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Multiphysics Numerical Modeling of Transient Transport of PFAS

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Abstract

The need to understand the fate and transport of Per- and Polyfluoroalkyl substances (PFAS) has grown due to the widespread contamination of the environment by them. PFAS are persistent, mobile, toxic manmade chemicals of great concern that contribute to the contamination of soil and groundwater. The presence of PFAS in unsaturated soil complicates their transport due to the impact of the air-water interface and solid-phase adsorption. The air-water interface can significantly increase the retention of PFAS during its transport. In this paper, a numerical model has been developed to study the transport of PFAS by coupling transient seepage and advection-dispersion, also accounting for the air-water interface and solid-phase adsorption. The numerical model was then used to study various scenarios.

I. Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetically fluorinated organic compounds of great concern due to the widespread contamination of the environment they cause. More than 4,000 PFAS compounds have been manufactured since the 1940s (Barzen-Hanson et al., 2017, Wang et al., 2017). This is due to PFAS's unique properties useful in industrial and commercial products such as fire resistance, dust suppression, oil repellence (lipophobic and hydrophobic properties), and remarkably high stability due to strong carbon-fluoride (C-F) bond (Buck et al., 2011). PFAS are known to be durable in the natural environment. The most common sources of PFAS in the environment are industrial facilities, landfills (leachate), wastewater treatment plants, consumer products (textile, cookware, etc.), and aqueous film-forming foams (AFFFs) (ITRC, 2018). AFFFs are fire-fighting foams that are used at airports, fire training facilities, and chemical refineries. PFAS are known to be mobile, persistent, and very toxic chemicals that spread widely in the environment (Rayne et al., 2009; Ahrens, 2011; Krafft and Riess, 2015) and can lead to soil and groundwater contamination; thus, causing health hazards via drinking water contamination. The most common forms of PFAS found in the environment are perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Lyu et al., 2018).

The need to understand the fate and transport of PFAs in the subsurface is crucial for Risk assessment as well as remediation of PFAS. Therefore, the objective of this research is to create a one-dimensional (1D) model coupling seepage and PFAS transport through the vadose zone and into groundwater by taking into consideration the advection, diffusion, and adsorption to the solid phase and air-water interfaces through different scenarios.

II. Materials and Methods

2.1 Materials

Given this work is a numerical model with no experimental validation yet, the parameters used in the simulations of PFAS transport were obtained from a study conducted by Guo et al. (2020) on Accusand soil. However, the model is set up in a way that various types of soils and scenarios can be studied using this model. Guo et al. (2020) discuss how each parameter was obtained from various researchers (Brusseau et al., 2007; Araujo et al., 2015; Schaefer et al., 2019; Xu and Eckstein, 1995). Table 1 shows some of the parameters used.

Table 1. Parameters used in the simulation

Parameters	Value	Unit
Bulk density, ρ_b	1.65	g/cm^3
Diffusion coefficient, D_0	5.4×10^{-6}	Cm^2/s
Fitting parameter, K_f	0.055	-
Fitting parameter, N	0.85	-
Aqueous Concentration, C	12	Mg/L
Surface tension, σ	71	Dyn/cm
Gas constant, R	8.314	J/K/mol
Temperature, T	293.15	K

2.2 Methods

In this study, two numerical models, seepage and contaminant transport, were created and later coupled to study the fate and transport of PFAS using the MATLAB platform. The models solve the transient second-order governing partial differential equations (PDEs) for seepage and PFAS transport using the finite-difference method (FDM). The soil domain of 5cm was discretized into a one-dimensional mesh to solve for hydraulic head for seepage and aqueous concentration for transport of PFAS. The forward difference (Equation 1) was used to simulate the first derivative with respect to space and time, and the central difference (Equation 2) was used for the second derivative with respect to space.

$$\frac{\partial f}{\partial x} = \frac{f(x_{i+1}) - f(x_i))}{dx} \text{ (Forward Difference)} \tag{1}$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}(f'_x) = \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{dx^2} \text{ (Central Difference)} \tag{2}$$
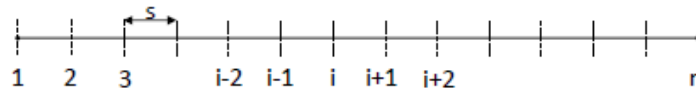

Figure 1. The schematic of the discretized domain.

2.2.1 Seepage

The transient seepage flow of water within the soil can be defined with the following 1D Equation by (Fredlund, 1997):

$$\vec{\nabla} \cdot v = -\frac{\partial \theta}{\partial t}, \tag{3}$$

where v is the seepage velocity and θ is the volumetric water content equal to $n.S_w$, where n is the soil porosity, and S_w is the degree of water saturation.

Darcy's law can be applied to Equation (3, $v = -k_z * i$), and any variation in the volumetric content can be computed based on the specific/elastic capacity (i.e., retention) of water, m_v, and temporal variations of the hydraulic head, h.

$$\frac{\partial}{\partial z}\left(-k_z \frac{\partial h}{\partial z}\right) = -m_V \frac{\partial h}{\partial t}, \qquad (4)$$

where k_z is the hydraulic conductivity given by Darcy's Law, $i = dh/dz$ is the hydraulic gradient. The specific or elastic capacity, m_v is assumed ≈ 0.001 m^{-1} within unsaturated soils and ≈ 0.00001 m^{-1} within saturated soils.

The finite-difference discretization of the 1D transient seepage Equation at Node i can, hence, be simplified to the following form.

$$h_{i-1}^{t+1}\left(\frac{k_i}{dz^2}\right) + h_i^{t+1}\left(\frac{-k_{i+1}}{dz^2} - \frac{k_i}{dz^2} - \frac{m_v}{dt}\right) + h_{i+1}^{t+1}\left(\frac{k_{i+1}}{dz^2}\right) = -\frac{m_v h_i^t}{dt}, \qquad (5)$$

where k_{i-1}, k_i, and k_{i+1} are the hydraulic conductivity at Nodes i-1, i, and i+1, respectively, while h_{i-1}, h_i, and h_{i+1} represent the hydraulic head at Nodes i-1, i, and i+1, respectively, over each time step. From the discretized equation, the hydraulic head can be determined at any node at any time. The Crank-Nicolson method was also used to update parameters within each time step such as the unsaturated hydraulic conductivity as shown by Equation (6).

$$k_i = \frac{k_0}{1 + a_1|h_i - z_i|^{a_2}} \qquad \blacktriangleright \qquad k_i = \frac{k_0}{1 + a_1\left|\frac{h_i^{tt} + h_i^{tt+1}}{2} - z_i\right|^{a_2}}, \qquad (6)$$

where k_{ii}= unsaturated hydraulic conductivity at Node ii, k_0= Saturated hydraulic conductivity, a_1 = constant (assumed 1), a_2 = constant (assumed 3), h= hydraulic (i.e., total) head, and z = elevation.

2.2.2 Transport of PFAS

Various transport processes exist that contribute to the fate of PFAS upon the surface deposition and subsequent infiltration of PFAS into the vadose zone (Sharifan et al., 2021). The vadose zone can be considered as a long-term source of PFAS for groundwater contamination (shin et al.,2011, Brusseau,2020) due to the amount of time PFAS can spend in this zone. PFAS will almost always interact with soils before impacting groundwater. Various factors can affect the transport of PFAS both in water and soil, more specifically the vadose zone where air and water coexist and can lead to fluid-fluid interfaces, e.g., air-water interface. PFAS are known to demonstrate surfactant-like properties, which makes their sorption to any fluid-fluid interface easier. PFAS accumulate at the air-water interface due to the hydrophobic and hydrophilic nature of PFAS at its tail and head, respectively, as shown by Figure 2. The unsaturated condition within the vadose zone provides a significant air-water interfacial area, A_{aw}, which can impact the overall PFAS migration (Sharifan, et al., 2021).
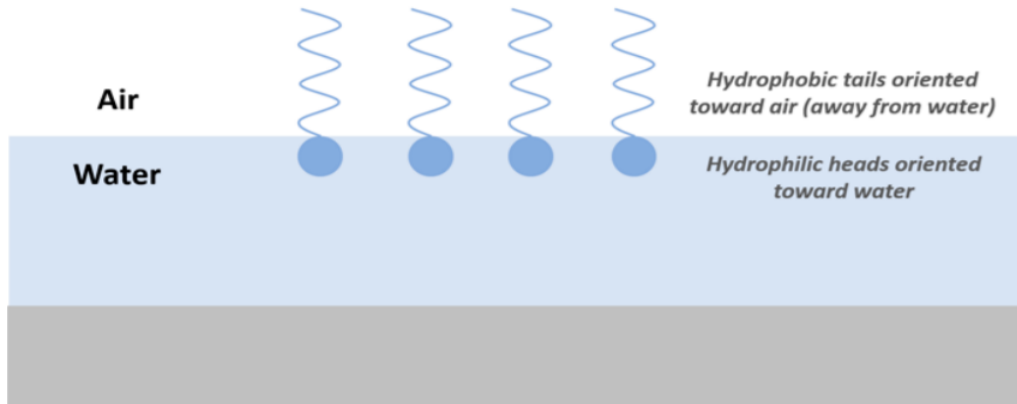

Figure 2. Example of expected orientation and accumulation of PFAS at air-water interface (D. Adamson, GSI)

Adsorption of PFAS to the air-water interface, C_{aw}, can be described by using Equation (7) (Guo et al., 2020; Brusseau, 2007; Kim et al., 1997; Anwar, 2001).

$$C_{aw} = A_{aw}K_{aw}C, \tag{7}$$

$$K_{aw} = \frac{-1}{RTC}\frac{\partial\sigma}{\sigma\, ln\, C} \tag{8}$$

where A_{aw} is the air-water interfacial area(cm^2/cm^3); K_{aw} is the air-water interfacial adsorption coefficient(cm^3/cm^2); R is the gas constant (in J/K/mol); σ is the interfacial tension (in dynes/cm); T is the temperature (°K); C the aqueous concentration of PFAS ($n\ \mu mol/cm^2$). On the other hand, the adsorption of PFAS to the solid-phase, C_s, can be described using a Freundlich isotherm like Equation (8) (Brusseau et al., 2019; