HWRS 505: Vadose Zone Hydrology

Lecture 22

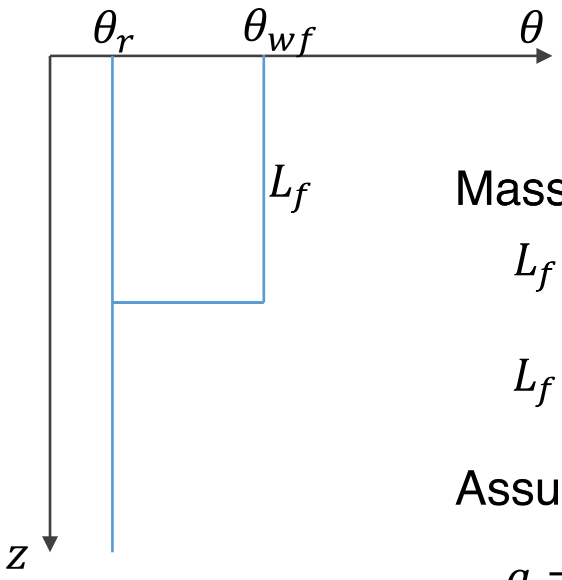
11/14/2023

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 Ksat/10. Ksat = 0.00825 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

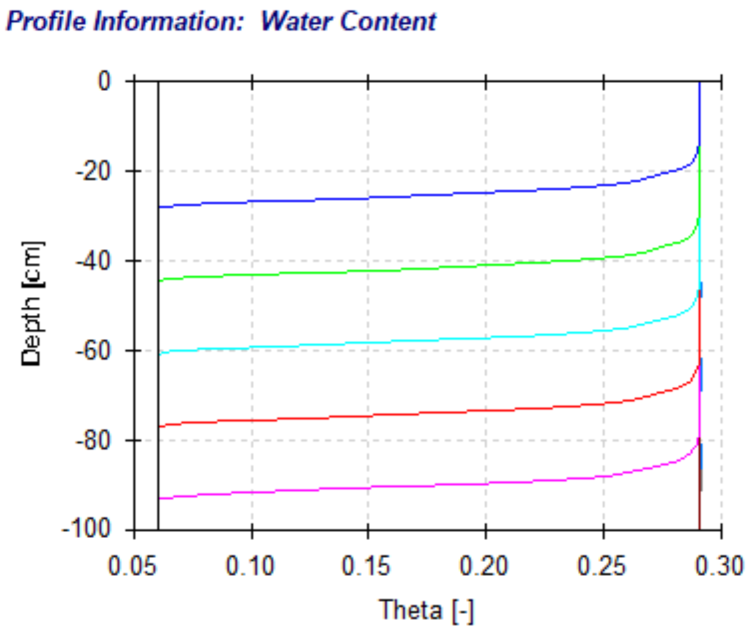
$$L_f(\theta_{wf} - \theta_r) = qt$$

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

Assuming water flow is only driven by gravity

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

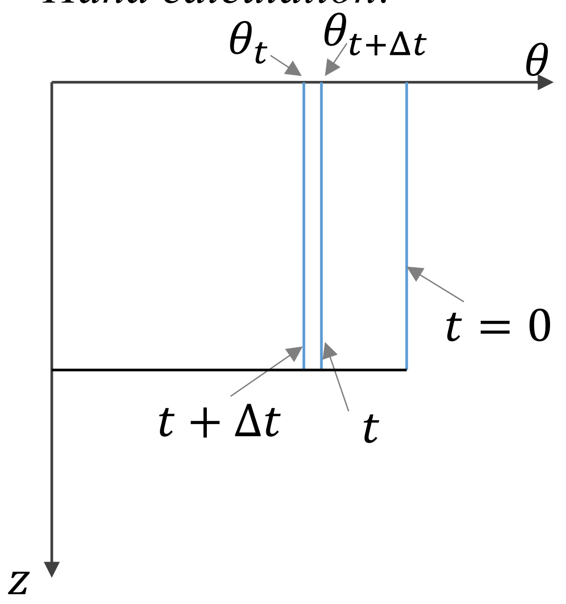
You can then back calculate θ_{wf} and determine L_f.



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:



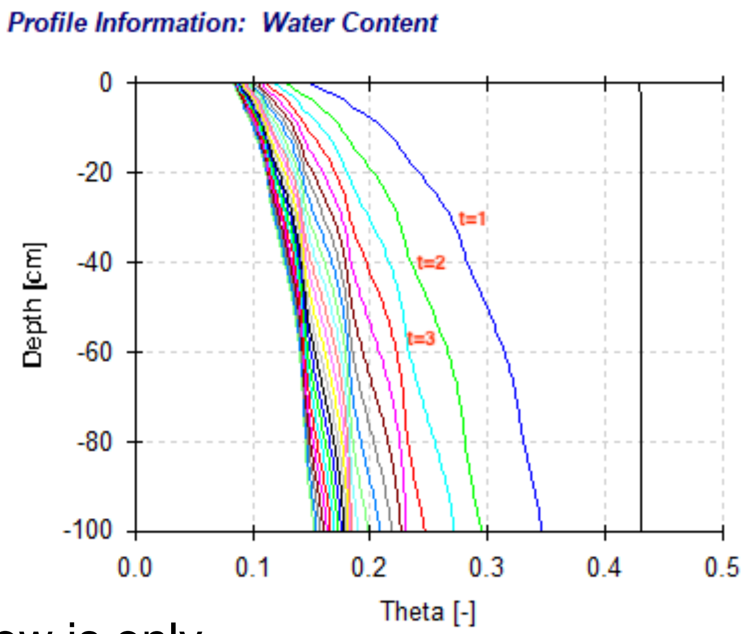
$$t \rightarrow t + \Delta t$$

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

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

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

Assuming water flow is only driven by gravity



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 filed 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 New York Times Magazine

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**

'Ticking time bomb': PFAS chemicals in drinking water alarm scientists over health risks

EPA under pressure to regulate PFAS, found in the water of nearly 2,800 cities

By Devin Dwyer, Stephanie Ebbs, and Jacqueline Yoo
August 10, 2021, 12:33 PM • 17 min read

'Forever chemicals' detected in water systems of nearly 2,800 US cities

ABC News' Devin Dwyer investigates the growing concern over PFAS contamination and... **Read M**
ABC News

abc NEWS

University of Arizona hydrologist Bo Guo calls the prevalence of synthetic chemicals in soils a "ticking time bomb" as the substances can slowly contaminate groundwater years after release.
ABC News

"They basically fulfill the characteristics of a ticking time bomb," said Dr. Bo Guo, a University of Arizona hydrologist and expert on per- and polyfluoroalkyl substances, or PFAS, which are commonly used in hundreds of consumer products and in firefighting foams, a top source of PFAS contamination.

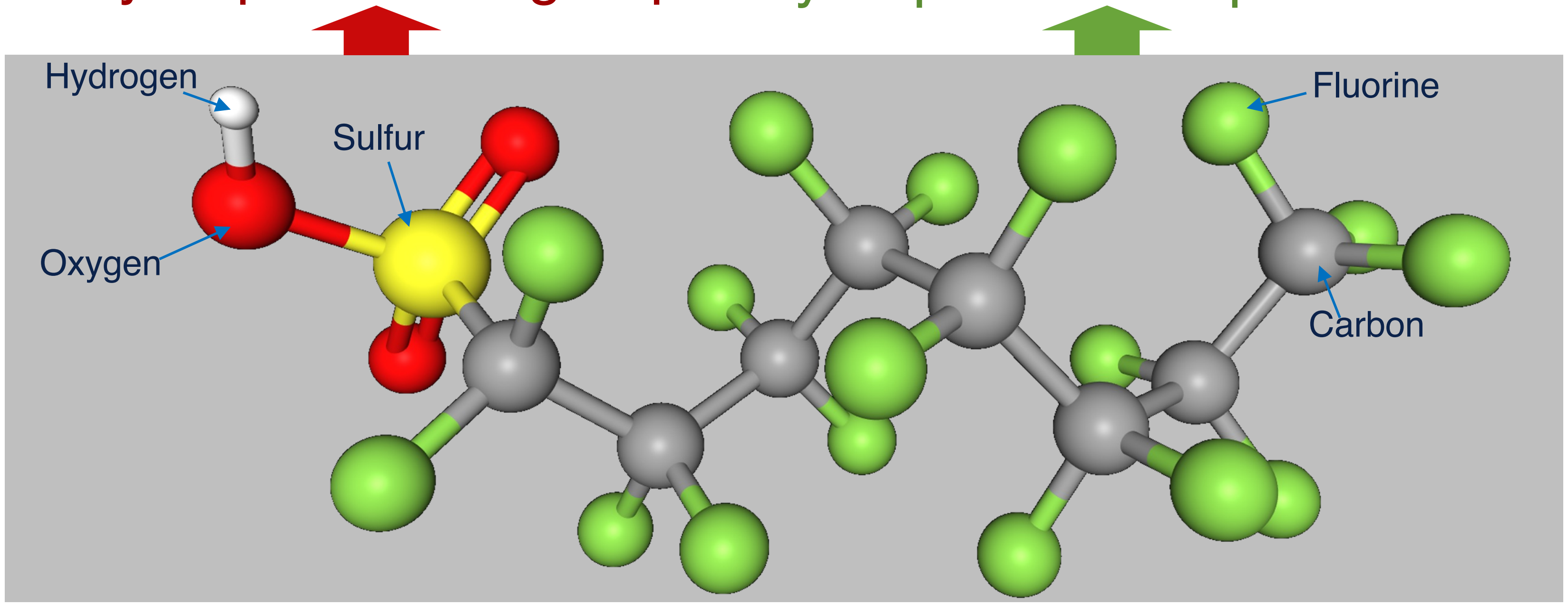
"They're very dangerous and they're migrating very slowly," Guo said of the heat-resistant chemicals.

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

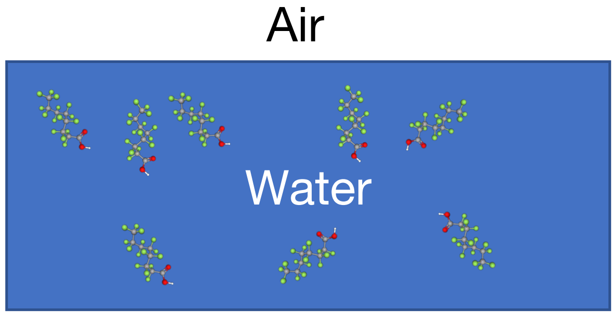
PFAS molecule (e.g., PFOS)

(“likes” water)
Hydrophilic headgroup

(“does not like” water)
Hydrophobic-oleophobic tail



- Surfactant (**Surf**ace **act**ive ag**ent**)
- Persistent (**C-F** bond)
- Toxic at **ppt** levels
- More than **9,000** compounds



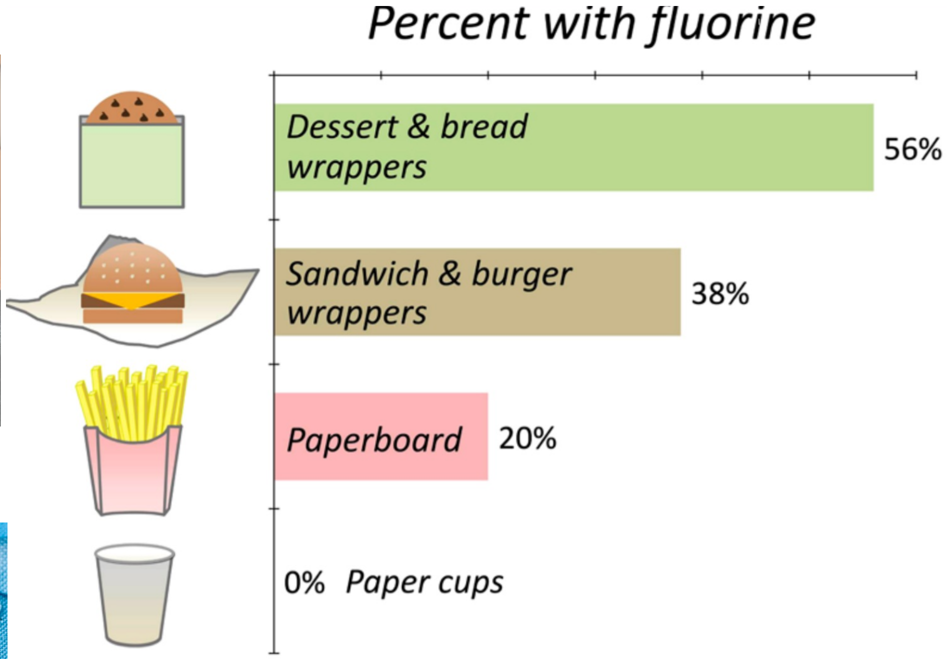
Accumulate at air–water interfaces

Used in our daily life and at military sites

“Perfect” chemicals if NOT toxic

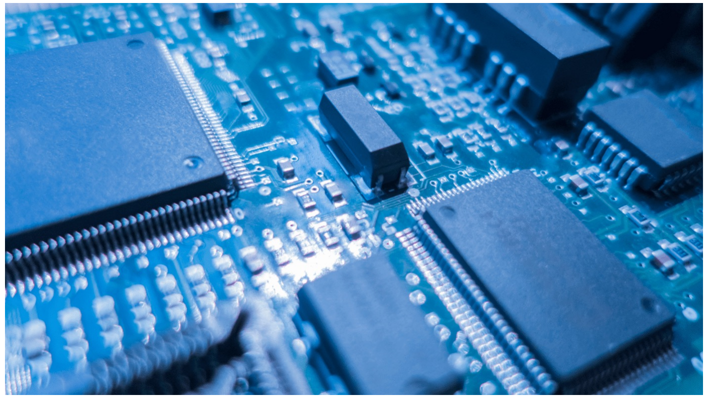
Non-stick, stain- and water-resistant coating

Food packaging



Schaider et al (2017)

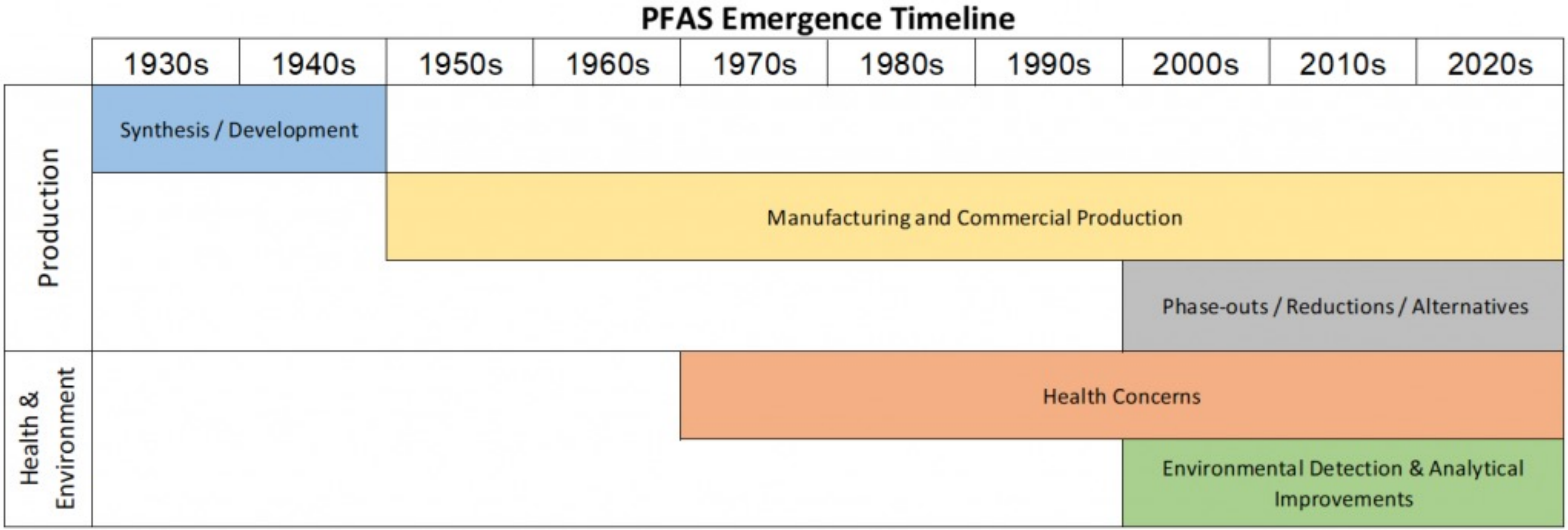
Semiconductor Industry



Fire fighting foam

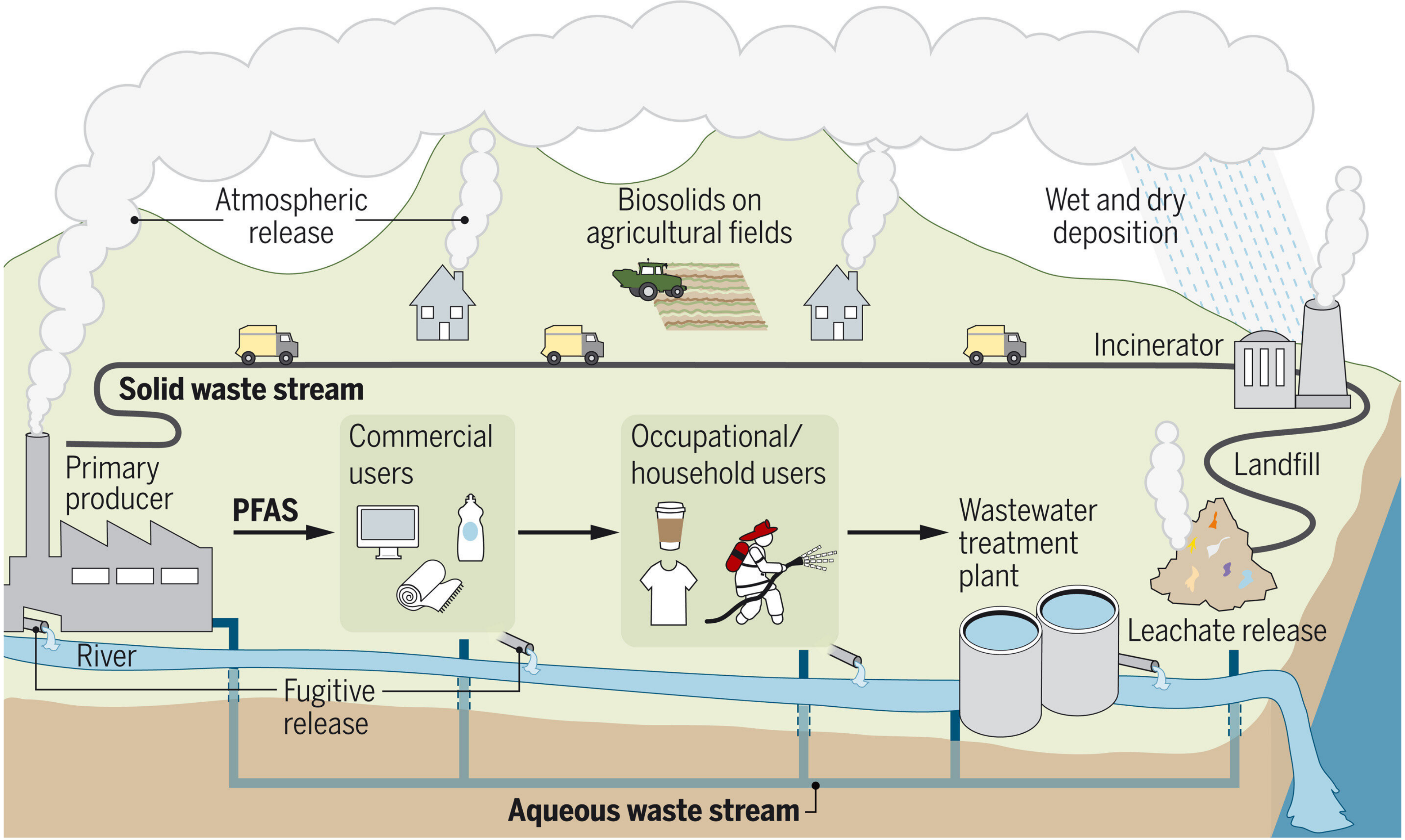
http://www.safetynews.co.nz/fire-fighting-foams-causing-sparks-fly/

General timeline of PFAS emergence and awareness



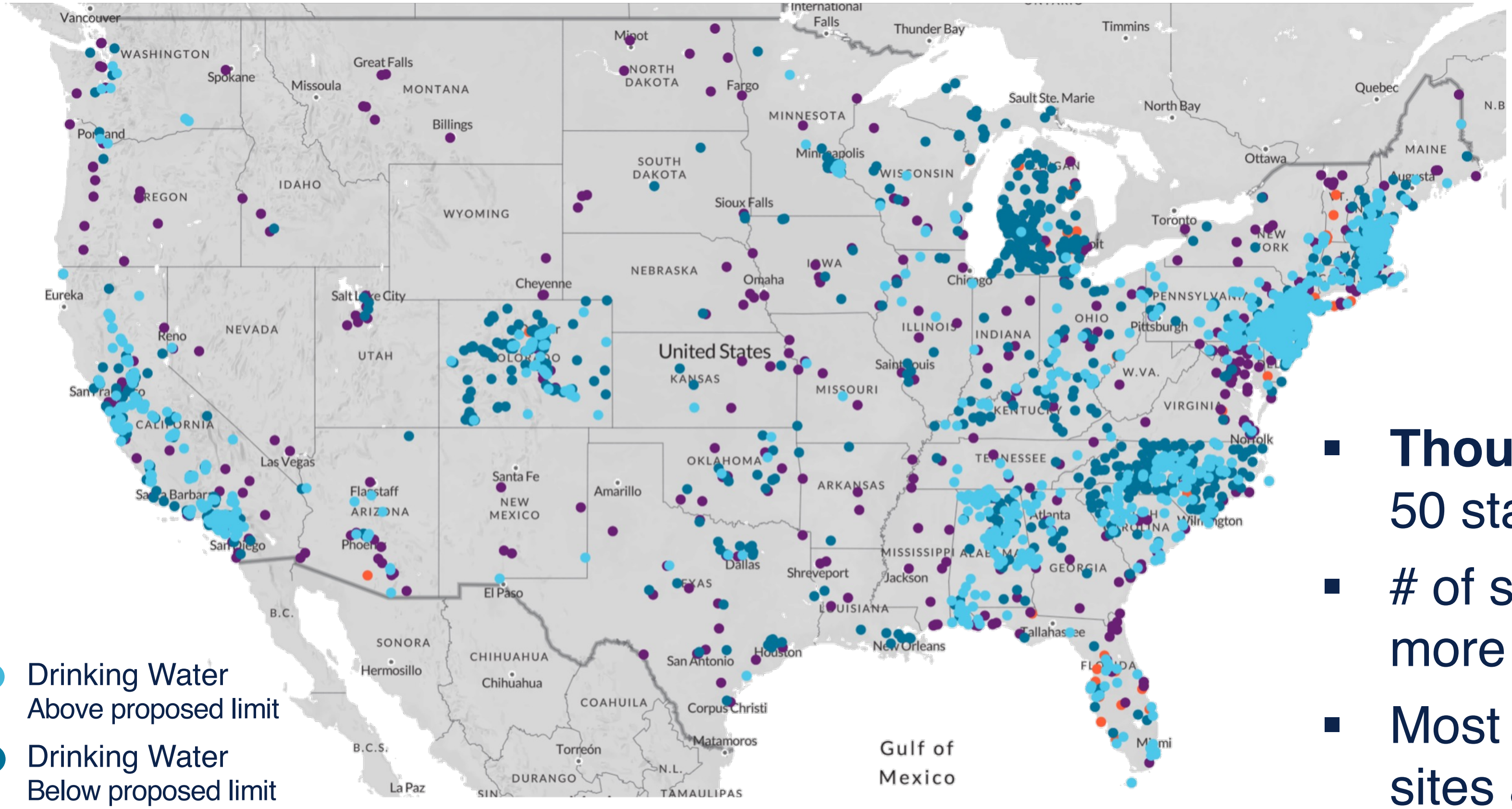
Source: J. Hale, Kleinfelder and ITRC PFAS fact sheets

PFAS releases to the environment



Source: Evich et al., 2022. Science.

