individual or multiple parameters.
- Three simulations are run side-by-side.
- Direct analysis of parameter sensitivity in SSLs and PFAS groundwater concentrations.



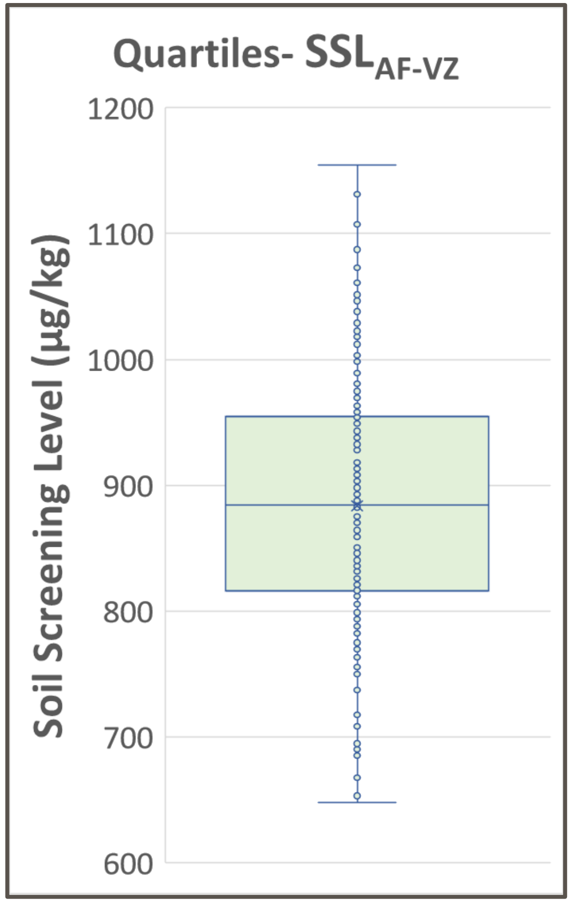
30% variation in solid–phase sorption coefficient ***K_d***

Results

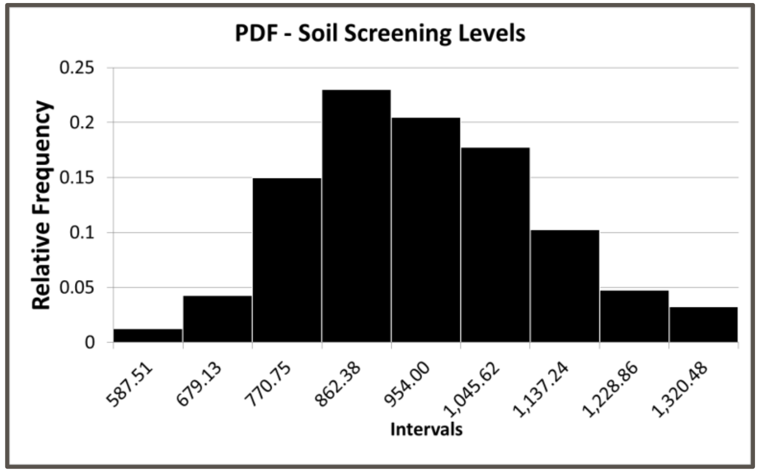
			Lower	**Base**	**Upper**
Soil Screening Level (PFAS-Leach)	***SSL***	µg/kg	3.39	2.34	1.78

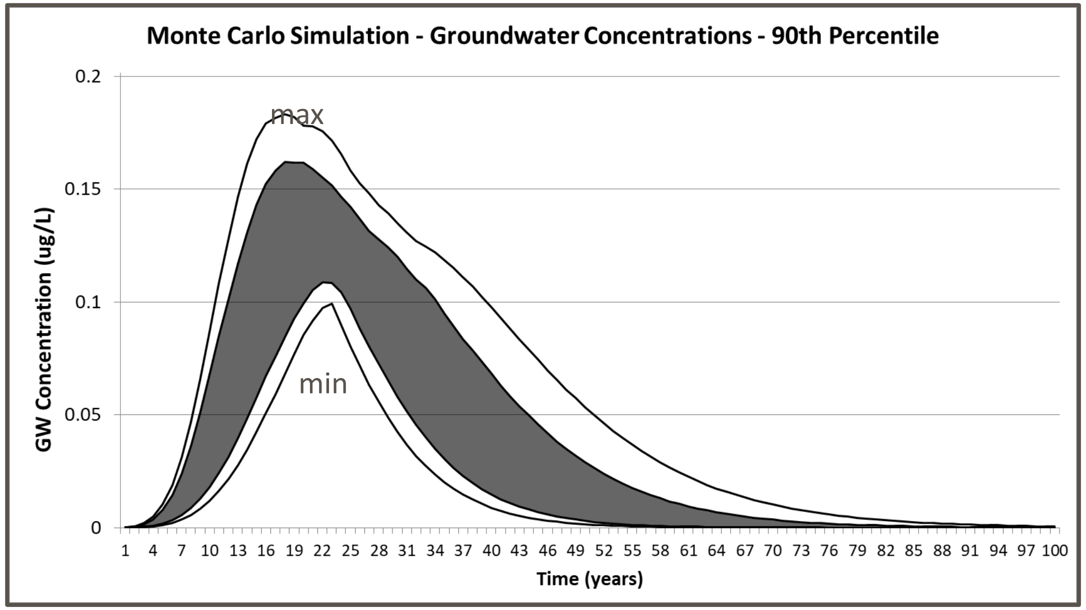
Module 2 – Monte Carlo Simulation

- Monte Carlo Simulation accounts for total uncertainty in parameter space
- Selected parameters can be sampled from a Normal distribution
- Percentile ranges of groundwater concentrations and SSLs are displayed


Quartiles- SSL$_{AF\text{-}VZ}$

PFPeA – Sandy Clay


PDF - Soil Screening Levels

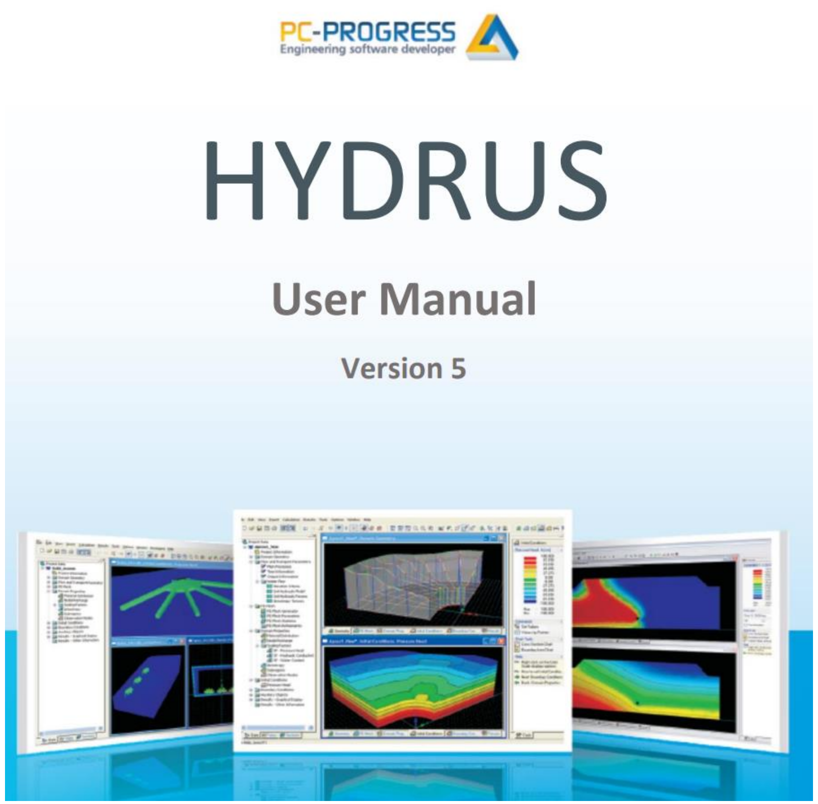

Monte Carlo Simulation - Groundwater Concentrations - 90th Percentile

Summary – 1-d Model

- Analytical model is fast and computationally efficient
  - Monte-Carlo simulation
  - Facilitates sensitivity analysis
- Simplifying assumptions limit the effective use cases of the 1-d model
  - Not applicable at site with significant heterogeneity or preferential flow
    - *Ensemble approaches can be used to approximate these cases*
- Excel-based modeling framework is user friendly, and straight-forward
- Can derive site-specific PFAS concentrations in groundwater
  - Leachate concentrations
  - Soil concentration profiles
  - Temporal and spatial PFAS distribution/mass transport

