CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

Avoiding Over Predicting PFAS Soil Porewater Concentrations: Implications for Hydrogeological Risk Assessment and Soil Remediation

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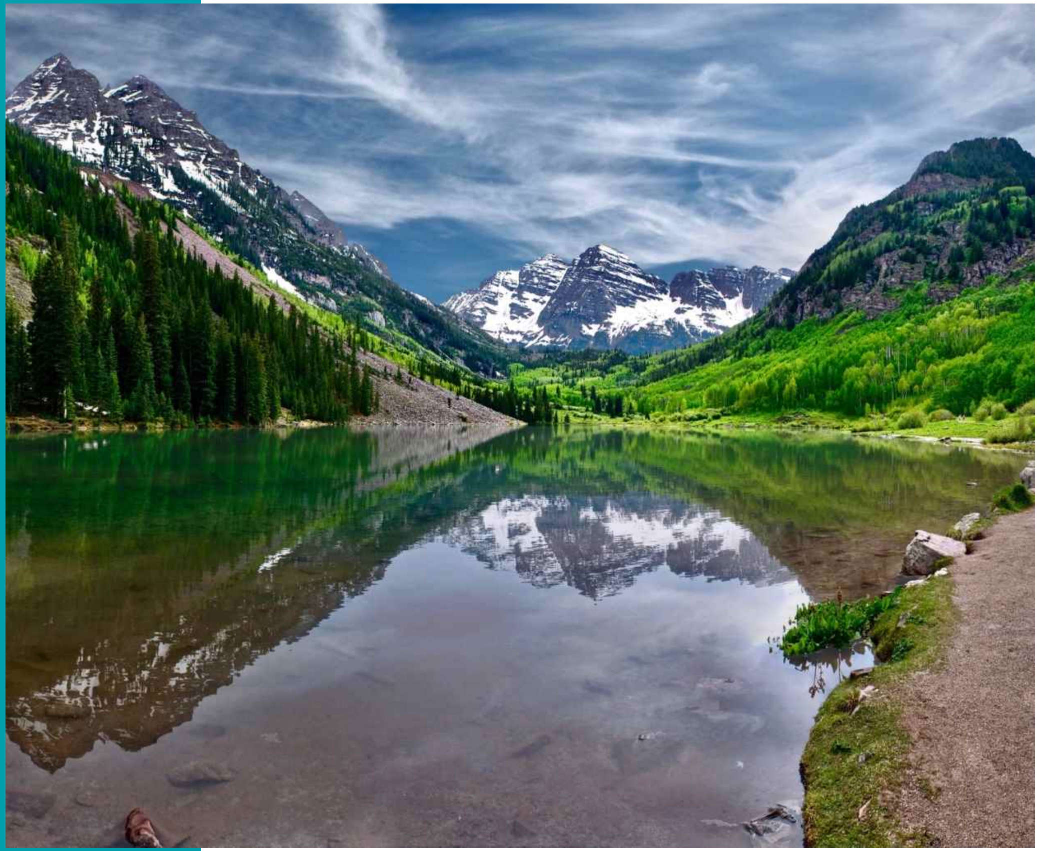
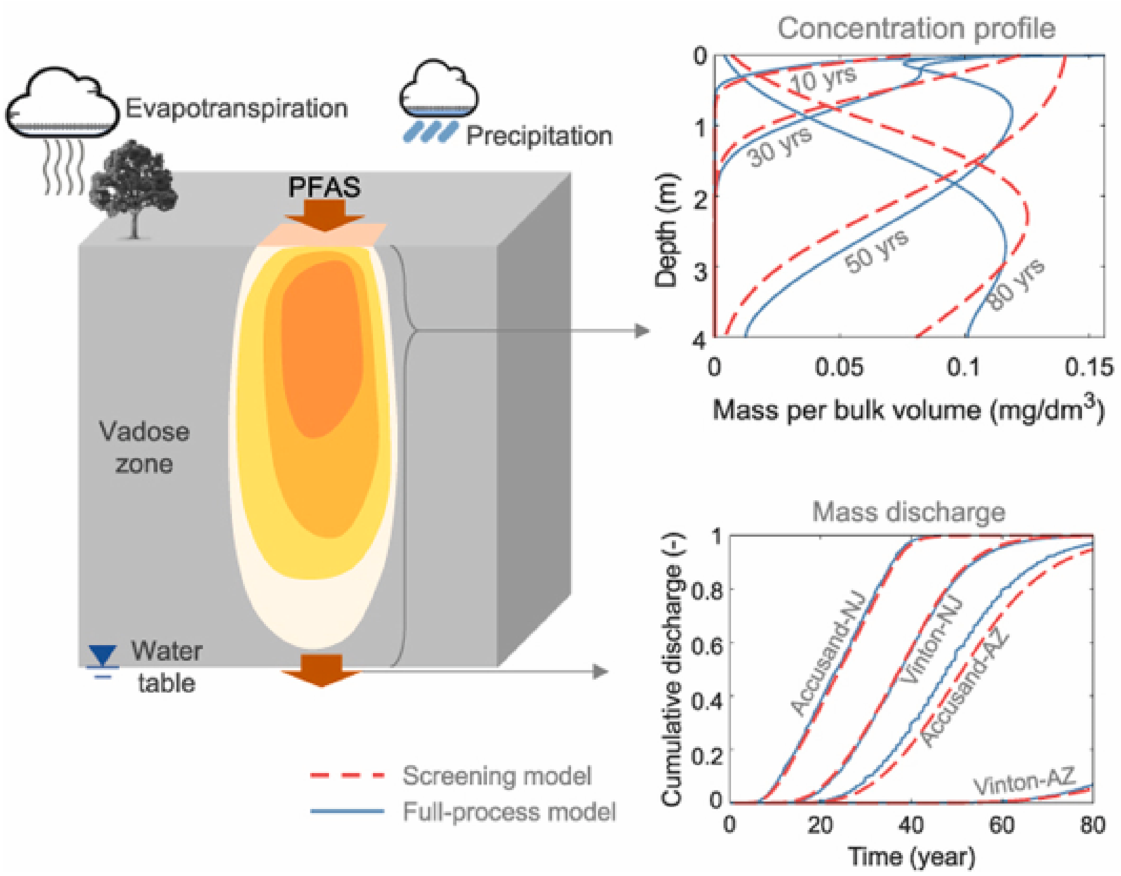


