

HWRS 505: Vadose Zone Hydrology

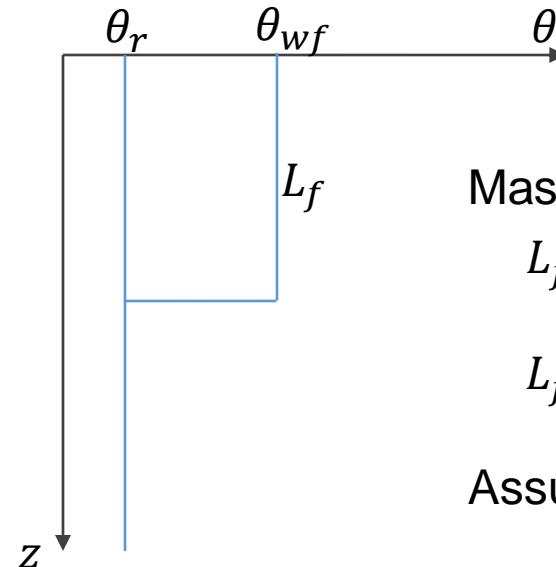
Lecture 22
11/14/2024

Today: Introduction to a group of emerging contaminants — PFAS

Comments on HW #4

1. (10 points) Construct a 100 cm long vertical column in HYDRUS 1D. Fill it with sand, initially at field capacity. Apply a flux equal to $K_{sat}/10$. $K_{sat} = 0.00825 \text{ cm/s}$. Calculate by hand the expected advance of the wetting front, assuming piston displacement. Run the HYDRUS model for this same elapsed time. Compare the water content profile that you calculated manually and numerically and discuss any significant differences.

Hand calculation:



Mass balance

$$L_f(\theta_{wf} - \theta_r) = qt$$

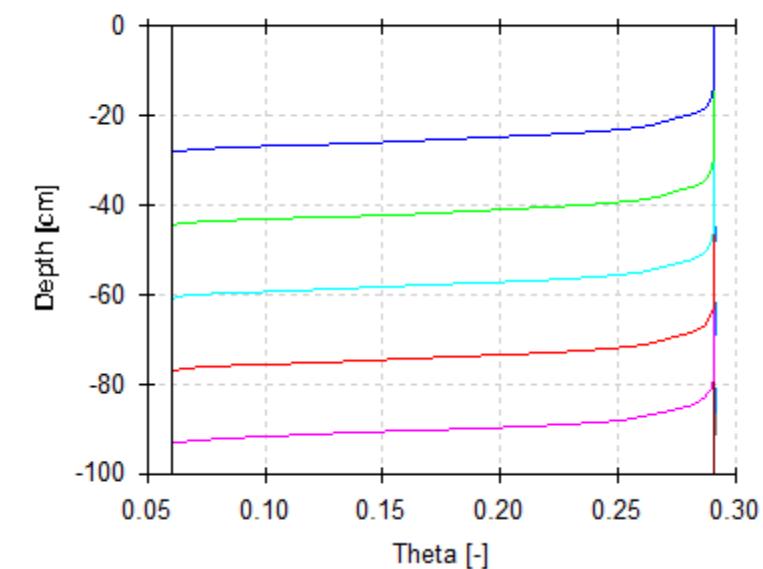
$$L_f = \frac{qt}{\theta_{wf} - \theta_r}$$

Assuming water flow is only driven by gravity

$$q = K(\theta_{wf})$$

You can then back calculate θ_{wf} and determine L_f .

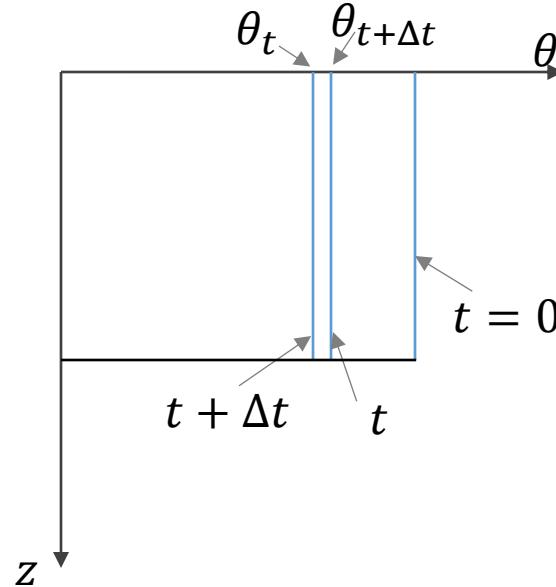
Profile Information: Water Content



Comments on HW #4

2. (10 points) Construct a 100 cm long vertical column in HYDRUS 1D. Fill it with sand, initially at a constant pressure head of 0 cm. Apply a flux equal to 0 at the top boundary and allow free drainage at the bottom. Calculate by hand the expected progression of drainage. Use a one hour time step. Assume that flux is constant over each hour and that the K of the medium is defined by the water content at the beginning of the time step. Run the HYDRUS model for these same conditions for 24 hours of simulated time. Compare the water content profile that you calculated manually and numerically and discuss any significant differences.

Hand calculation:



$$t \rightarrow t + \Delta t$$

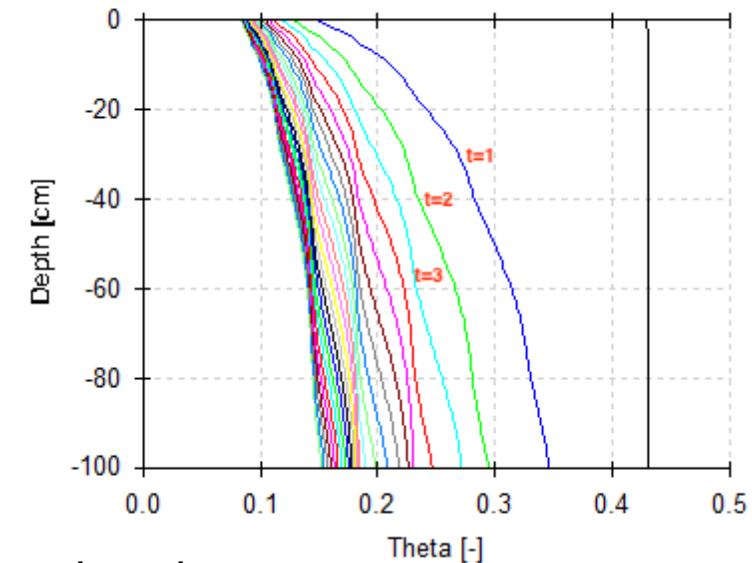
$$(\theta_{t+\Delta t} - \theta_t)L = -q_t \Delta t$$

$$\begin{aligned}\theta_{t+\Delta t} &= \theta_t - q_t \Delta t / L \\ &= \theta_t - K(\theta_t) \Delta t / L\end{aligned}$$

$$q = K(\theta_{wf})$$

Assuming water flow is only driven by gravity

Profile Information: Water Content



Comments on HW #4

3. (5 points; for graduate students only) For those of you who are enrolled in HWRS 505, you will need to do a final project for this class. There are two options for the final project: 1) choose a research topic of interest related to processes in the vadose zone, read 3 to 5 relevant papers and provide a critical review of their research questions, methodologies, results, and implications; 2) choose a research problem in your own field of interest and apply the concepts and research tools covered in class to systematically tackle the problem. For either option, you will need to summarize your key findings in a formal report and deliver a presentation in class. The purpose of this question in HW #4 is for you to get the project going. Please come up with a potential topic that you would like to pursue. Write down your topic and provide a plan to execute the project.

Comments:

- 1) Try to narrow down your topic.
- 2) It would be better that the 3-5 papers are closely related to each other.
- 3) Be somewhat selective of the Journals in which the papers are published.

Review of Lecture 22

Inverse modeling (parameter estimation) using HYDRUS-1D

- The forward model is transient (vs. steady-state in the spreadsheet model)
- How does the error in your observation impact your estimated parameter?
- What happens when we try to estimate multiple parameters?
- We only used the observed data at one location. What happens when you have multiple types of observation data at multiple locations



THE TRUTH HAS A MAN ON THE INSIDE.



A TODD HAYNES FILM

DARK WATERS

MARK RUFFALO ANNE HATHAWAY TIM ROBBINS BILL CAMP VICTOR GARBER AND BILL PULLMAN

FROM PARTICIPANT, WHO BROUGHT YOU SPOTLIGHT AND THE POST

PARTICIPANT PRESENTS A WILLIAMS/KILLER CONTENT PRODUCTION

A TODD HAYNES FILM "DARK WATERS" MARK RUFFALO ANNE HATHAWAY TIM ROBBINS BILL CAMP VICTOR GARBER AND BILL PULLMAN

PRODUCED BY LAURA ROSENTHAL CO-PRODUCED BY MARCELLA ZARVOS WRITTEN BY CHRISTOPHER PETERSON DIRECTED BY AFFONSO GONCALVES AGE RATED BY HANNAH BEAHLER

PRODUCED BY EDWARD LACHMAN AD PROPS BY JEFF SKOLL, JONATHAN KONG, ROBERT KESSEL, MICHAEL SLEDO PROPS BY MARK RUFFALO, CHRISTINE VACHON, PAMELA KOFFLER

SCREENPLAY BY MARIO CORREA AND MATTHEW MICHAEL CARNahan DIRECTED BY TODD HAYNES

NOVEMBER 10 FOCUS FEATURES

SCREENPLAY BY MARIO CORREA AND MATTHEW MICHAEL CARNahan DIRECTED BY TODD HAYNES

The cover features a black and white photograph of a man standing in a field of tall grass, looking towards the right. In the foreground, the front of a pickup truck is visible. The title "The New York Times Magazine" is at the top, with "FEATURE" below it. The date "January 2016" is in the top right corner. The main headline "The Lawyer Who Became DuPont's Worst Nightmare" is in large, bold, white letters. Below the headline is a summary of the story, followed by a large callout at the bottom.

FEATURE

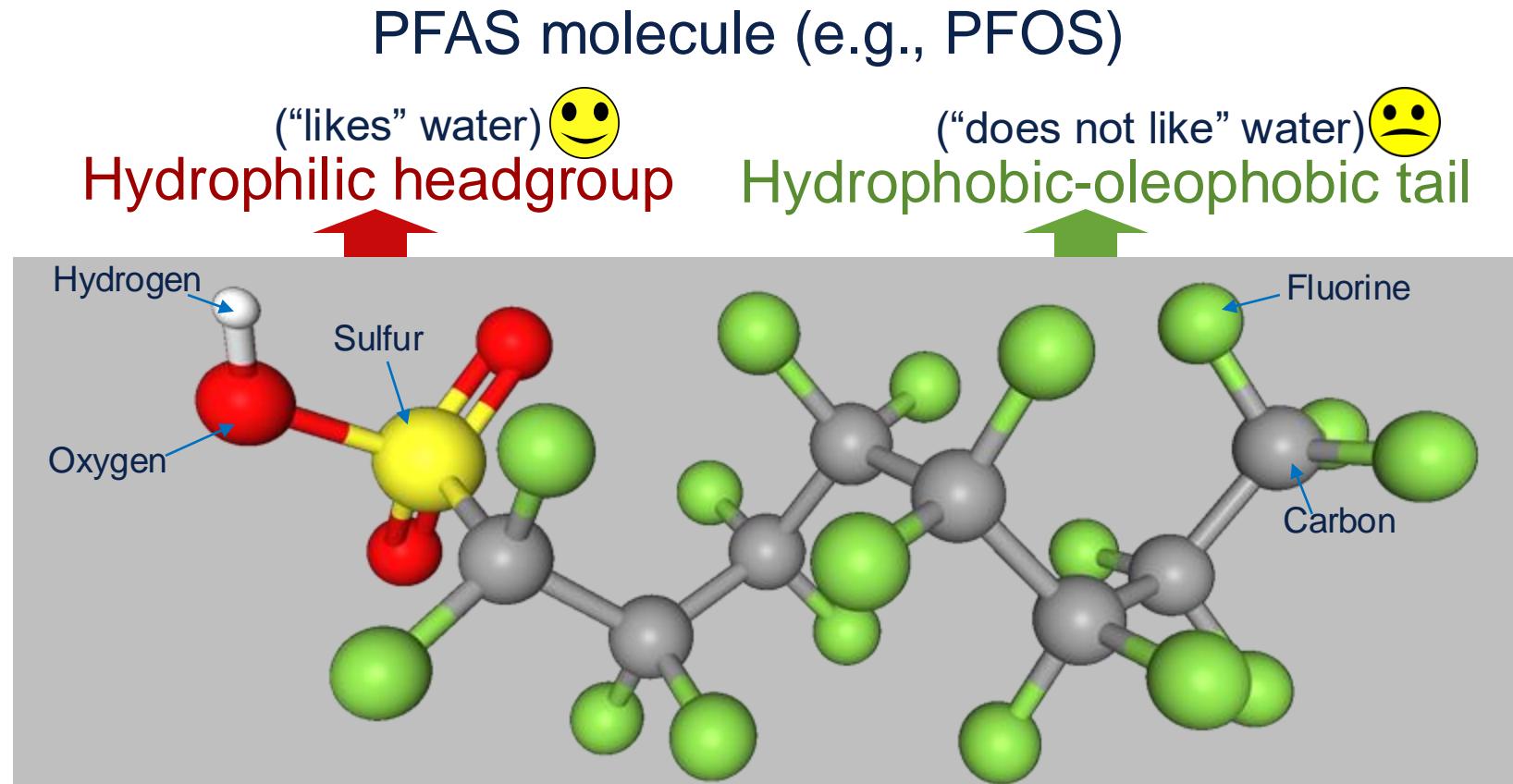
January 2016

The Lawyer Who Became DuPont's Worst Nightmare

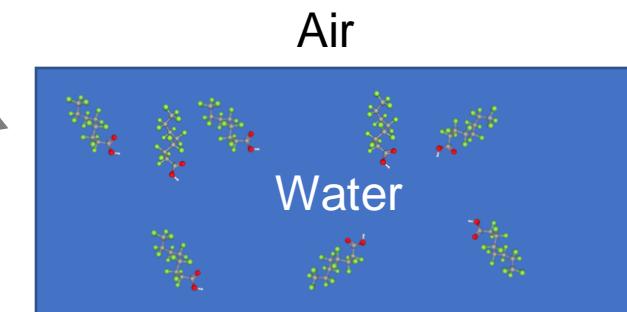
Rob Bilott was a corporate defense attorney for eight years. Then he took on an environmental suit that would upend his entire career — and expose a brazen, decades-long history of chemical pollution.

Based on a true story – Lawsuit against DuPont led to total settlement of \$753 million

What are PFAS (Per- and poly-FluoroAlkyl Substances)?