PFAS Transport 2D and 3D models

- Hydrus
  - Air-water interfacial sorption (limited options)
  - Rate-limited adsorption
- MODFLOW-USG
  - Air-water interfacial sorption
  - No rate-limited sorption
- PFLOTRAN

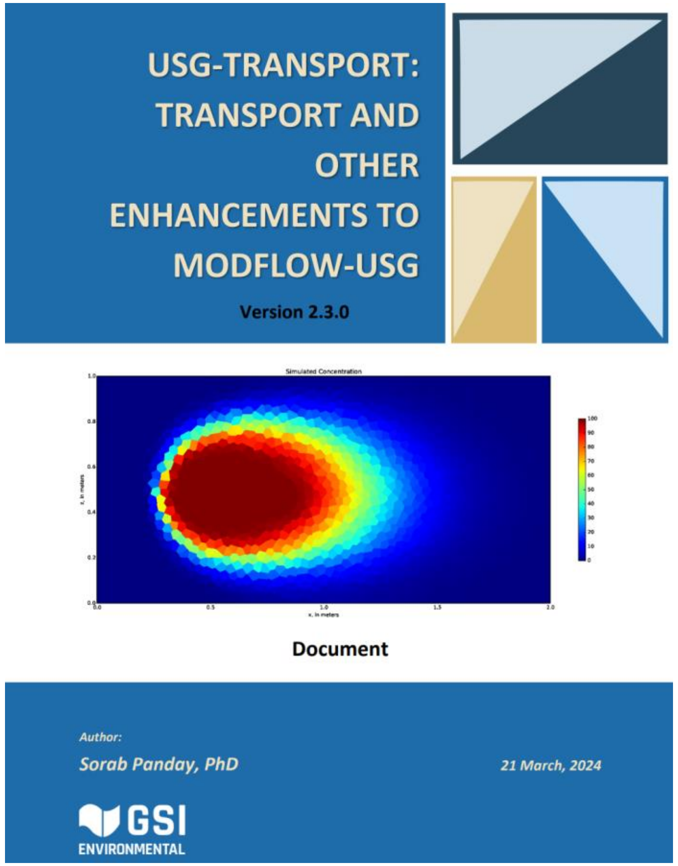


PC-PROGRESS
Engineering software developer

HYDRUS

User Manual

Version 5



USG-TRANSPORT: TRANSPORT AND OTHER ENHANCEMENTS TO MODFLOW-USG

Version 2.3.0

Document

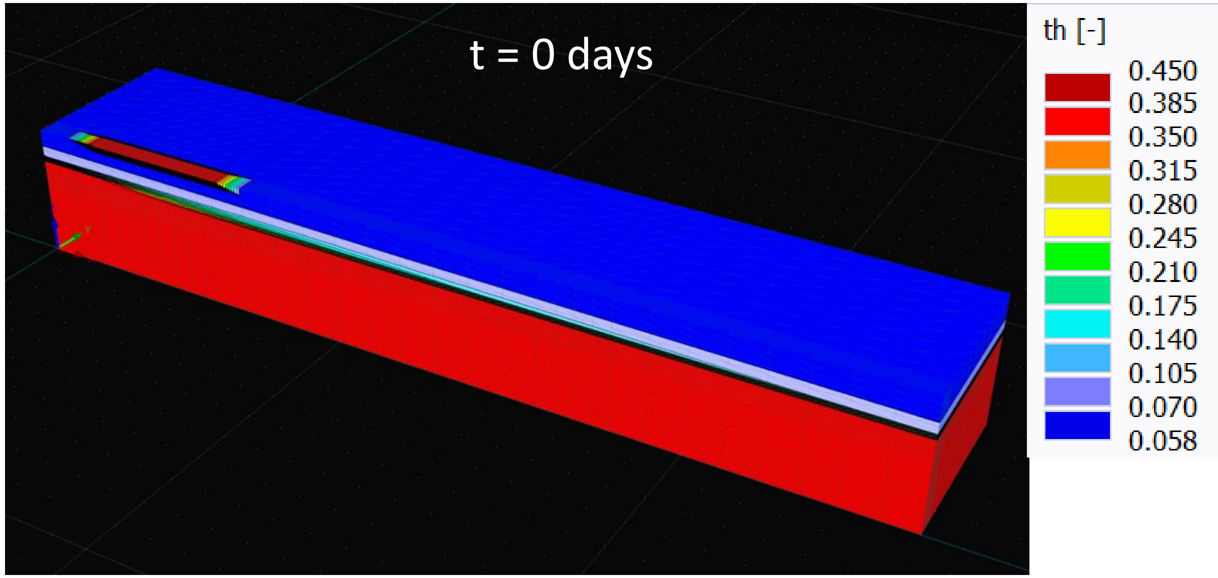
Author:
Sorab Panday, PhD

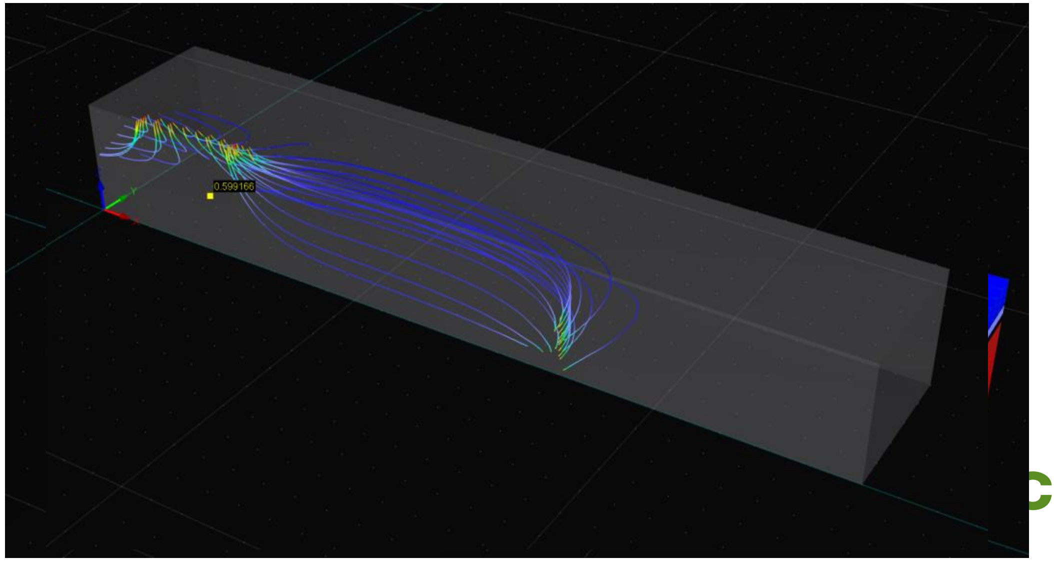
21 March, 2024

GSI ENVIRONMENTAL

Hydrus 3D Example – PFAS from Landfill Leachate

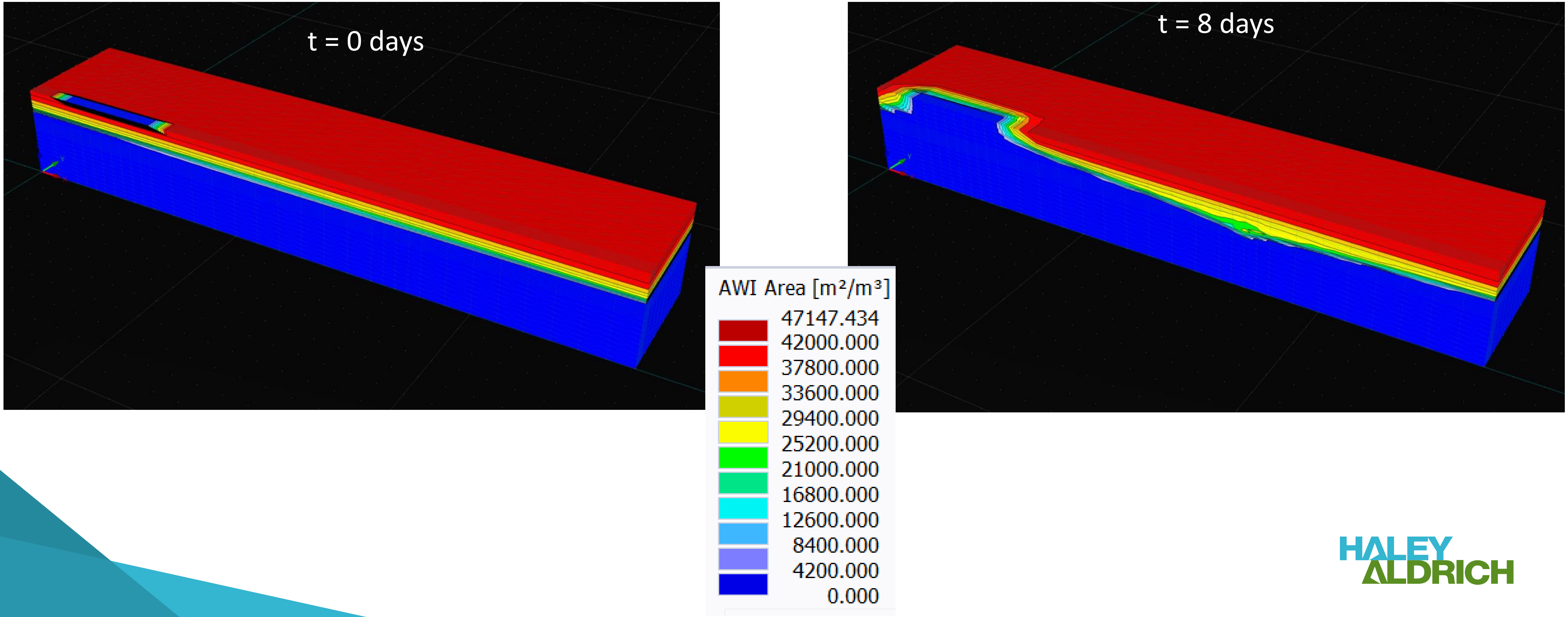
- PFAS in landfill leachate released over a 24-hour period
- Simulation time of 200 hours
- Air-water interfacial sorption only
- Pumping well downgradient