PFAS are widely spread in the environment



Drinking Water
Above proposed limit

Drinking Water
Below proposed limit

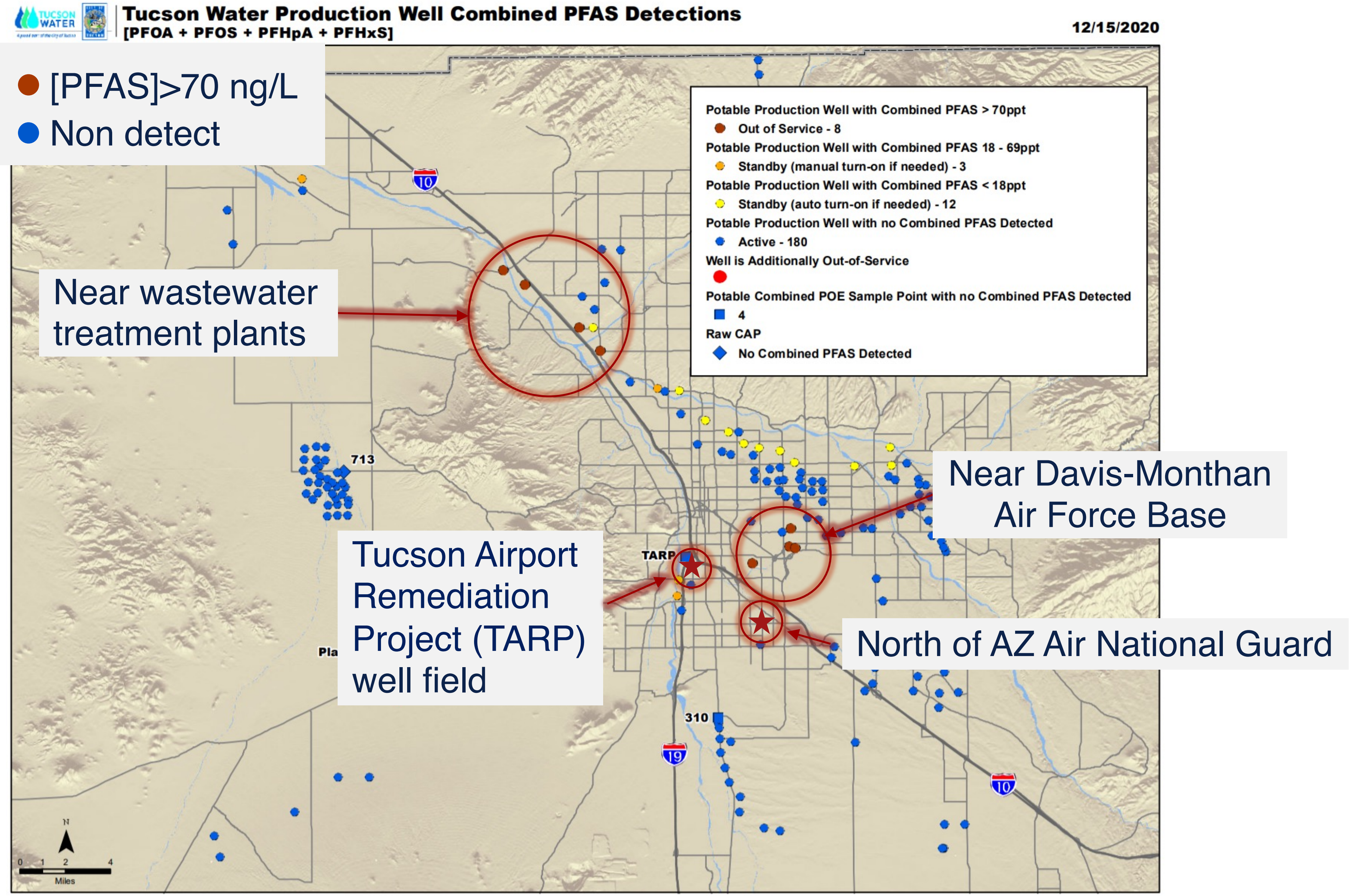
Military Sites

Other Known Sites

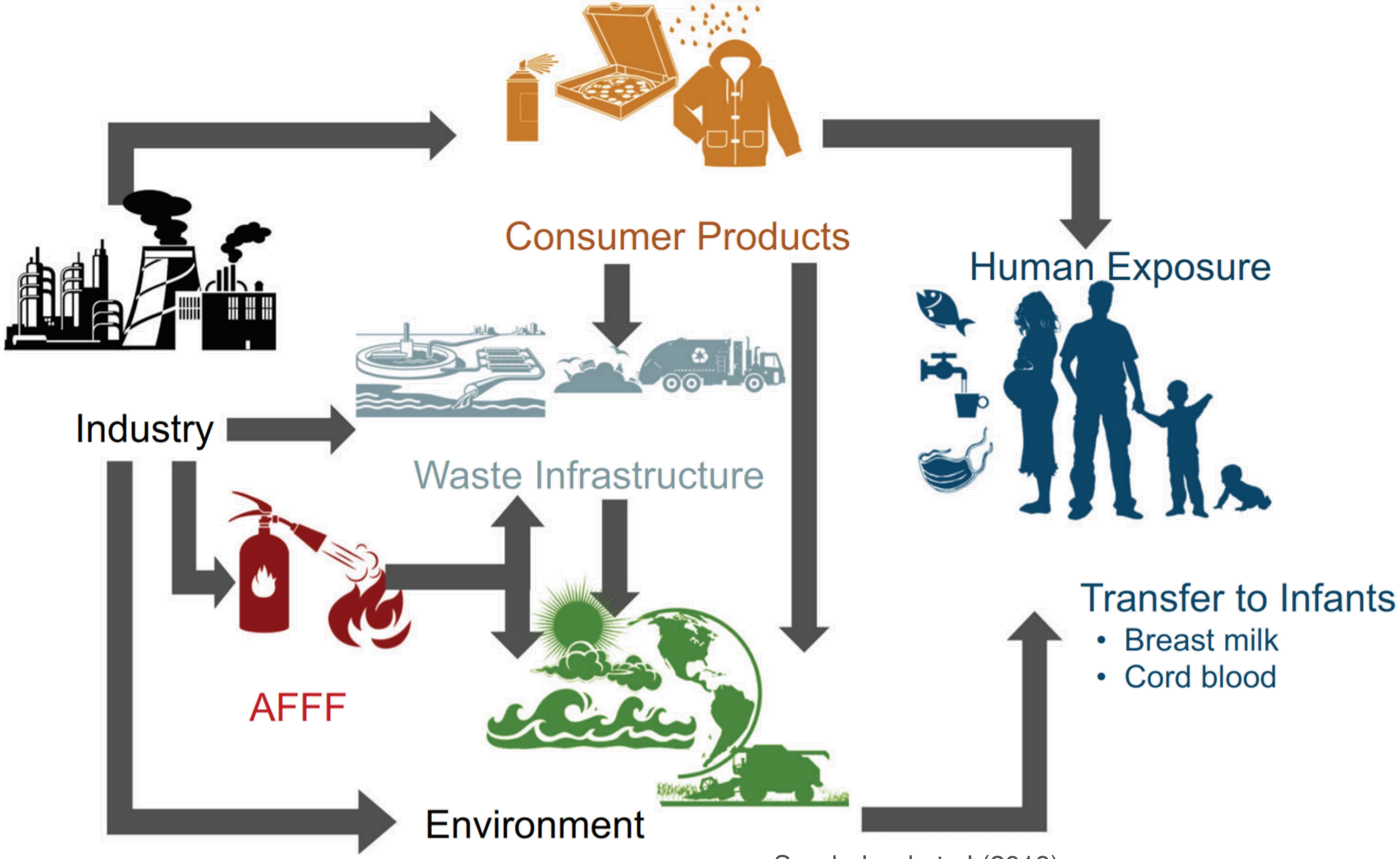
- **Thousands** of contamination sites in 50 states.
- # of sites are rapidly **growing** as more investigations are carried out.
- Most drinking water contamination sites are **above** the EPA proposed maximum contaminant level (**MCL**).

https://www.ewg.org/interactive-maps/pfas_contamination/map/

PFAS contamination in Tucson, AZ



97% of US residents have PFAS in their blood



Sunderland et al (2019)

What we know about health effects of PFAS exposure?

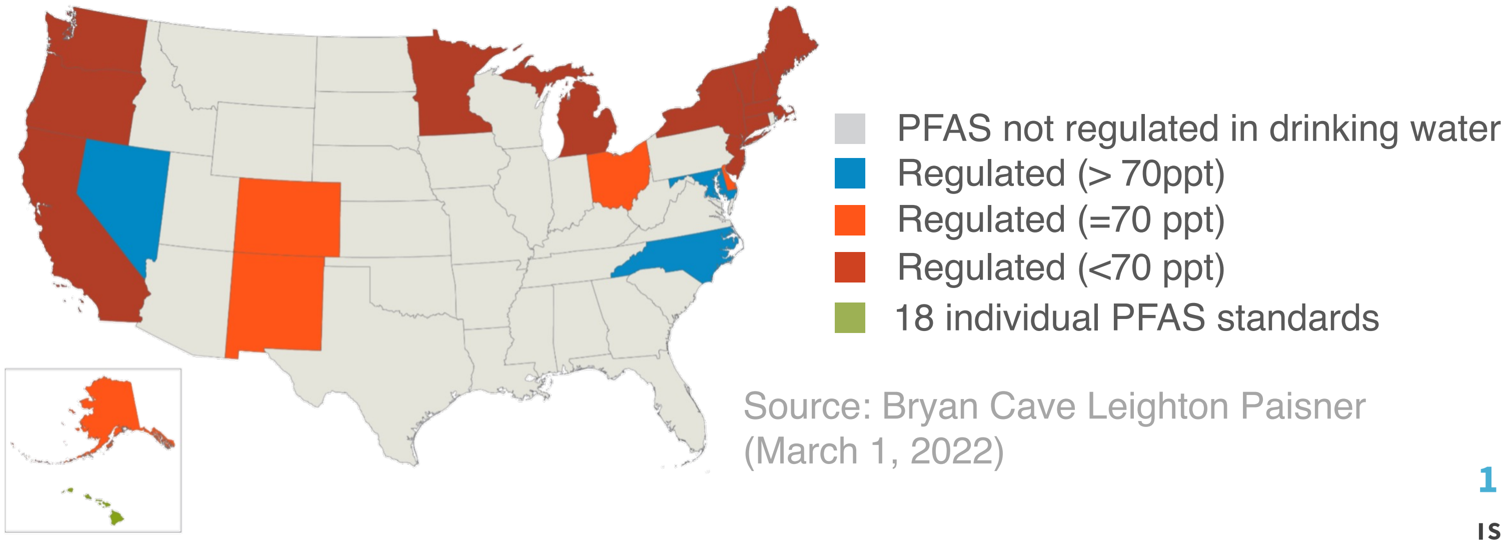
- **According to EPA, exposure to certain levels of PFAS may lead to:**
  - *Reproductive effects* such as decreased fertility or increased high blood pressure in pregnant women.
  - *Developmental effects* or delays in children, including low birth weight, accelerated puberty, bone variations, or behavioral 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 plaintifs 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)."

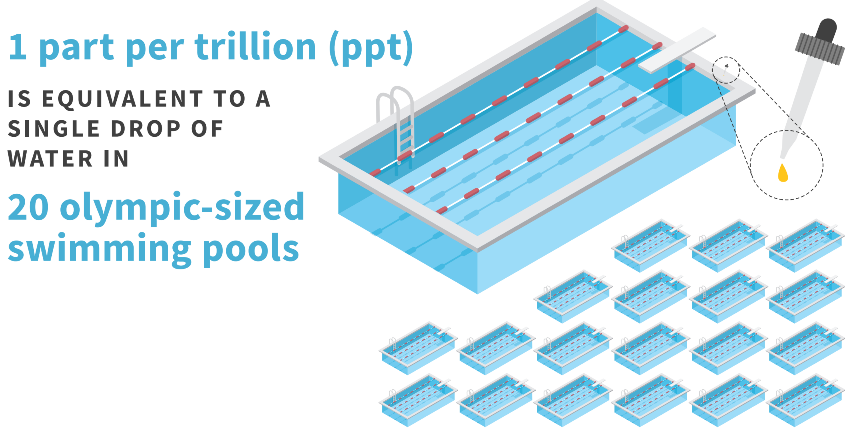
https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas
https://pfasproject.com/parkersburg-west-virginia/

Regulation of PFAS in drinking water in the US



Source: Bryan Cave Leighton Paisner (March 1, 2022)

- 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



https://www.michigan.gov/

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

How do the proposed MCLs compare to other contaminants?

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

Groundwater contaminant	Regulatory criteria (μg/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

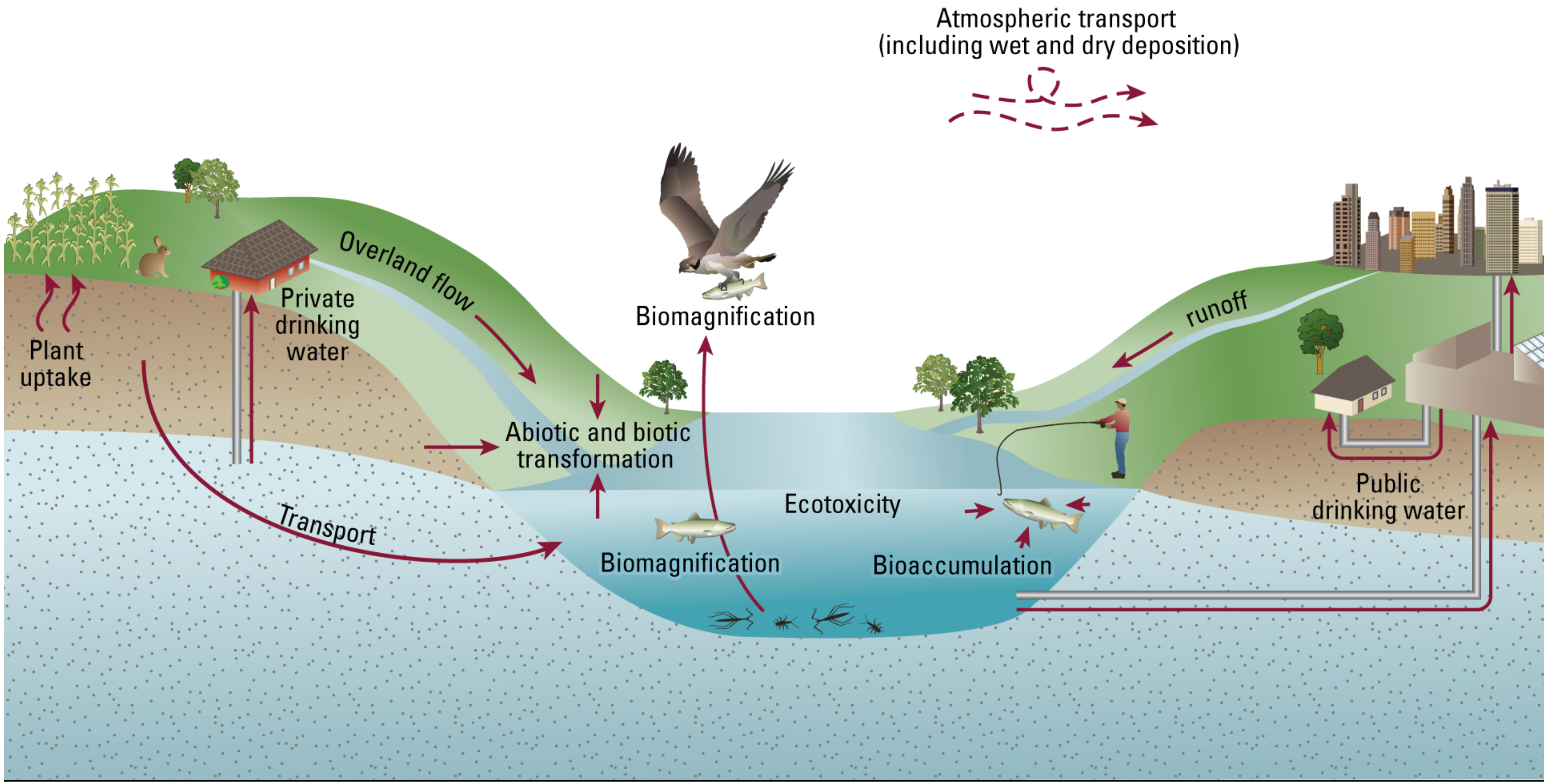
Tucson Airport Remediation Project (TARP) was created 1994 to treat TCE, and then later 1,4-Dioxane.

- 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?

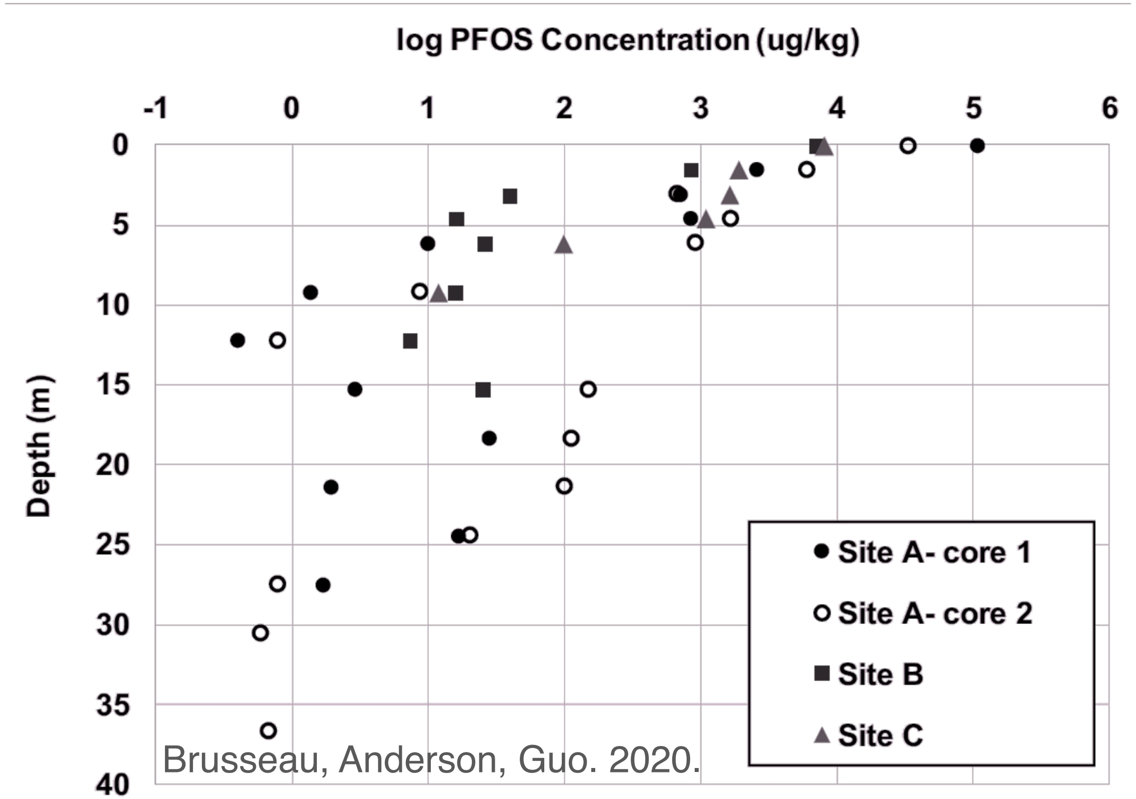
PFAS fate and transport in the environment



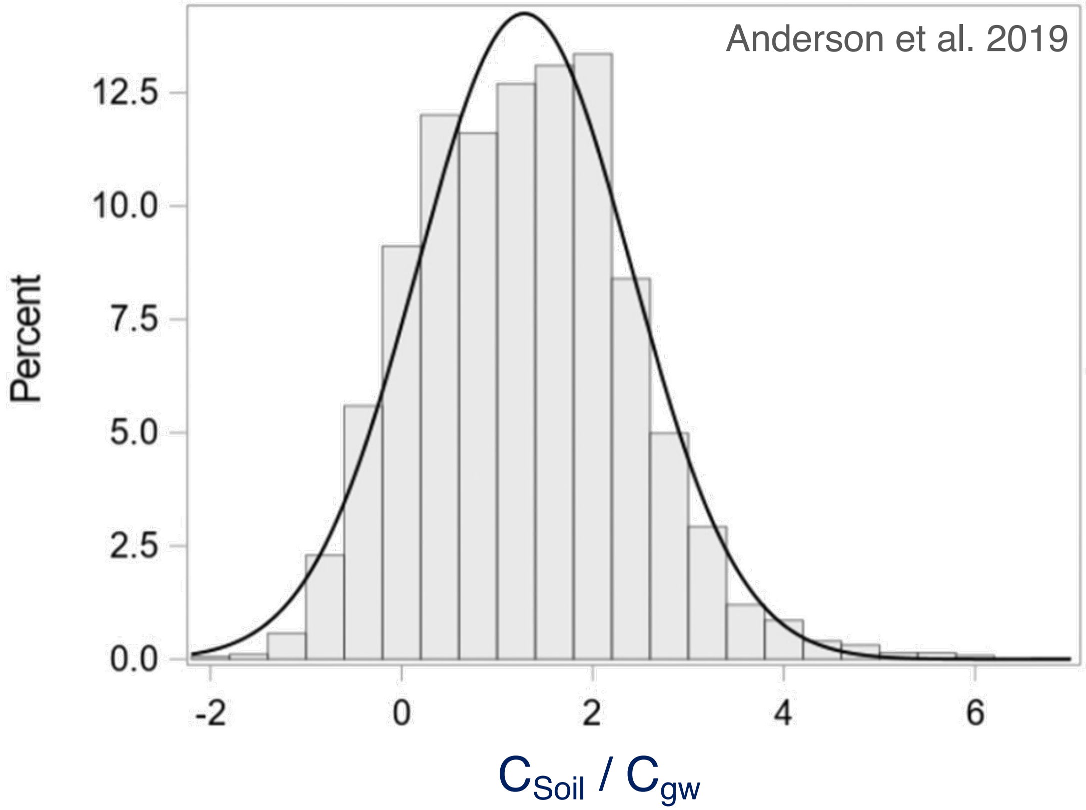
Source: USGS

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

Field data: concentrations in soil vs. groundwater



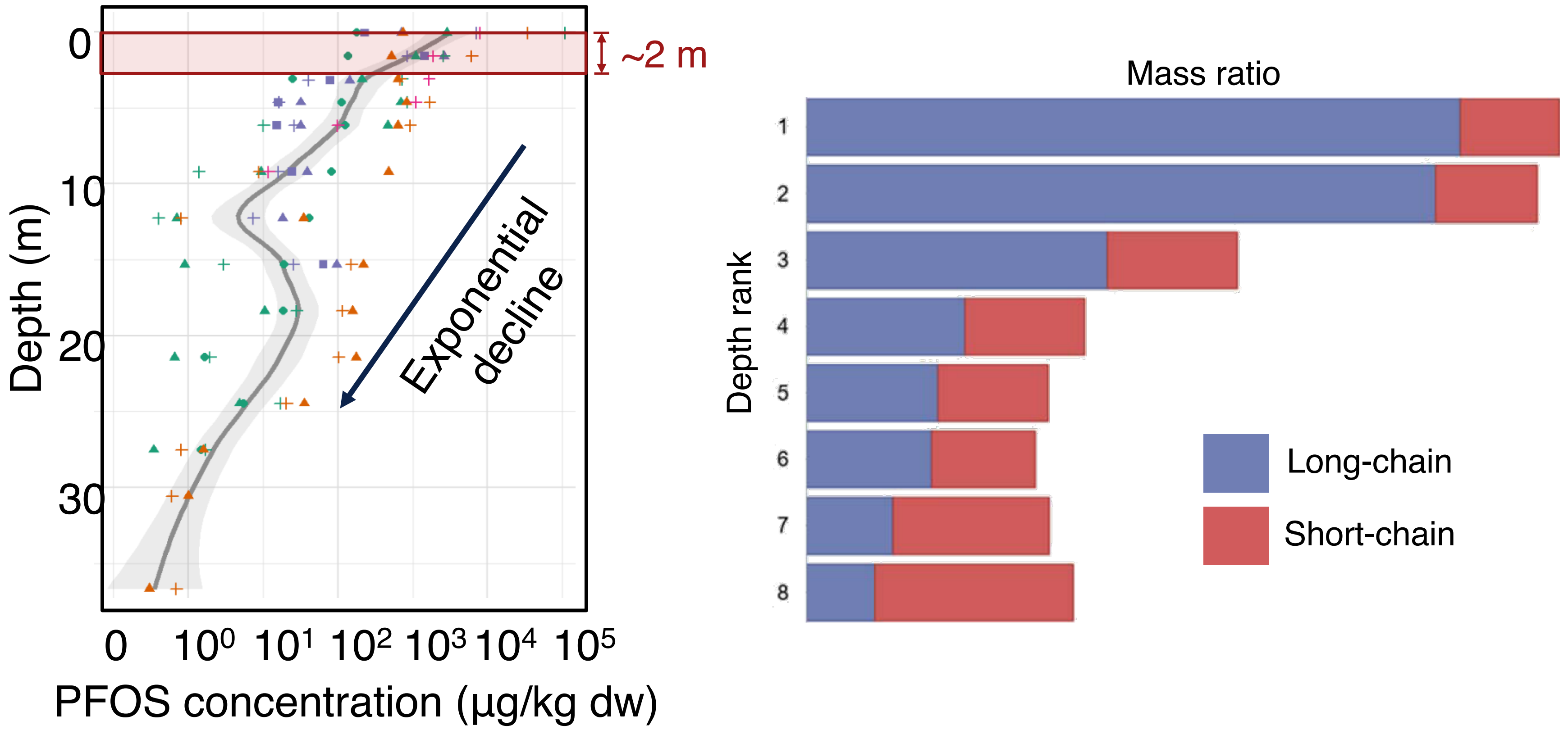
PFOS concentration in soil



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.

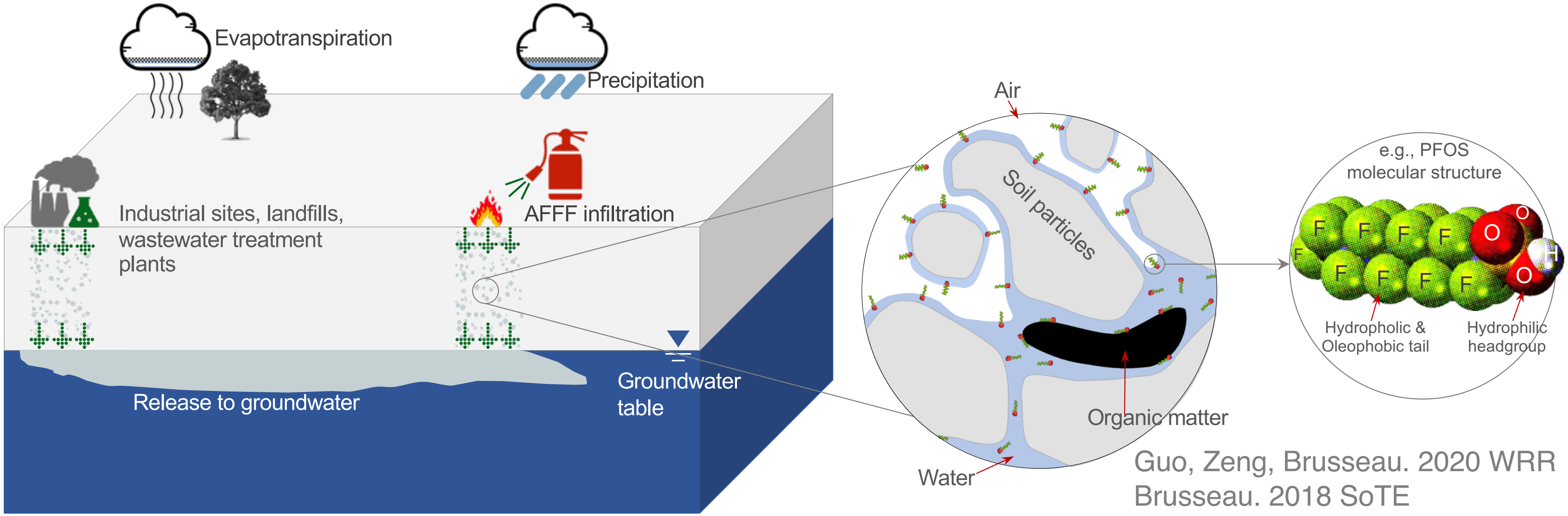
Anderson et al. 2019
Brusseau, Anderson, Guo. 2020.

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



Guo, Zeng, Brusseau. 2020 WRR
Brusseau. 2018 SoTE

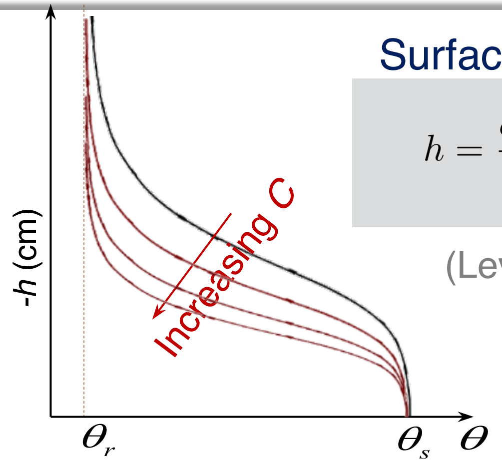
Unique physicochemical properties:

- 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:

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



Surfactant-induced flow

$$h = \frac{\sigma(C)\cos\gamma(C)}{\sigma_0 \cos\gamma_0} h_0$$

(Leverett J scaling)

PFAS transport:

$$\frac{\partial(\theta C)}{\partial t} + \boxed{\rho_b \frac{\partial C_s}{\partial t}} + \boxed{\frac{\partial C_{aw}}{\partial t}} + \underbrace{\nabla \cdot (\theta \boldsymbol{v} C)}_{\text{Advection}} - \underbrace{\nabla \cdot \left(\theta \boldsymbol{D} \frac{\partial C}{\partial z}\right)}_{\text{Dispersion}} = 0$$

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

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

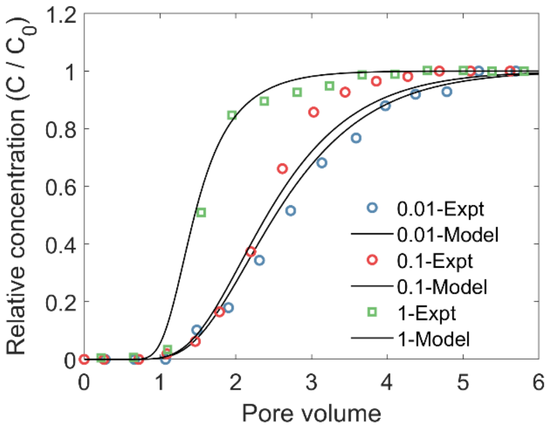
Kinetic

Guo, Zeng, Brusseau. 2020 WRR
Zeng & Guo. 2021 AWR

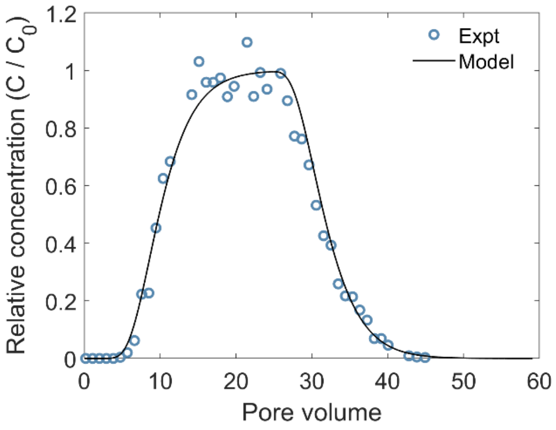
θ	Water content
σ	Surface tension
h	Pressure head
K	Hydraulic conductivity
γ	Contact angle
v	Pore-water velocity
D	Dispersion coefficient
C	Aqueous concentration
$C_{s,1}$	Instantaneous SPA
$C_{s,2}$	Kinetic SPA
$C_{aw,1}$	Instantaneous AWIA
$C_{aw,2}$	Kinetic AWIA
K_f, N	Freundlich parameters
F_s	Fraction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

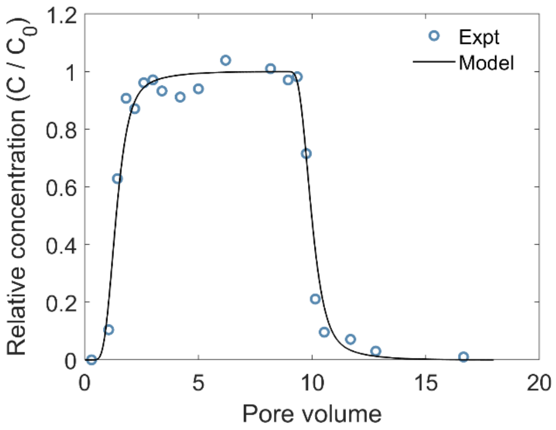
Experimental data set #1
PFOA (1 mg/L, 0.1 mg/L, 0.01 mg/L)
Measured data: Lyu et al., 2018



Experimental data set #2
PFOS (0.1 mg/L)
Measured data: Brusseau et al., 2021



Experimental data set #3
GenX (10 mg/L)
Measured data: Yan et al., 2021

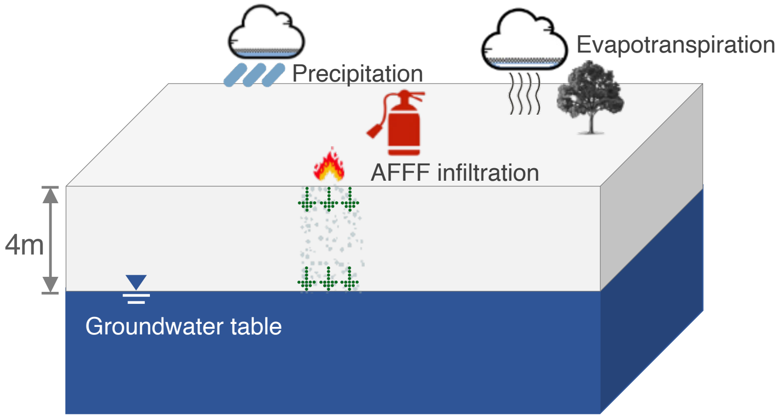


➢ Independent model predictions match well with experimental data.

