Groundwater Modeling and Complexity in PFAS Modeling

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Outline

- Overview of groundwater modeling
- Analytical models (BioChlor, REMChlor,…etc.)
- Numerical models (MODFLOW, MT3D, RT3D)
- Numerical modeling for unsaturated zone
- PFAS fate and transport (demo from a journal article applying modified HYDRUS)
- Things to Note

Common Types of GW Models

- Groundwater flow modeling
  - Movement of water by solving the Darcy's Equation
- Fate and Transport modeling (solve ADE)
  - In Saturated Zone
    - No air in pore space ($\theta = \theta_s$; $K = K_s$)
    - Analytic model (homogeneous and isotropic)
    - Numerical model (heterogeneous and anisotropic)
      - Heterogenous K is not uniform in space i.e., different at every node (location)
      - Anisotropic $Kx \neq Ky \neq Kz$
  - In Vadose Zone
    - Air in pore spaces [$\theta \leq \theta_s$; $K = K(\theta)$]
    - Solve Richard's Equation for flow
    - Complexity at air-water interface when VOCs or SVOCs are modeled
- Particle Tracking Modeling (MODPATH)
  - Direction of water particle movements with GW flow (forward/backward tracking)

Analytical Model for Saturated Zone

- Unidirectional flow (groundwater flows in one direction)
- 3D Dispersion (Dx, Dy, Dz)
- ADE:

$$R\frac{\partial \mathrm{C}}{\partial \mathrm{t}} = -\left(\mathrm{v_x}\frac{\partial \mathrm{C}}{\partial \mathrm{x}}\right) + \left(\mathrm{D_x}\frac{\partial^2 \mathrm{C}}{\partial \mathrm{x}^2} + \mathrm{D_y}\frac{\partial^2 \mathrm{C}}{\partial \mathrm{y}^2} + \mathrm{D_z}\frac{\partial^2 \mathrm{C}}{\partial \mathrm{z}^2}\right) + \frac{\mathrm{W}}{n}\mathrm{C_0} - \frac{Q}{n}\mathrm{C} - \lambda$$

- Domenico Solution:

$$\mathrm{C(x,y,z,t)} = \frac{\mathrm{C_0}}{8}\left[erfc\left(\frac{\mathrm{x - v_x t}}{2\sqrt{\mathrm{D_x t}}}\right)\right]$$

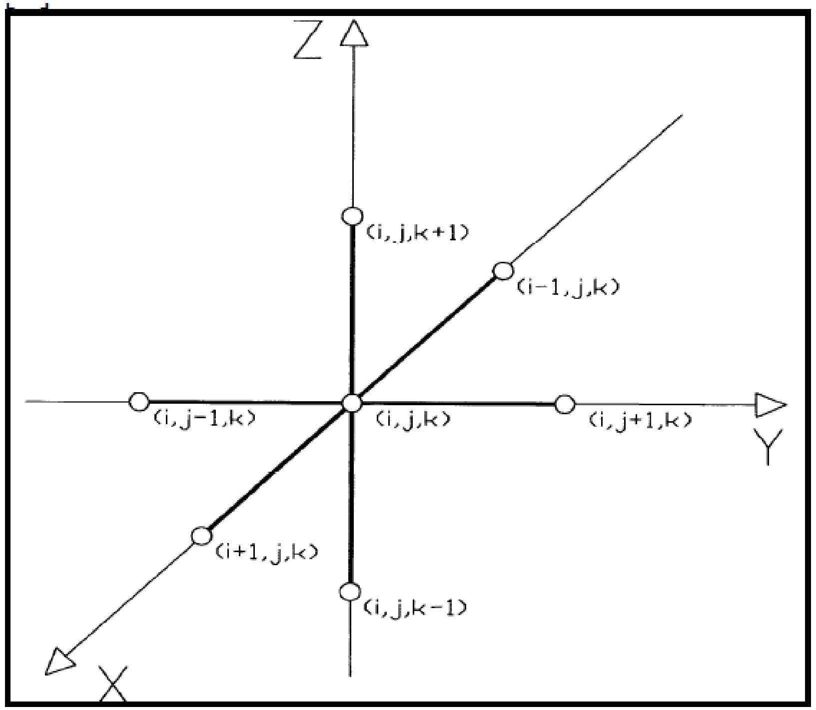
$$\left[erf\left(\frac{\mathrm{y} + {}^{\mathrm{Y_S}}\!/\!{}_{2}}{2\sqrt{\mathrm{D_y t}}}\right) - erf\left(\frac{\mathrm{y} - {}^{\mathrm{Y_S}}\!/\!{}_{2}}{2\sqrt{\mathrm{D_y t}}}\right)\right]\left[erf\left(\frac{\mathrm{z} + {}^{\mathrm{Z_S}}\!/\!{}_{2}}{2\sqrt{\mathrm{D_z t}}}\right) - erf\left(\frac{\mathrm{z} - {}^{\mathrm{Z_S}}\!/\!{}_{2}}{2\sqrt{\mathrm{D_z t}}}\right)\right]$$

- REMChlor is not Domenico-based model
- Analytical models are useful for screening level applications (e.g., BIOCHLOR, BIOSCREEN, REMChlor, REMFuel)

Numerical Model for Saturated Zone

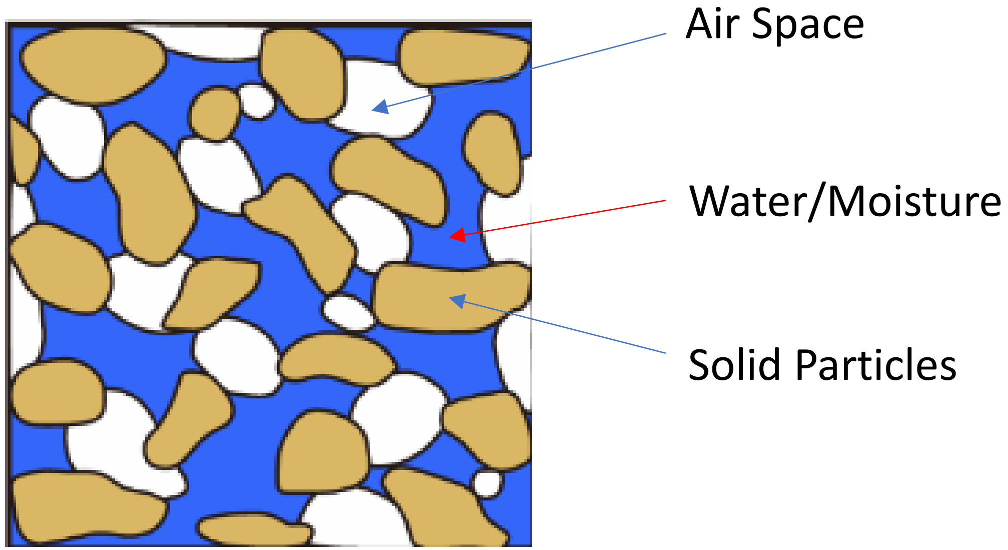
- Flow equation for a complex system in porous media

$$\frac{\partial}{\partial x}\cdot\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\cdot\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\cdot\left(K_{zz}\frac{\partial h}{\partial z}\right)-W=S_s\cdot\frac{\partial h}{\partial t}$$



- Solves the ADE numerically using FDM or FEM.
- MODFLOW is built for porous media modeling, but people still use it for fractured rocks.
- Models for fractured rock systems are available.
- MODLOW can model dual porosity (mobile and immobile)