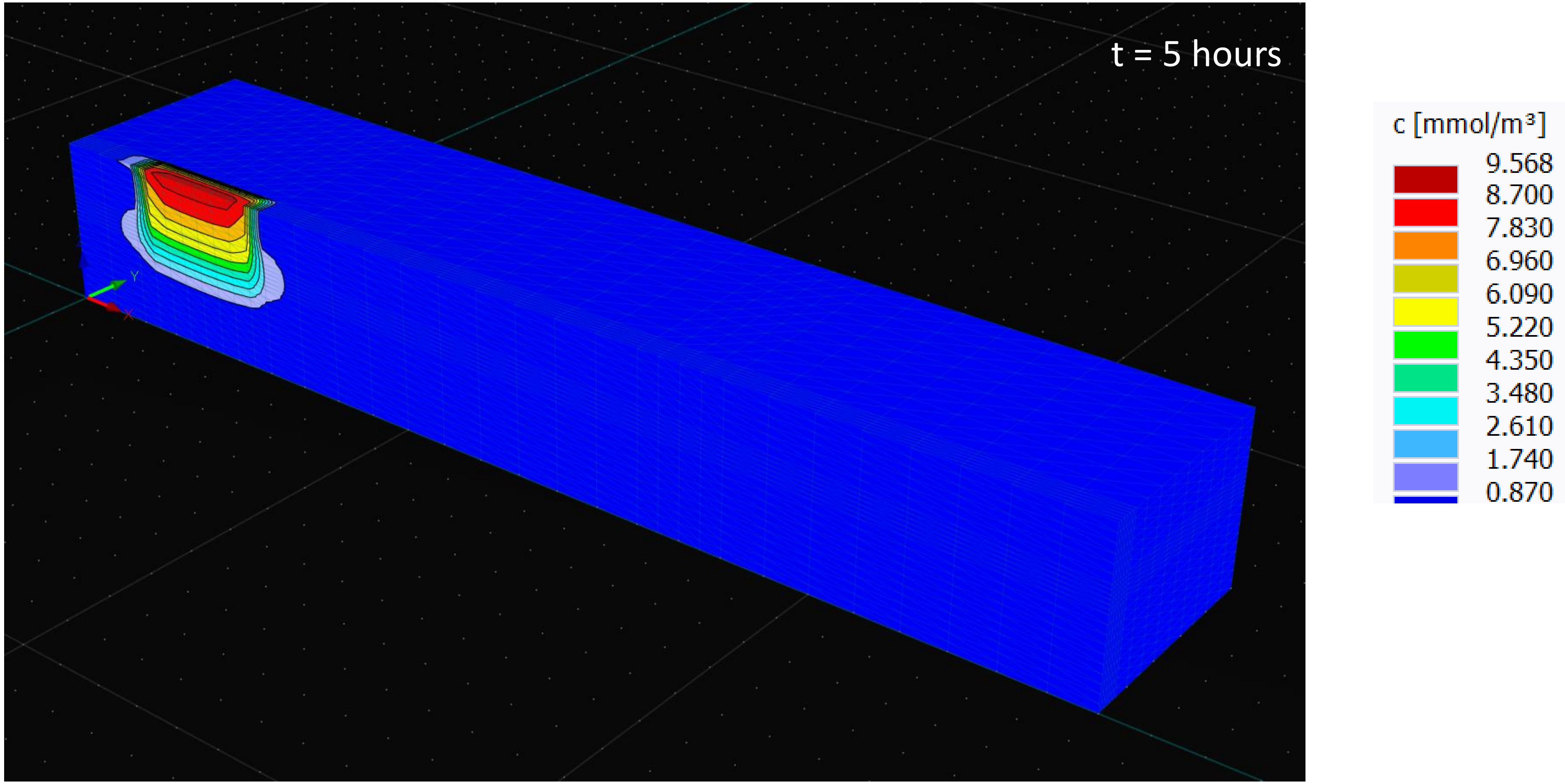


Hydrus 3D Example – PFAS from Landfill Leachate

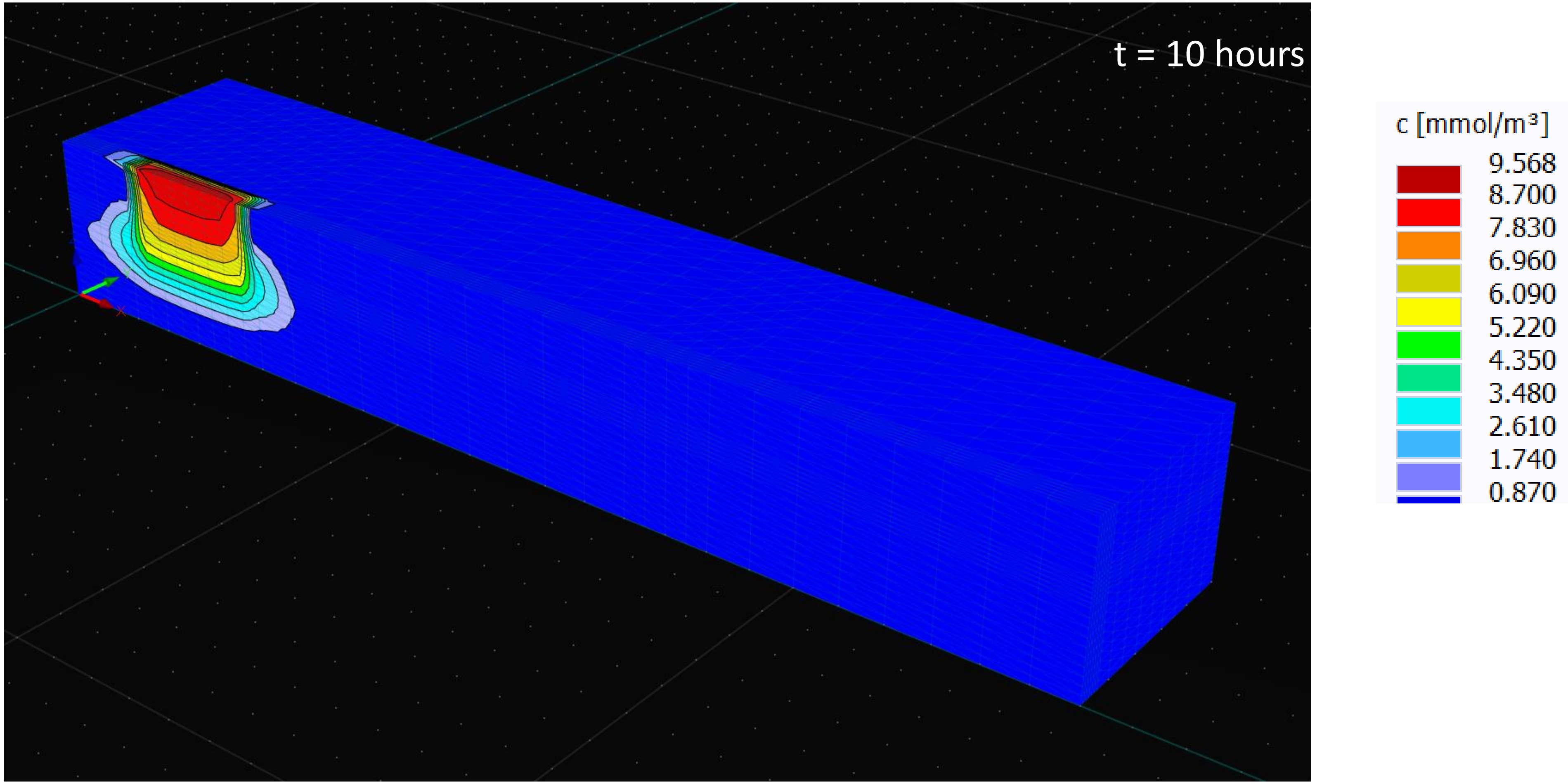
Air-water interfacial area follows same pattern as moisture content



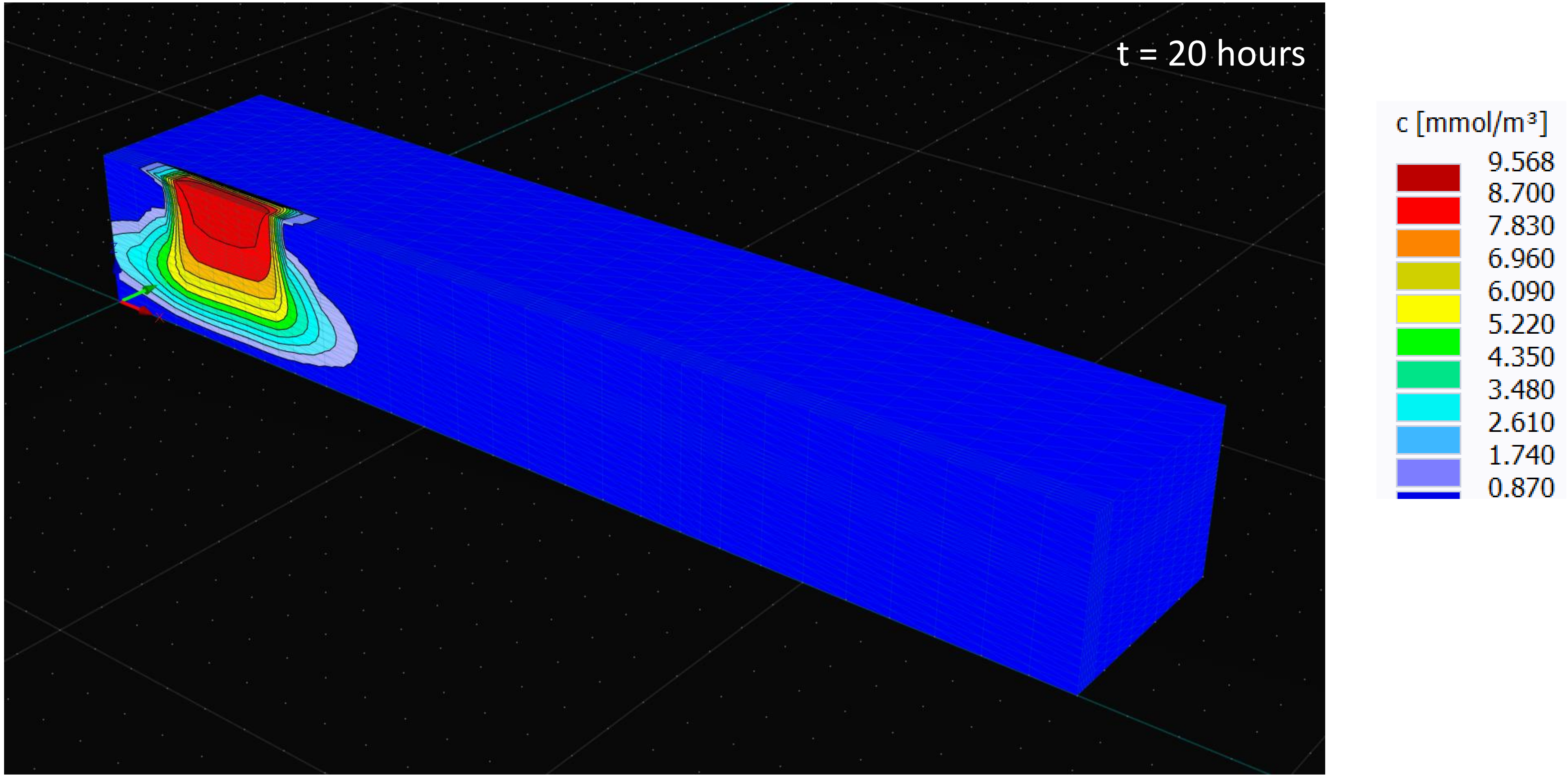
Hydrus 3D Example – PFAS from Landfill Leachate



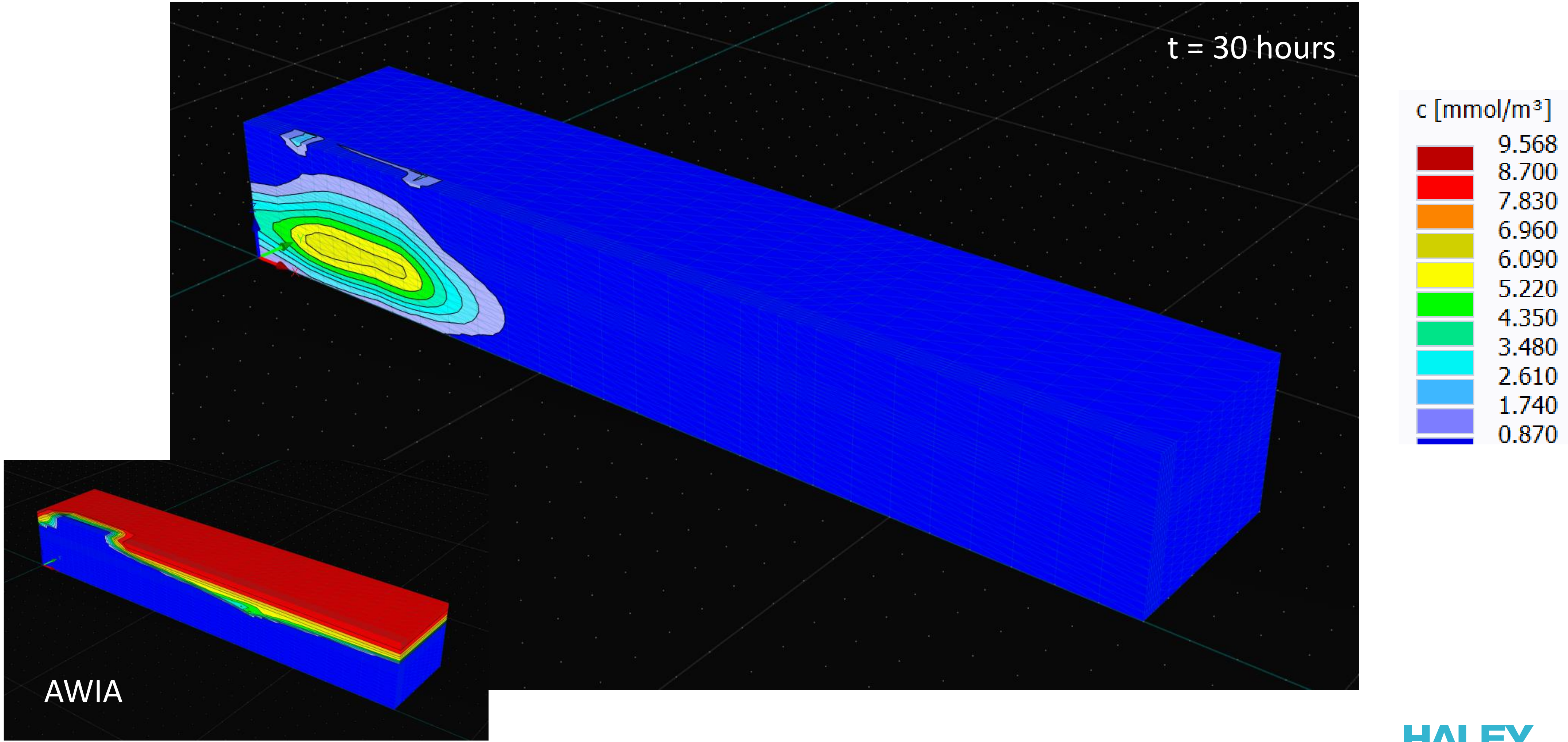
Hydrus 3D Example – PFAS from Landfill Leachate



Hydrus 3D Example – PFAS from Landfill Leachate

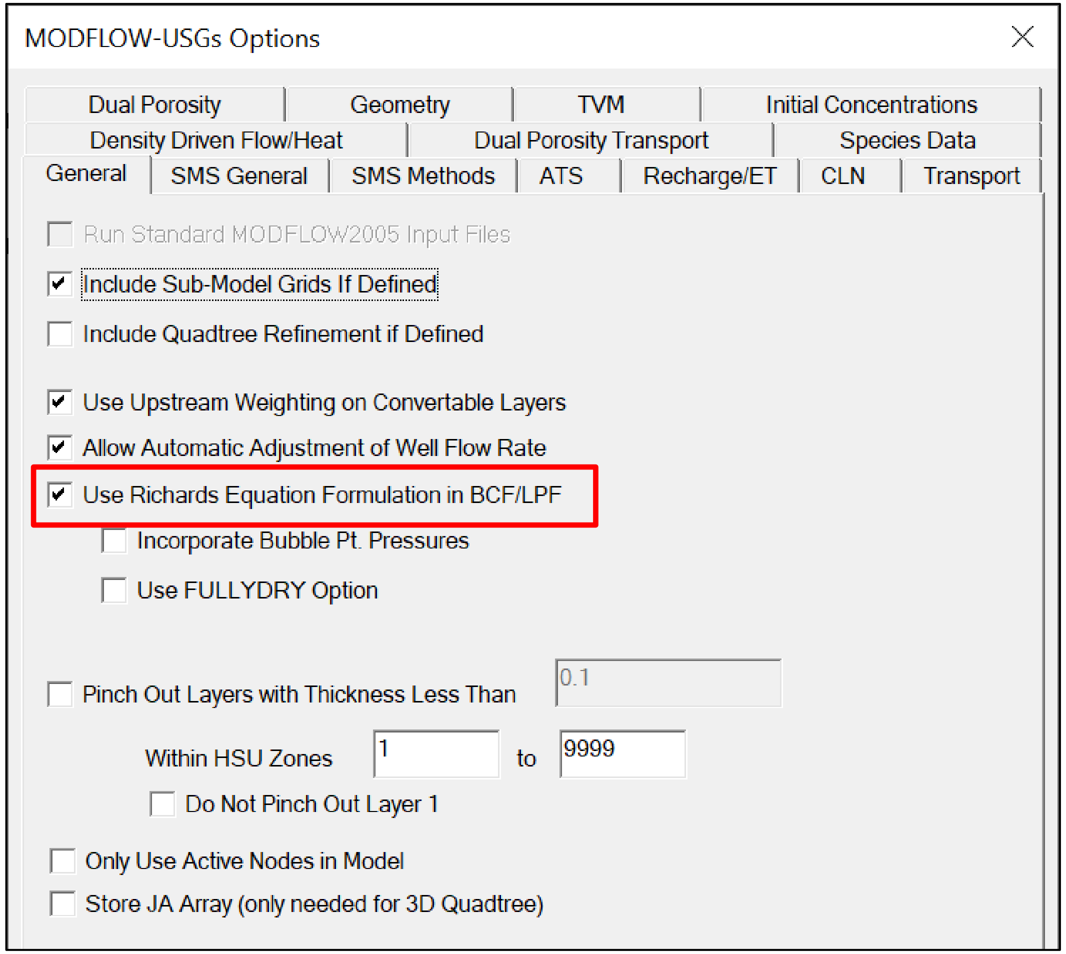


Hydrus 3D Example – PFAS from Landfill Leachate



MODFLOW-USG PFAS Option

- USG-Transport version 2.3.0 (Panday 2024)
- Unsaturated zone flow and transport
  - Richard's equation
    - Brooks-Corey
    - van Genuchten
  - PFAS transport
- Most of the options available in Groundwater Vistas version 9