- Surfactant (**Surface active agent**)
- Persistent (**C-F bond**)
- Toxic at **ppt** levels
- More than **9,000** compounds

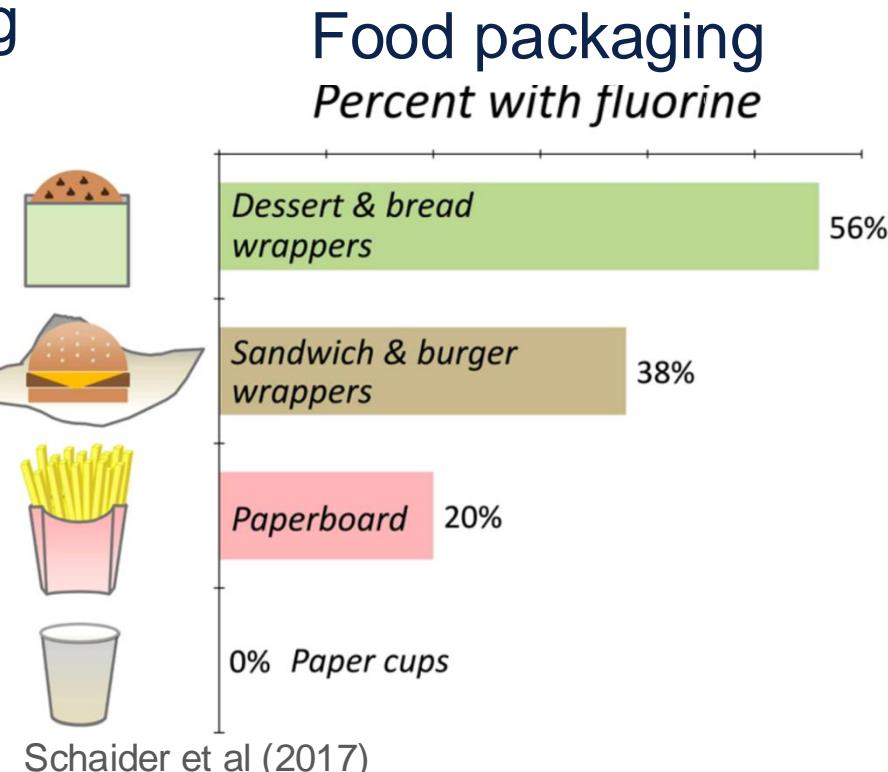


Accumulate
at air–water
interfaces

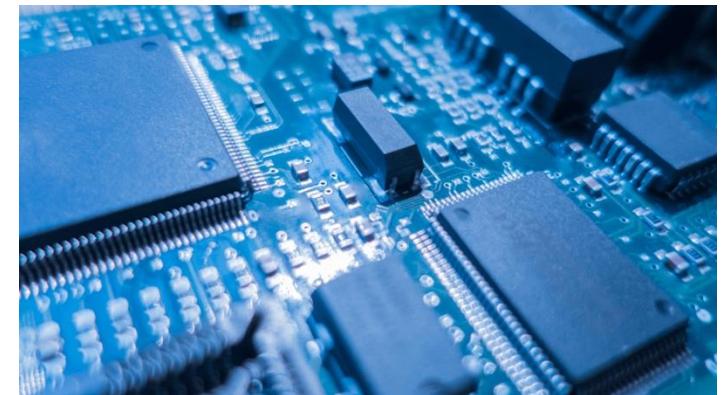
Used in our daily life and at military sites

“Perfect” chemicals if NOT toxic

Non-stick, stain- and water-resistant coating



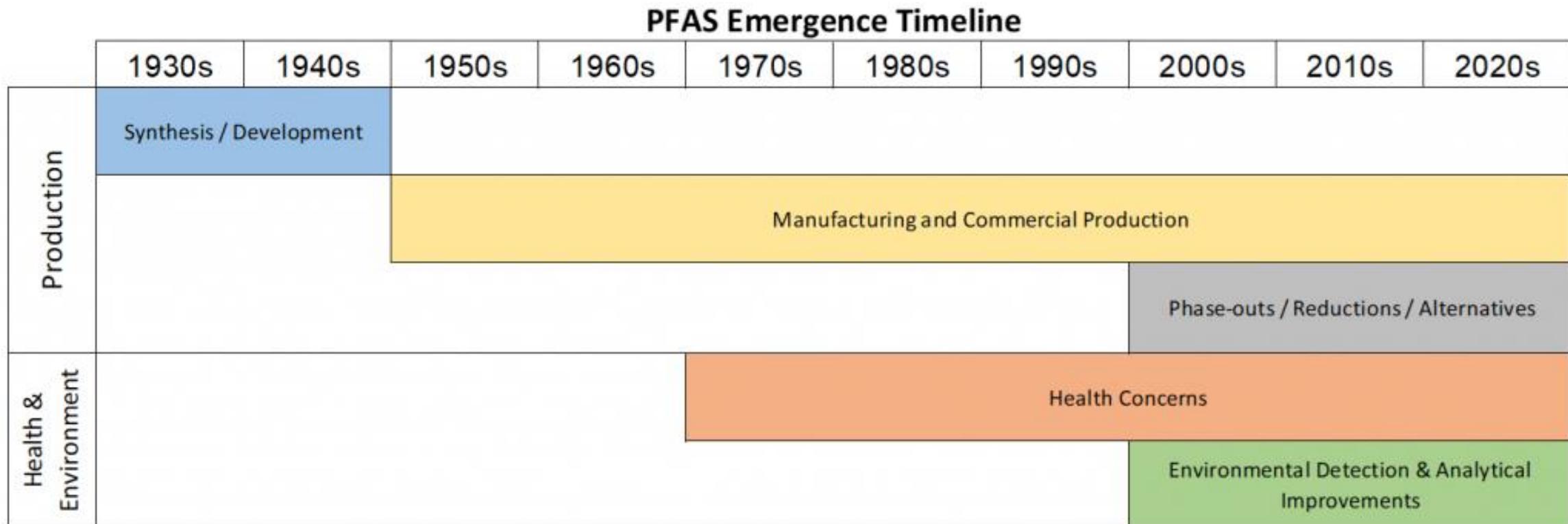
Semiconductor Industry



Fire fighting foam

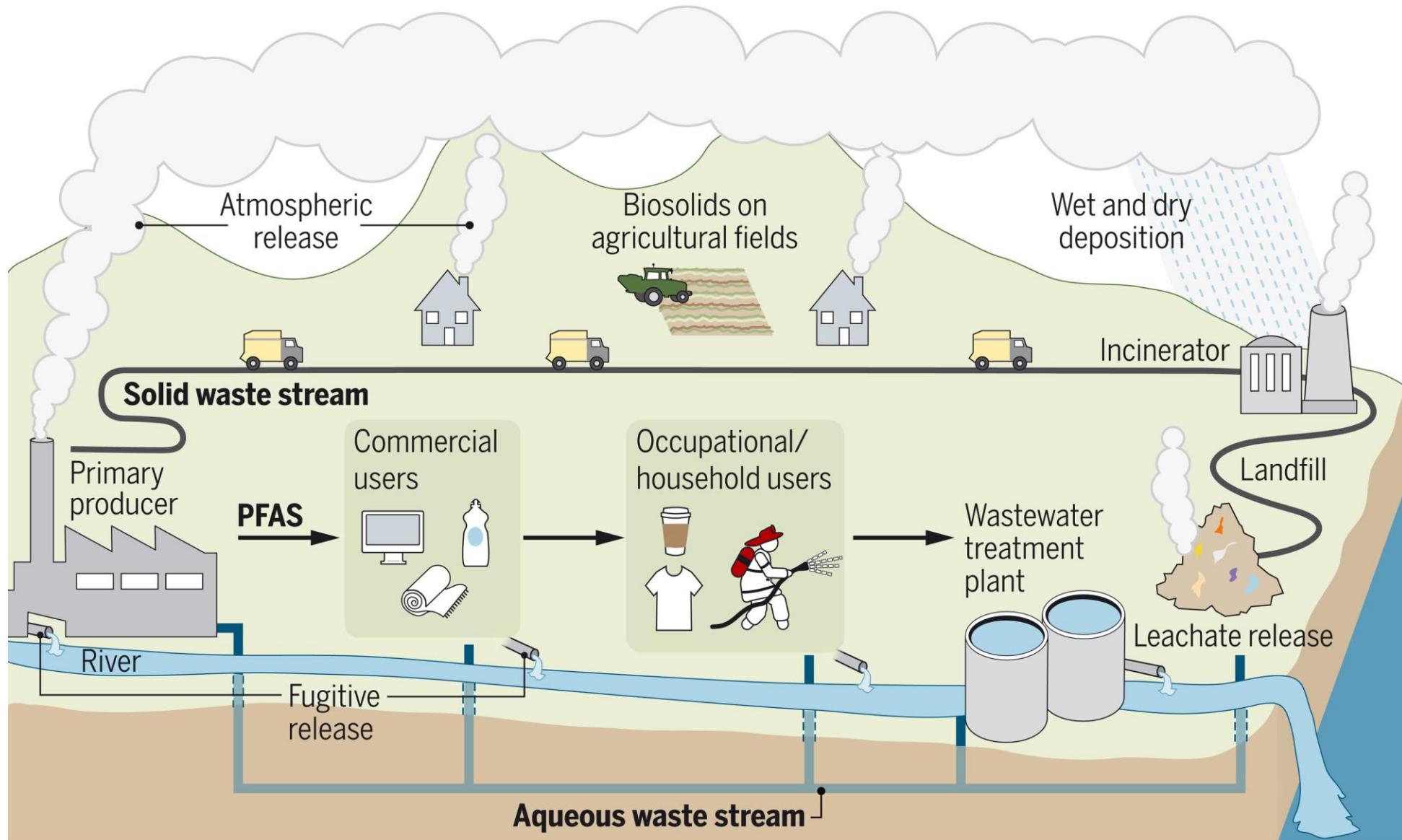


General timeline of PFAS emergence and awareness



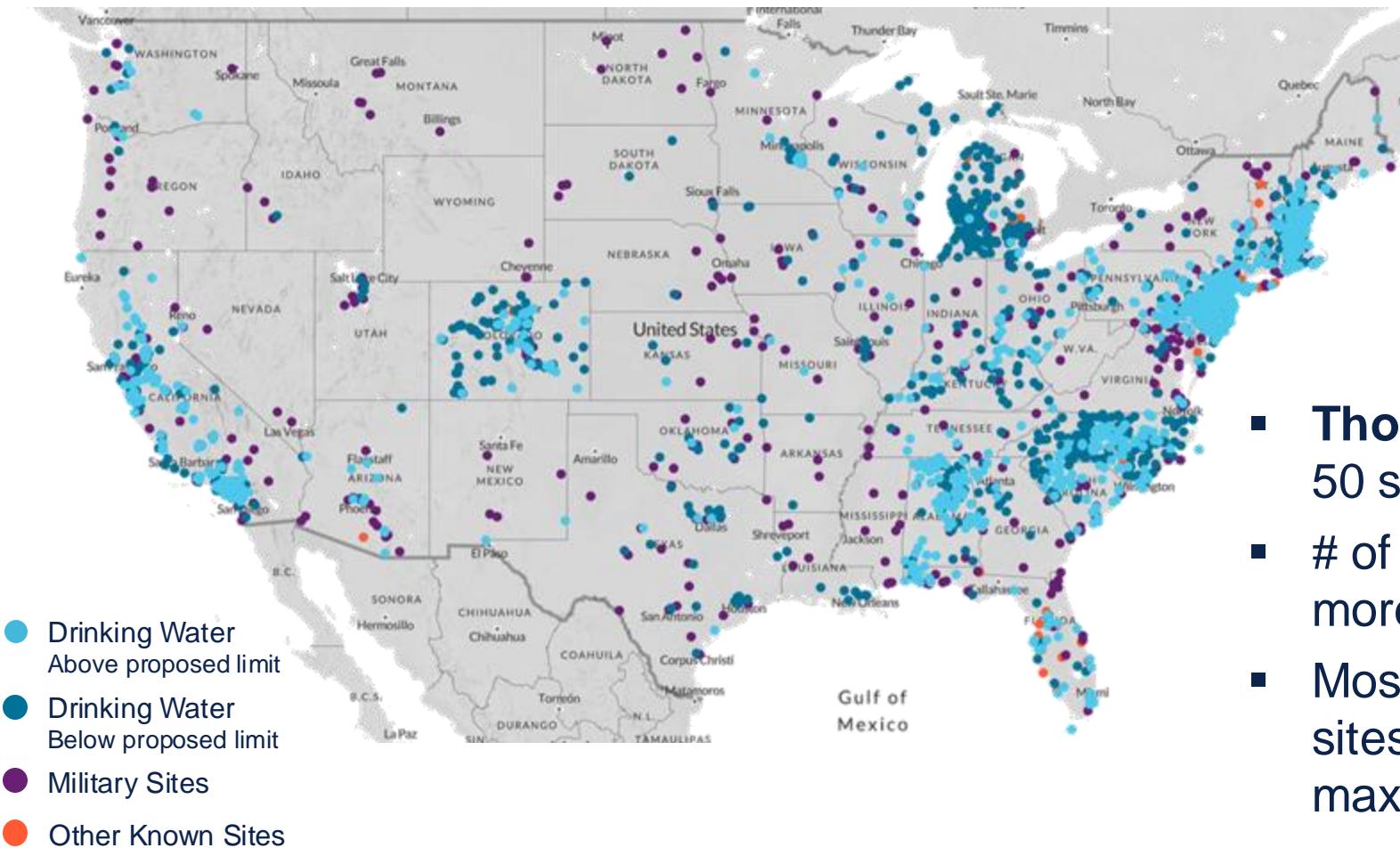
Source: J. Hale, Kleinfelder and ITRC PFAS fact sheets

PFAS releases to the environment



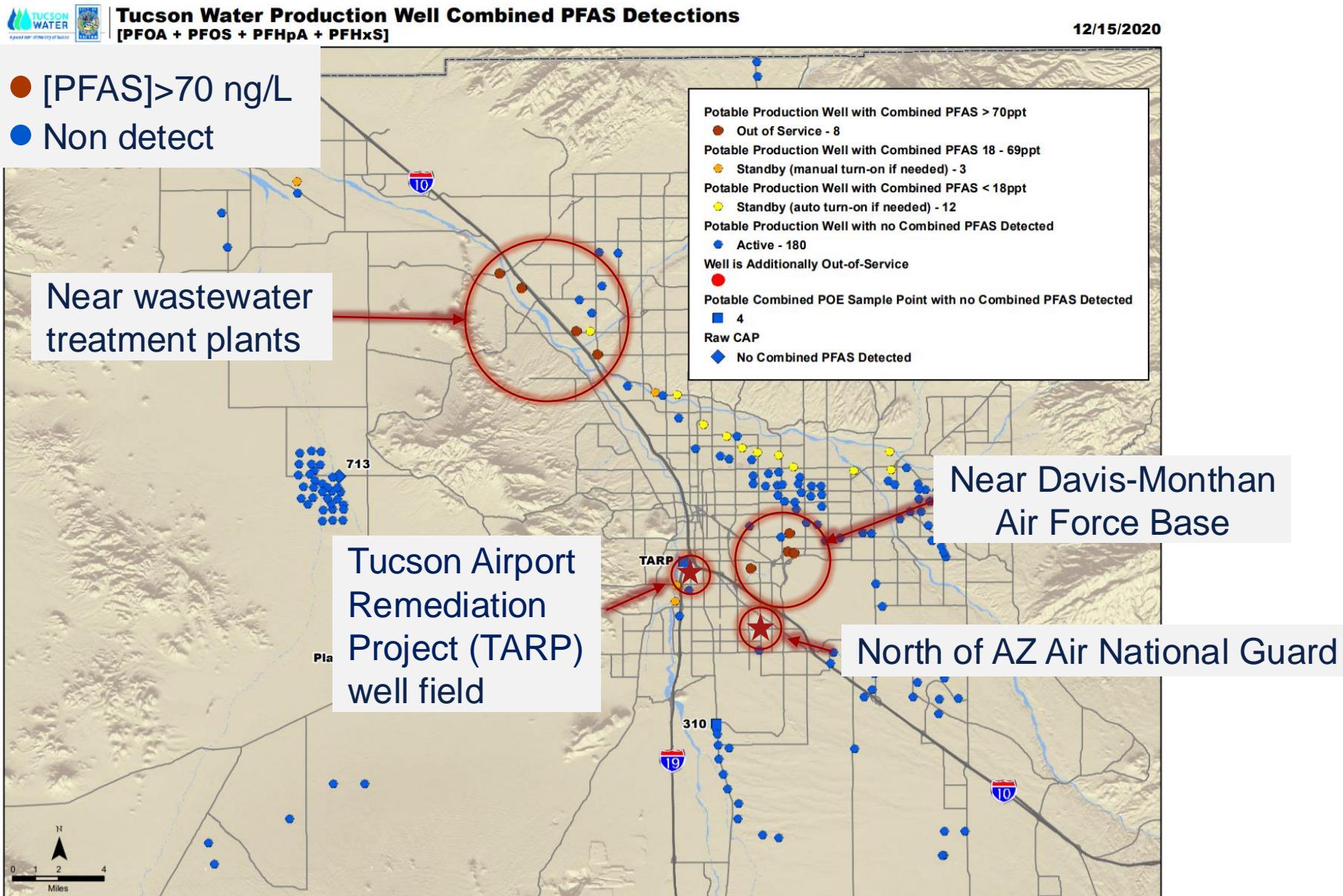
Source: Ewich et al., 2022. *Science*.

