

Fate and Transport of PFAS in the vadose zone: *controlling processes, mathematical formulation, and practical modeling approaches*

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PFAS are widely spread in the environment



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 proposed maximum contaminant level (MCL).

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



Adsorb at airwater interfaces

Used in our daily life and at military sites

"Perfect" chemicals if NOT toxic

Non-stick, stain- and water-resistant coating



Percent with fluorine Dessert & bread wrappers Sandwich & burger wrappers 38% Paperboard 20% 0% Paper cups Schaider et al (2017)

Food packaging

Fire fighting foam

56%



http://www.safetynews.co.nz/fire-fightingfoams-causing-sparks-fly/ 4

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 are the primary processes controlling PFAS leaching in soils?

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

PFAS transport in the vadose zone : physical & chemical processes



Unique physicochemical properties:

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

PFAS transport in the vadose zone: mathematical formulation



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

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



Two soil types (Accusand vs. Vinton)



Three representative PFAS



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

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.

Short-chain vs. long-chain

PFBS in vadose zone (%)

100

75

50

0





- PFBS, PFHxS, and PFOS reach groundwater table at t = 0.6yrs, 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- \succ chain PFAS reach much deeper depth.

Field data: spatial variation of concentrations in soils



PFAS concentration profiles in the soil

- > 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



PFAS contamination at a fire-training area (FTA)

- Area: 30 m × 30 m.
- o 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





Water saturation

Time: 0 years





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



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.

More complex heterogeneities



- Stochastically generated heterogeneous parameter fields based on field measurements.
- Geochemical properties correlate with hydraulic parameters.

Preferential flow uniquely accelerated PFAS leaching in the vadose zone





Zeng & Guo. 2023 GRL

Can we develop simplified models for practical screening-type analysis?

PFAS transport in the vadose zone: simplified mathematical model



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

Guo, Zeng, Brusseau, Zhang. AWR. 2022

25

Model validation: vs. miscible-displacement experiments



- > Analytical solutions are identical to the numerical solutions of the full-process model.
- > Independent model predictions match well with experimental data.

Model validation: vs. full-process model

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



Two soil types (Accusand vs. Vinton)



- ✓ Fire training: one session every 10 days lasting for 30 years
- ✓ Representative PFAS mixture in 1% diluted AFFF solution PFPeA: 0.23 mg/L, PFOA: 0.9 mg/L, PFHxS: 7.1 mg/L, PFOS: 100 mg/L





Simulated long-term PFAS leaching in the vadose zone

PFAS retention in the vadose zone and mass discharge to groundwater



Analytical model matches remarkably well with the full-process model for all four PFAS.

Simulated long-term PFAS leaching in the vadose zone





The concentration profiles simulated by the analytical model agrees well with those by the full-process model.

Applying the analytical model as a screening-type tool

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



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

✓ Six soils and nine PFAS in 1% diluted AFFF solution







Simulated long-term PFAS leaching in the vadose zone

PFAS retention in the vadose zone



- PFAS retention increases with chain length and varies among different soils.
- Finer-grain soils may have weaker retention than coarser-grain soils due to reduced AWIA resulting from greater Sw and reduced air-water interfacial area.



 Zeng, J. and Guo, B., 2021. Multidimensional simulation of PFAS transport and leaching in the vadose zone: Impact of surfactant-induced flow and subsurface heterogeneities. *Advances in Water Resources*, *155*, p.104015.

The presence of multicomponent PFAS and hydrocarbon surfactants retention in the vadose zone

 Guo, B., Saleem, H. and Brusseau, M.L., 2023. Predicting Interfacial Tension and Adsorption at Fluid–Fluid Interfaces for Mixtures of PFAS and/or Hydrocarbon Surfactants. *Environmental Science & Technology.*

□ The impact of thin water films in controlling PFAS transport in water-unsaturated soils

 Chen, S. and Guo, B., 2023. Pore-scale modeling of PFAS transport in water-unsaturated porous media: Air–water interfacial adsorption and mass-transfer processes in thin water films. *Water Resources Research*, p.e2023WR034664.



PFAS-LEACH: Predicting PFAS Leaching in Source Zones



Take-home message

- We develop mathematical models with varying complexity representing PFAS-specific transport processes.
- Air-water interfacial adsorption leads to strong retention of (long-chain) PFAS.
- Surfactant-induced flow appears to have a minor impact on long-term PFAS leaching.
- Preferential flow destructs air-water interfaces and accelerates PFAS leaching to deep vadose zone.
- The simplified model provides an efficient and accurate screening-type tool for quantifying vadose-zone PFAS leaching.