MODFLOW-USGs Options

☐ Run Standard MODFLOW2005 Input Files

☑ Include Sub-Model Grids If Defined

☐ Include Quadtree Refinement if Defined

☑ Use Upstream Weighting on Convertable Layers

☑ Allow Automatic Adjustment of Well Flow Rate

☑ Use Richards Equation Formulation in BCF/LPF

☐ Incorporate Bubble Pt. Pressures

☐ Use FULLYDRY Option

☐ Pinch Out Layers with Thickness Less Than 0.1

Within HSU Zones 1 to 9999

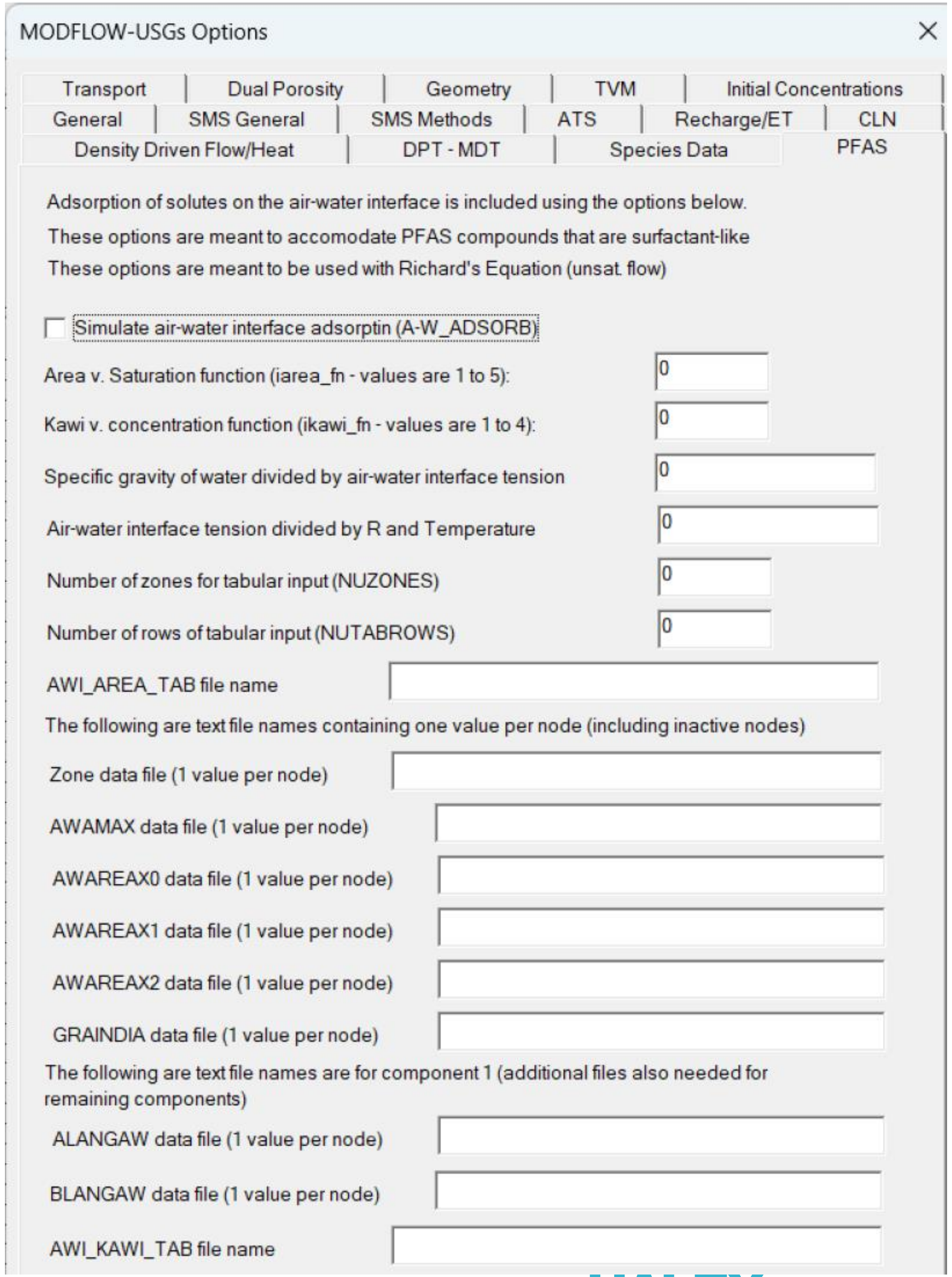
☐ Do Not Pinch Out Layer 1

☐ Only Use Active Nodes in Model

☐ Store JA Array (only needed for 3D Quadtree)

PFAS Transport

- AWIA-saturation relationship (iarea_fn)
  - linear and non-linear S_w
  - tabular input
- Air-water partitioning coefficient (ikawi_fn)
  - Langmuir isotherm
  - tabular input



Adsorption of solutes on the air-water interface is included using the options below.
These options are meant to accomodate PFAS compounds that are surfactant-like
These options are meant to be used with Richard's Equation (unsat. flow)

☐ Simulate air-water interface adsorptin (A-W_ADSORB)

Area v. Saturation function (iarea_fn - values are 1 to 5): 0

Kawi v. concentration function (ikawi_fn - values are 1 to 4): 0

Specific gravity of water divided by air-water interface tension 0

Air-water interface tension divided by R and Temperature 0

Number of zones for tabular input (NUZONES) 0

Number of rows of tabular input (NUTABROWS) 0

AWI_AREA_TAB file name

The following are text file names containing one value per node (including inactive nodes)

Zone data file (1 value per node)

AWAMAX data file (1 value per node)

AWAREAX0 data file (1 value per node)

AWAREAX1 data file (1 value per node)

AWAREAX2 data file (1 value per node)

GRAINDIA data file (1 value per node)

The following are text file names are for component 1 (additional files also needed for remaining components)

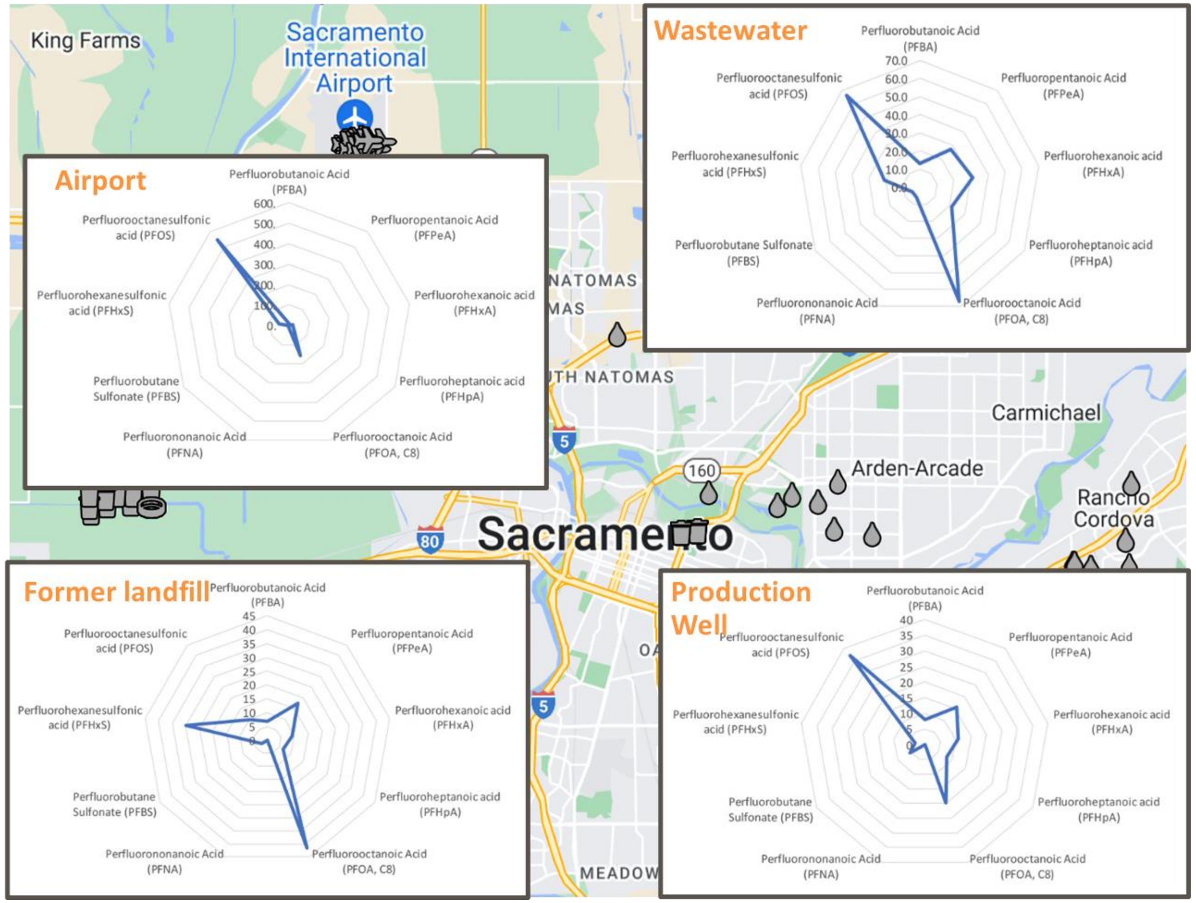
ALANGAW data file (1 value per node)

BLANGAW data file (1 value per node)