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

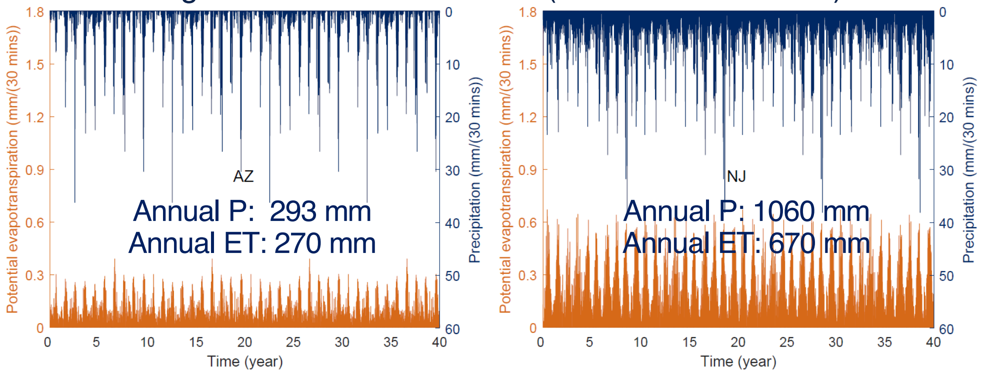


✓ Fire training: one session every 10 days lasting for 30 years

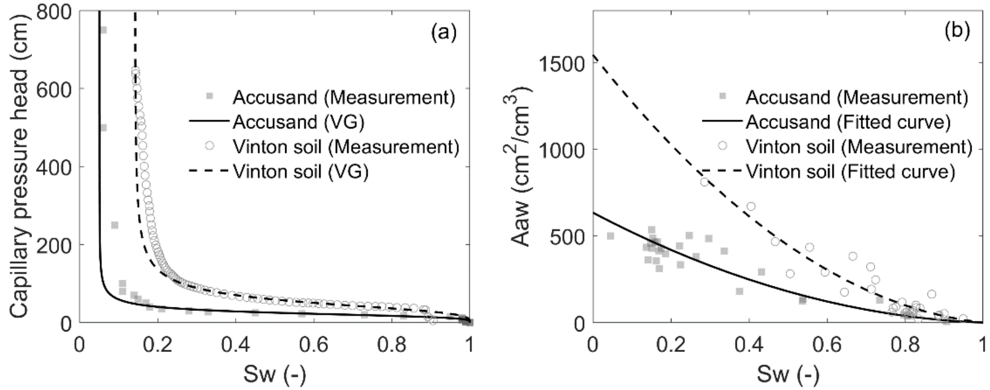
✓ Representative PFAS mixture in 1% diluted AFFF solution

PFOS: 100 mg/L, PFHxS: 7.1 mg/L, PFBS: 1.4 mg/L

High resolution rainfall data (semi-arid vs. humid)

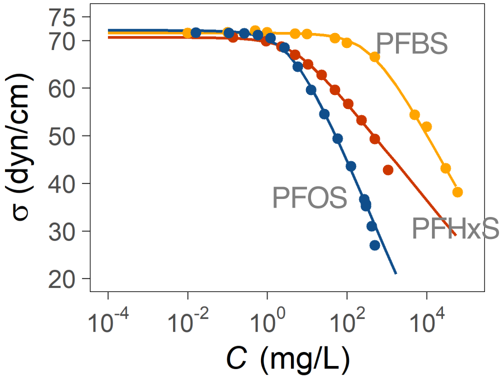


Two soil types (Accusand vs. Vinton)

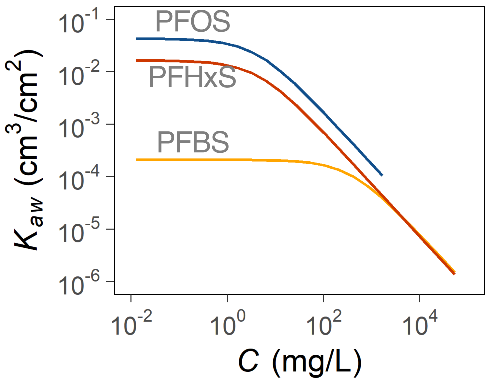


Soil water characteristics | Air-water interfacial area

Three representative PFAS



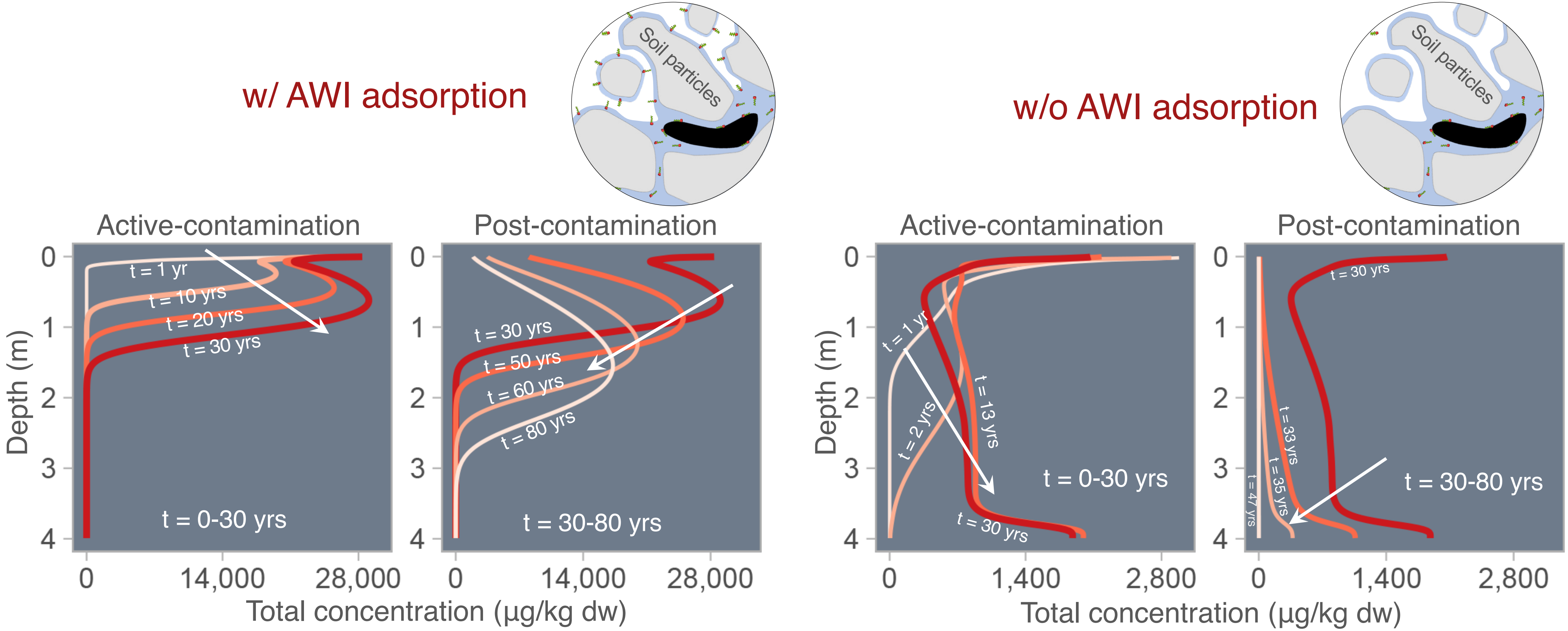
Surface tension data



Air-water interfacial adsorption coeff.

Numerical simulation: PFAS migration at a fire training area

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

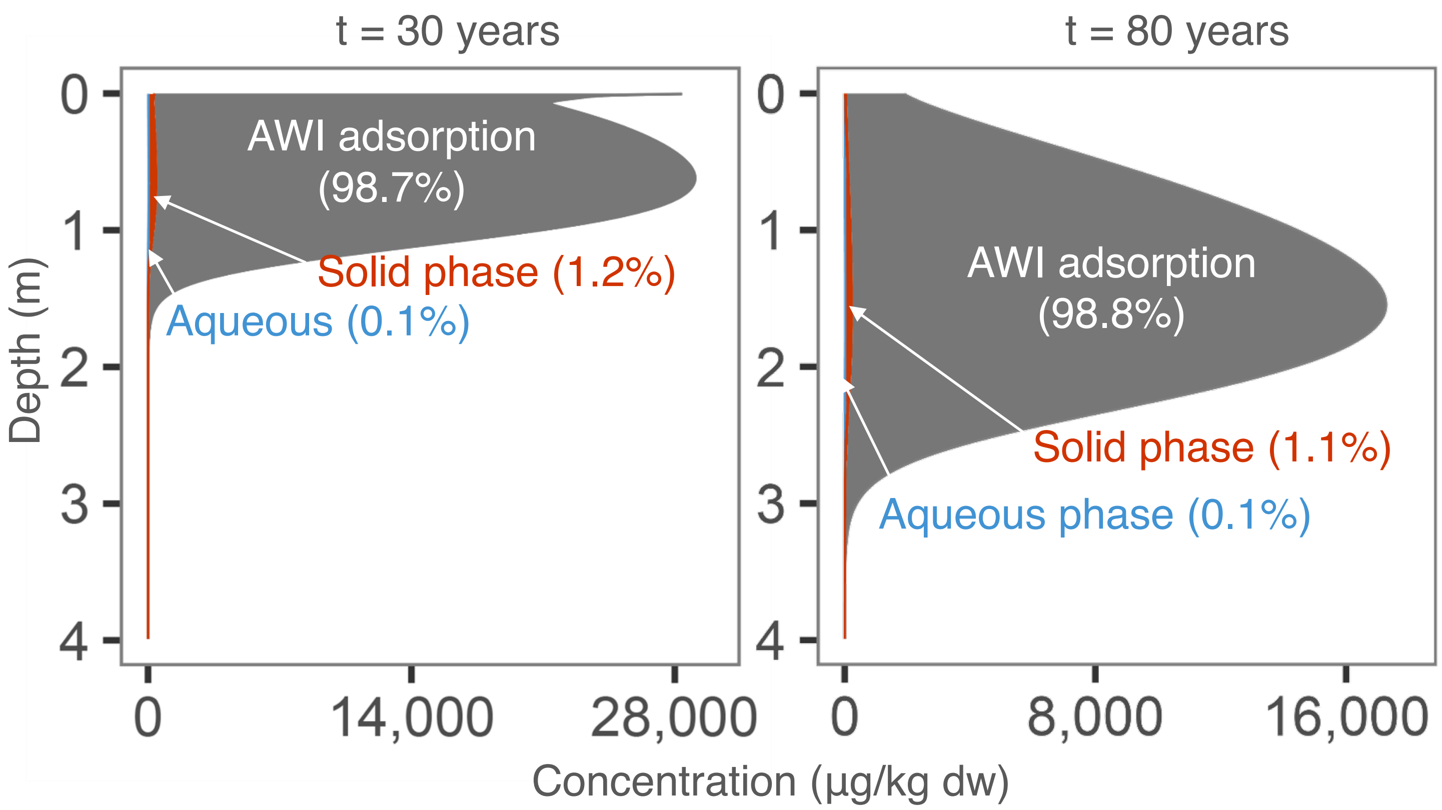


➢ Air-water interfacial adsorption significantly reduces the PFOS leaching in soils.

Guo, Zeng, Brusseau. 2020 WRR

Numerical simulation: PFAS migration at a fire training area

- Retention and leaching of PFOS: mass distribution in soils

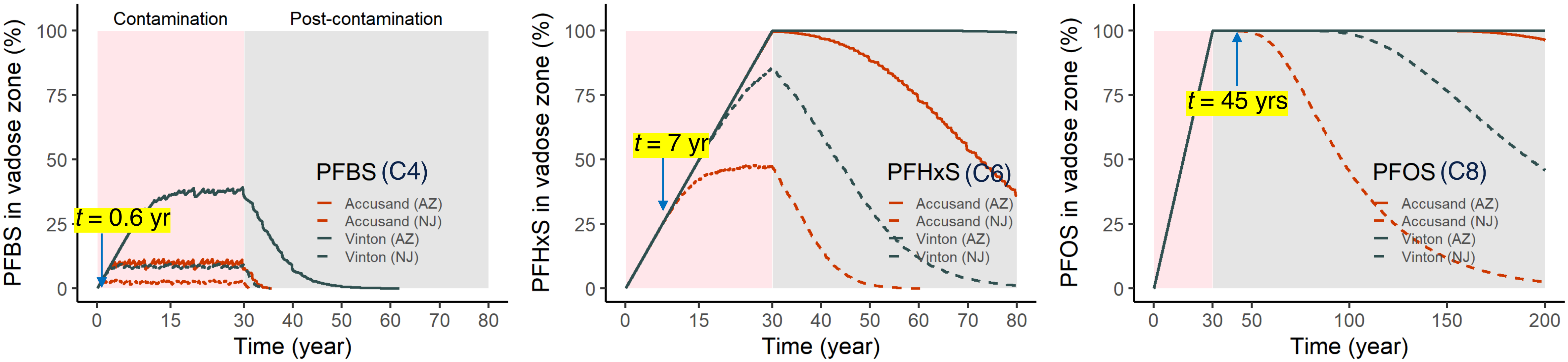


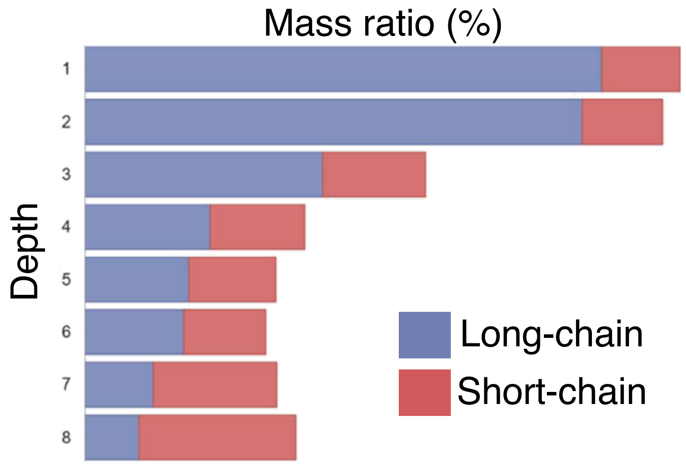
- The majority (>98%) of PFOS in the soil is adsorbed at the air-water interfaces.
- Only 0.1% and ~1% of PFOS in aqueous and solid phase.
- C in soils >> C in groundwater.

Guo, Zeng, Brusseau. 2020 WRR

Numerical simulation: PFAS migration at a fire training area

- Short-chain vs. long-chain



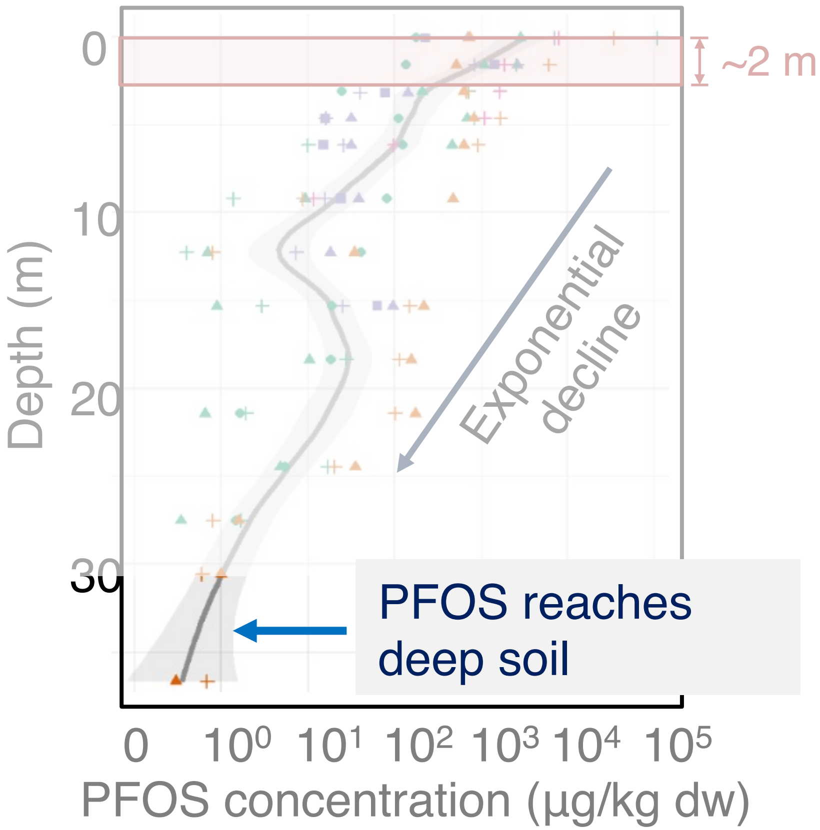


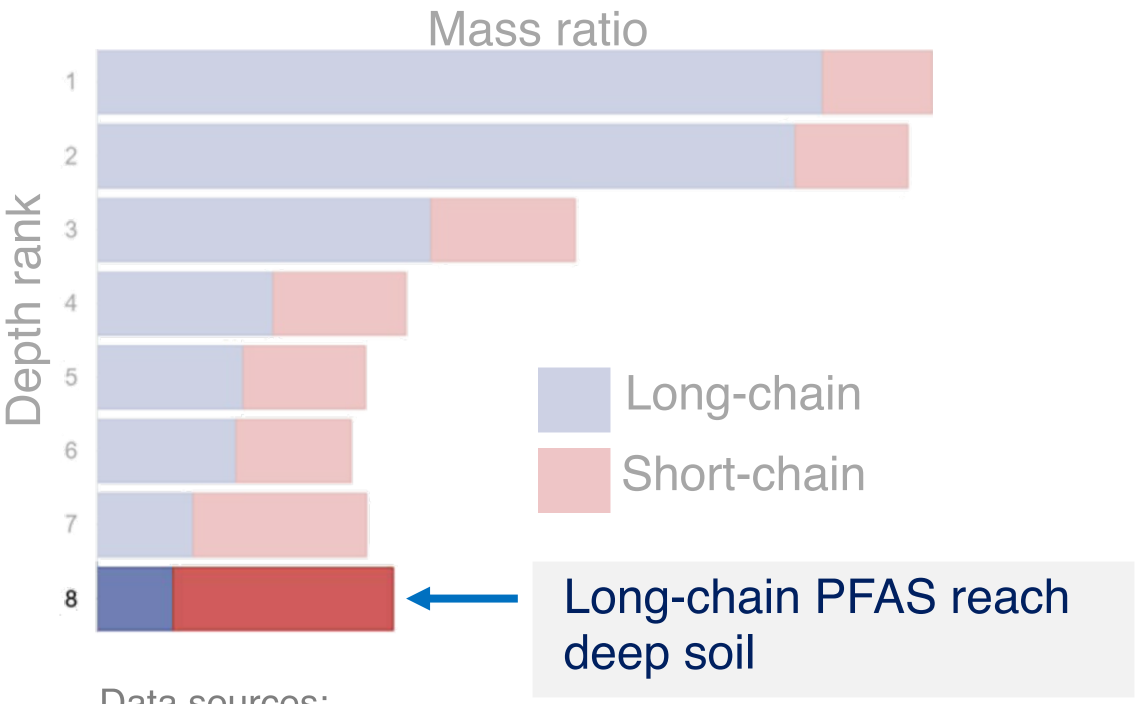
- PFBS, PFHxS, and PFOS reach groundwater table at t = 0.6 yrs, 7 yrs, and 45 yrs.
- PFOS is much more strongly retained in the soil than PFBS and PFHxS.
- Long-chain PFAS is retained in the shallow soil; while short-chain PFAS reach much deeper depth.

Zeng, Brusseau & Guo. 2021 JH

Field data: spatial variation of concentrations in soils

PFAS concentration profiles in the soil





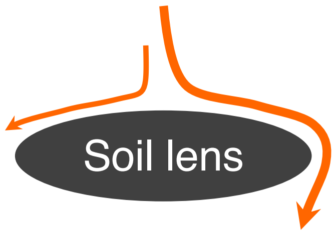
Data sources:
Brusseau, Anderson, Guo. 2020. SoTE
Dauchy et al. 2019