Unsaturated Soil Structure



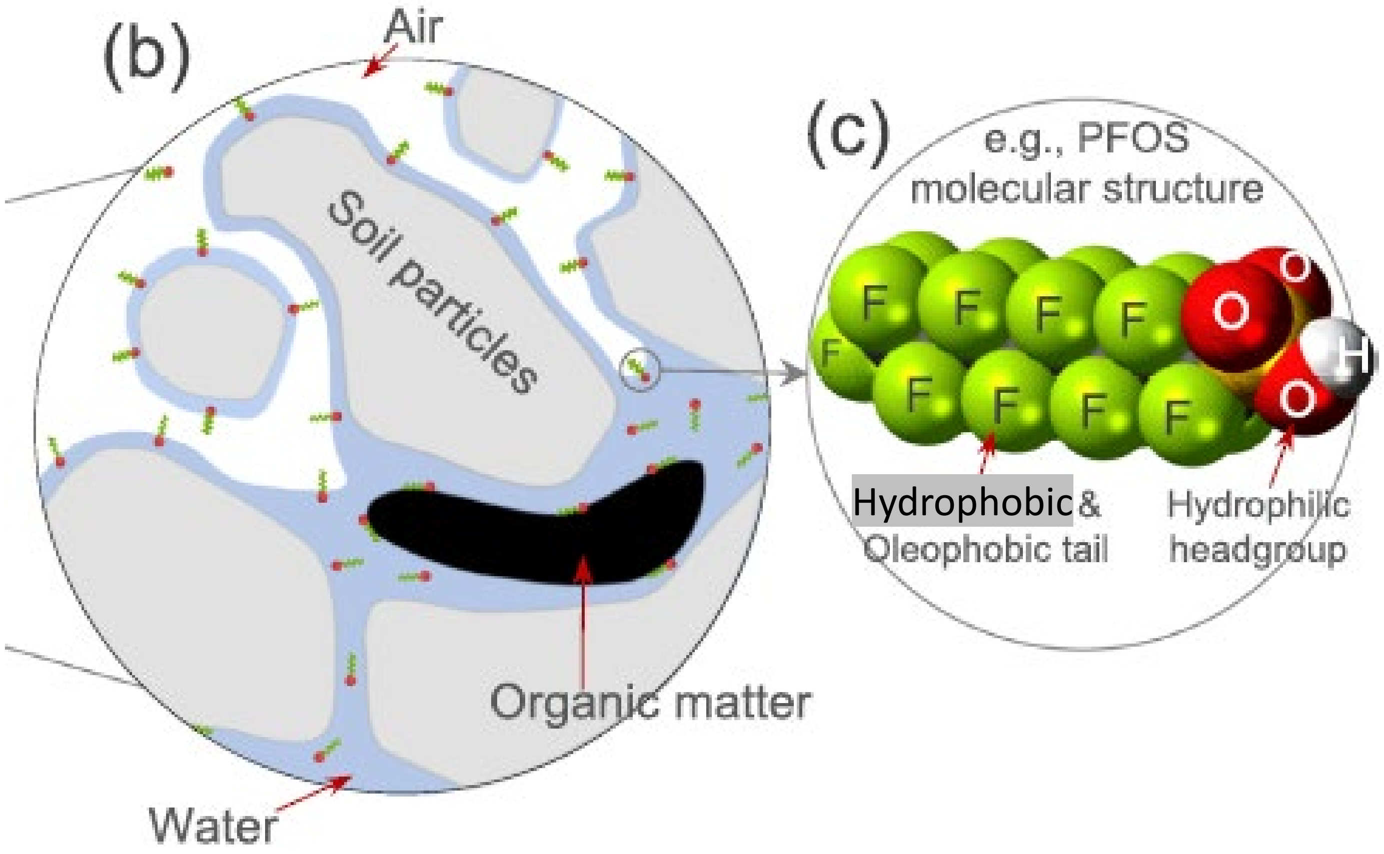
3 Interfaces in vadose zone:

- Air-Water interface
- Solid-Water interface
- Air-Solid interface

When saturated ($\theta = \theta_s$), only Solid-Water interface

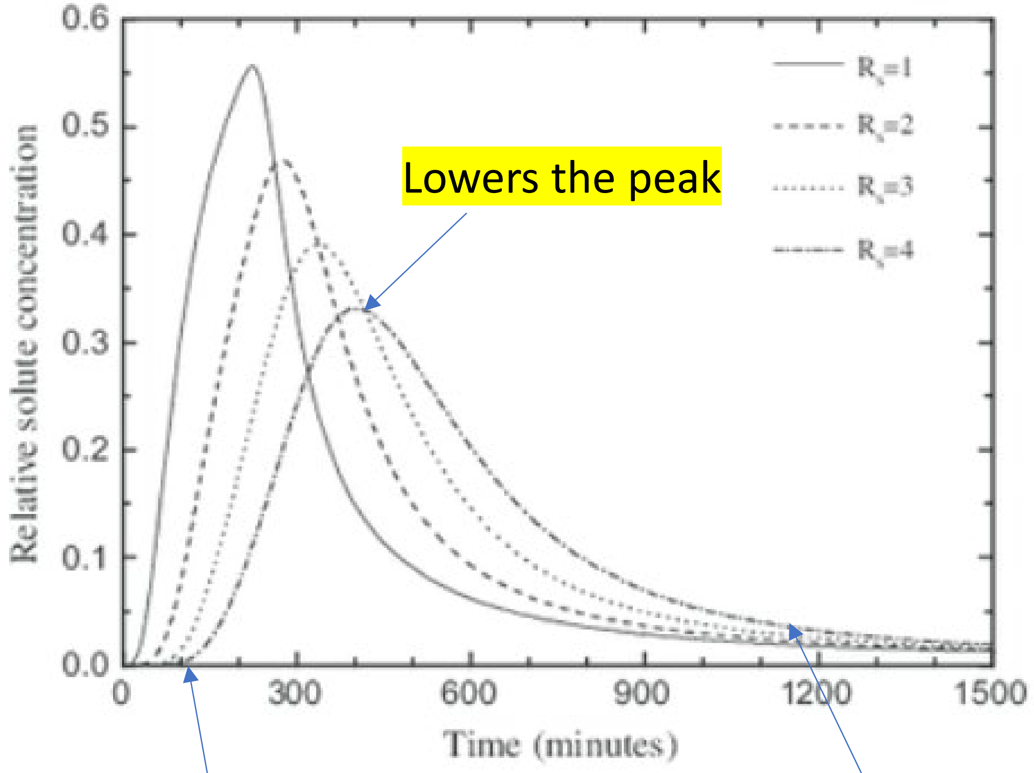
PFAS fate and transport mechanism

- PFAS has tendency to aggregate at air-water interfaces
- Air-Water interface will contribute as an additional retardation to Soil-Water partitioning.
- Longer-chain PFAS compounds are likely to be less mobile in vadose zone compared to the shorter-chain PFAS compounds.



From Guo et al. (2020)

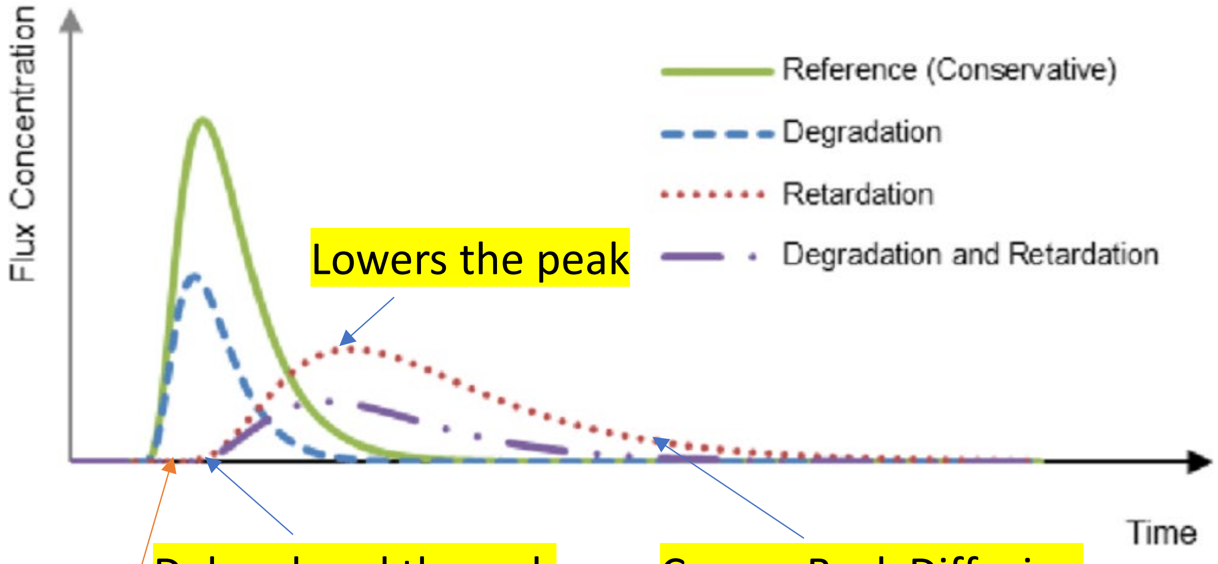
Effect of Retardation Factor and Biodegradation on Plume Migration