AWI_KAWI_TAB file name

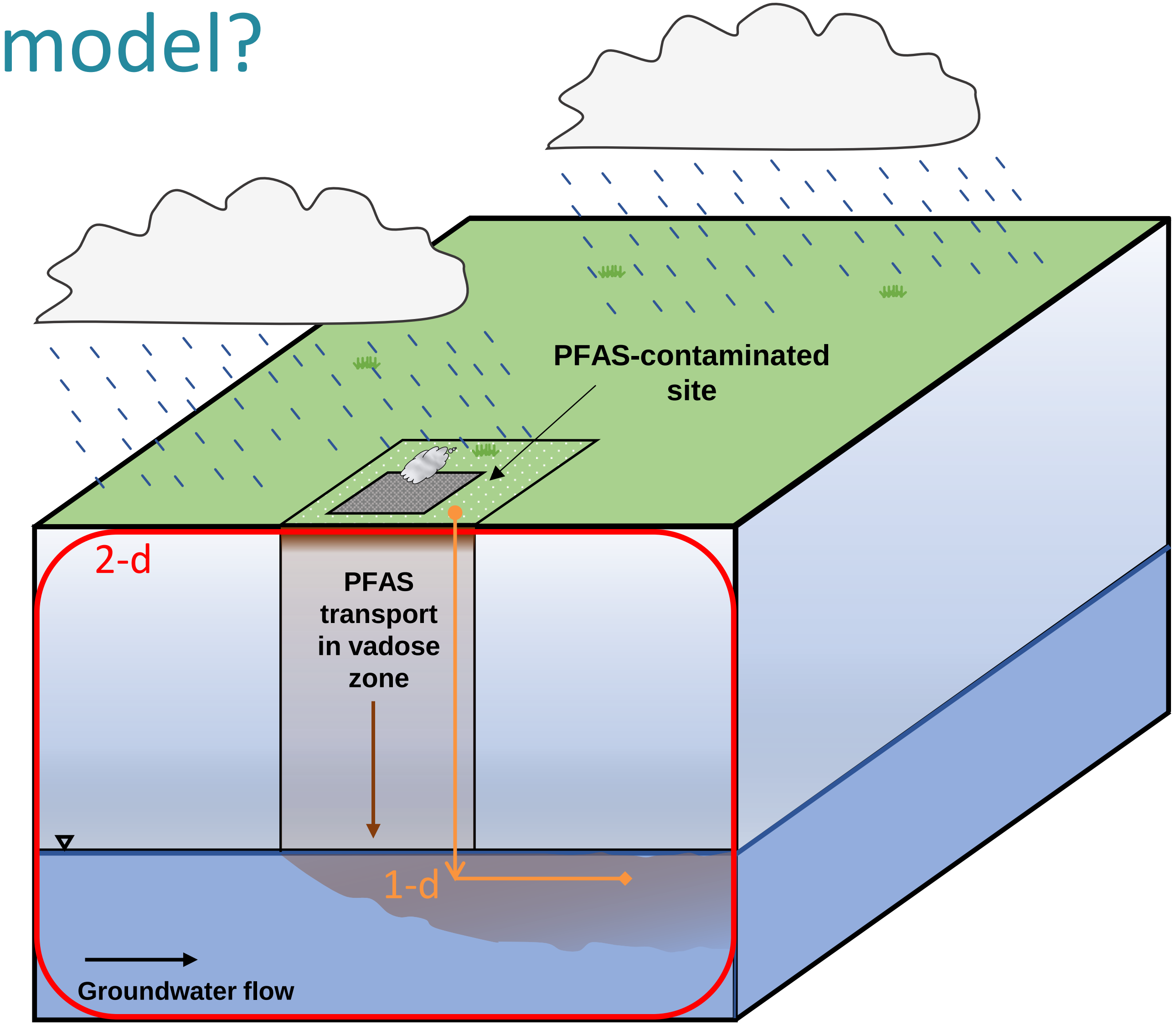
Summary – 2D/3D Numerical Models

- Represent soil and aquifer heterogeneity
- Recharge and infiltration dynamics, pumping and regional flow
- Soil hydraulic and PFAS chemical parameters
- Larger computational effort, limited visualization options, numerical solution challenges
- 1-D analytical models can complement complex 2D/3D models
  - most sensitive parameters
  - which PFAS is most mobile



What do we need for a PFAS model?

- Model objective(s)
- Conceptual site model & data
- Vadose zone flow parameters
- Groundwater flow parameters
- Recharge
- Estimated soil surface area or air-water interfacial area
- PFAS-specific sorption coefficients



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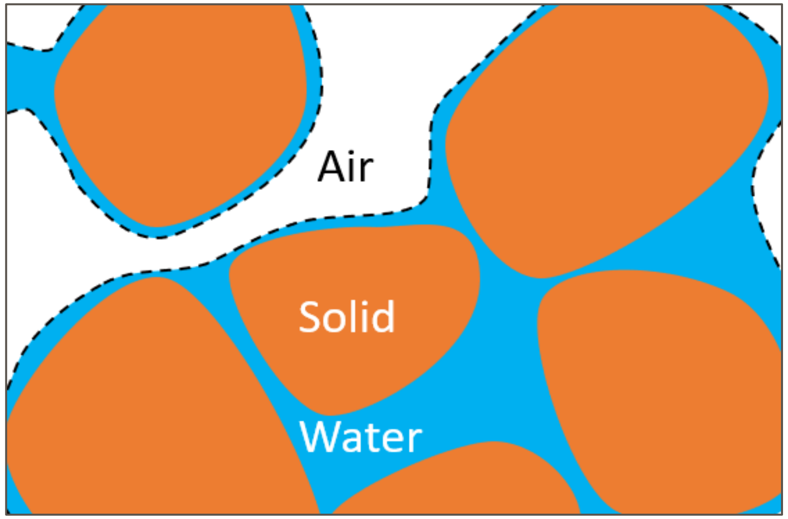
Knowledge Gaps

- Field-scale air-water interfacial area
- Impact of co-contaminants
- Transport in thin water films
- Competitive sorption
- Representativeness of laboratory-scale data
- Many more (Guo & Brusseau 2024, SERDP-ESTCP PFAS Report, 2022)