- 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

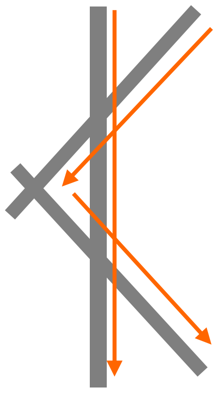
Hypothesis

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

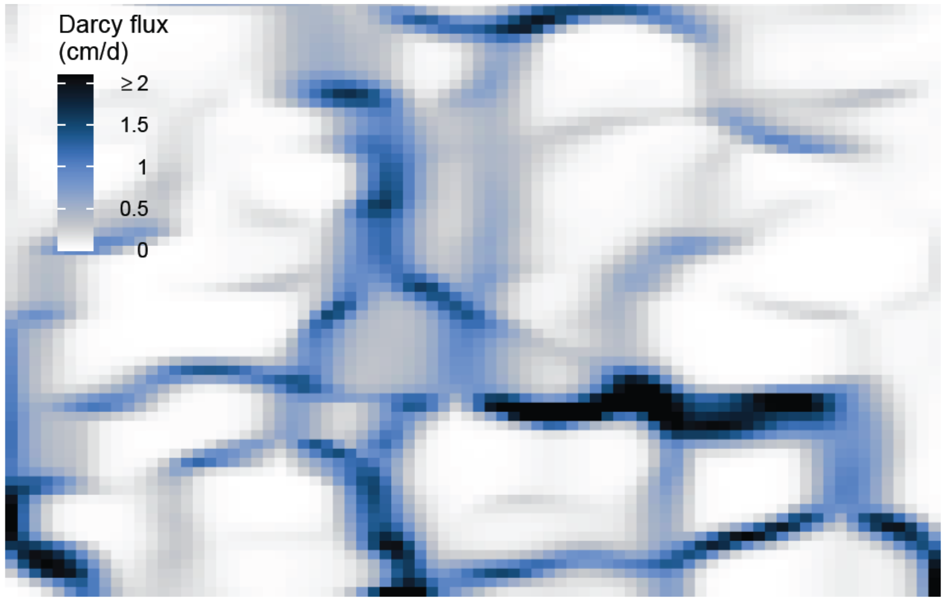
Preferential flow



- Funnel flow

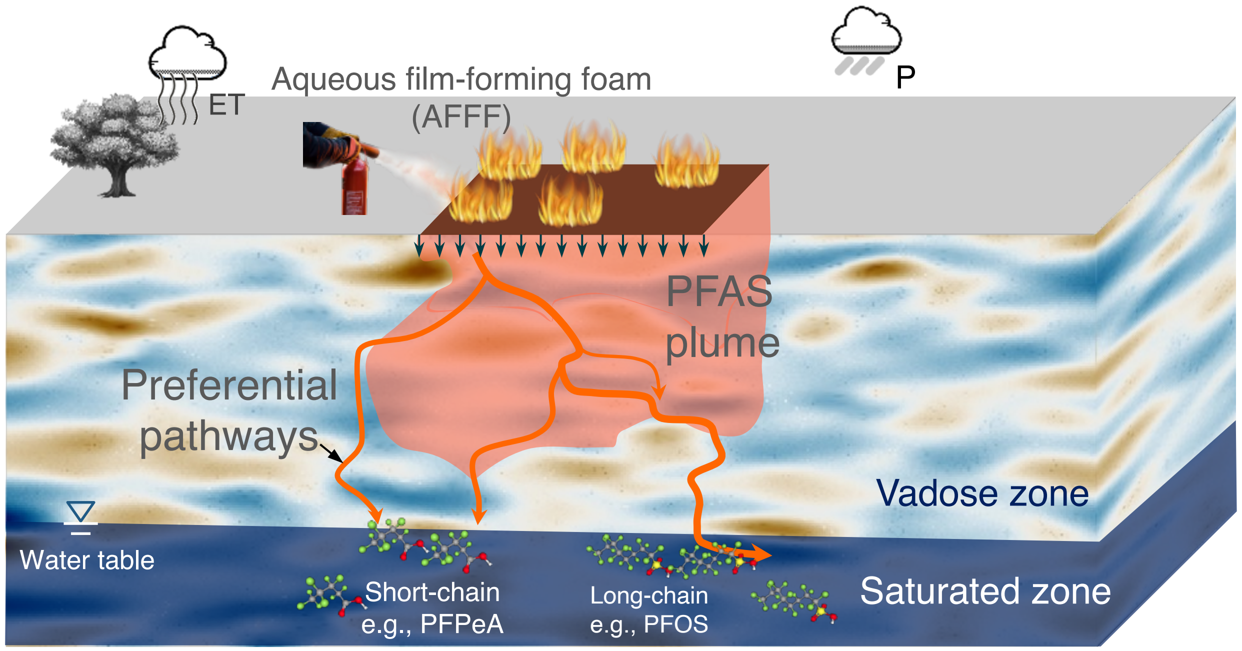


- Macropores/Fractures
- Other high-conductivity channels



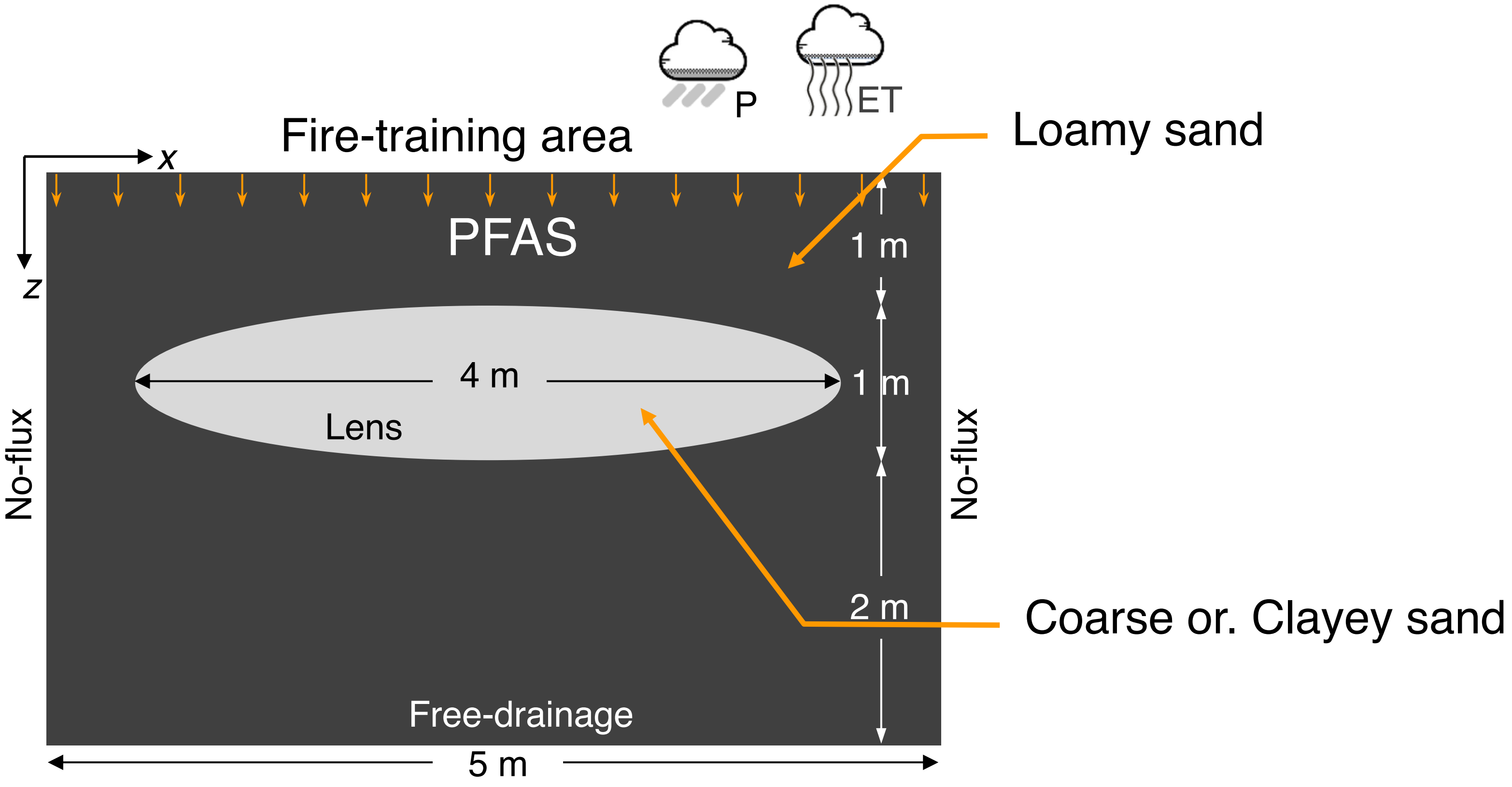
PFAS contamination at a fire-training area (FTA)

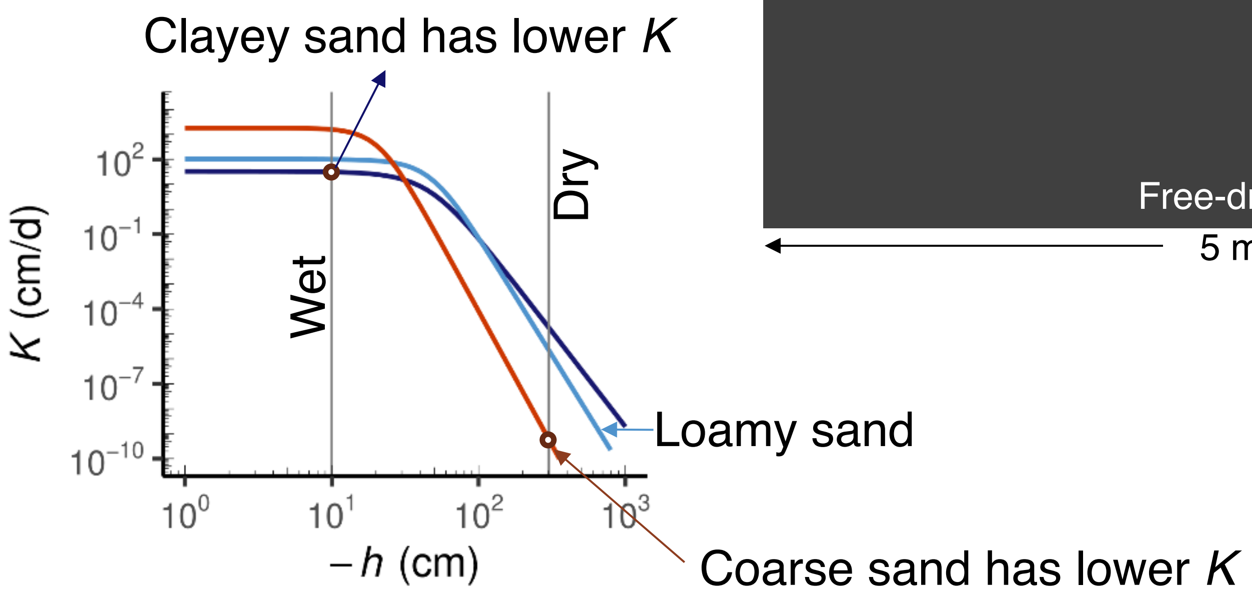
- Area: 30 m × 30 m.
- 1% diluted AFFF.
- Fire training: 30 min per 10 days for 30 yrs.
- Water table is deeper than 4 m.

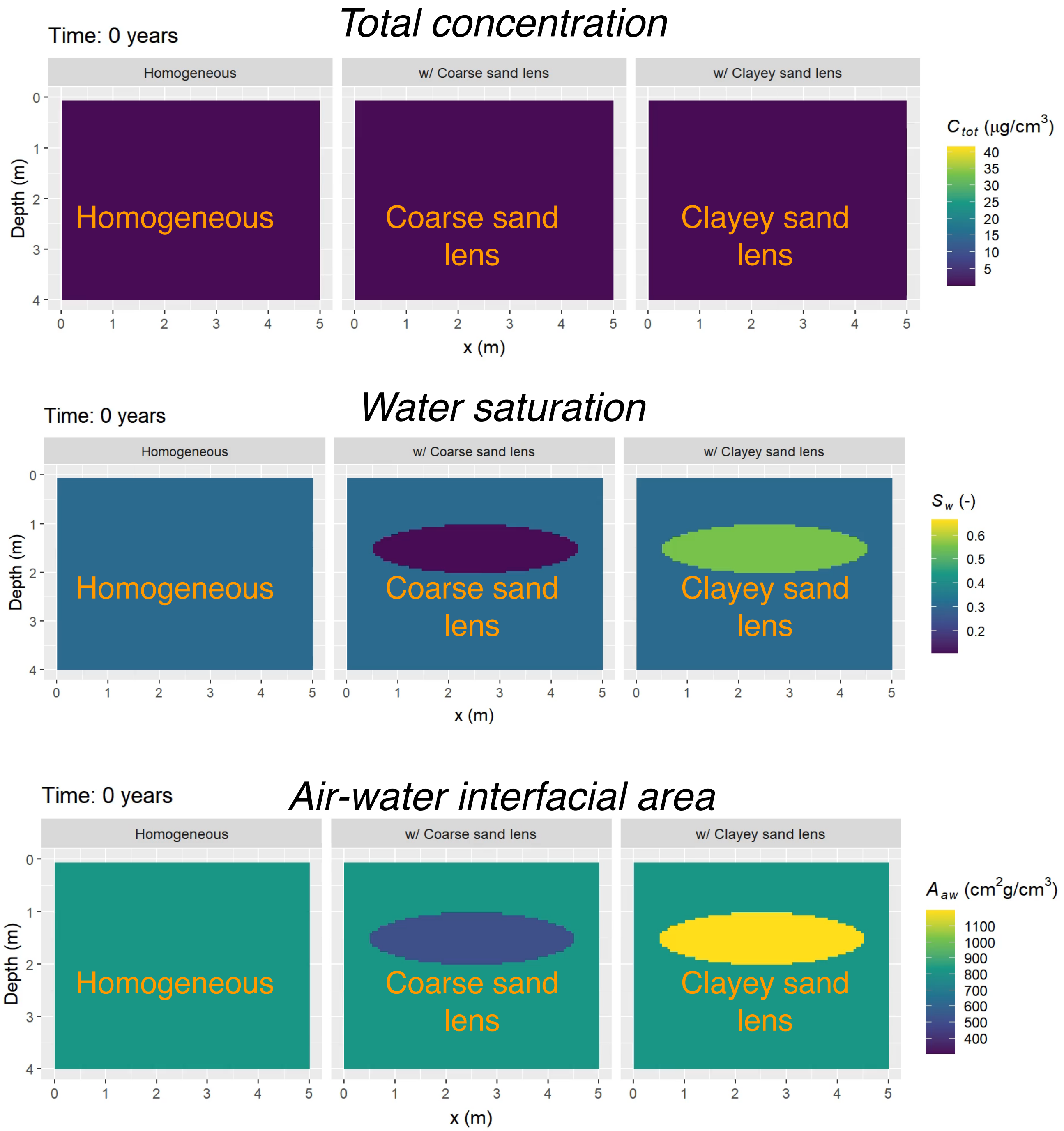


(Zeng, Guo, 2021; Guo, Zeng, Brusseau, 2020)

Soil lenses


P
ET
Fire-training area
Loamy sand
x
z
PFAS
1 m
4 m
1 m
Lens
No-flux
No-flux
2 m
Coarse or. Clayey sand
Free-drainage
5 m


Clayey sand has lower K
10^{2}
10^{-1}
10^{-4}
10^{-7}
10^{-10}
K (cm/d)
Wet
Dry
Loamy sand
10^{0}
10^{1}
10^{2}
10^{3}
$-h$ (cm)
Coarse sand has lower K

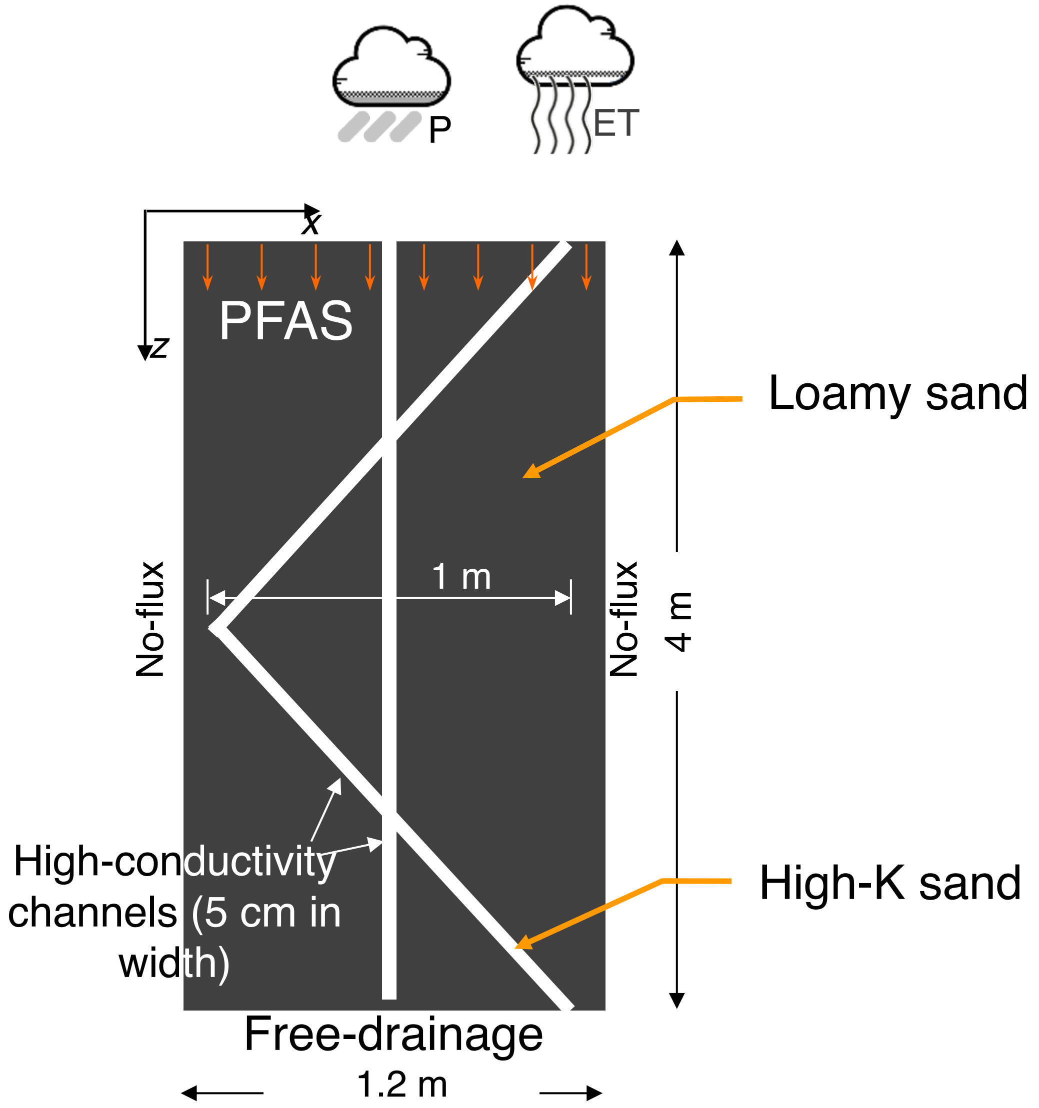


Accelerated leaching caused by soil lenses

- 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.