Lowers the peak

Causes Back Diffusion

Delays breakthrough



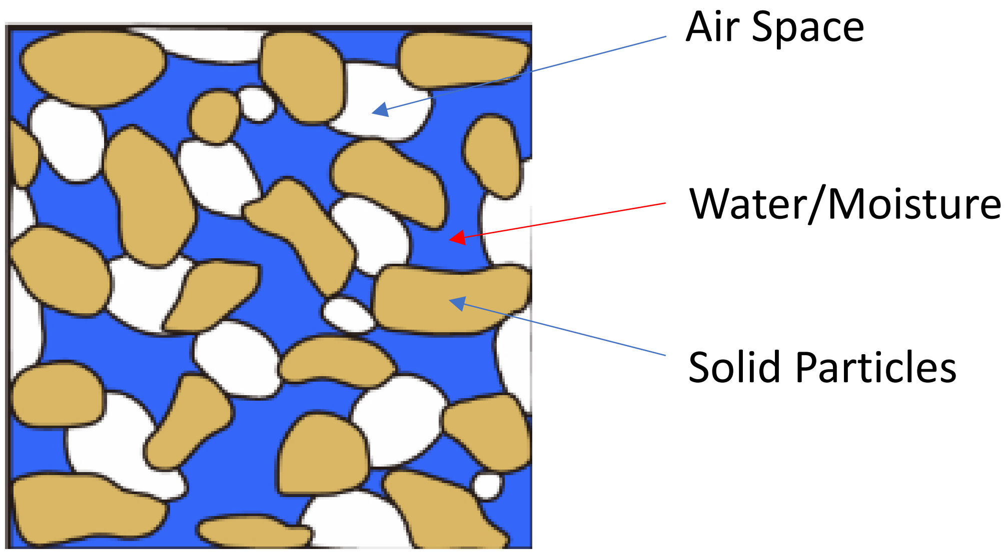
Lowers the peak

Delays breakthrough

Causes Back Diffusion

Although PFAS breakthrough gets delayed because of air pockets, the leading front may be higher than the cleanup goal (which is in ppt)!!

Modeling for Unsaturated Soil



In Vadose Zone:

- Air in pore spaces [$\theta \leq \theta_s$; $K = K(\theta)$]
- Complexity at air-water interface when VOCs or SVOCs are modeled (Henry's Law)
- Solve Richard's Equation for flow

Richard's Equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K\left(\frac{\partial h}{\partial x} + \cos\alpha\right)\right] - S$$

where,

- Moisture Content (θ) changes with time and space,
- Pressure/suction potential (h) = $f(x, \theta)$
- α = angle with vertical axis in the direction of flow

Vadose Zone Hydraulic Properties (VG Model)

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{[1+|\alpha h|^n]^m} & h < 0 \\ \theta_s & h \geq 0 \end{cases}$$

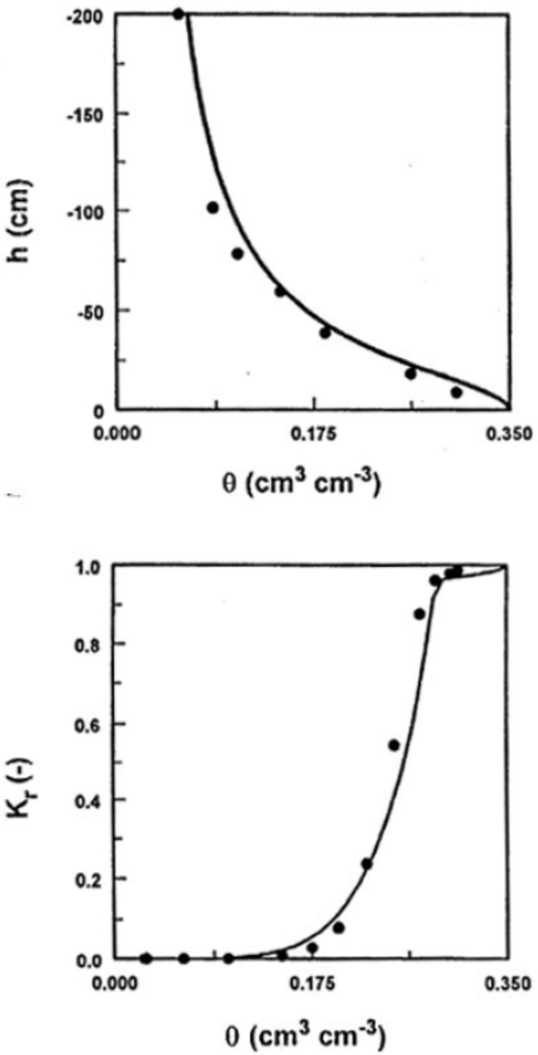
$$K(h) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2$$