Risks from PFAS leaching to groundwater

Long-term impacts to groundwater due to PFAS leaching in vadose zone

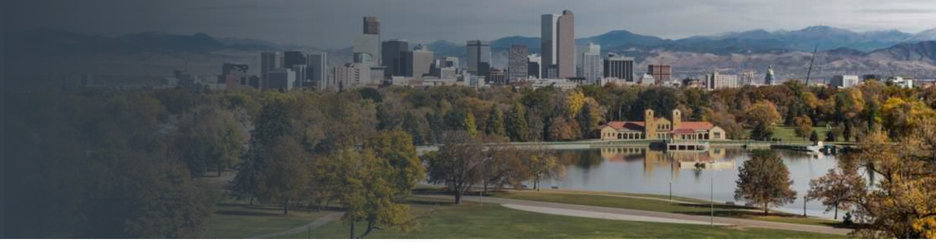
Need to quantify PFAS discharge due to leaching

Partitioning-based alternative to direct measurement



Guo et al. 2022

Predicting PFAS porewater concentration



“Total dissolution” model

Organic chemical model

(Feenstra et al. 1991)

Comprehensive PFAS Retention Model

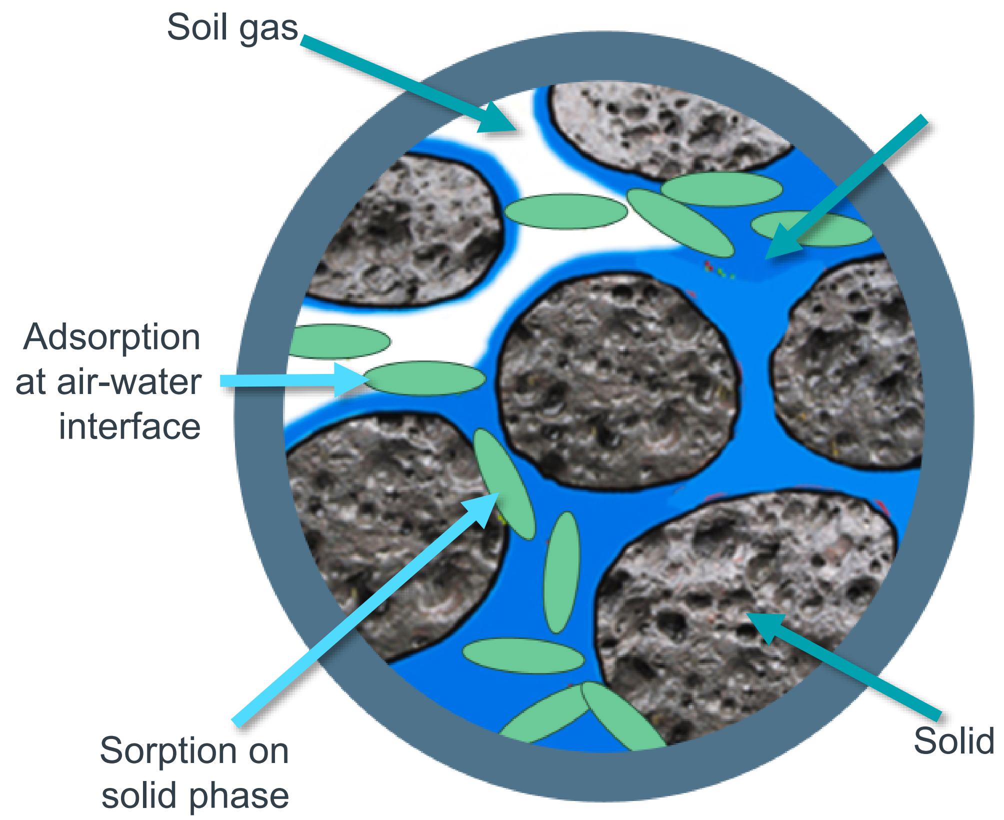
(Brusseau et al. 2019)

Phase	Source Zone	Plume
Aqueous		
Sorbed by solid phase		
Vapour		
Adsorbed at air-water interface		
Adsorbed at air-NAPL interface		
Adsorbed at NAPL-water interface		
Absorbed by NAPL		

PFAS partitioning behaviour

Phase	Source Zone	Plume
Aqueous	Most	Most
Sorbed by solid phase	Most	Most
Vapour	Some	Some
Adsorbed at air-water interface	Many	Many
Adsorbed at air-NAPL interface	Some	N/A
Adsorbed at NAPL-water interface	Many	N/A
Absorbed by NAPL	Many	N/A

After Brusseau et al. 2019



After Brusseau & Guo. 2022

Total & porewater PFAS concentrations

Total soil concentration

$$C_t = \frac{C_p \theta_w R_d}{\rho_b}$$

$$R_d = \left(1 + \underbrace{\overset{\text{Solid}}{K_d * \frac{\rho_b}{\theta_w}} + \overset{\text{Vapour}}{K_a \frac{\theta_a}{\theta_w}} + \overset{\text{NAPL}}{K_n \frac{\theta_n}{\theta_w}}}_{\text{Phases}} + \underbrace{\overset{\text{Air-water}}{K_{aw} * \frac{A_{aw}}{\theta_w}} + \overset{\text{NAPL-water}}{K_{nw} * \frac{\theta_{nw}}{\theta_w}} + \overset{\text{Air-NAPL}}{K_{an} * \frac{\theta_{an}}{\theta_w}}}_{\text{Phase interfaces}} + \overset{\text{Colloidal}}{K_c * X_c}\right)$$

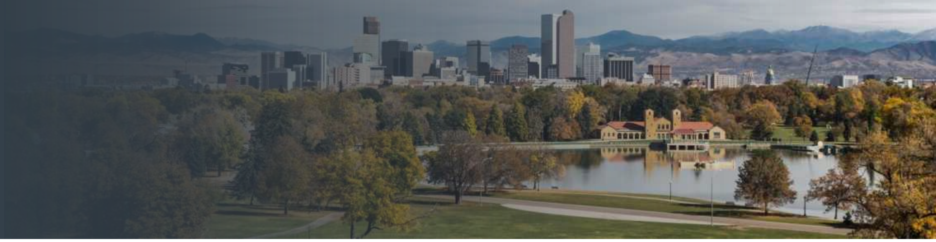
Porewater concentration

$$C_p = \frac{C_t \rho_b}{\theta_w + K_d \rho_b + K_{aw} A_{aw}}$$

<u>Assumptions:</u>
NAPL absent
Non-volatile PFAS
Colloidal material absent
Sorption coefficients effectively linear

After Brusseau & Guo. 2022

PFAS partitioning model application



Soil properties

- 10 soils
  Sandy, silty or clayey
- Organic content
  f_{oc} 0.1 to 4.9%
- PSD
- Bulk density (ρ_b)
- Porosity (θ)

Chemical parameters

- C_t 1,500 µg/kg
- PFOS
  K_d 3.2 to 34 cm^3/g
  K_{aw} 0.05 cm^2
- PFBS
  K_d 0.05 to 0.41 cm^3/g
  K_{aw} 0.00017 cm^2

Approach

- Water saturation 0.1 to 1 (s_w)
- Water-filled porosity (θ_w)
- Air-water interface surficial area (A_{aw})

Concentration estimates

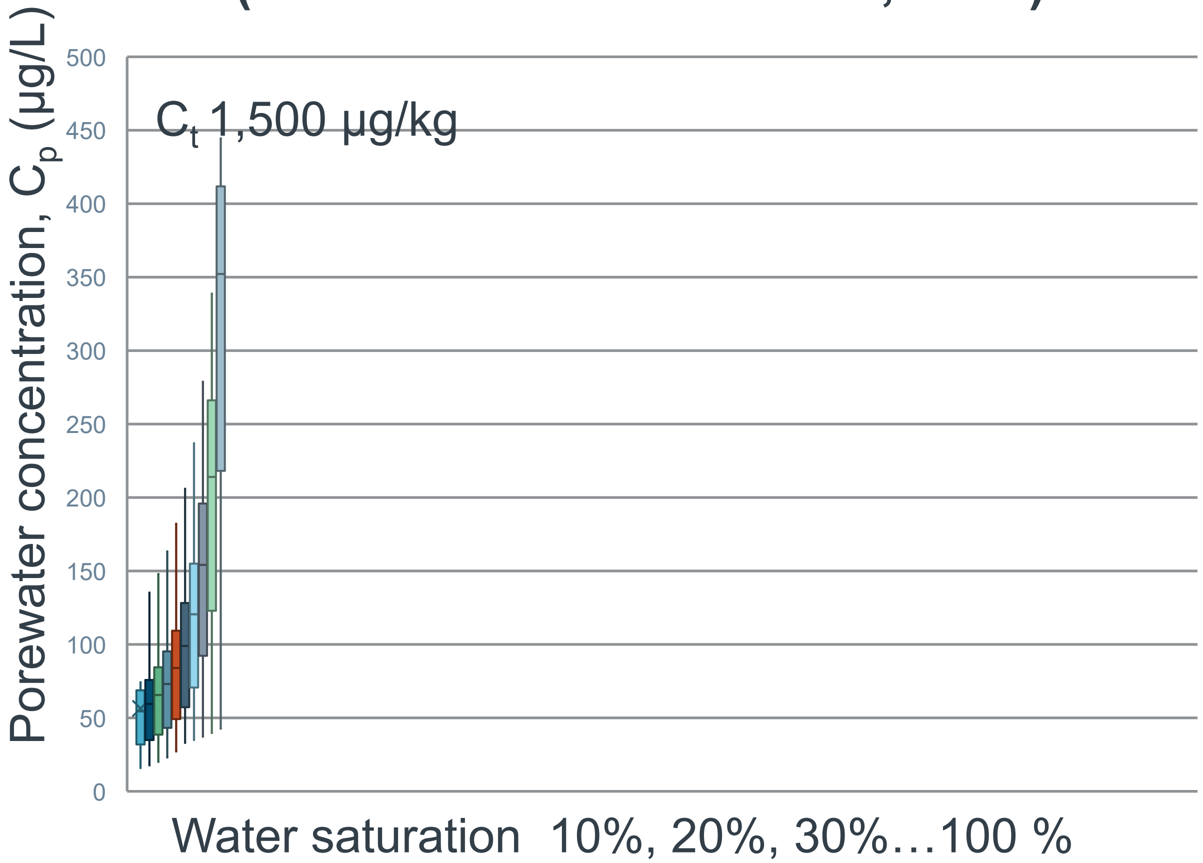
- Porewater concentration (C_p)
- Air-water concentration to solid phase concentration ratio (C_{aw}/C_s)

Nguyen et al. 2020, Brusseau et al. 2019, Brusseau & Guo 2022, Endo et al., 2023

Comparison between porewater concentration predictive models

Predicted **PFOS** retention in vadose zone (10 soils)

PFAS Partitioning Model (based on Brusseau et al., 2019)

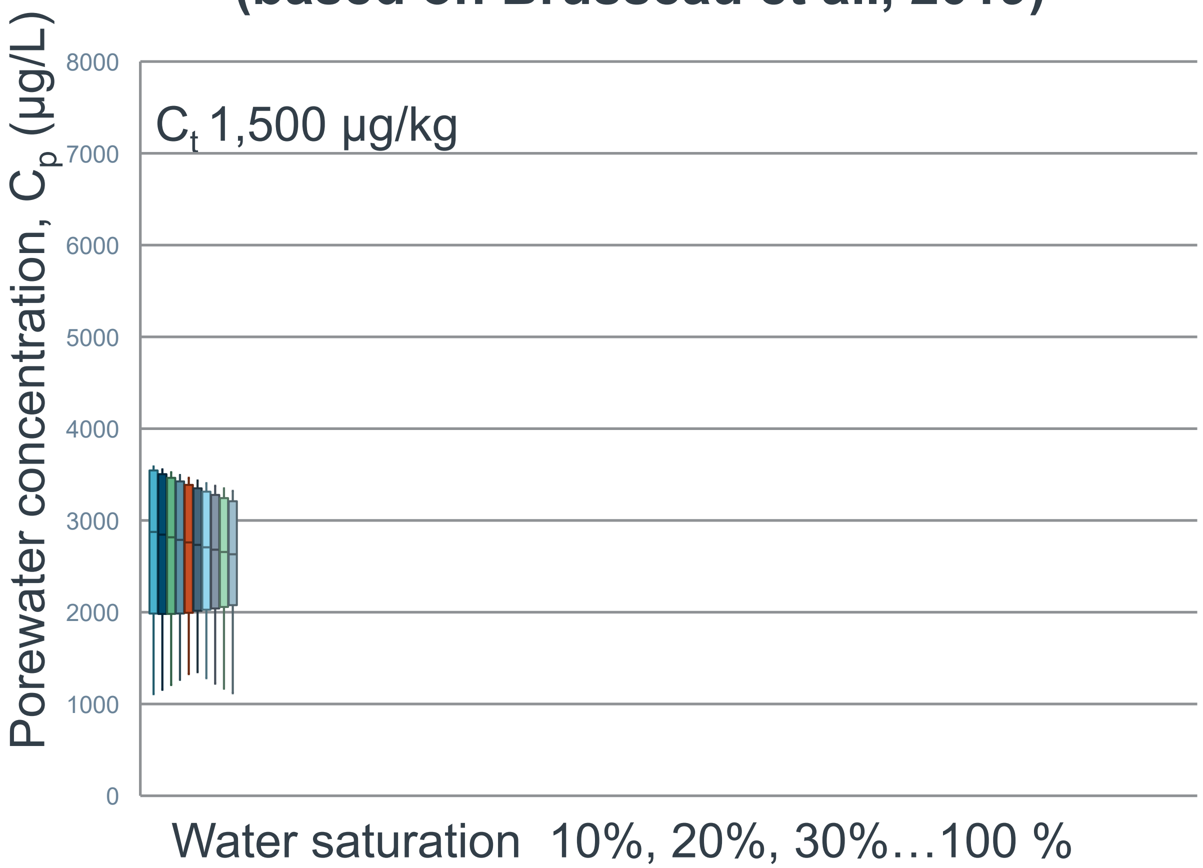


Conventional Partitioning Model (Feenstra et al., 1991)

“Total Dissolution” Model

Predicted PFBS retention in vadose zone (10 soils)

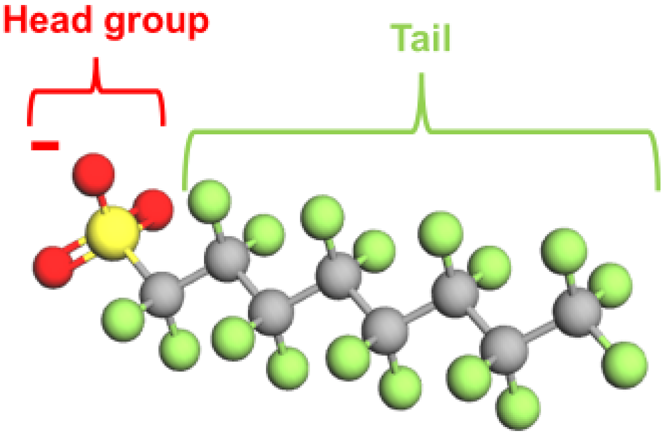
PFAS Partitioning Model (based on Brusseau et al., 2019)



Conventional Partitioning Model (Feenstra et al., 1991)

“Total Dissolution” Model

Differing sorption behaviour of long & short chain PFAS

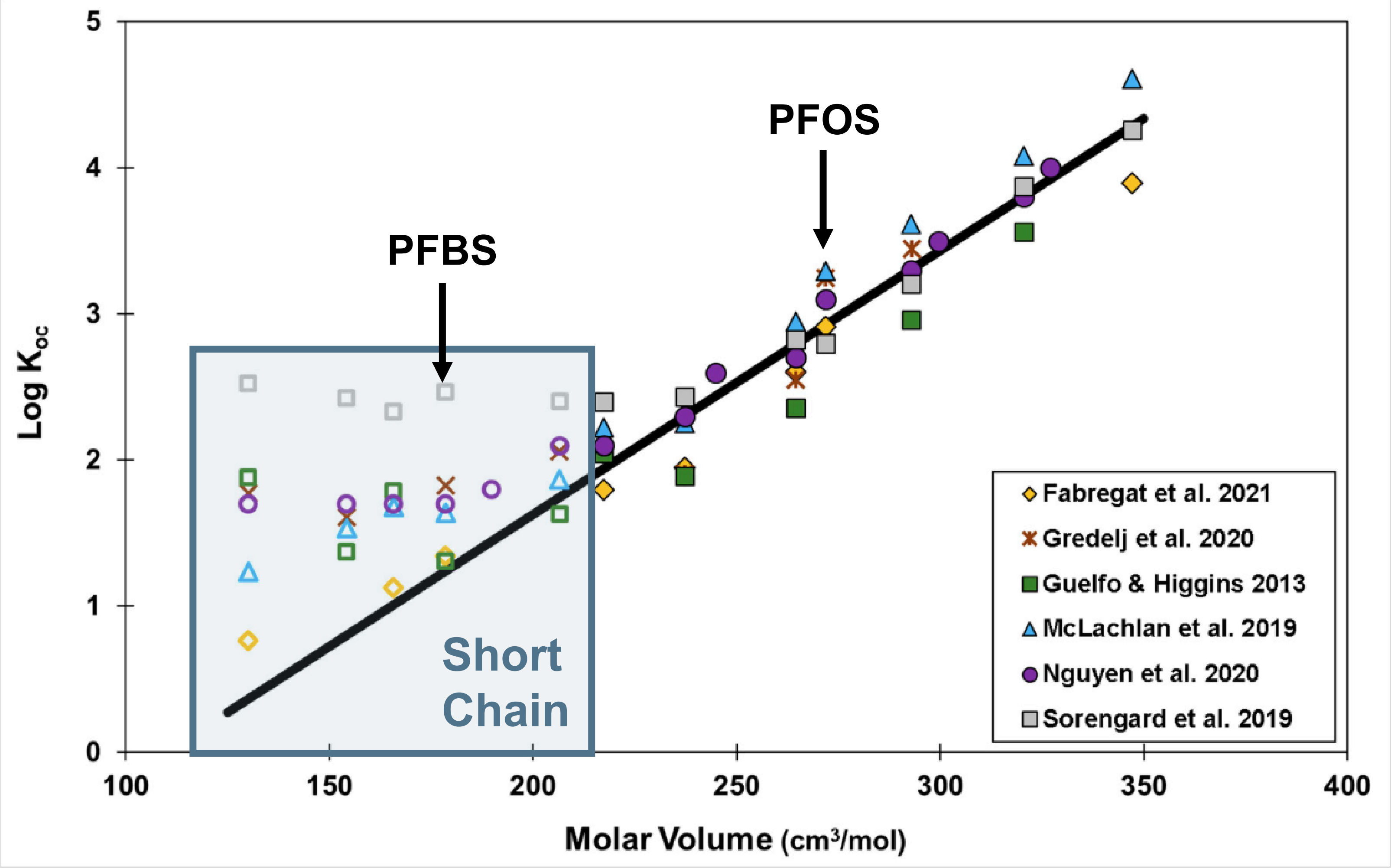


Long chain PFAS

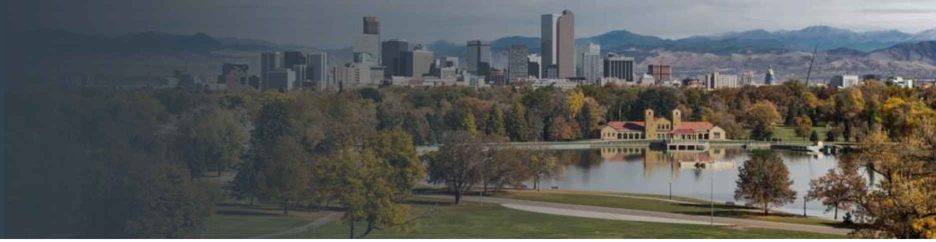
Hydrophobic interaction of tail group

Short chain PFAS

Electrostatic interactions of charged head group

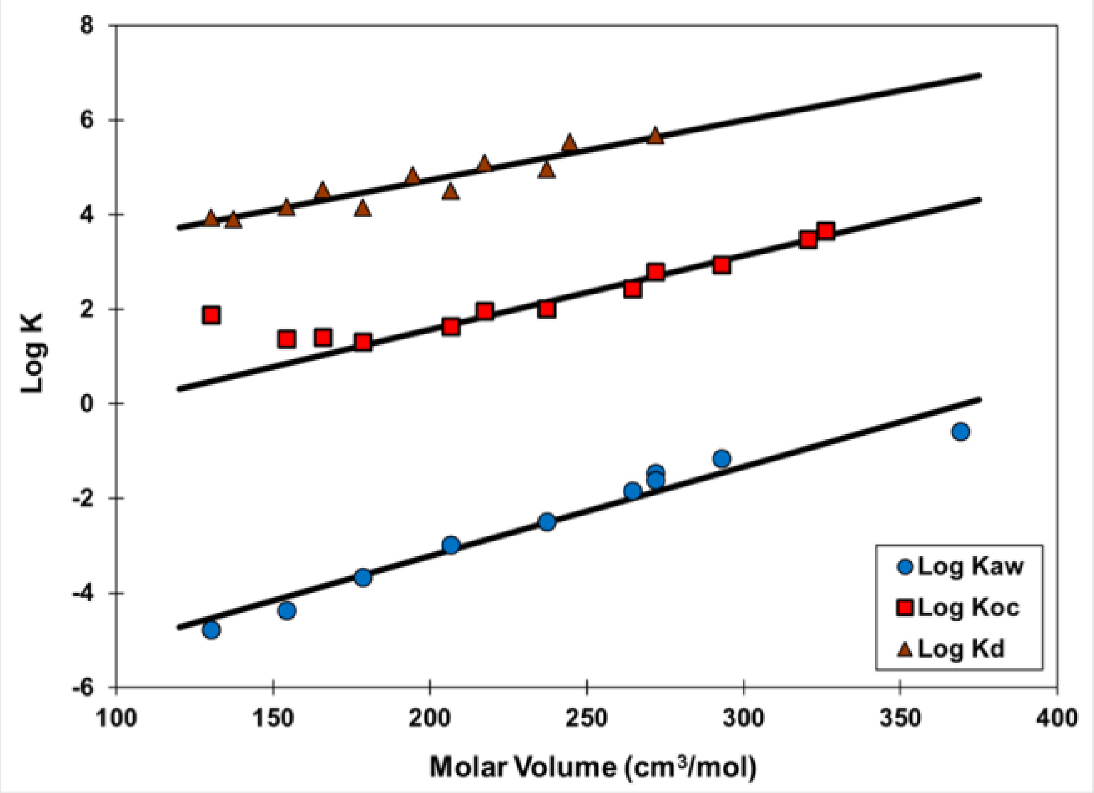