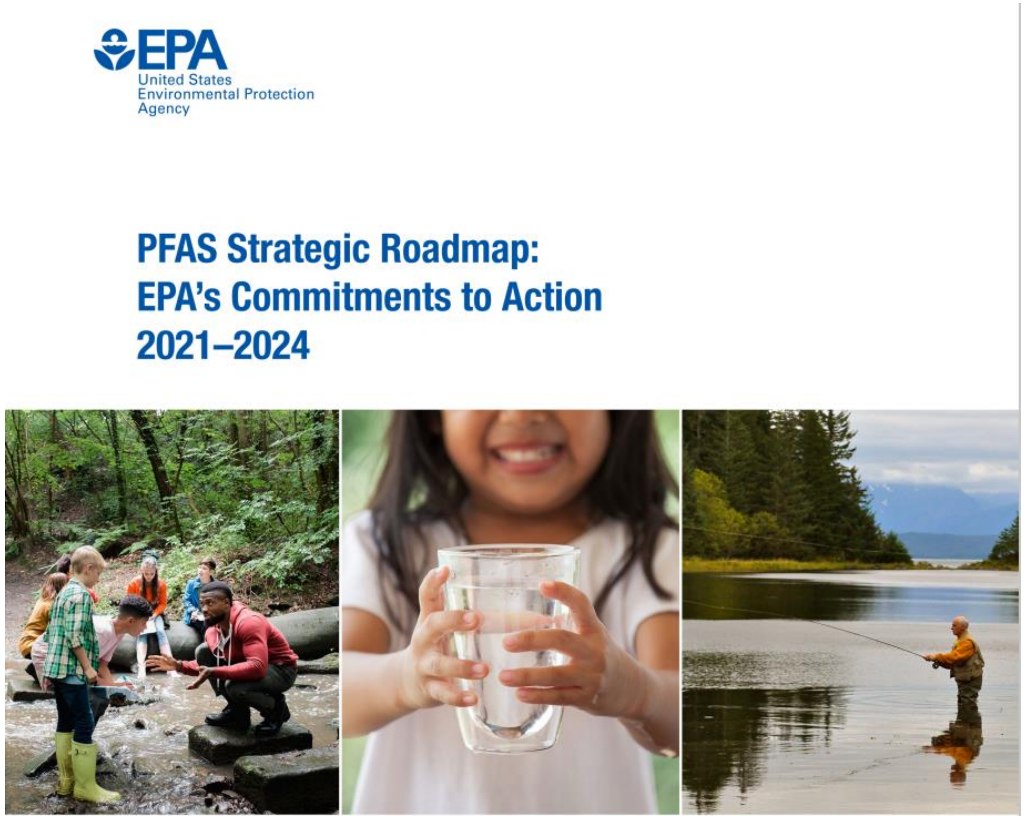

REPORT

Summary Report: Strategic Workshop on Management of PFAS in the Environment

NOVEMBER 2022

Ongoing Research

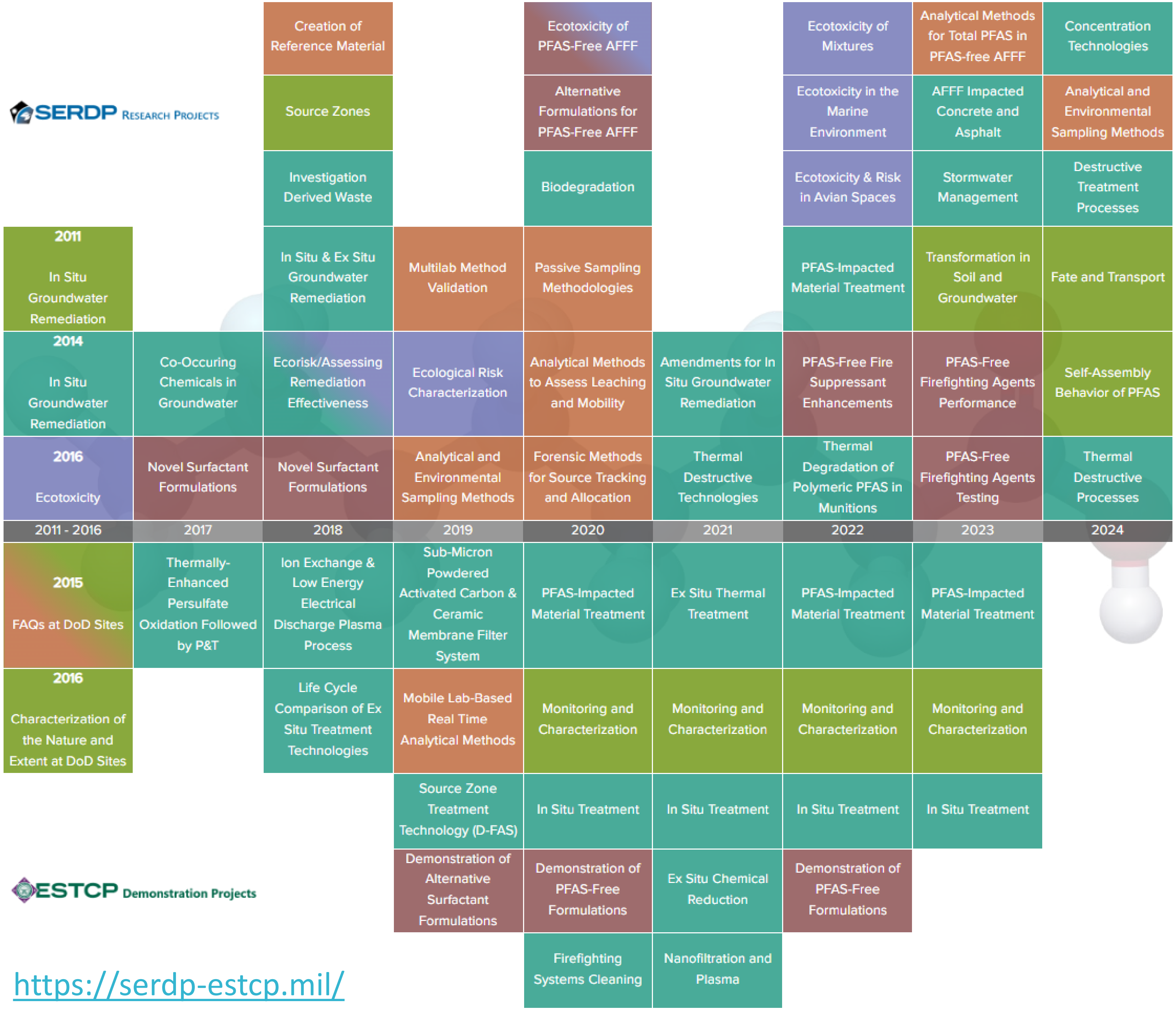
- EPA's "Whole-of-Agency" approach – Research + Restrict + Remediate
  - Vapor intrusion
  - Analytical methods
  - Field measurement standards
  - Toxicity assessments
- Department of Defense's SERDP-ESTCP
  - Complete destruction technologies
  - In-situ treatment/immobilization methods
  - In-situ monitoring tools/technologies
  - Modeling & decision support tools
  - Background PFAS



EPA
United States
Environmental Protection
Agency

PFAS Strategic Roadmap:
EPA's Commitments to Action
2021–2024

www.epa.gov/pfas



SERDP Research Projects

2011 - 2016	2017	2018	2019	2020	2021	2022	2023	2024
		Creation of Reference Material		Ecotoxicity of PFAS-Free AFFF		Ecotoxicity of Mixtures	Analytical Methods for Total PFAS in PFAS-free AFFF	Concentration Technologies
		Source Zones		Alternative Formulations for PFAS-Free AFFF		Ecotoxicity in the Marine Environment	AFFF Impacted Concrete and Asphalt	Analytical and Environmental Sampling Methods
		Investigation Derived Waste		Biodegradation		Ecotoxicity & Risk in Avian Spaces	Stormwater Management	Destructive Treatment Processes
2011 In Situ Groundwater Remediation		In Situ & Ex Situ Groundwater Remediation	Multilab Method Validation	Passive Sampling Methodologies		PFAS-Impacted Material Treatment	Transformation in Soil and Groundwater	Fate and Transport
2014 In Situ Groundwater Remediation	Co-Occuring Chemicals in Groundwater	Ecorisk/Assessing Remediation Effectiveness	Ecological Risk Characterization	Analytical Methods to Assess Leaching and Mobility	Amendments for In Situ Groundwater Remediation	PFAS-Free Fire Suppressant Enhancements	PFAS-Free Firefighting Agents Performance	Self-Assembly Behavior of PFAS
2016 Ecotoxicity	Novel Surfactant Formulations	Novel Surfactant Formulations	Analytical and Environmental Sampling Methods	Forensic Methods for Source Tracking and Allocation	Thermal Destructive Technologies	Thermal Degradation of Polymeric PFAS in Munitions	PFAS-Free Firefighting Agents Testing	Thermal Destructive Processes

ESTCP Demonstration Projects

2011 - 2016	2017	2018	2019	2020	2021	2022	2023	2024
2015 FAQs at DoD Sites	Thermally-Enhanced Persulfate Oxidation Followed by P&T	Ion Exchange & Low Energy Electrical Discharge Plasma Process	Sub-Micron Powdered Activated Carbon & Ceramic Membrane Filter System	PFAS-Impacted Material Treatment	Ex Situ Thermal Treatment	PFAS-Impacted Material Treatment	PFAS-Impacted Material Treatment	
2016 Characterization of the Nature and Extent at DoD Sites		Life Cycle Comparison of Ex Situ Treatment Technologies	Mobile Lab-Based Real Time Analytical Methods	Monitoring and Characterization	Monitoring and Characterization	Monitoring and Characterization	Monitoring and Characterization	
			Source Zone Treatment Technology (D-FAS)	In Situ Treatment	In Situ Treatment	In Situ Treatment	In Situ Treatment	
			Demonstration of Alternative Surfactant Formulations	Demonstration of PFAS-Free Formulations	Ex Situ Chemical Reduction	Demonstration of PFAS-Free Formulations		
				Firefighting Systems Cleaning	Nanofiltration and Plasma			

https://serdp-estcp.mil/

SERDP-ESTCP projects at H&A

Title	Collaborators	Funding Source
Optimized numerical models using environmental sequence stratigraphy	Aquaveo, Seequent	ESTCP
Demonstration of PFAS destruction in a concentrate waste	UC Riverside	ESTCP
Demonstration of a treatment train for PFAS removal and destruction in groundwater	Allonnia	AFCEC
Development of in situ microcosm for PFAS precursor assessment	UC Riverside	SERDP
Transformation of PFAS precursor in soil and groundwater	UC Riverside, NCSU	SERDP
A novel in-situ subsurface PFAS destruction strategy that uses ligand-coordinated zero-valent metals at ambient conditions	Univ. Texas at Austin, UC Riverside	SERDP
Lab and field validation of an acetylene sampler for quantifying abiotic transformation of chlorinated solvents	UM Lowell	SERDP
Enhanced in situ aerobic cometabolic biodegradation of chlorinated solvents, 1,4-dioxane, and other recalcitrant compounds in deep, large, dilute plumes	North Carolina State University	ESTCP
Development of a reliable method for performing compound-specific isotope analysis on low levels of 1,4-dioxane in groundwater	Univ. Waterloo	SERDP
New laser induced fluorescence tool for high-resolution real-time mapping of chlorinated solvent DNAPL	Dakota Technologies	ESTCP

AFCEC BAA = Air Force Civil Engineer Center Broad Agency Announcement

ESTCP = Environmental Security Technology Certification Program

SERDP = Strategic Environmental Research and Development Program

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Thank You