$$m = 1 - 1/n \ , \quad n > 1$$

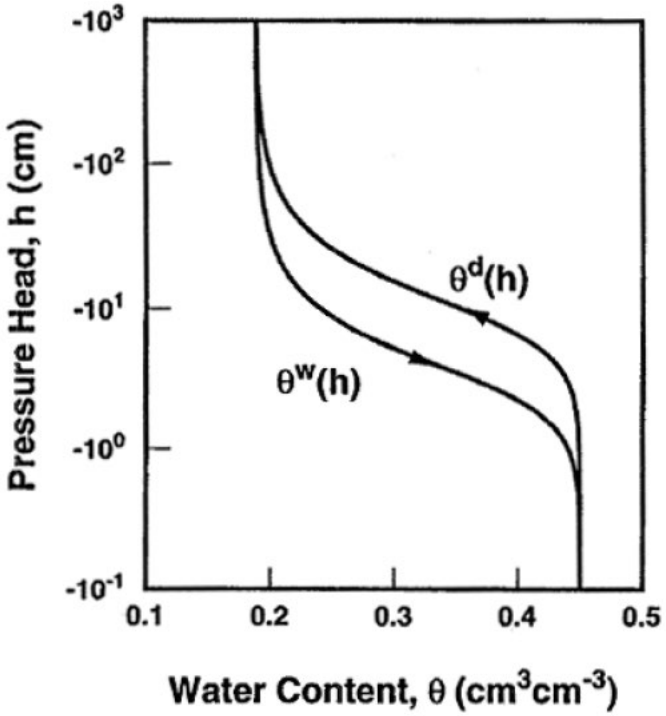
$K_r = S_e^l [1 - (1 - S_e^{1/m})^m]^2$

$K_{us} = K_s \,.\, K_r$

$K_r \leq 1$

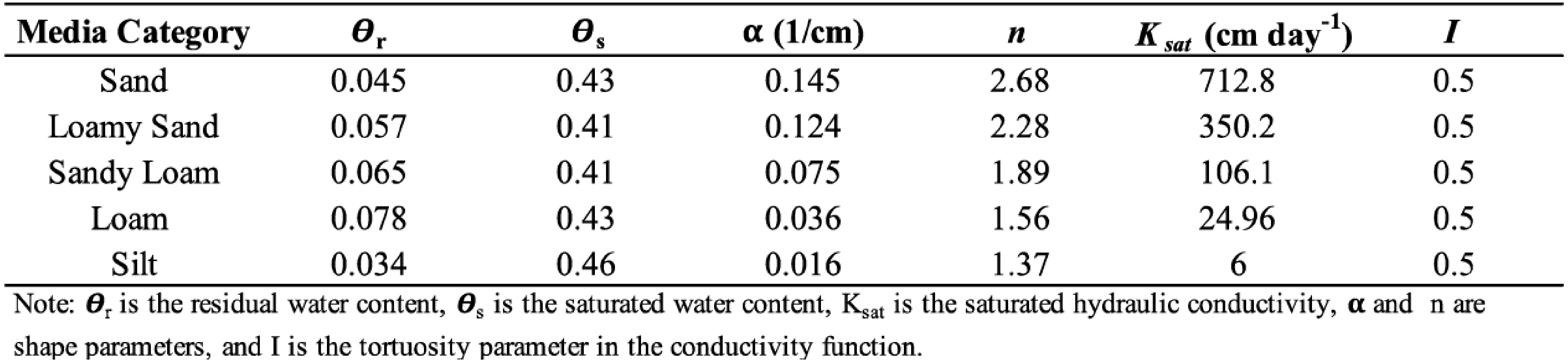


Suction potential (h) and K are functions of moisture content



Hysteresis during wetting and drying

VG Parameters for different soil types

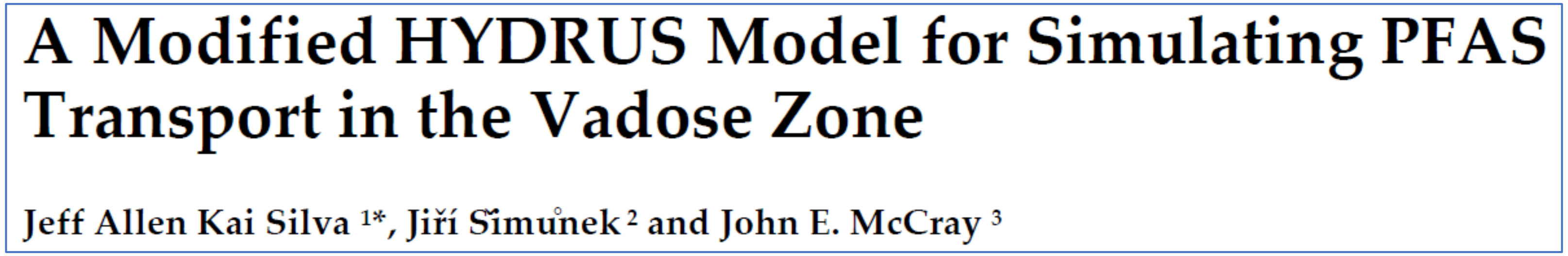


Media Category	**θ_r**	**θ_s**	**α (1/cm)**	***n***	**K_{sat} (cm day^{-1})**	***I***
Sand	0.045	0.43	0.145	2.68	712.8	0.5
Loamy Sand	0.057	0.41	0.124	2.28	350.2	0.5
Sandy Loam	0.065	0.41	0.075	1.89	106.1	0.5
Loam	0.078	0.43	0.036	1.56	24.96	0.5
Silt	0.034	0.46	0.016	1.37	6	0.5

Note: θ_r is the residual water content, θ_s is the saturated water content, K_{sat} is the saturated hydraulic conductivity, **α** and n are shape parameters, and I is the tortuosity parameter in the conductivity function.

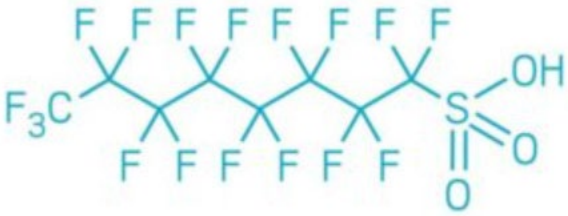
α and *n* are called VG parameters and are often calibrated

PFAS Transport in Vadose Zone

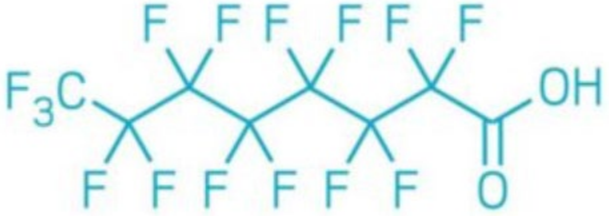


A Modified HYDRUS Model for Simulating PFAS Transport in the Vadose Zone

Jeff Allen Kai Silva [1*], Jiří Šimůnek [2] and John E. McCray [3]

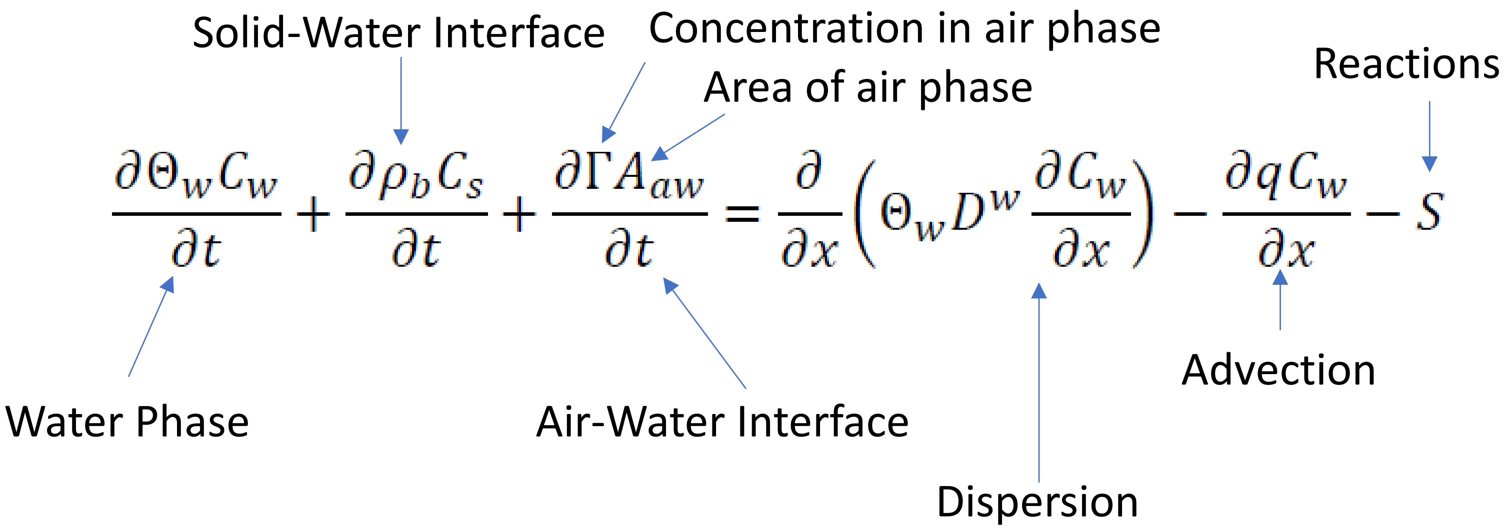


PFOS



PFOA

Advection-Dispersion Equation for PFAS in the vadose zone:



Solid-Water Interface

Concentration in air phase

Area of air phase

Reactions

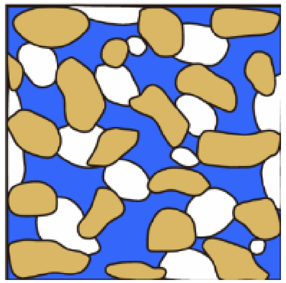
$$\frac{\partial \Theta_w C_w}{\partial t} + \frac{\partial \rho_b C_s}{\partial t} + \frac{\partial \Gamma A_{aw}}{\partial t} = \frac{\partial}{\partial x}\left(\Theta_w D^w \frac{\partial C_w}{\partial x}\right) - \frac{\partial q C_w}{\partial x} - S$$

Water Phase

Air-Water Interface

Advection

Dispersion



PFAS Fate and Transport Processes

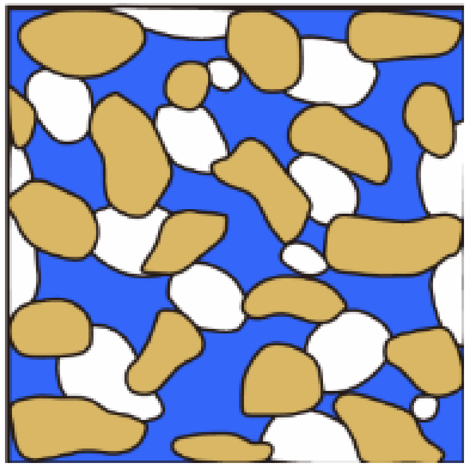
- Sorption between solid-water phases:

$$C_s = \frac{k_D {C_w}^{\beta}}{1 + \eta {C_w}^{\beta}}$$

Given the input values, it could be Linear, Freundlich or Langmuir isotherms. **At low PFAS concentration, linear relationship can be assumed.**