Brusseau, 2024



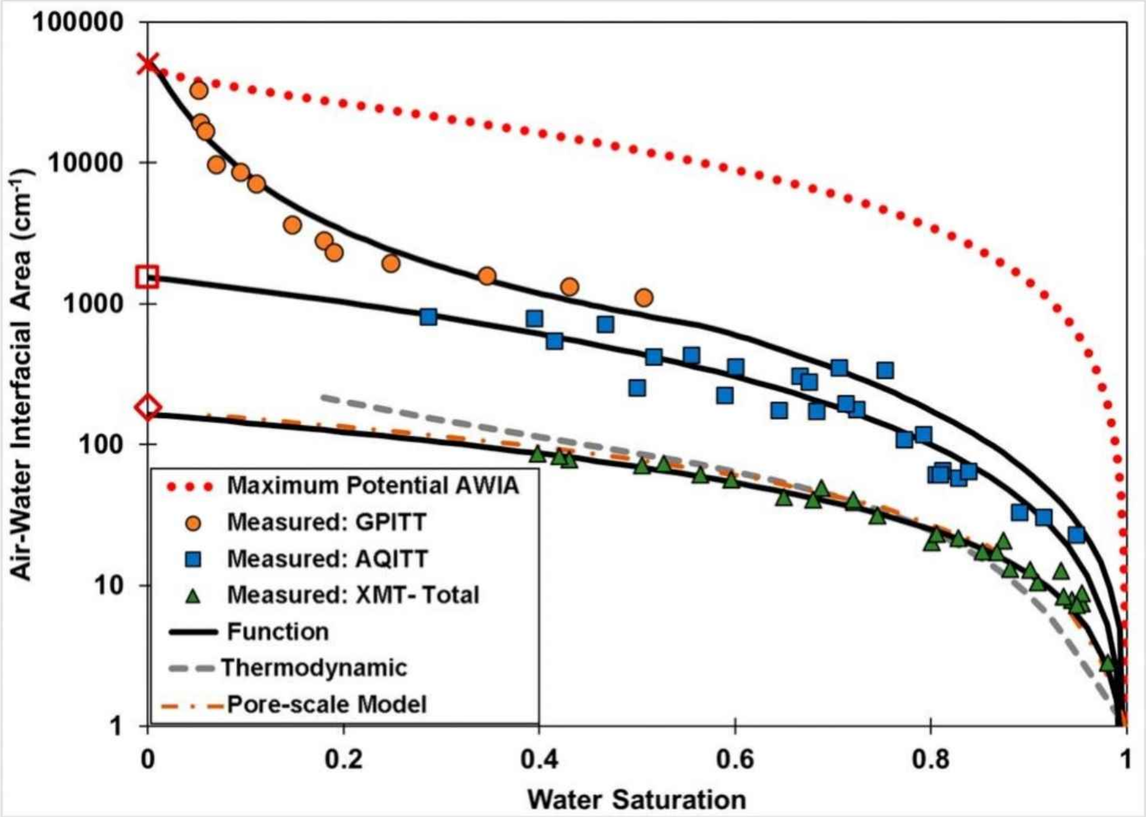
Retention at air-water interface

Retention governed by air-water interfacial area



Brusseau, 2024

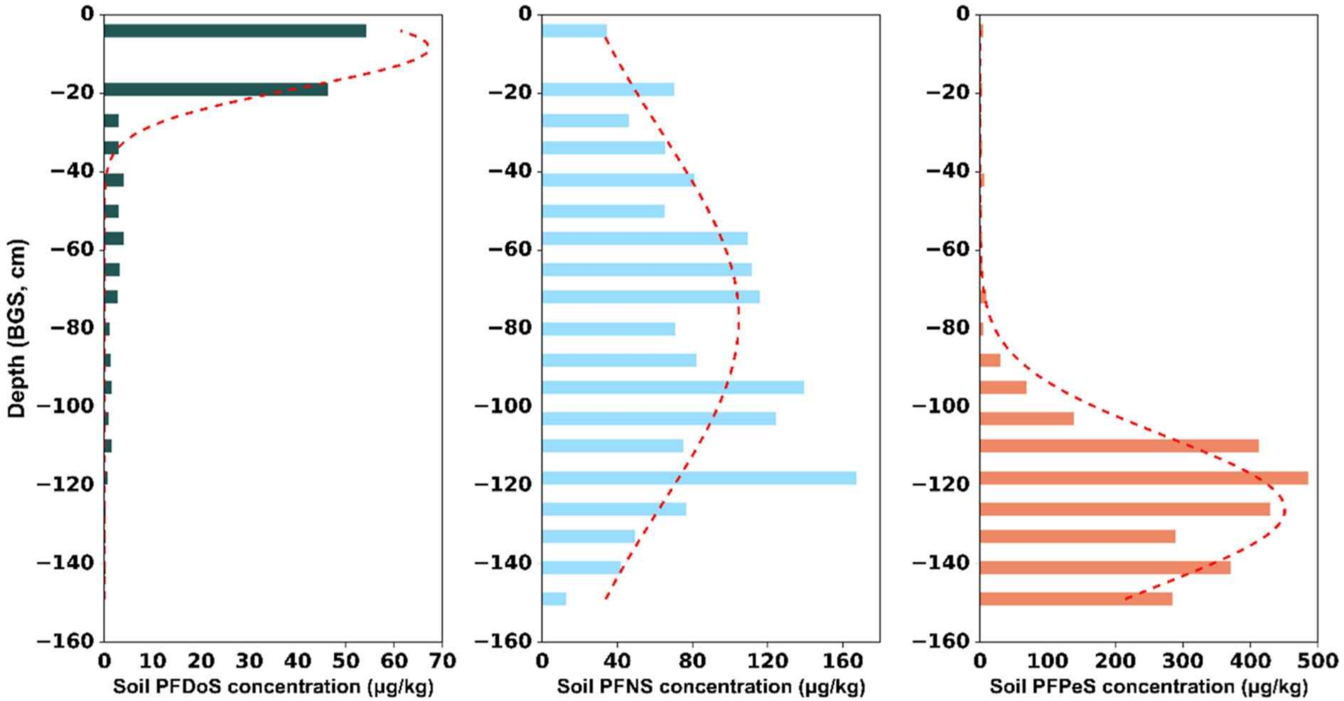
Air-water interfacial area varies with water saturation



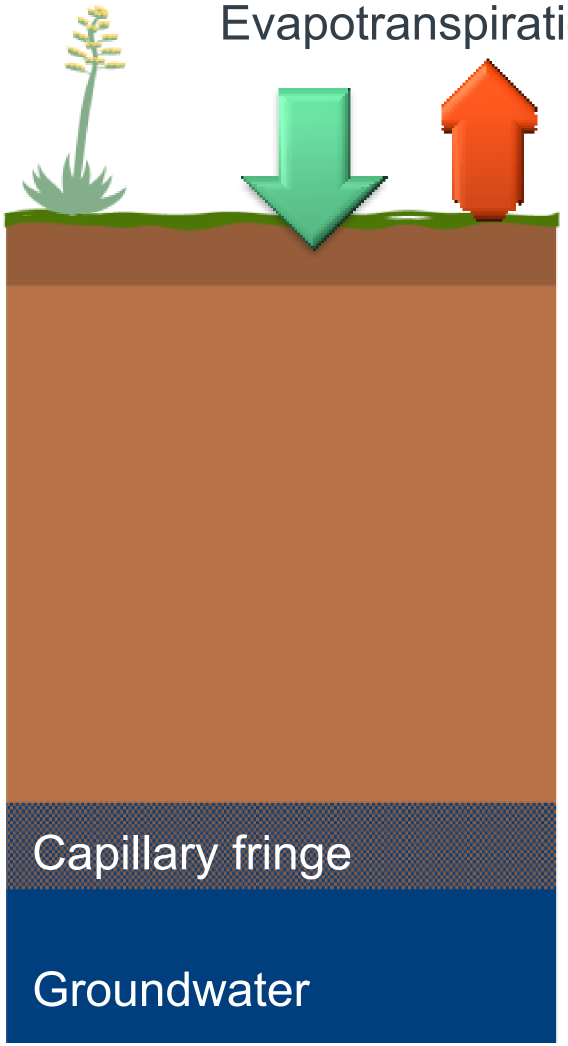
Brusseau, 2023

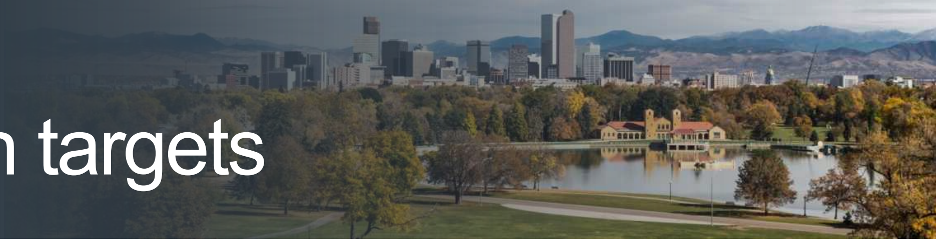
PFAS retention at vadose zone scale

Long chain → **Short chain**



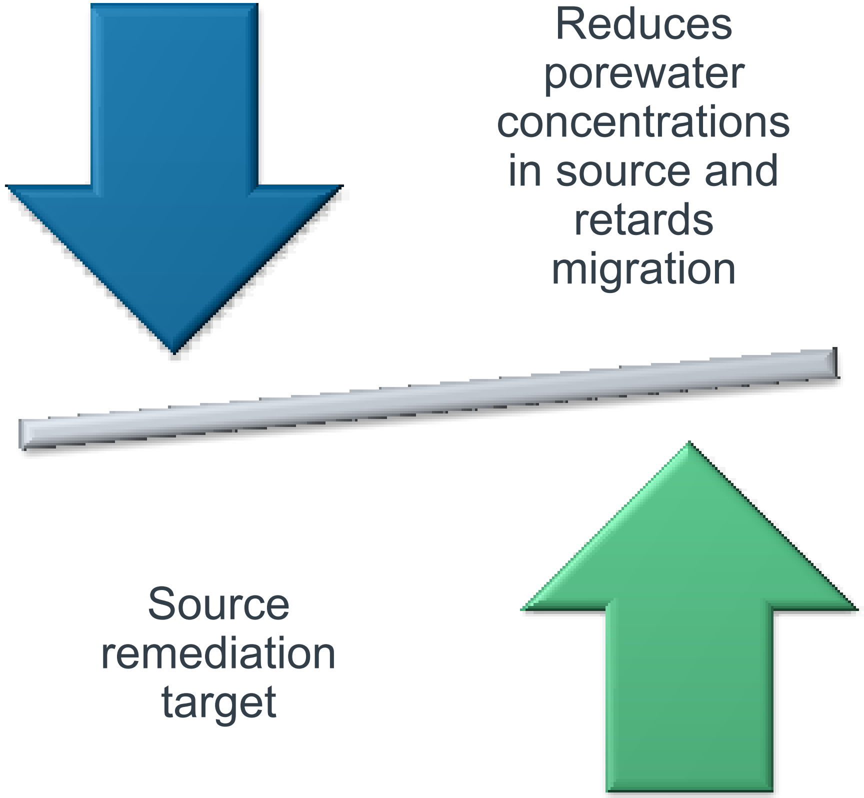
Bigler et al., 2024





Implications for risk assessment & remediation targets

Considering PFAS partitioning behaviour



PFAS leaching mass discharge overpredicted if retention ignored

Considering vadose zone dynamics further improves representativeness

Available modeling approaches and tools available to **support pragmatic decision-making for PFAS in soil**

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Thank you for your attention