PFAS are widely spread in the environment

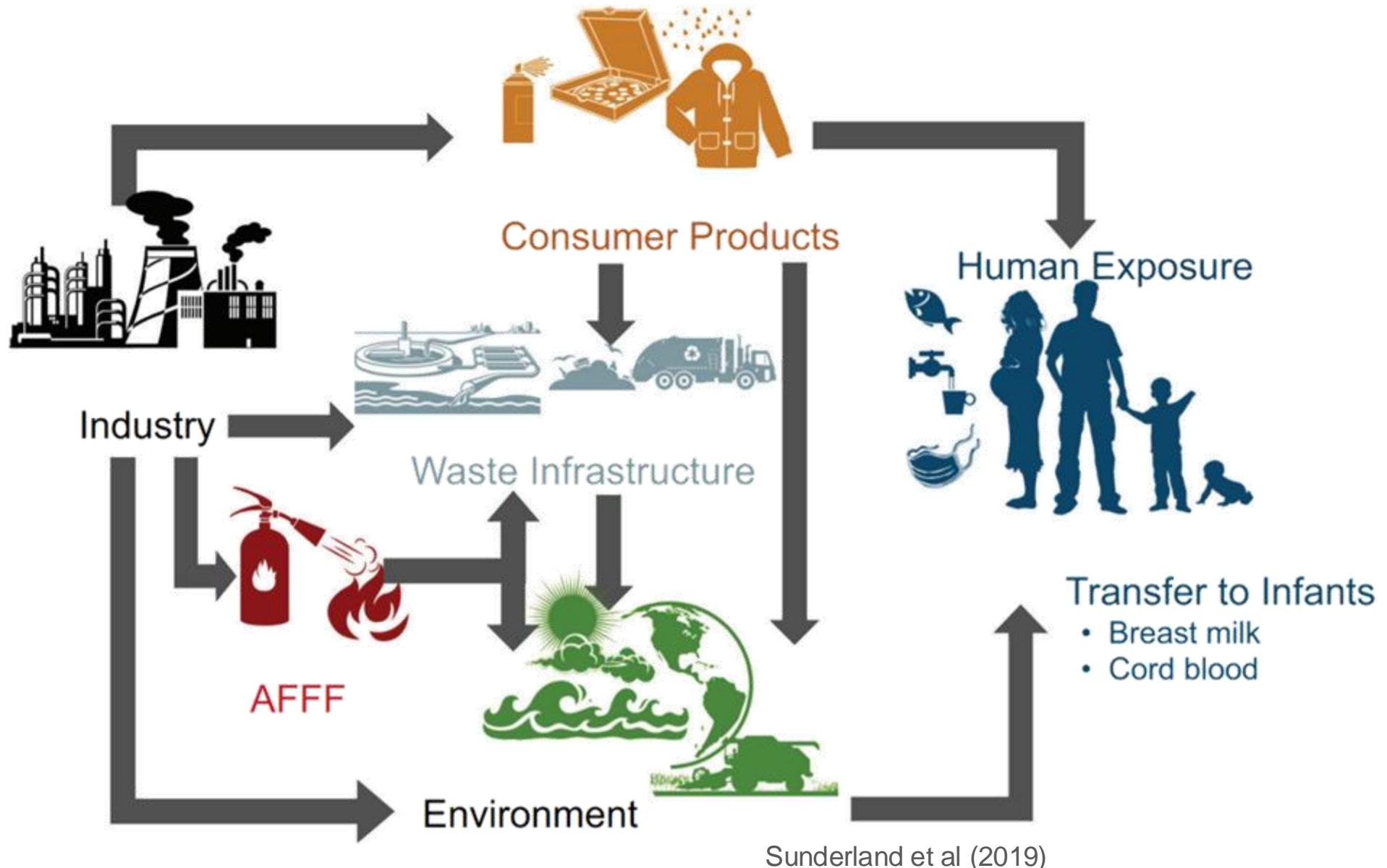


- Thousands of contamination sites in 50 states.
- # of sites are rapidly **growing** as more investigations are carried out.
- Most drinking water contamination sites are **above** the EPA proposed maximum contaminant level (**MCL**).

PFAS contamination in Tucson, AZ



97% of US residents have PFAS in their blood

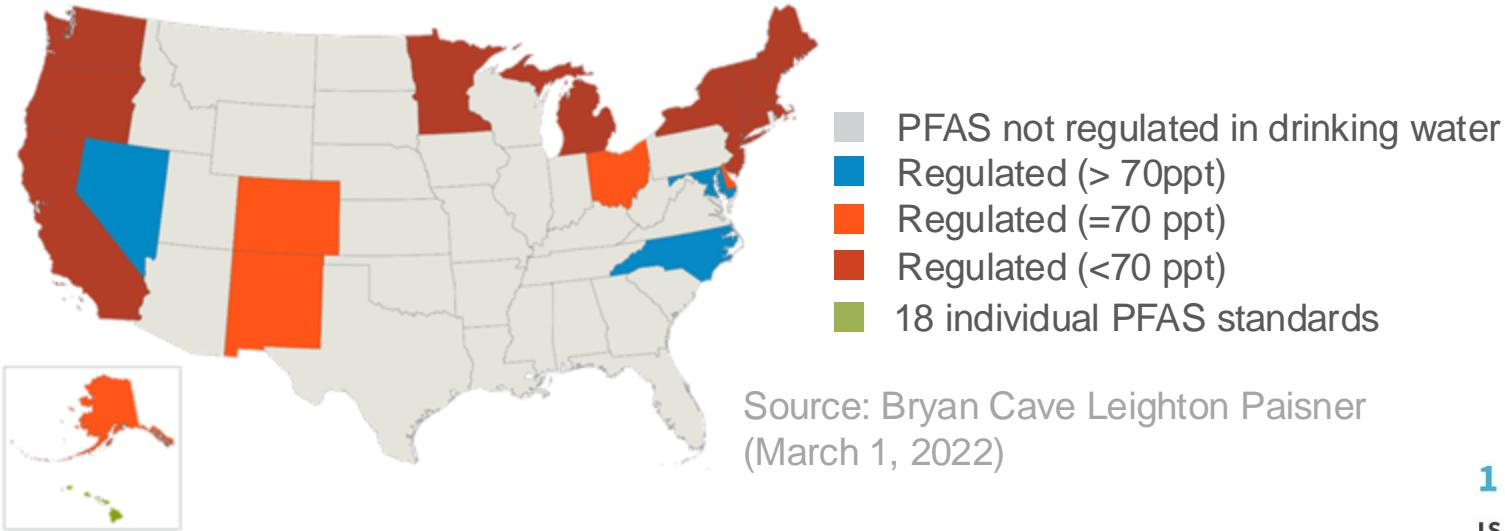


What we know about health effects of PFAS exposure?

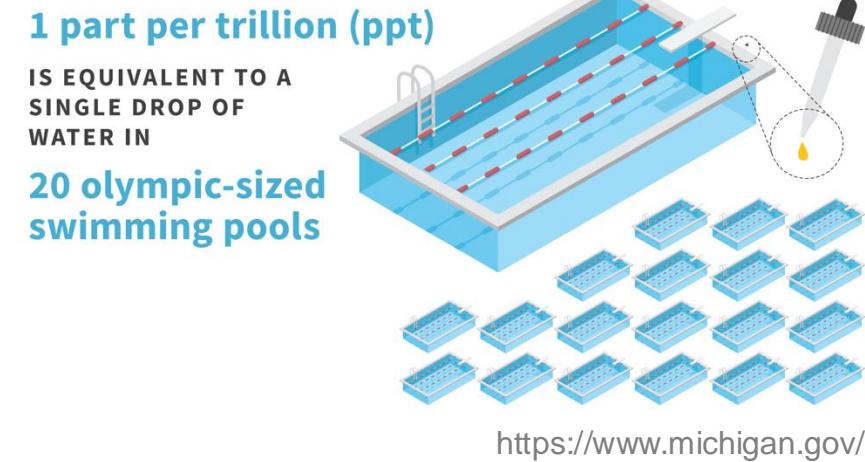
- According to EPA, exposure to certain levels of PFAS may lead to:
 - Reproductive effects such as decreased fertility or increased high blood pressure in pregnant women.
 - Developmental effects or delays in children, including low birth weight, accelerated puberty, bone variations, or behavioral changes.
 - Increased risk of some cancers, including prostate, kidney, and testicular cancers.
 - Reduced ability of the body's immune system to fight infections, including reduced vaccine response.
 - Interference with the body's natural hormones.
 - Increased cholesterol levels and/or risk of obesity.
- Residents in Parkersburg, West Virginia affected by PFAS contamination have higher rates of various health problems including cancers (Robert Bilott's lawsuit against DuPont. **Movie: Dark Waters**)

"In 2004, DuPont settled Bilott's class-action suit, which now applied to 80,000 plaintiffs in 6 water districts, for \$343 million. The settlement also included the creation of a C8 Science Panel and funding of a study to collect medical information on the exposed population and determine whether PFOA exposure actually posed harm. The project was complete in 2013, and linked PFOA exposure to 6 diseases: ulcerative colitis, pregnancy-induced hypertension, thyroid disease, testicular cancer, and kidney cancer (Lerner, 2015)."

Regulation of PFAS in drinking water in the US



- Not regulated yet by EPA, but States are aggressively setting their own regulatory standards
- EPA proposed unprecedented MCLs (March 14, 2023)
 - PFOA = 4 parts per trillion (ppt or ng/L)
 - PFOS = 4 parts per trillion (ppt or ng/L)
 - PFNA, PFHxS, PFBS, HFPO-DA (GenX): Hazard Index = 1



$$\text{Hazard Index} = \frac{[\text{PFNA}]}{10 \text{ ppt}} + \frac{[\text{PFHxS}]}{9 \text{ ppt}} + \frac{[\text{PFBS}]}{2000 \text{ ppt}} + \frac{[\text{GenX}]}{10 \text{ ppt}}$$

How do the proposed MCLs compare to other contaminants?

Regulatory criteria for contaminant group (Newell et al., 2020)

Groundwater contaminant	Regulatory criteria ($\mu\text{g/L}$)	Source
Many CVOCs such as TCE, PCE	5	Maximum concentration limit (MCL) for many CVOCs
1,4-Dioxane	0.46	USEPA drinking water screening level
Benzene	5	MCL for benzene
MTBE	13	California maximum contaminant limit for drinking water (2017)
PFOA/PFOS	0.004	EPA proposed MCLs

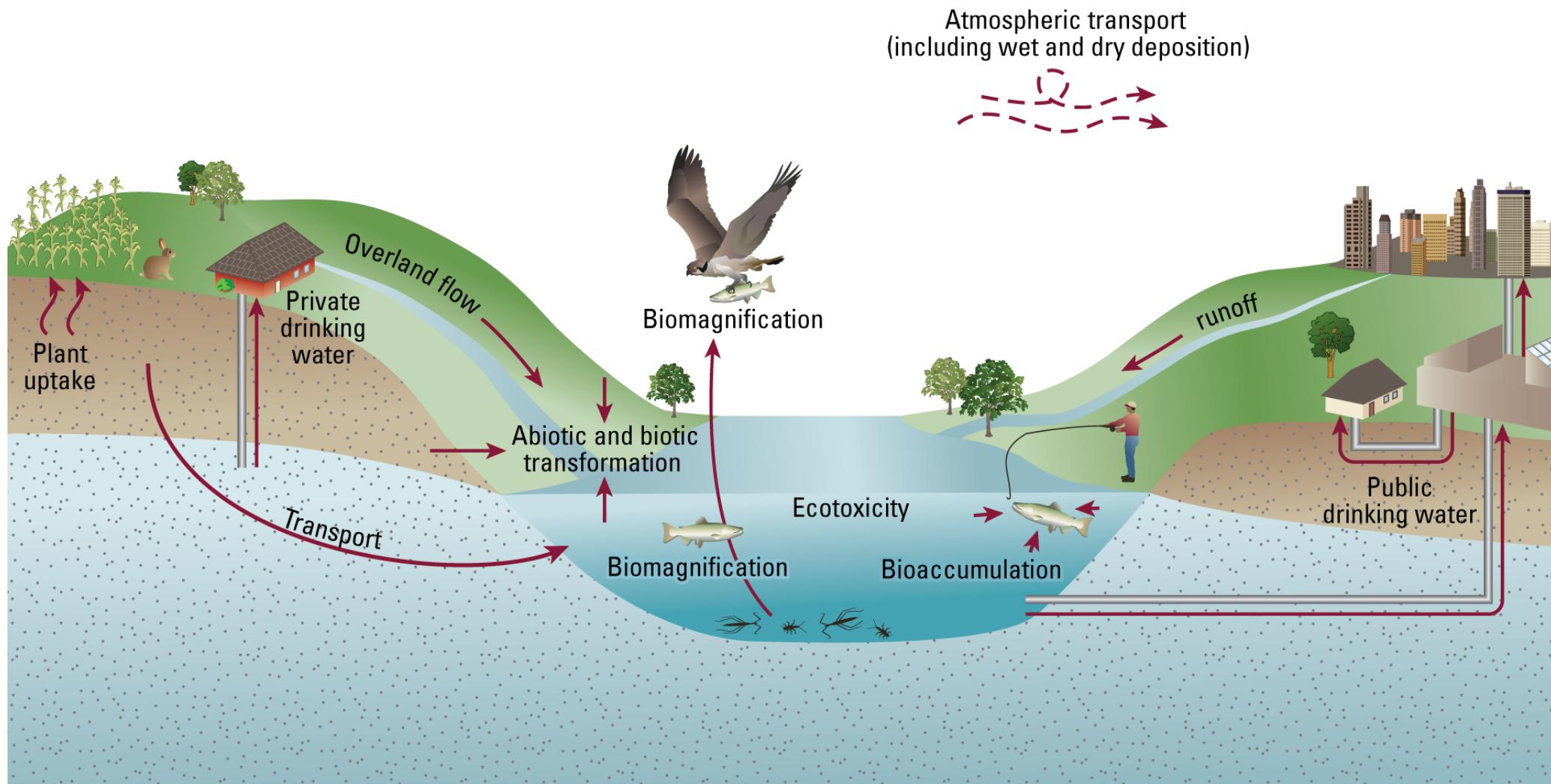
Tucson Airport Remediation Project (TARP) was created 1994 to treat TCE, and then later 1,4-Dioxane.

- The MCLs for PFAS are 100 to 1000 times lower than many other groundwater contaminants.

Abbreviations: CVOC, chlorinated volatile organic compound; MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; USEPA, U.S. Environmental Protection Agency.

How can hydrology help solve the PFAS problem?

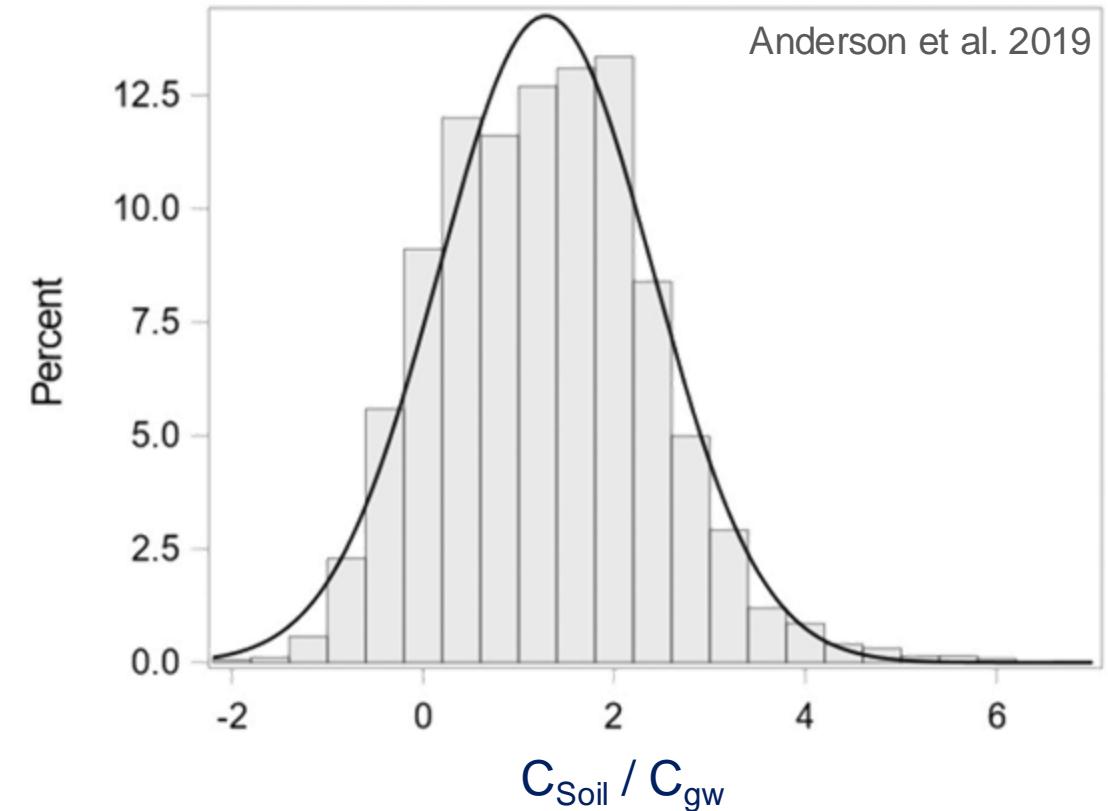
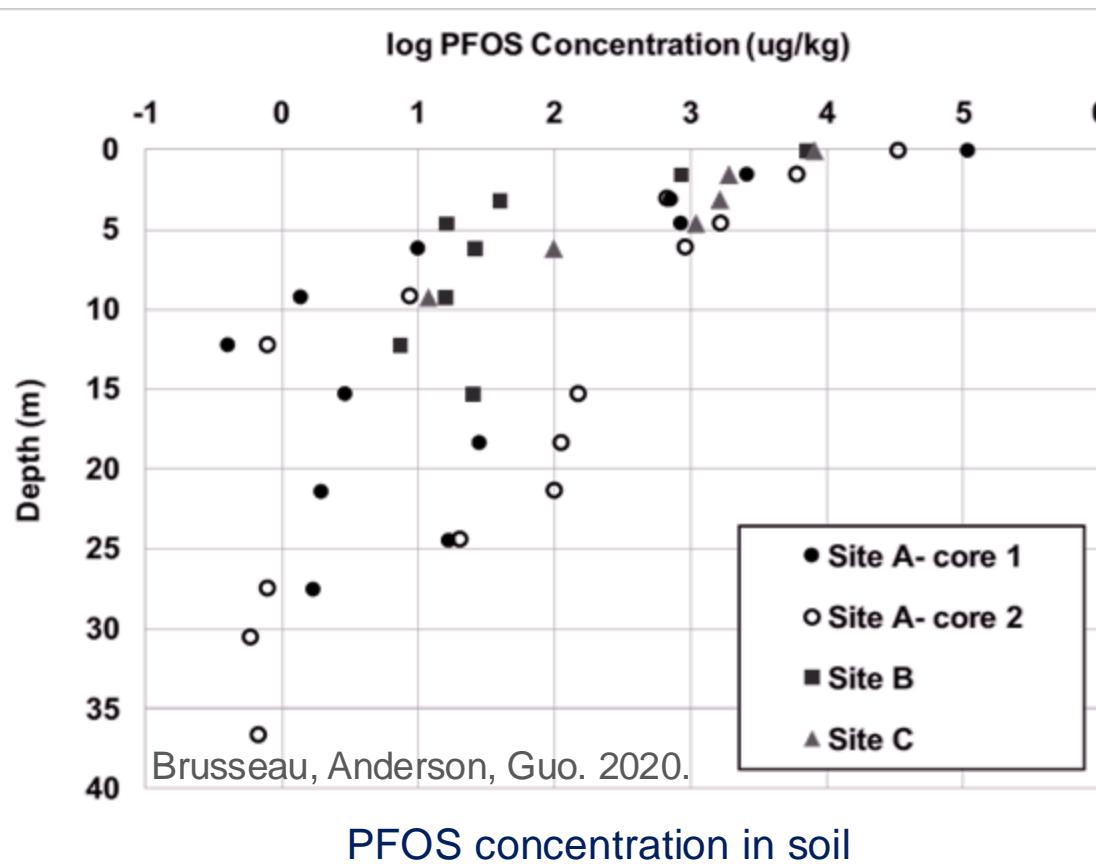
PFAS fate and transport in the environment



Source: USGS

- Water cycle is a major driver of PFAS movement in the environment.

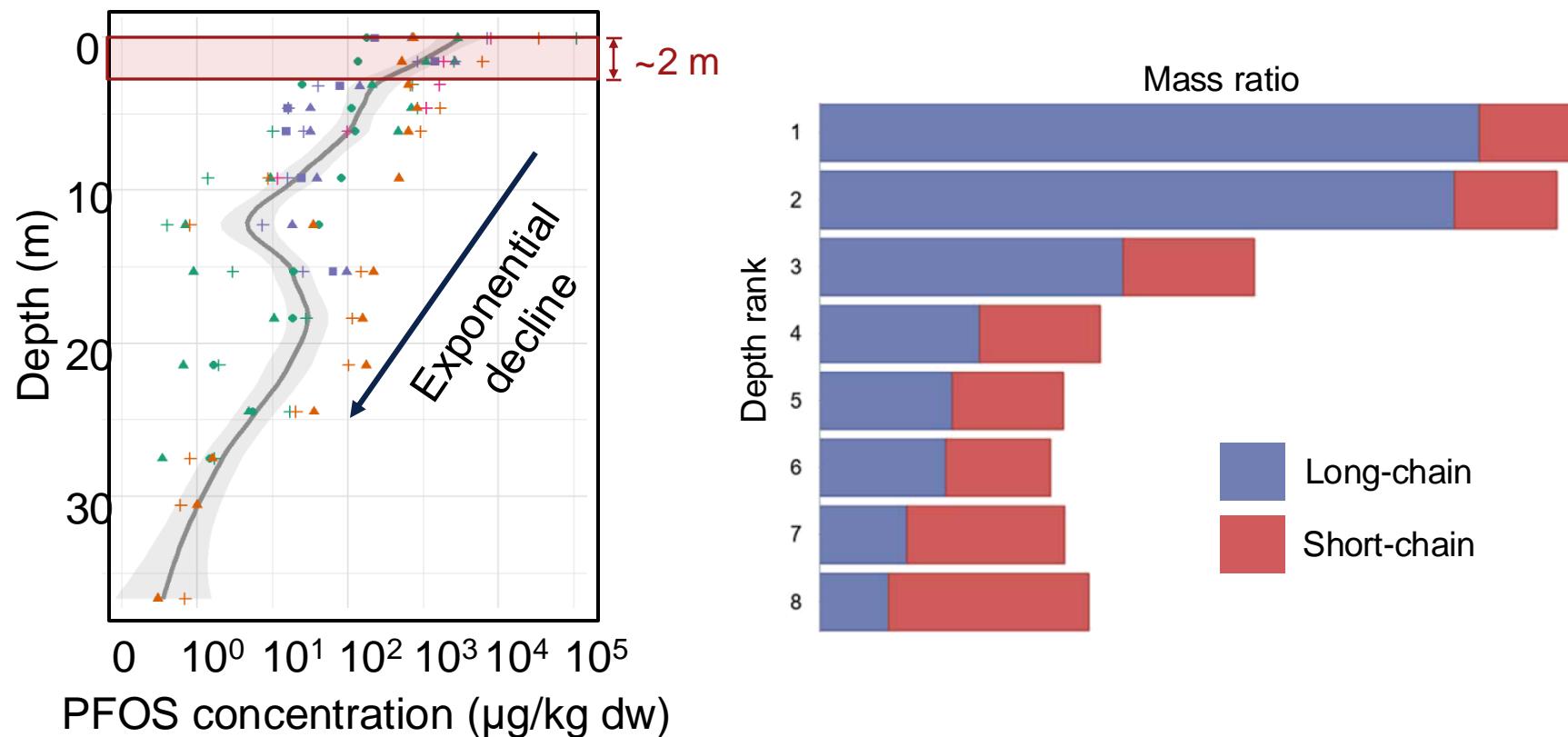
Field data: concentrations in soil vs. groundwater



Ratio between soil and groundwater PFAS concentrations (324 sites across 56 military installations throughout the continental U.S.)

- Concentrations in soils are generally much greater than that in groundwater.

Field data: spatial variation of concentrations in the soil



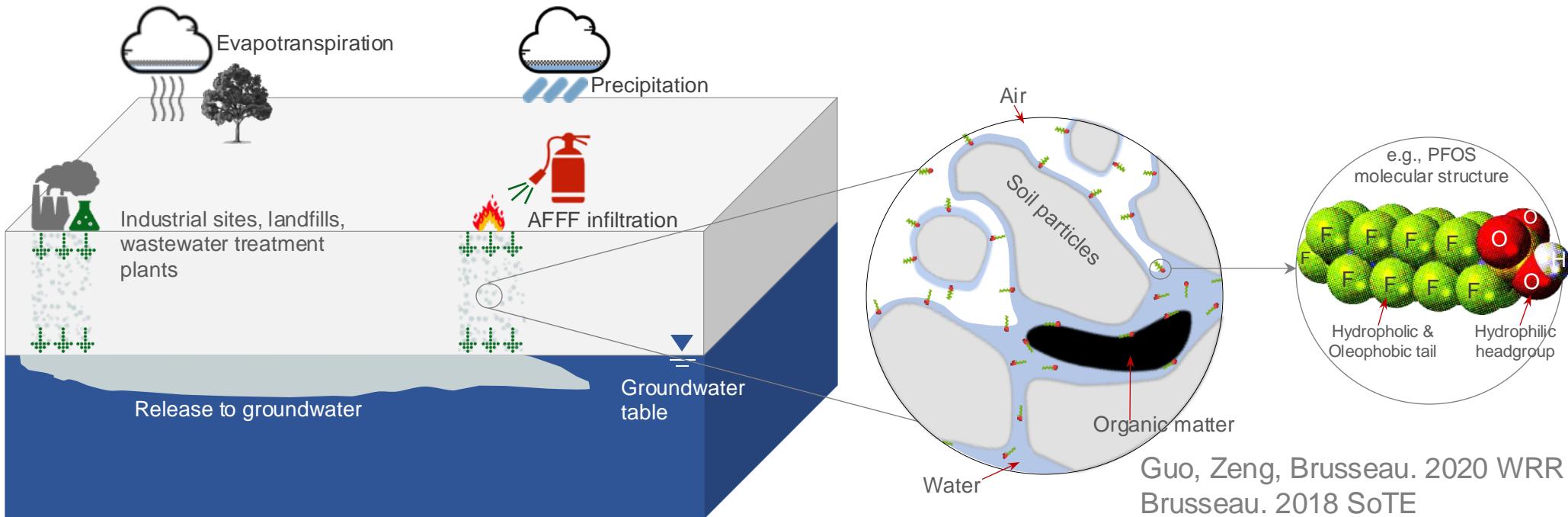
- Soils appear to act as significant source zones of PFAS.
- Long-chain PFAS tend to retain in shallow soil, while short-chain PFAS migrate to deeper depth.

Overarching Questions

What processes control PFAS leaching in soils?

What are the long-term mass discharge rates to groundwater?

PFAS transport in soils: physical & chemical processes



Unique physicochemical properties:

- As surfactants
 - ✓ PFAS tend to accumulate at solid surfaces and air-water interfaces in soils.
 - ✓ PFAS present in pore water can modify surface tension.