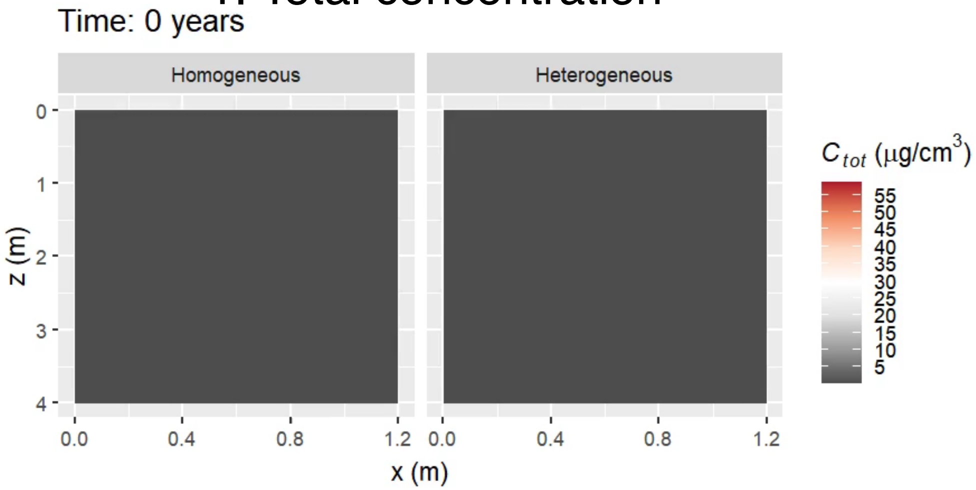
Zeng & Guo. 2021 AWR

Macropores/Fractures

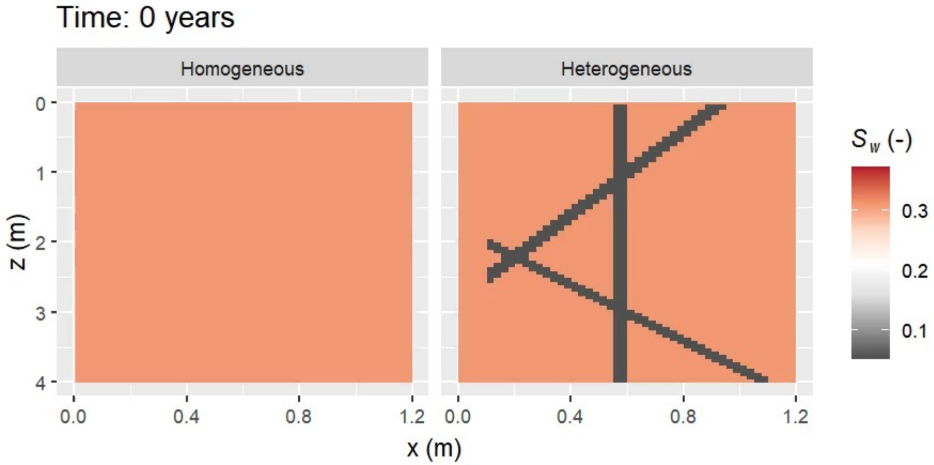


Early arrival and horizontal spreading caused by macropores/fractures

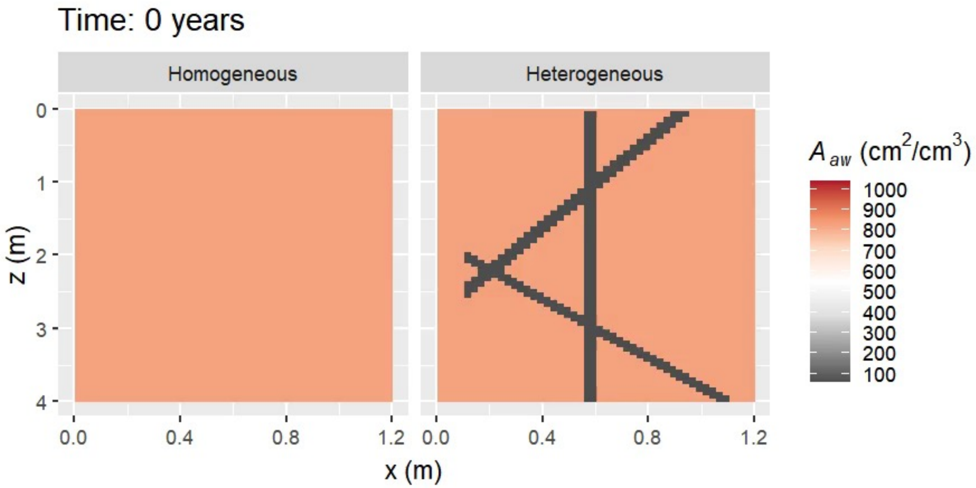
1. Total concentration



2. Water saturation



3. Air-water interfacial area

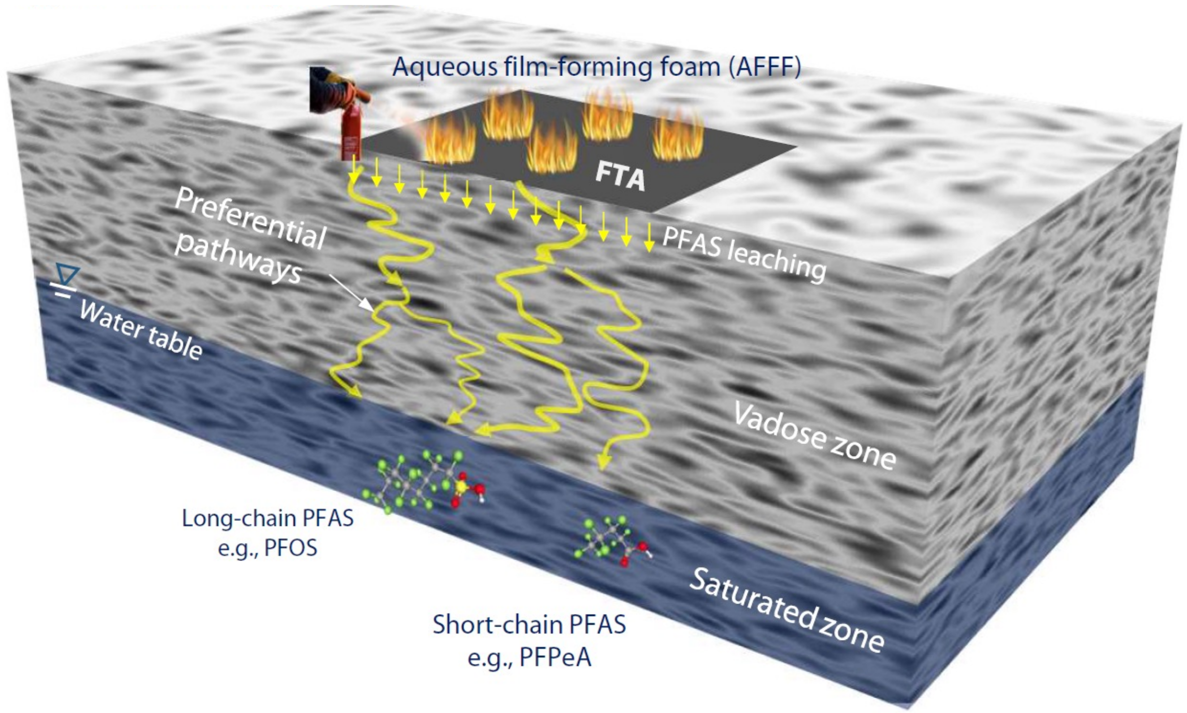


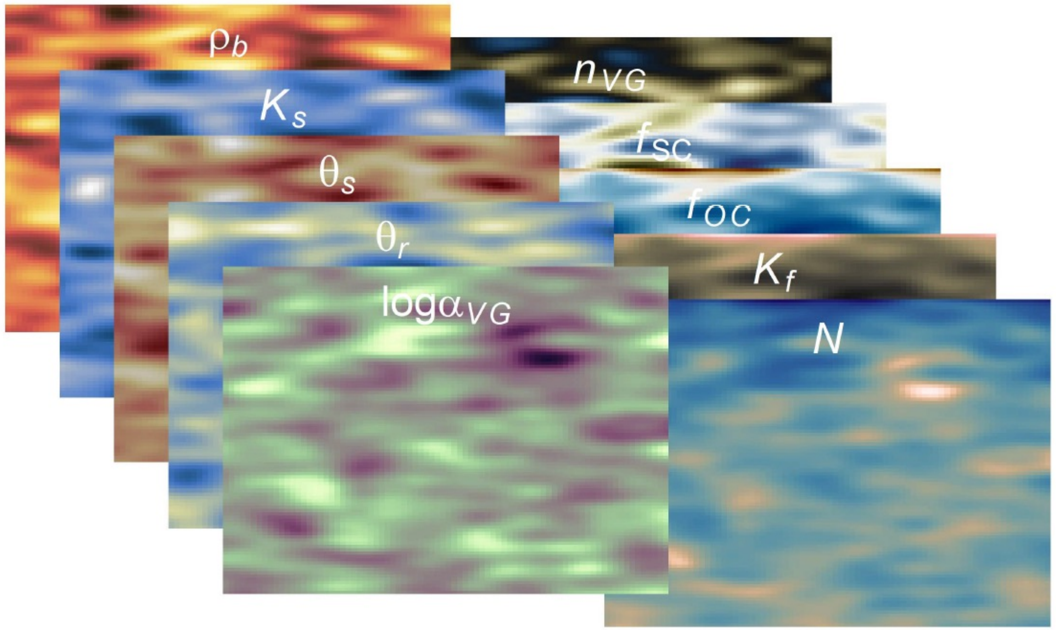
- During the early time, high-conductivity channels accelerate PFAS leaching;
- During the late time, the leaching efficiency is reduced due to "shortcut-circuiting" channels surrounding the soil matrix.

Zeng & Guo. 2021 AWR

More complex heterogeneities

(Stochastically generated heterogeneous fields)

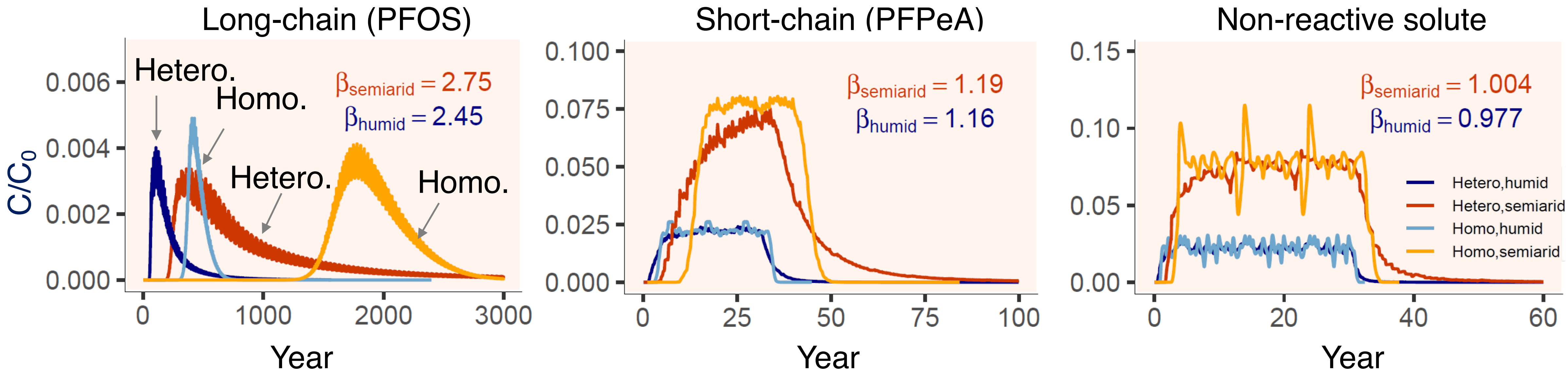




Zeng & Guo. 2023 GRL

Preferential flow uniquely accelerated PFAS leaching in soil

Breakthrough concentration (C/C_0)



Zeng & Guo. 2023 GRL

Testing the mathematical models using pilot-scale experiments

ESTCP
Project ER21-5041

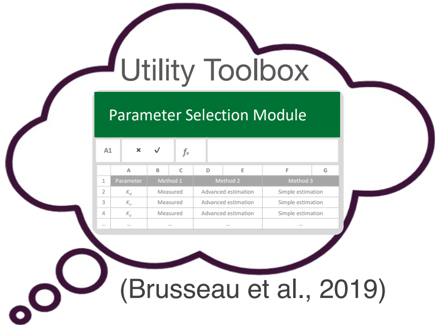

Excavating the soil cores and monolith from the Davis Monthan AFB (Tucson, AZ)


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

PFAS-LEACH: Predicting PFAS Leaching in Source Zones

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

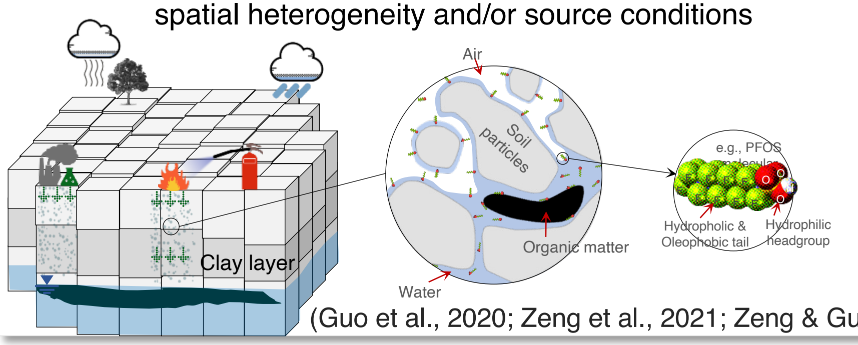
- i. **Three simulators spanning wide range of complexity**
- ii. **Comprehensive parameter selection module**
- iii. **Documentation and user manual**



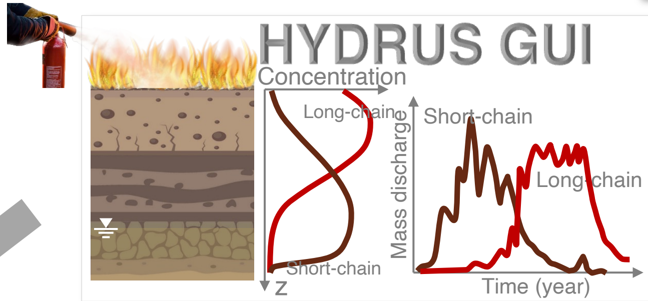
(Brusseau et al., 2019)

Tier 1 – PFAS-LEACH-COMP

Feature: Full-process model in 3D
Anticipated application: Sites w/ sufficient data; complex spatial heterogeneity and/or source conditions



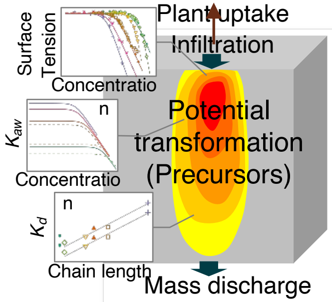
(Guo et al., 2020; Zeng et al., 2021; Zeng & Guo, 2021)



Tier 2 – PFAS-LEACH-HYDRUS

Feature: Implemented in HYDRUS-1D GUI
Anticipated application: Insignificant lateral heterogeneity; efficient uncertainty quantification

(Zeng et al., 2021)



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)

ESTCP Project ER21-5041
"Development and demonstration of PFAS-LEACH"

Computational Cost/Input Parameters

Model Complexity

THIS IS JUST THE BEGINNING

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.

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