- Guo, B., Saleem, H. and Brusseau, M.L., 2023. Predicting Interfacial Tension and Adsorption at Fluid–Fluid Interfaces for Mixtures of PFAS and/or Hydrocarbon Surfactants. *Environmental Science & Technology*. 2023, 57, 21, 8044–8052
- Zeng, J. and Guo, B., 2023. Reduced accessible air–water interfacial area accelerates PFAS leaching in heterogeneous vadose zones. *Geophysical Research Letters*, 50(8), p.e2022GL102655.
- Brusseau, M.L. and Guo, B., 2023. Revising the EPA dilution-attenuation soil screening model for PFAS. *Journal of Hazardous Materials Letters*, 4, p.100077.
- Chen, S. and Guo, B., 2023. Pore-scale modeling of PFAS transport in water-unsaturated porous media: Air–water interfacial adsorption and mass-transfer processes in thin water films. *Water Resources Research*, p.e2023WR034664.
- Guo, B., Zeng, J., Brusseau, M.L. and Zhang, Y., 2022. A screening model for quantifying PFAS leaching in the vadose zone and mass discharge to groundwater. *Advances in Water Resources*, 160, p.104102.
- Zeng, J., Brusseau, M.L. and Guo, B., 2021. Model validation and analyses of parameter sensitivity and uncertainty for modeling long-term retention and leaching of PFAS in the vadose zone. *Journal of Hydrology*, 603, p.127172.
- Zeng, J. and Guo, B., 2021. Multidimensional simulation of PFAS transport and leaching in the vadose zone: Impact of surfactant-induced flow and subsurface heterogeneities. *Advances in Water Resources*, 155, p.104015
- Guo, B., Zeng, J. and Brusseau, M.L., 2020. A mathematical model for the release, transport, and retention of pfas in the vadose zone. *Water Resources Research*, *56*(2), p.e2019WR026667.







Approaching PFAS Data - Integrating an Array of Visualizations into the Conceptual Site Model

Dr. Ryan David Swanson Dr. Jim Montague Jeffrey Temple





Restoring the Environment. Protecting Our Future.



OCTOBER 3-5, 2023



CULPRITS & CHALLENGES

- Low health advisory levels
- 8 PFAS with RSLs
- Relative concentrations can be critical in
 - Identifying sources
 (e.g., wastewater
 effluent, AFFF,
 landfill leachate)
 - Locating source areas,
 - Delineating unique plumes
 - Quantifying PFAS



NOTE: Many of our sites are sensitive, so their locations have been masked.



OUR FOCUS & GOAL

- CERCLA sites in the Remedial Investigation phase
- Comingled plumes including from AFFF and non-AFFF sources
- Conceptual Site Model development that
 support better informed
 environmental restoration decisions



Source: L. Trozzolo, TRC, and C. Higgins, Colorado School of Mines.



TODAY'S TOPICS

- Multiple flavors of pie (charts)
- Stacking blocks
- Stacking rings

No one approach is sufficient, but these are some of our favorite methods.



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EMIE

CONTAMINANTS

This figure transmits data, not knowledge: Okay for the site



HOW CAN WE BEST TRANSMIT KNOWLEDGE?



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PFAS Analyte Name	Abbreviation	breviation Type	
Perfluorobutanoic Acid	PFBA	Perfluoroalkyl carboxylic acids	4
Perfluoropentanoic Acid	PFPeA	Perfluoroalkyl carboxylic acids	5
Perfluorohexanoic Acid	PFHxA	Perfluoroalkyl carboxylic acids	6
Perfluoroheptanoic Acid	PFHpA	Perfluoroalkyl carboxylic acids	7
Perfluorooctanoic Acid	PFOA	Perfluoroalkyl carboxylic acids	8
Perfluorononanoic Acid	PFNA	Perfluoroalkyl carboxylic acids	9
Perfluorodecanoic Acid	PFDA	Perfluoroalkyl carboxylic acids	10
Perfluoroundecanoic Acid	PFUnA	Perfluoroalkyl carboxylic acids	11
Perfluorododecanoic Acid	PFDoA	Perfluoroalkyl carboxylic acids	12
Perfluorotridecanoic Acid	PFTrDA	Perfluoroalkyl carboxylic acids	13
Perfluorotetradecanoic Acid	PFTeDA	Perfluoroalkyl carboxylic acids	14
Perfluorobutane Sulfonic Acid	PFBS	Perfluoroalkane sulfonic acids	4
Perfluoropentane Sulfonic Acid	PFPeS	Perfluoroalkane sulfonic acids	5
Perfluorohexane Sulfonic Acid	PFHxS	Perfluoroalkane sulfonic acids	6
Perfluoroheptane Sulfonic Acid	PFHpS	Perfluoroalkane sulfonic acids	7
Perfluorooctane Sulfonic Acid	PFOS	Perfluoroalkane sulfonic acids	8
Perfluorononane Sulfonic Acid	PFNS	Perfluoroalkane sulfonic acids	9
Perfluorodecane Sulfonic Acid	PFDS	Perfluoroalkane sulfonic acids	10

~2 Hues (red & green) with 3 Different Saturations

Terminal

Perfluoroalkyl carboxylic acids (PFCAs) Decreasing Mobility

Terminal

Perfluoroalkane sulfonic acids
(PFSAs)

Decreasing Mobility





FLAVOR #1



This figure transmits data, not knowledge.

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	and the second	-	2									PFOA	0.35	PFOA	0.2	PFOA	0.5

HOW CAN WE BEST TRANSMIT KNOWLEDGE?



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PFAS Analyte Name	Abbreviation	Туре	No. of Carbons
4:2 Fluorotelomer Sulfonic Acid	4:2 FTS	Fluorotelomer sulfonic acids	6
6:2 Fluorotelomer Sulfonic Acid	6:2 FTS	Fluorotelomer sulfonic acids	8
8:2 Fluorotelomer Sulfonic Acid	8:2 FTS	Fluorotelomer sulfonic acids	10
Perfluorobutanoic Acid	PFBA	Perfluoroalkyl carboxylic acids	4
PerfluoropentanoicAcid	PFPeA	Perfluoroalkyl carboxylic acids	5
Perfluorohexanoic Acid	PFHxA	Perfluoroalkyl carboxylic acids	6
PerfluoroheptanoicAcid	PFHpA	Perfluoroalkyl carboxylic acids	7
Perfluorooctanoic Acid	PFOA	Perfluoroalkyl carboxylic acids	8
PerfluorononanoicAcid	PFNA	Perfluoroalkyl carboxylic acids	9
PerfluorodecanoicAcid	PFDA	Perfluoroalkyl carboxylic acids	10
PerfluoroundecanoicAcid	PFUnA	Perfluoroalkyl carboxylic acids	11
PerfluorododecanoicAcid	PFDoA	Perfluoroalkyl carboxylic acids	12
PerfluorotridecanoicAcid	PFTrDA	Perfluoroalkyl carboxylic acids	13
PerfluorotetradecanoicAcid	PFTeDA	Perfluoroalkyl carboxylic acids	14
Perfluorobutane Sulfonic Acid	PFBS	Perfluoroalkane sulfonic acids	4
Perfluoropentane Sulfonic Acid	PFPeS	Perfluoroalkane sulfonic acids	5
Perfluorohexane Sulfonic Acid	PFHxS	Perfluoroalkane sulfonic acids	6
Perfluoroheptane Sulfonic Acid	PFHpS	Perfluoroalkane sulfonic acids	7
Perfluorooctane Sulfonic Acid	PFOS	Perfluoroalkane sulfonic acids	8
PerfluorononaneSulfonic Acid	PFNS	Perfluoroalkane sulfonic acids	9
Perfluorodecane Sulfonic Acid	PFDS	Perfluoroalkane sulfonic acids	10
N-Methyl PerfluorooctanesulfonamidoaceticAcid	NMeFOSAA	Perfluorooctane sulfonamidoacetic acids	11
N-Ethyl Perfluorooctanesulfonamidoacetic Acid	NEtFOSAA	Perfluorooctane sulfonamidoacetic acids	12
Perfluorooctane Sulfonamide	PFOSA	Perfluoroalkane sulfonamides	8
Perfluoroalkyl ether carboxylic acid	GenX	Per- and Polyfluoroether carboxylic acids	6
		RE	MTFO

Precursors

Terminal Perfluoroalkyl carboxylic acids (PFCAs) Decreasing Mobility

Terminal Perfluoroalkane sulfonic acids (PFSAs) Decreasing Mobility

Precursors



Altered to Highlight PFOS/PFOA FLAVOR #2

4:2 FTS	
6:2 FTS	
8:2 FTS	
PFBA	PFBS
PFPeA	PFPeS
PFHxA	PFHxS
PFHpA	PFHpS
PFOA	PFOS
PFNA	PFNS
PFDA	PFDS
PFUnA	NMeFOSAA
PFDoA	NEtFOSAA
PFTrDA	PFOSA
PFTeDA	GenX











Concentric circles - PFAS at depth at approximately 5-ft intervals - innermost is shallowest; outermost is deepest -White areas - cleaner; redder areas - more impacted









AFFF Release Area



Concentric circles - PFAS at depth at approximately 5-ft intervals - innermost is shallowest; outermost is deepest -White areas - cleaner; redder areas - more impacted

<1/2 RSL 1/2 RSL - RSL RSL - 2x RSL

2x RSL - 5x RSL 5x RSL - 10x RSL >10x RSL

WHY THIS WORKS:

PFOS in soil is the highest PFAS relative to the respective RSL at all locations, so we focus exclusively on a single analytremtec

IG CONTAMINANTS OCTOBER 3-5, 2023

CONCLUSIONS

- Characterizing PFAS contamination is complex, with constantly changing targets.
- We highlighted ways to look at the whole suite of data, a trio of analytes, and just PFOS.
- Our figures should consider transmitting knowledge-not just data.
- No one approach will be sufficient, but many complementary approaches can be extremely valuable.



OCTOBER 3-5, 2023

QUESTIONS?

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