PFAS transport in soils: mathematical formulation

Variably saturated flow:

$$\frac{\partial \theta}{\partial t} - \nabla \cdot [\mathbf{K}(\theta) \nabla (h - z)] = 0$$

PFAS transport:

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

Advection Dispersion

Nonlinear and rate-limited solid-phase adsorption (SPA)

$$C_{s,1} = F_s K_f C^N$$

Instantaneous

$$\frac{dC_{s,2}}{dt} = \alpha_s [(1 - F_s) K_f C^N - C_{s,2}]$$

Kinetic

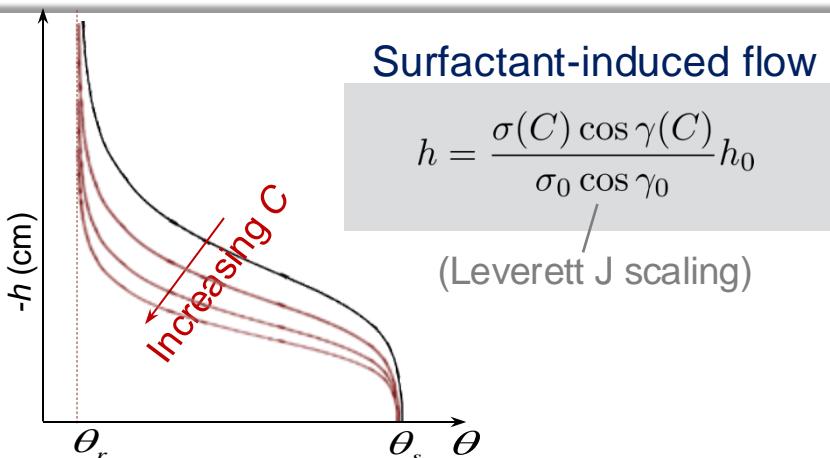
Nonlinear and rate-limited air-water interfacial adsorption (AWIA)

$$C_{aw} = F_{aw} A_{aw} K_{aw} C$$

Instantaneous

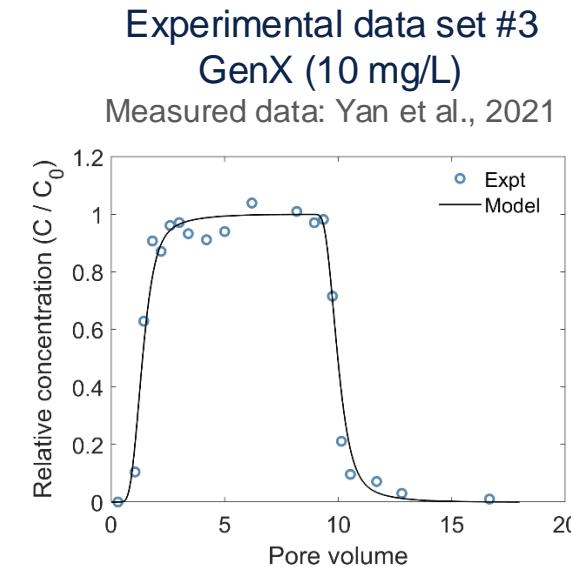
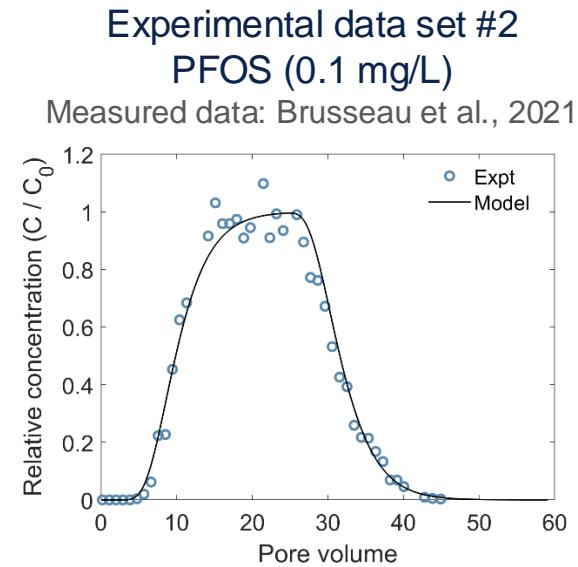
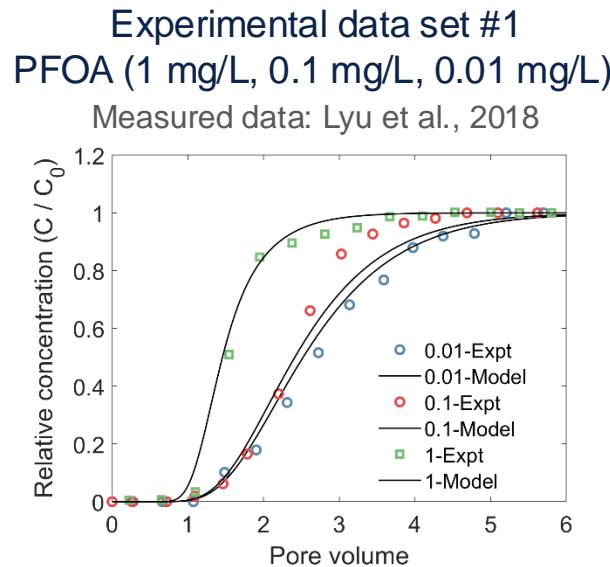
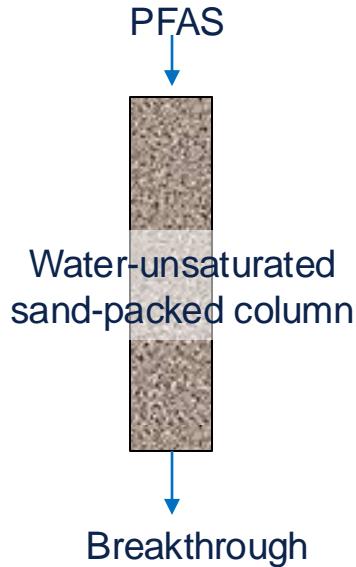
$$\frac{dC_{s,aw}}{dt} = \alpha_{aw} [(1 - F_{aw}) A_{aw} K_{aw} C - C_{aw,2}]$$

Kinetic



θ	Water content
σ	Surface tension
h	Pressure head
K	Hydraulic conductivity
γ	Contact angle
v	Pore-water velocity
D	Dispersion coefficient
C	Aqueous concentration
$C_{s,1}$	Instantaneous SPA
$C_{s,2}$	Kinetic SPA
$C_{aw,1}$	Instantaneous AWIA
$C_{aw,2}$	Kinetic AWIA
K_f, N	Freundlich parameters
F_s	Fraction of instantaneous sites
A_{aw}	Air-water interfacial area
K_{aw}	AWIA coefficient
F_{aw}	Fraction of instantaneous sites

Model validation: vs. miscible-displacement experiments



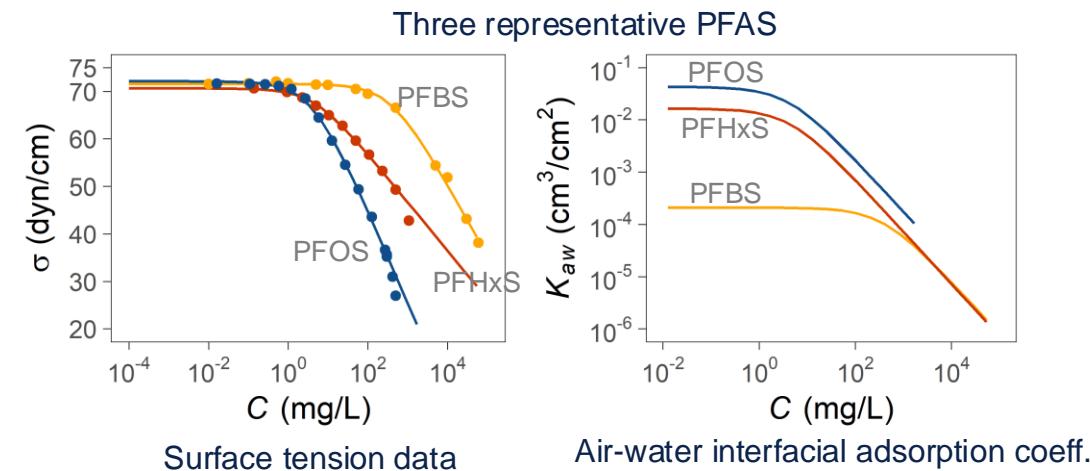
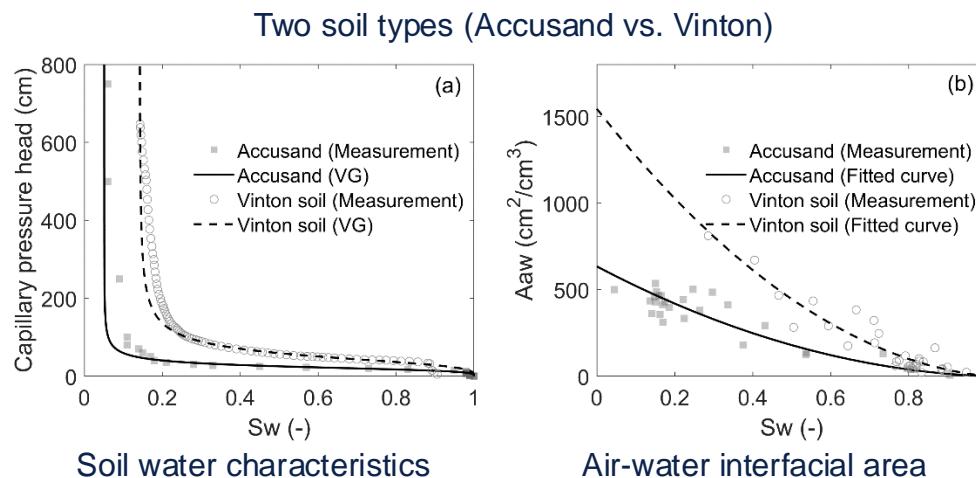
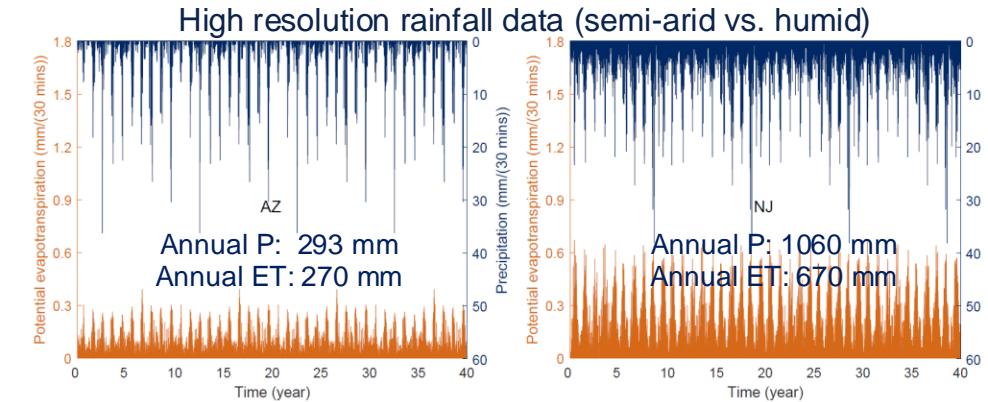
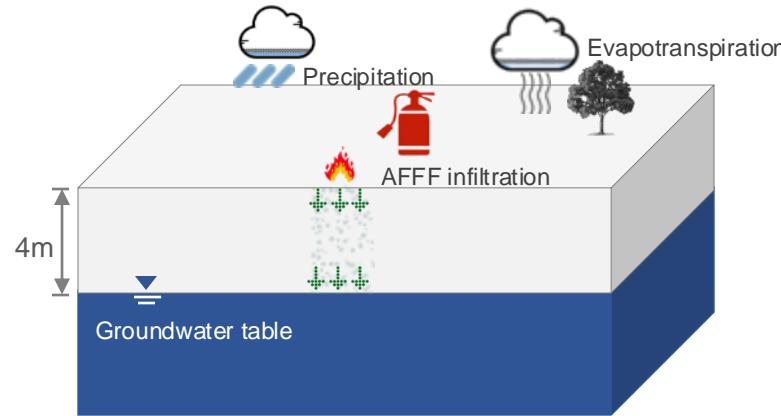
- Independent model predictions match well with experimental data.

Zeng, Brusseau, Guo. 2021 JH
Guo, Zeng, Brusseau, Zhang. 2022 AWR

Numerical simulation: PFAS migration at a fire training area

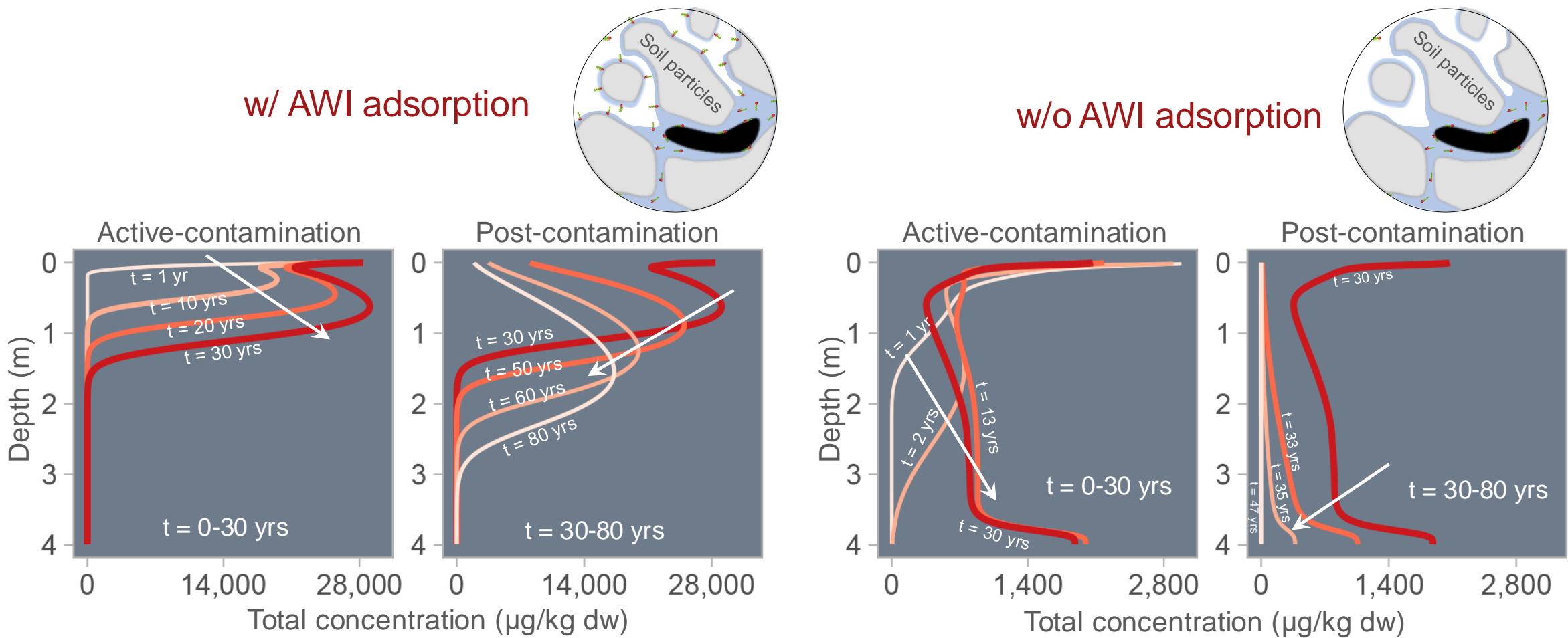
- PFAS contamination scenario at an AFFF-impacted fire training area site

- ✓ Fire training: one session every 10 days lasting for 30 years
- ✓ Representative PFAS mixture in 1% diluted AFFF solution
PFOS: 100 mg/L, PFHxS: 7.1 mg/L, PFBS: 1.4 mg/L



Numerical simulation: PFAS migration at a fire training area

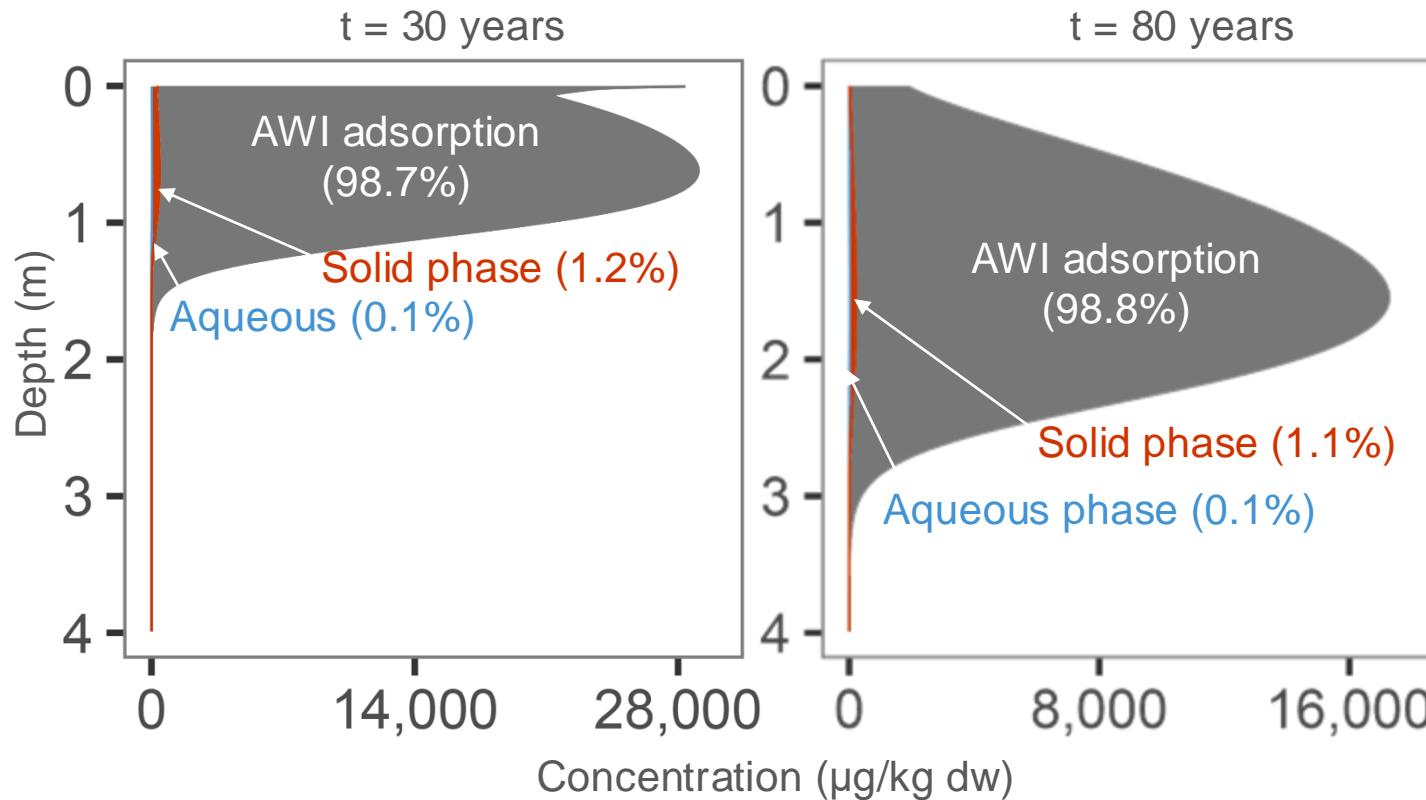
- Retention and leaching of PFOS: temporal evolution of spatial profiles



➤ Air-water interfacial adsorption significantly reduces the PFOS leaching in soils.

Numerical simulation: PFAS migration at a fire training area

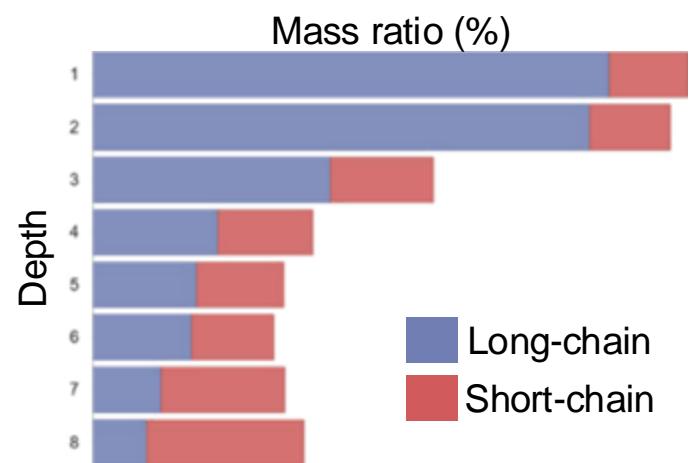
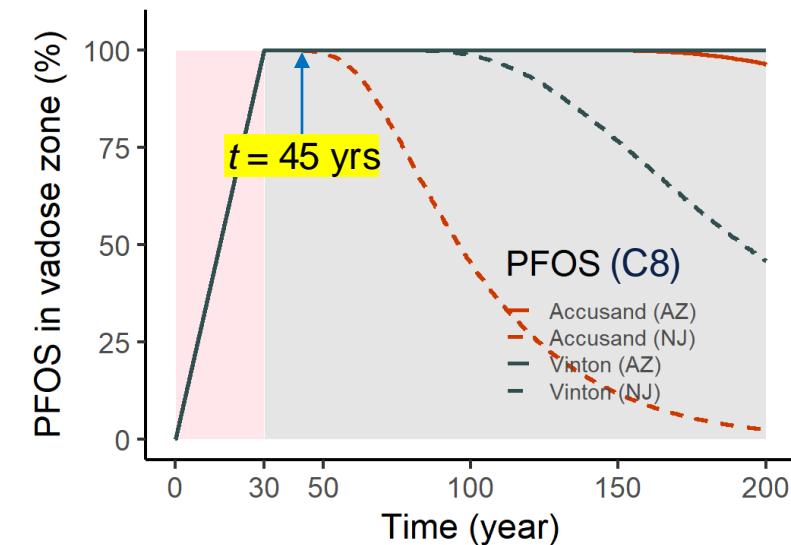
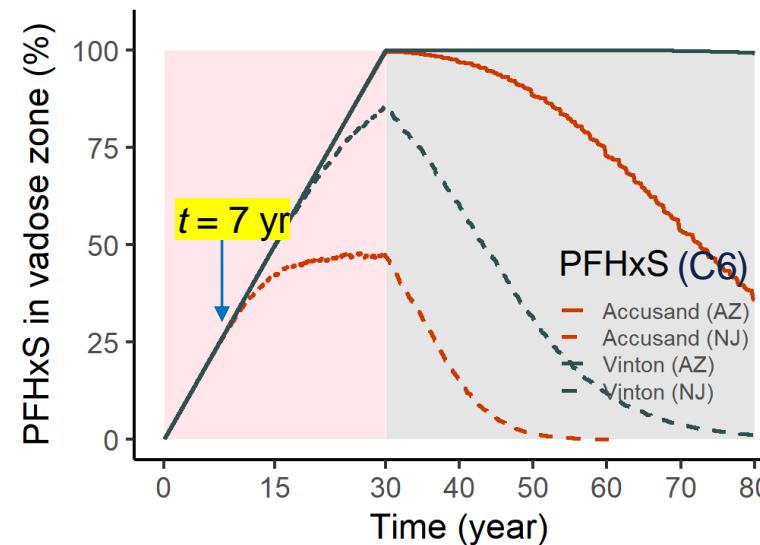
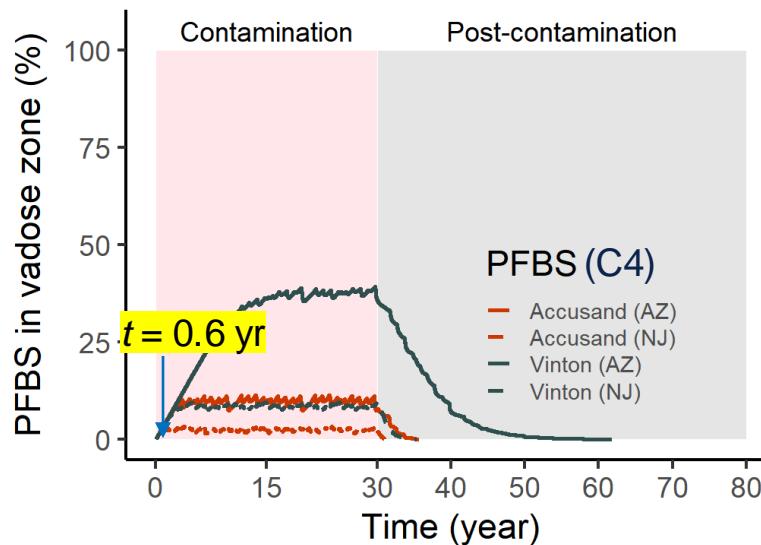
- Retention and leaching of PFOS: mass distribution in soils



- The majority (>98%) of PFOS in the soil is adsorbed at the air-water interfaces.
- Only 0.1% and ~1% of PFOS in aqueous and solid phase.
- C in soils >> C in groundwater.

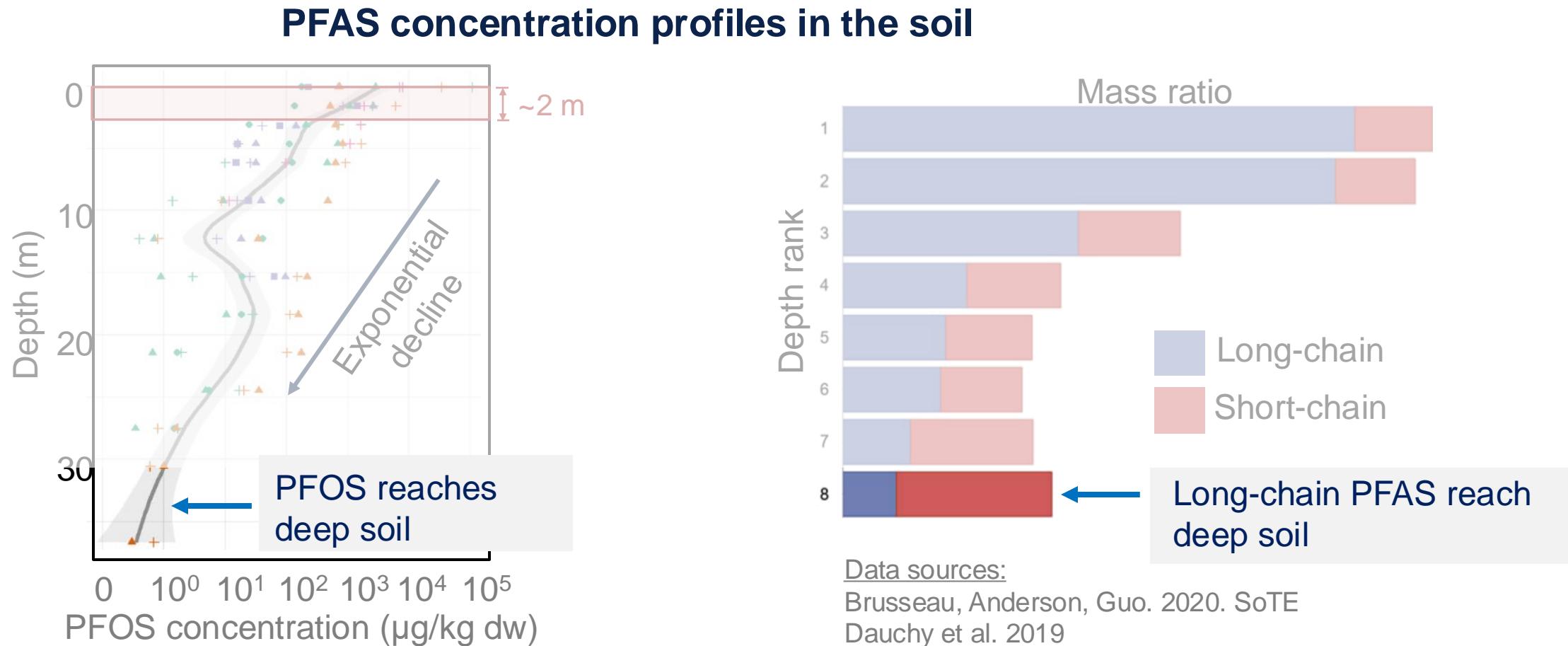
Numerical simulation: PFAS migration at a fire training area

- Short-chain vs. long-chain



- PFBS, PFHxS, and PFOS reach groundwater table at $t = 0.6$ yrs, 7 yrs, and 45 yrs.
- PFOS is much more strongly retained in the soil than PFBS and PFHxS.
- Long-chain PFAS is retained in the shallow soil; while short-chain PFAS reach much deeper depth.

Field data: spatial variation of concentrations in soils

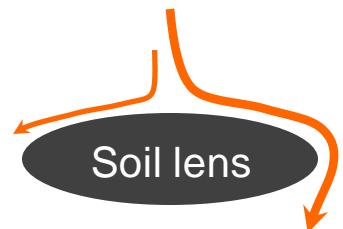


- The simulations capture strong retention of long-chain PFAS in shallow soil
- But they fail to represent leaching to deep soil and early arrival to groundwater

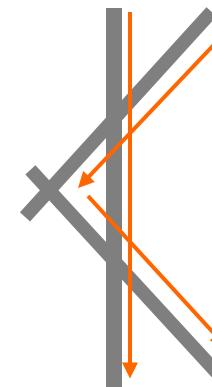
Hypothesis

Heterogeneity-generated preferential flow leads to long-chain PFAS leaching to deep soil.

Preferential flow



- Funnel flow

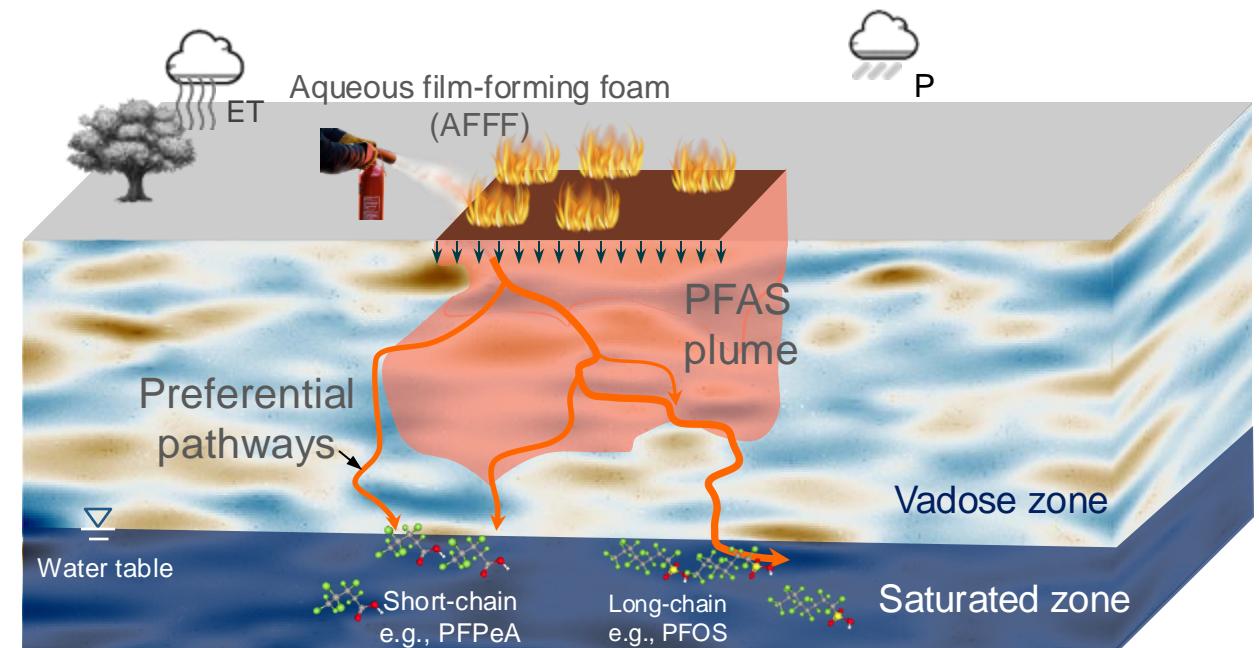


- Macropores/Fractures
- Other high-conductivity channels



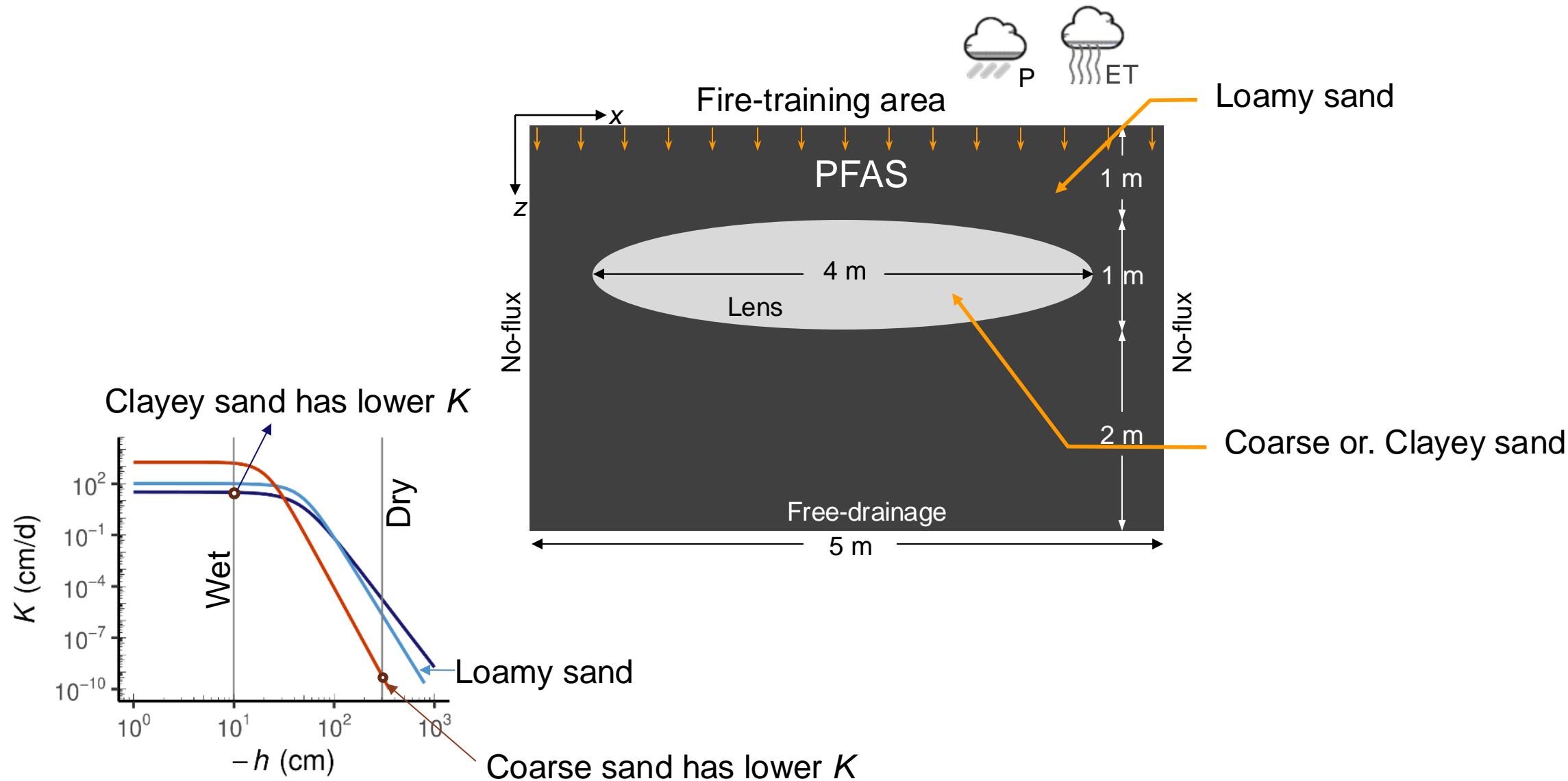
PFAS contamination at a fire-training area (FTA)

- Area: 30 m × 30 m.
- 1% diluted AFFF.
- Fire training: 30 min per 10 days for 30 yrs.
- Water table is deeper than 4 m.



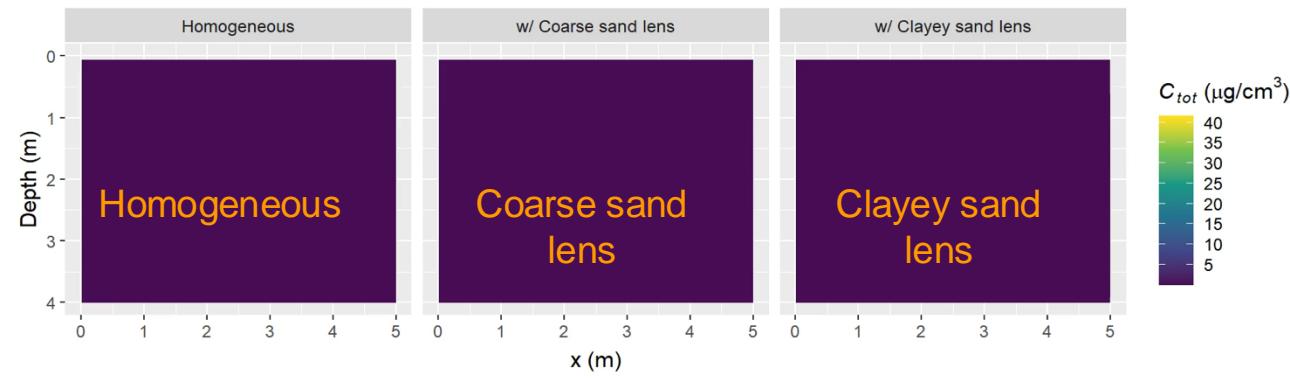
(Zeng, Guo, 2021; Guo, Zeng, Brusseau, 2020)

Soil lenses



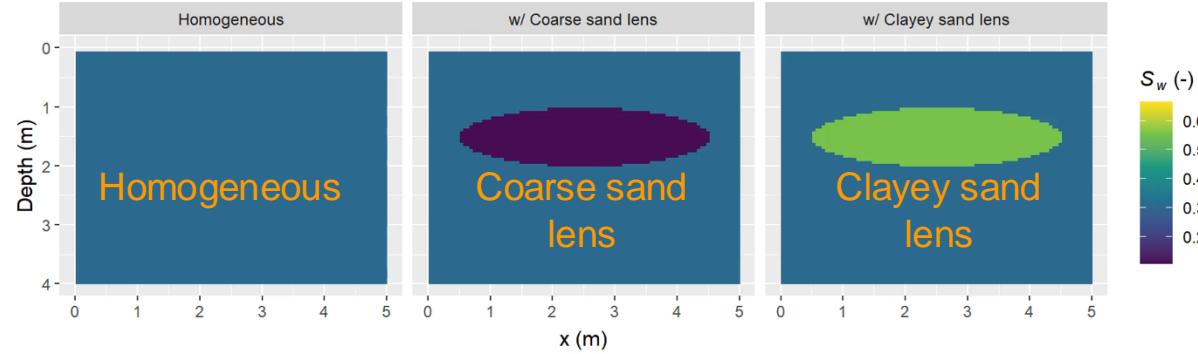
Time: 0 years

Total concentration



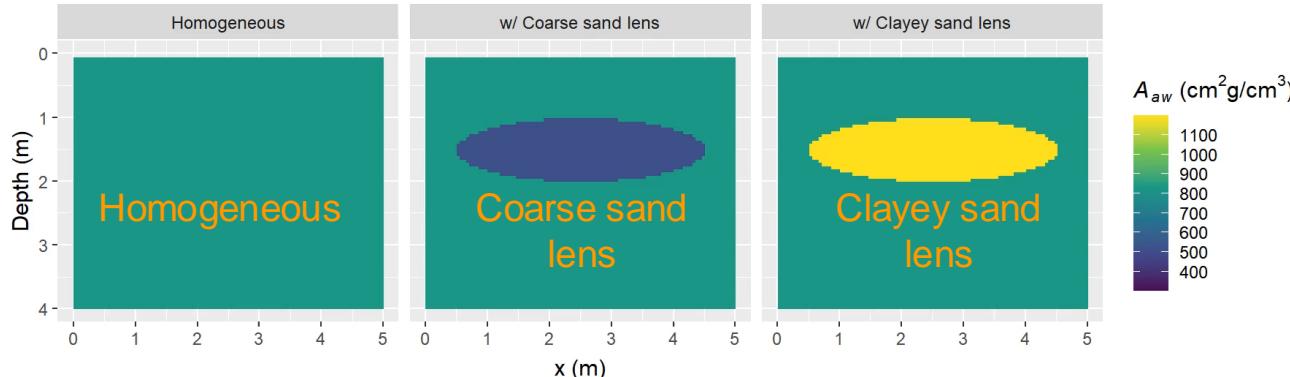
Time: 0 years

Water saturation



Time: 0 years

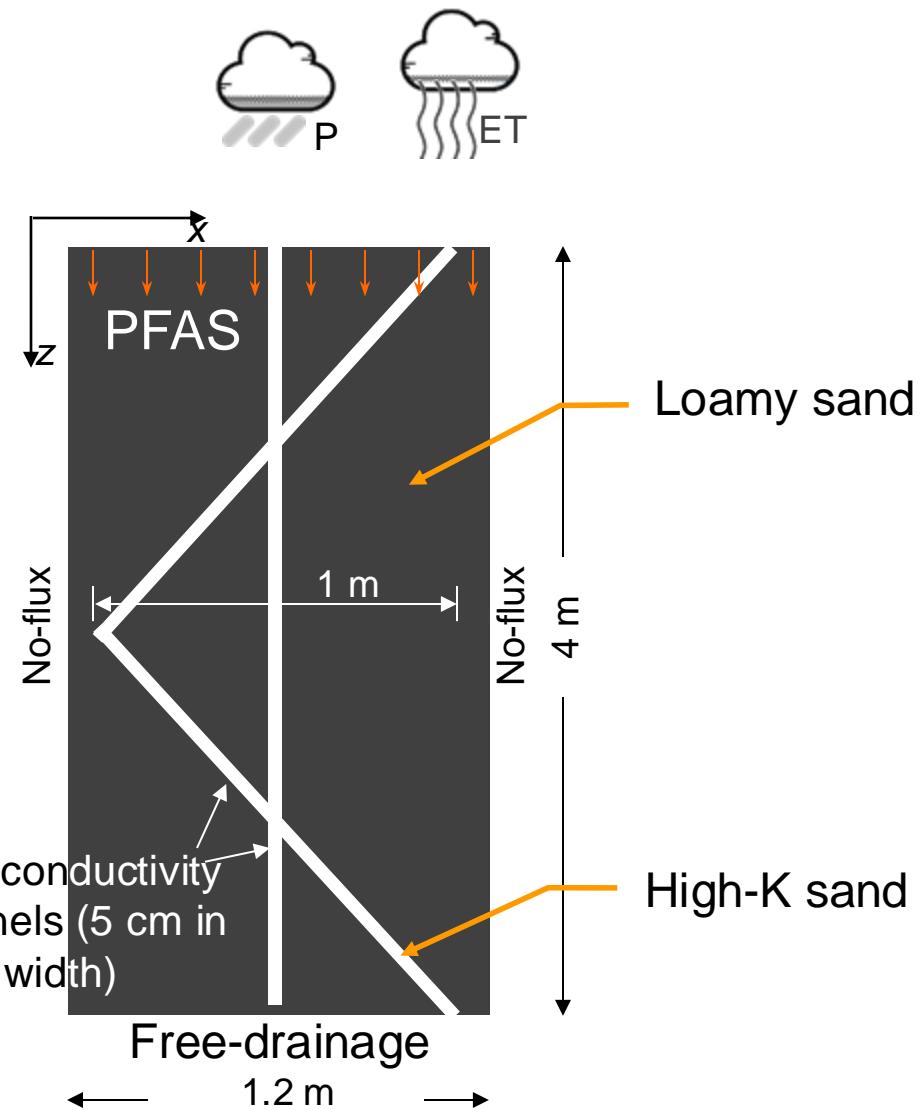
Air-water interfacial area



Accelerated leaching caused by soil lenses

- PFAS leaching is accelerated in the presence of the preferential flow pathways.
- Along these flow pathways, air-water interfaces are destructed, which further accelerates PFAS migration.
- This is a phenomenon **unique** for PFAS, especially those long-chain compounds.

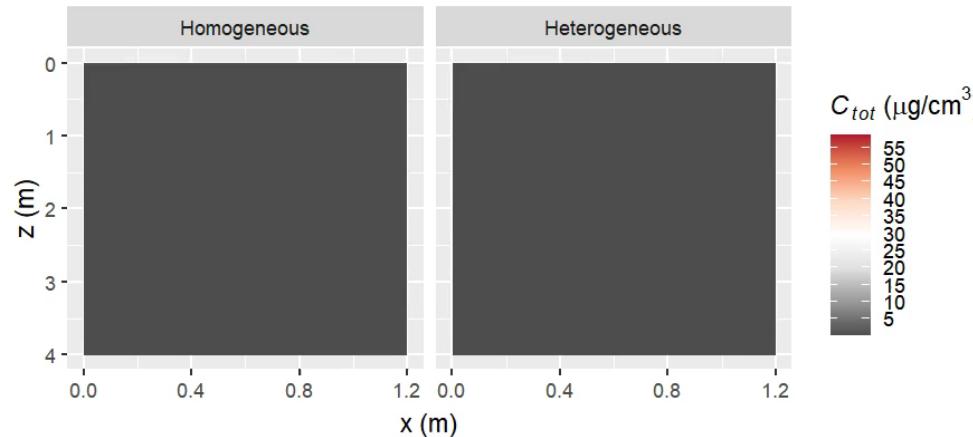
Macropores/Fractures



Early arrival and horizontal spreading caused by macropores/fractures

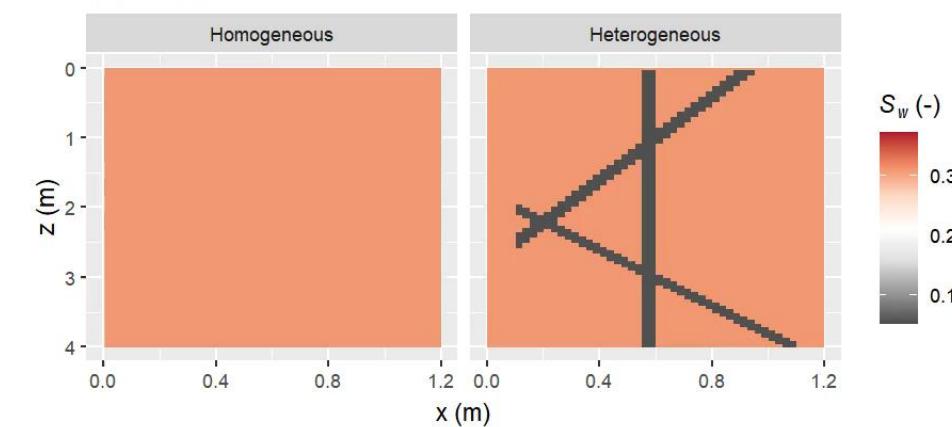
1. Total concentration

Time: 0 years



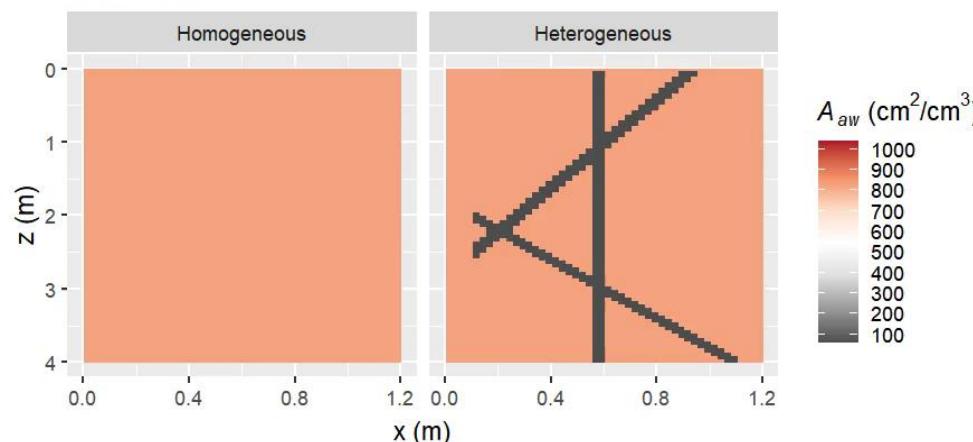
2. Water saturation

Time: 0 years



3. Air-water interfacial area

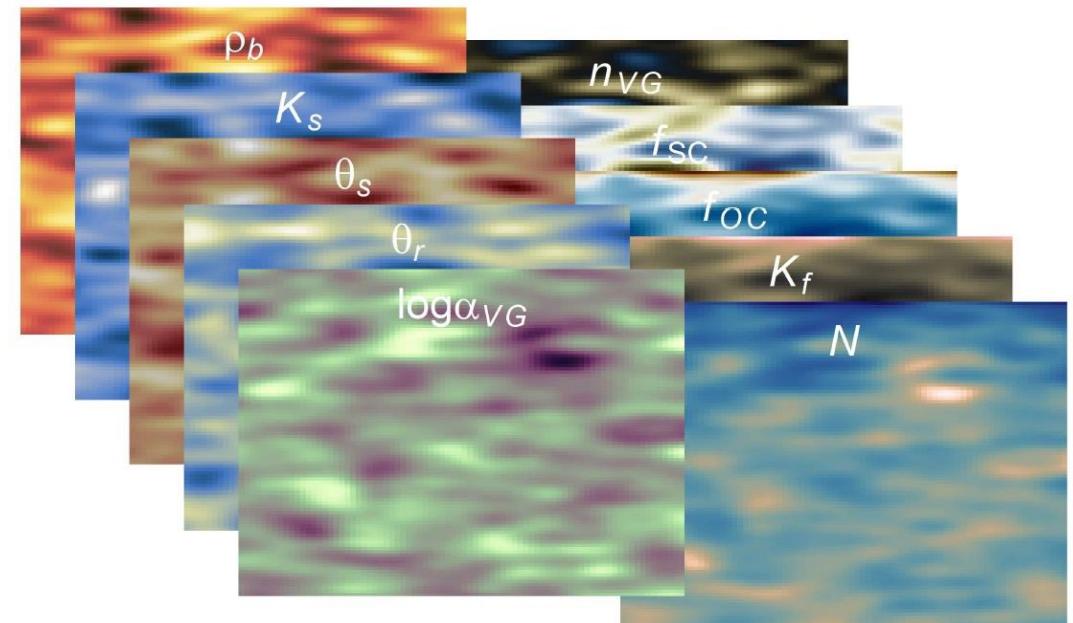
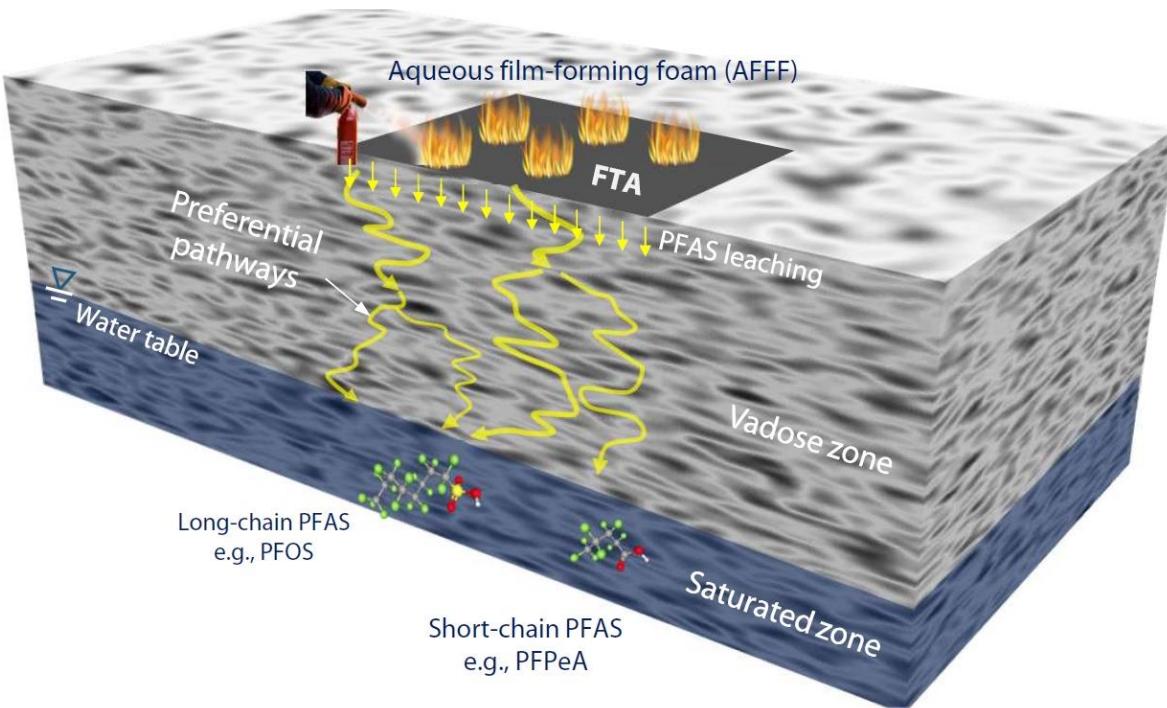
Time: 0 years



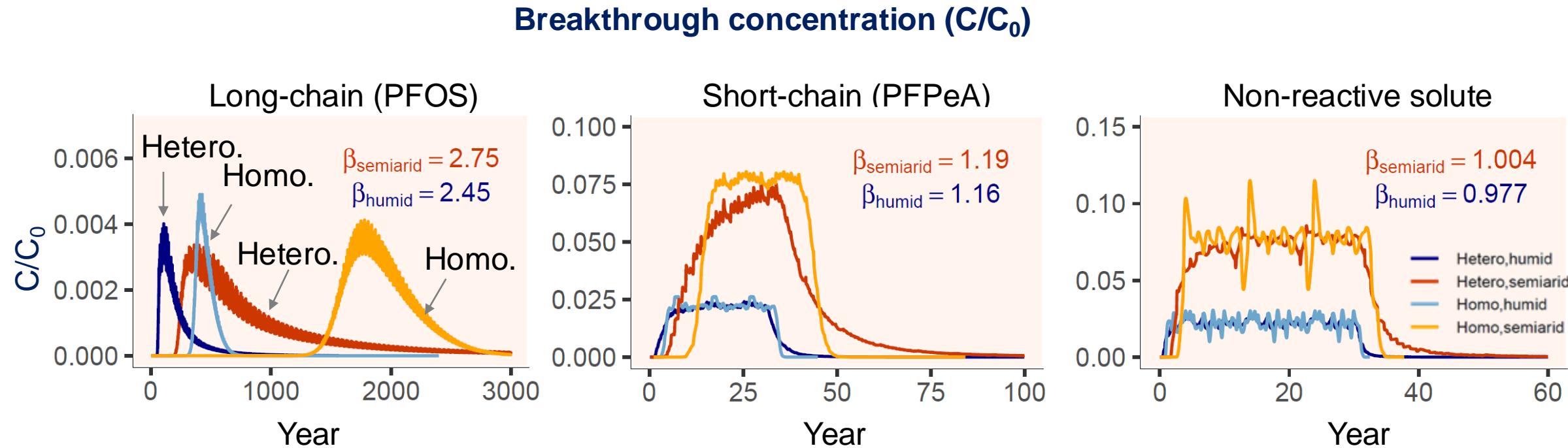
- During the early time, high-conductivity channels accelerate PFAS leaching;
- During the late time, the leaching efficiency is reduced due to “shortcut-circuiting” channels surrounding the soil matrix.

More complex heterogeneities

(Stochastically generated heterogeneous fields)



Preferential flow uniquely accelerated PFAS leaching in soil



Testing the mathematical models using pilot-scale experiments



Excavating the soil cores and monolith from the Davis Monthan AFB (Tucson, AZ)



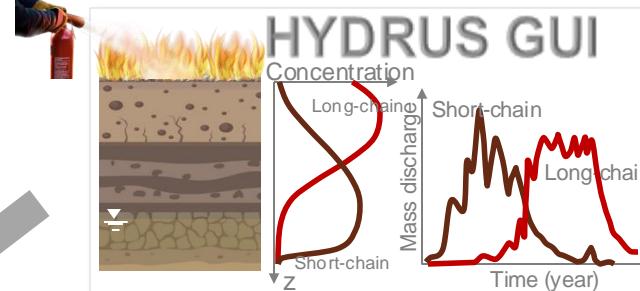
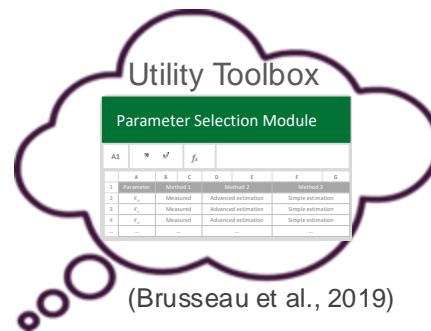
Soil cores and monolith transported to the laboratory (Dr. Mark Brusseau) at the University of Arizona

PFAS-LEACH: Predicting PFAS Leaching in Source Zones

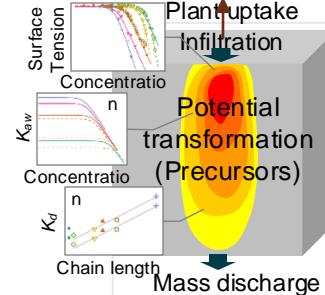
Computational Cost/Input Parameters ↑

PFAS-LEACH – A Comprehensive Decision Support Platform for Predicting PFAS Leaching in Source Zones

- i. Three simulators spanning wide range of complexity
- ii. Comprehensive parameter selection module
- iii. Documentation and user manual



Tier 3 – PFAS-LEACH-Screening



Feature: Implemented in Excel

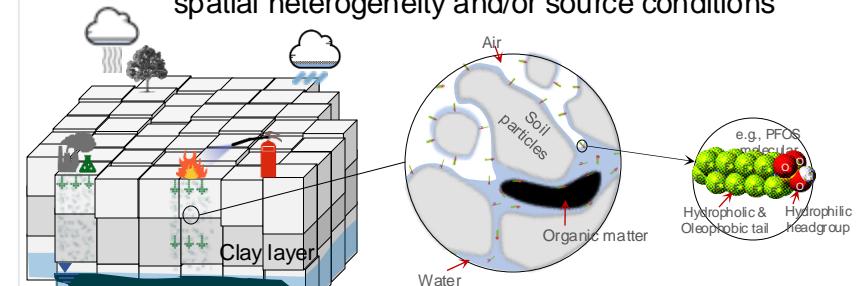
Anticipated application: Limited data; early stage of site management; order-of-magnitude estimate with uncertainty range

(Guo et al., 2022)

Tier 1 – PFAS-LEACH-COMP

Feature: Full-process model in 3D

Anticipated application: Sites w/ sufficient data; complex spatial heterogeneity and/or source conditions



(Guo et al., 2020; Zeng et al., 2021; Zeng & Guo, 2021)

Tier 2 – PFAS-LEACH-HYDRUS

Feature: Implemented in HYDRUS-1D GUI

Anticipated application: Insignificant lateral heterogeneity; efficient uncertainty quantification

(Zeng et al., 2021)

ESTCP Project ER21-5041
“Development and demonstration of PFAS-LEACH”

Model Complexity →

THIS IS JUST THE BEGINNING



EAR 2023351
EAR 2054575
CAREER 2237015



Project ER21-5041

Take-home message

- PFAS are wide spread in the environment.
- Soils above the groundwater have become significant reservoirs of PFAS.
- PFAS fate and transport in the environment are unique compared to conventional contaminants.
- Computer models can be used to assess contamination risks and assist remedial design.