- Sorption between Air-Water Interface (AWI) assumed Langmuir isotherm for Γ (PFAS concentration in the air phase):

$$\Gamma(C_w) = \frac{\Gamma_{max} K_{L,aw} C_w}{1 + K_{L,aw} C_w}$$



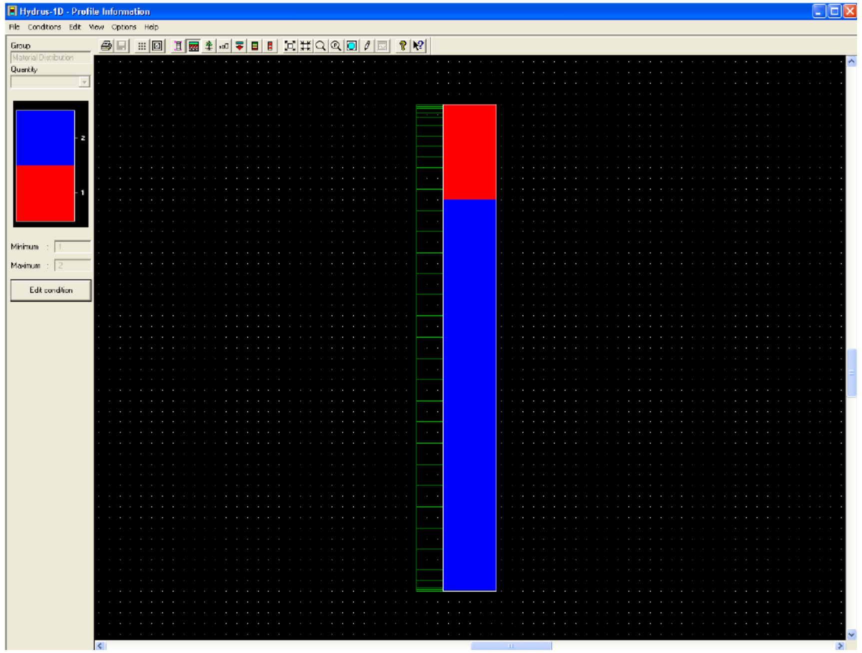
- AWI sorption is instantaneous and reversible (i.e., as the pores get saturated, mass in the air phase will transfer to the water phase)
- If $K_{aw} = f(C_w)$ at high concentration of PFAS (adds more complexity)
- PFAS retention in AWI is proportional to A_{aw} ; and $A_{aw} \infty 1/\theta_w$
- $A_{aw} = f(\theta_w)$ is calculated from soil-water retention curve (h vs. θ_w)
- *Surface tension (σ) driven flow is possible at high concentration, PFAS> 10 mg/L*
- *Viscosity of PFAS can reduce K_{unsat} during infiltration during AFFF application*

$$\frac{dA_{aw}(\Theta)}{d\Theta} = \frac{P_{aw}}{\sigma_o} = \frac{\rho_w g h}{\sigma_o}$$

Surface Tension

How to Setup Model

Model Boundary



Group: Material Distribution

Minimum : 1

Maximum : 2

Column Study Data for Calibration (Lyu et al. 2018)

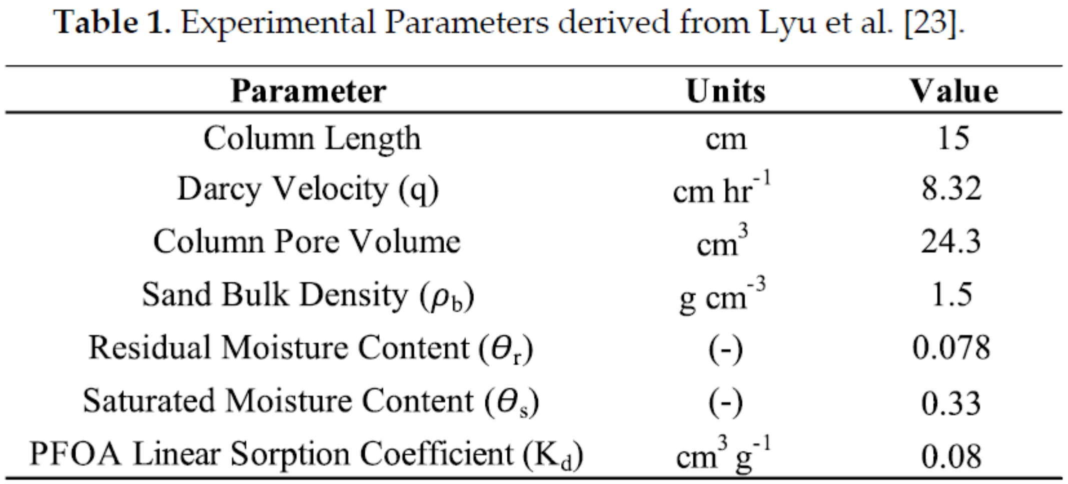


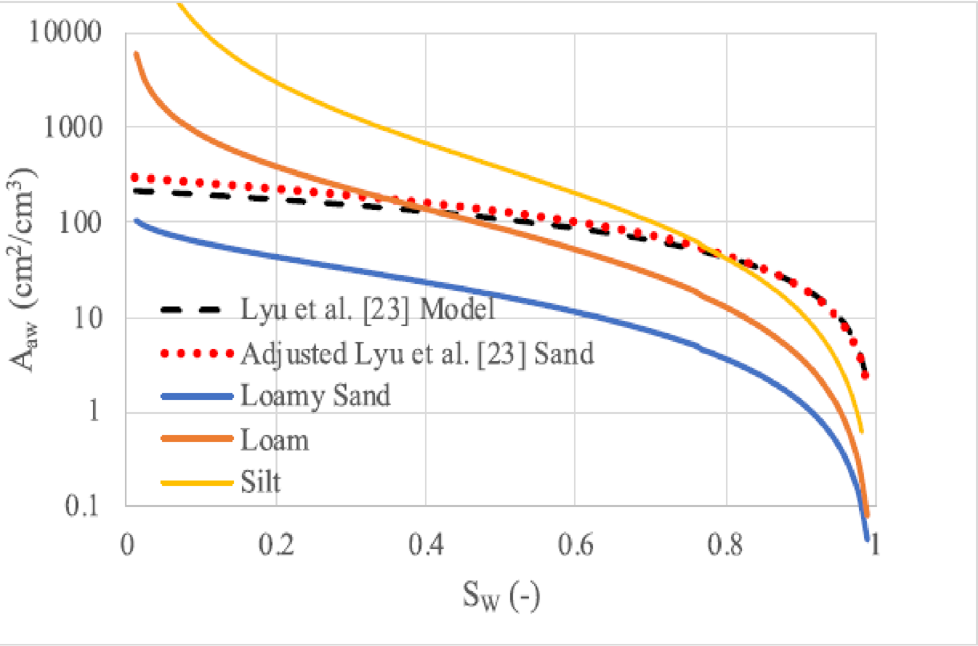
Table 1. Experimental Parameters derived from Lyu et al. [23].

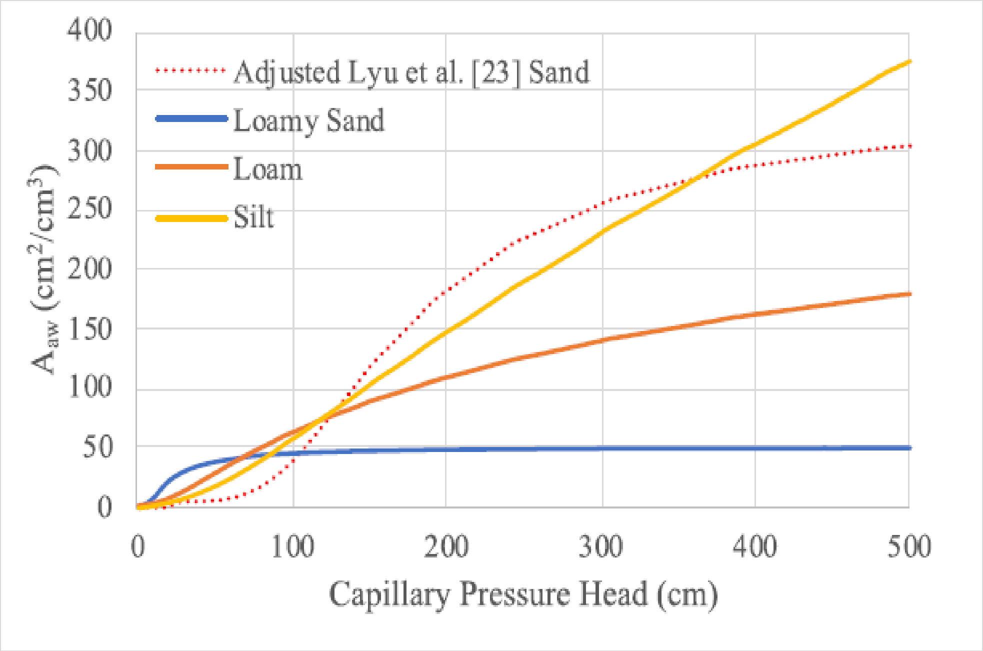
Parameter	Units	Value
Column Length	cm	15
Darcy Velocity (q)	$cm\ hr^{-1}$	8.32
Column Pore Volume	cm^3	24.3
Sand Bulk Density (ρ_b)	$g\ cm^{-3}$	1.5
Residual Moisture Content (θ_r)	(-)	0.078
Saturated Moisture Content (θ_s)	(-)	0.33
PFOA Linear Sorption Coefficient (K_d)	$cm^3\ g^{-1}$	0.08

Flow Model Boundary: Constant moisture content at the top and bottom.

Transport Model Boundary: Concentration flux at the top; Zero-conc. gradient at the bottom.

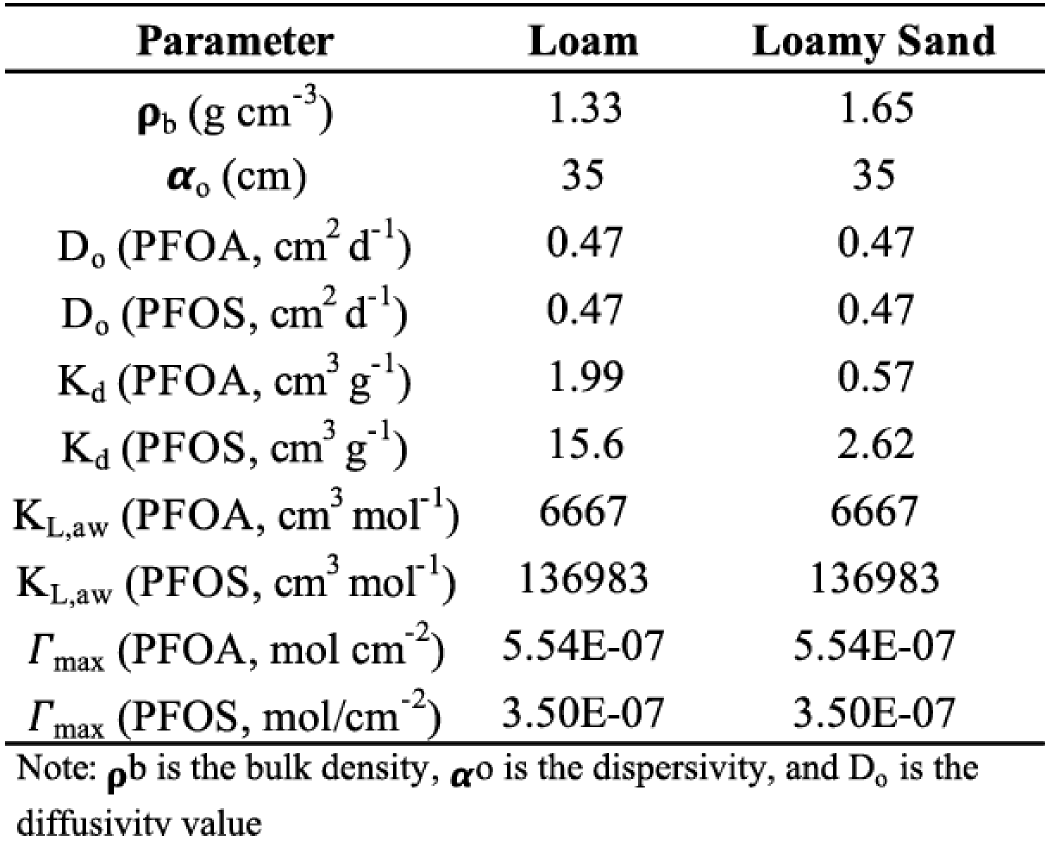
Model Calibration





- First, VG parameters (α, n and K) were adjusted to match the A_{aw} vs. S_w ; where, ($S_w=\theta_w/\theta_s$)
- Assumed, $A_{aw} = (1- S_w)A_{max}$ for the modeled quartz sand;
- Next, match the breakthrough concentrations (C/C_0 vs. t)
- Loamy sand, Loam and Silt are 3 different soil types with known VG parameter values
- As S_w increases to 1 (i.e., $\theta_w=\theta_s$), A_{aw} approaches to zero.
- Pressure head, $h \propto 1/\theta_w \propto A_{aw}$

Model Simulations for PFOA and PFOS leaching

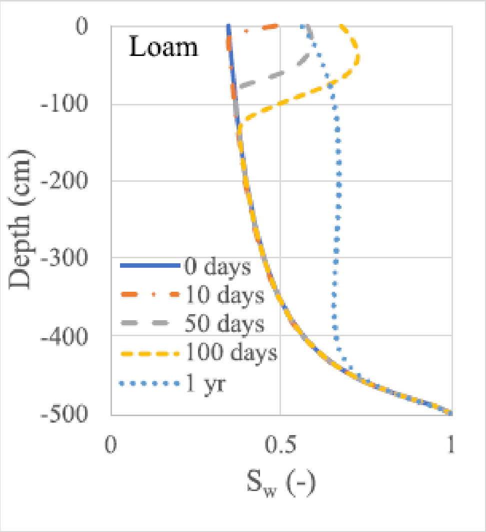


Parameter	**Loam**	**Loamy Sand**
ρ_b (g cm^{-3})	1.33	1.65
α_o (cm)	35	35
D_o (PFOA, cm^2 d^{-1})	0.47	0.47
D_o (PFOS, cm^2 d^{-1})	0.47	0.47
K_d (PFOA, cm^3 g^{-1})	1.99	0.57
K_d (PFOS, cm^3 g^{-1})	15.6	2.62
$K_{L,aw}$ (PFOA, cm^3 mol^{-1})	6667	6667
$K_{L,aw}$ (PFOS, cm^3 mol^{-1})	136983	136983
Γ_{max} (PFOA, mol cm^{-2})	5.54E-07	5.54E-07
Γ_{max} (PFOS, mol/cm^{-2})	3.50E-07	3.50E-07

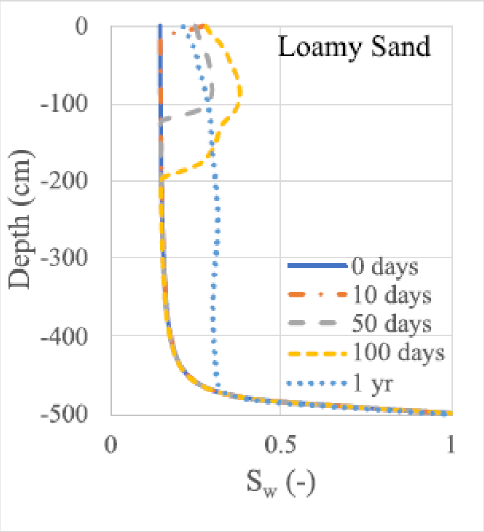
Note: ρb is the bulk density, αo is the dispersivity, and D_o is the diffusivity value

- Flow Model:
  - Z= 500 cm deep domain
  - h=0 at Z= 500 cm (Water Table)
  - Rainfall and ET as function of time at the top boundary
- Transport Model (boundary conditions):
  - Initial Source Concentration = 1 mg/L
  - Mass in the solid phase at the top 100 cm (source),
  - In 15 years, pore water conc. reduces to 0.5 mg/L)
  - Concentration flux at the top and zero conc. gradient at water table (bottom)

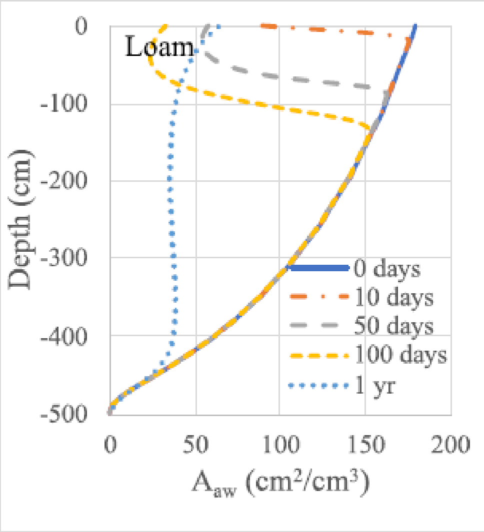
Simulation results



(a)



(b)



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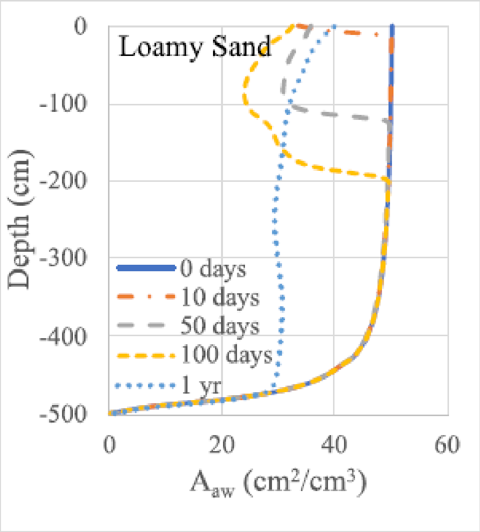
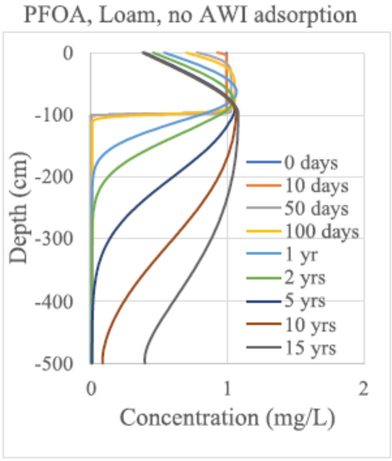


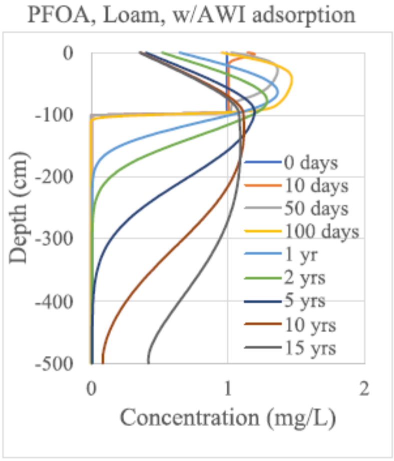
(d)

- Above figures show hydraulic behavior with advancement of the wetting front toward water table at the bottom
- A_{aw} approaches to zero at 100% saturation near the water table
- Loam shows more sensitivity to A_{aw} with increase of θ_w than loamy sand [Figures (c) and (d) above]
- These figures entirely depend on hydraulic properties, not based on PFOA/PFOS

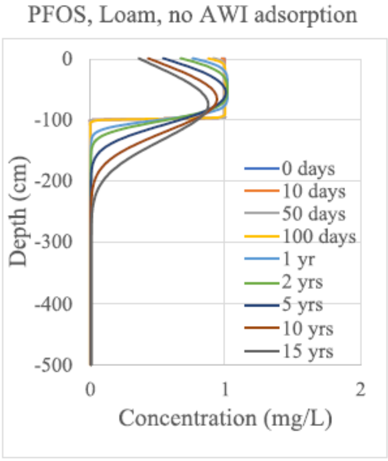
PFOA and PFOS results


PFOA, Loam, no AWI adsorption

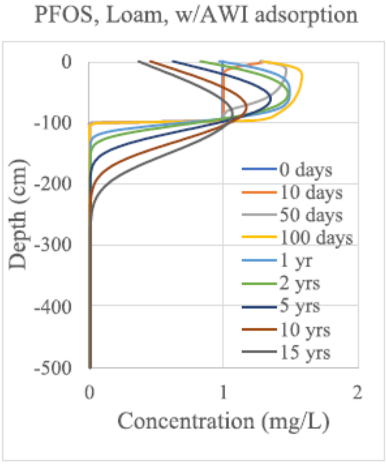
(a)


PFOA, Loam, w/AWI adsorption

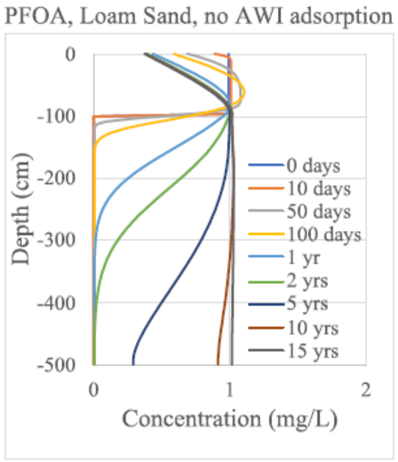
(b)


PFOS, Loam, no AWI adsorption

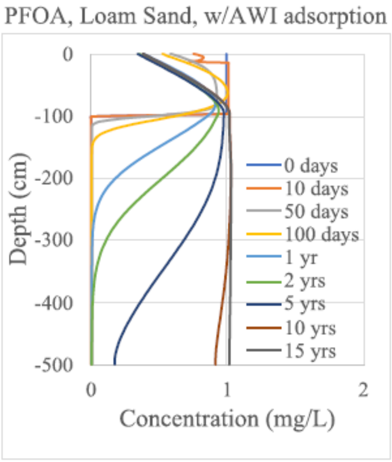
(c)


PFOS, Loam, w/AWI adsorption

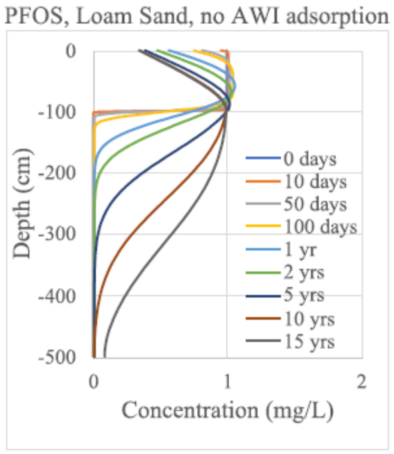
(d)


PFOA, Loam Sand, no AWI adsorption

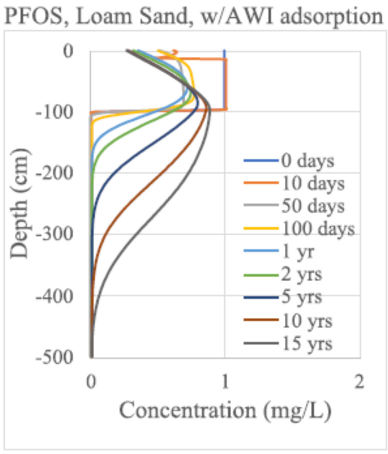
(e)


PFOA, Loam Sand, w/AWI adsorption

(f)


PFOS, Loam Sand, no AWI adsorption

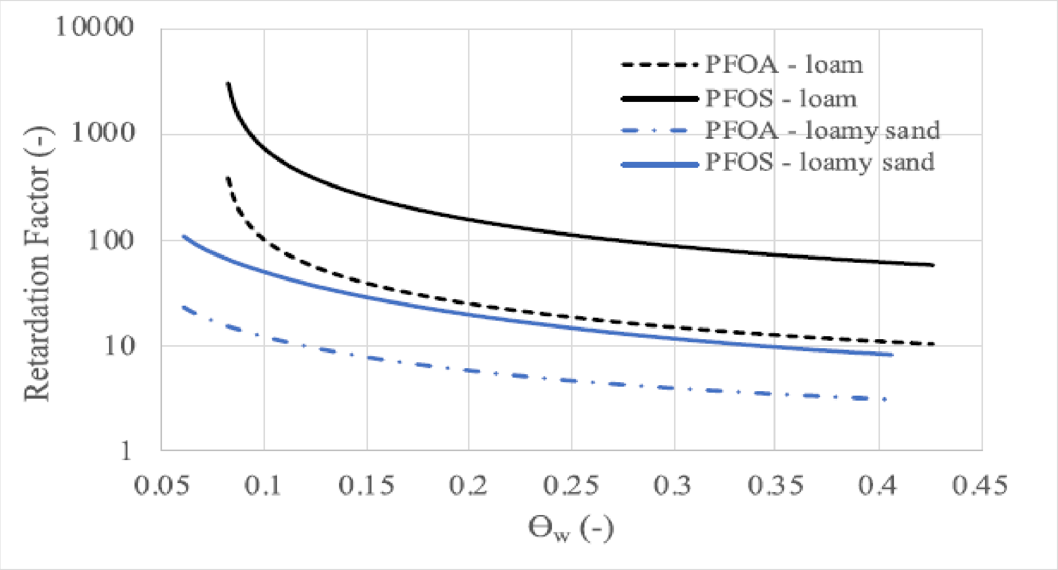
(g)


PFOS, Loam Sand, w/AWI adsorption

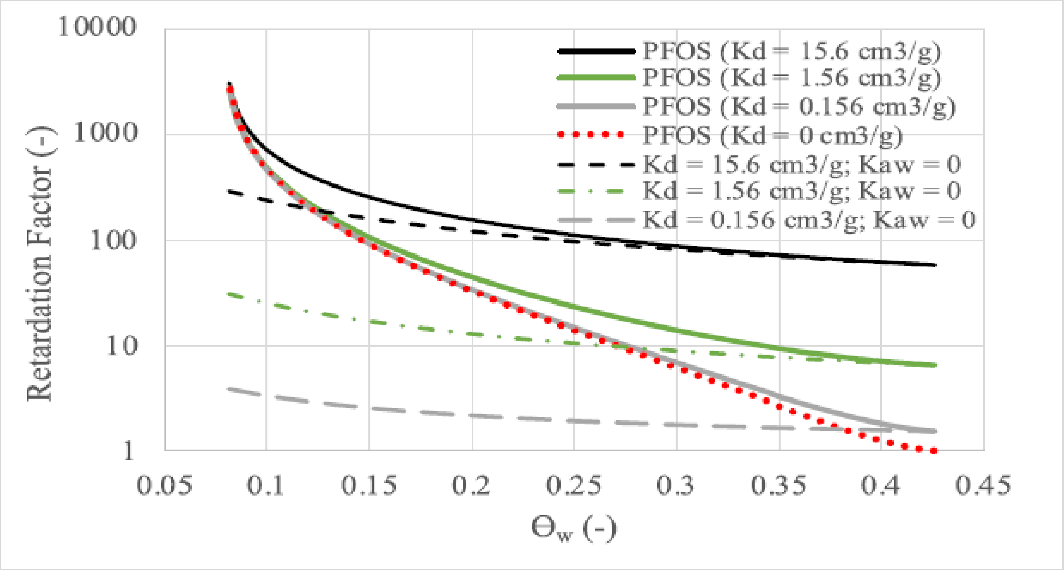
(h)

- Solid Phase sorption with/without AWI Sorption are compared here.
- In Loamy Sand, reduction of A_{aw} was much smaller with the wetting front (previous slide); hence AWI sorption was more significant than Loam soil.
- Solid Phase sorption is dominant for both PFOA and PFOS than AWI Sorption (contradicts other research findings). May be because the mass transfers from air to water as the soil gets wet.
- K_d value has a significant role in comparing sorption results.

Sensitivity of K_d



(a)



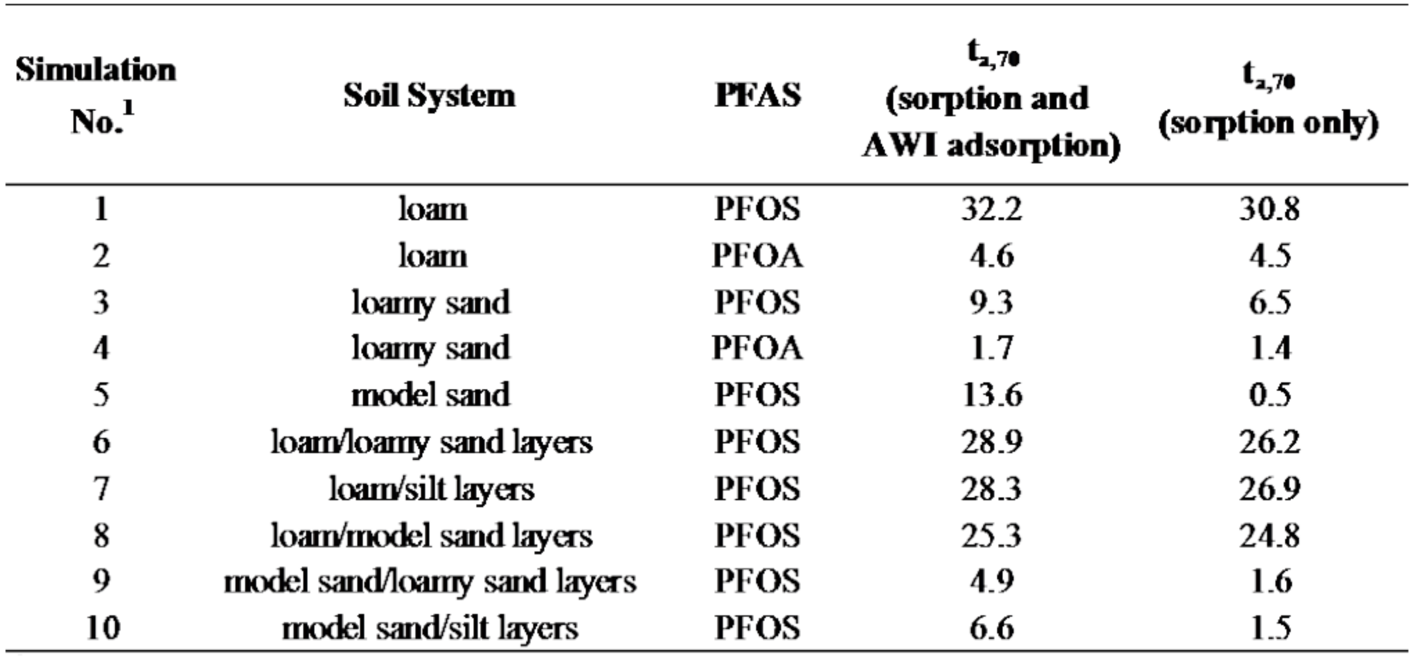
(b)

$$R_f = 1 + \frac{\rho_b K_d}{\Theta_w} + \frac{k_{aw} A_{aw}}{\Theta_w}$$

Retardation due to AWI

- K_{aw}= 0 means no AWI sorption (at saturation, no sorption due to AWI. PFAS reverse back to water)
- At low θ_w value, AWI sorption has significant contribution to Rf
- At low K_d value, AWI sorption is dominant until near saturation (θ_s)

AWI sorption for different soil types



Simulation No.[1]	Soil System	PFAS	$t_{a,70}$ (sorption and AWI adsorption)	$t_{a,70}$ (sorption only)
1	loam	PFOS	32.2	30.8
2	loam	PFOA	4.6	4.5
3	loamy sand	PFOS	9.3	6.5
4	loamy sand	PFOA	1.7	1.4
5	model sand	PFOS	13.6	0.5
6	loam/loamy sand layers	PFOS	28.9	26.2
7	loam/silt layers	PFOS	28.3	26.9
8	loam/model sand layers	PFOS	25.3	24.8
9	model sand/loamy sand layers	PFOS	4.9	1.6
10	model sand/silt layers	PFOS	6.6	1.5

$t_{a,70}$ is the number of years to reach 70 ng/L at the water table

- PFOS takes longer to reach water table than PFOA, because of higher K_d value.
- Travel time is faster for sandy soils, because of high K value and lower surface tension.
- AWI sorption is mostly not significant, although PFOS in model sand (calibrated sand) shows a different result.

Things to Note

- Modeling of solute transport in vadose zone is complex.
- Soil hydraulic properties vary with change in moisture content. Need to calibrate the relationship between (hydraulic properties)
  - h vs. θ,
  - A_{aw} vs. θ
  - K vs. θ
- VG model is a good place to start for calibrating soil hydraulic properties
- For PFAS, AWI can add to the sorption and retain the contaminant in the air pockets. However, as air pockets disappear due to infiltration, contaminant mass will reverse back to water phase (cause a spike in concentration).
- AWI could have relatively significant contribution to retardation when K_d value of the contaminant is low (may apply to short-chain PFAS)
- Requires a lot of effort in data collection to calibrate a model.

Questions??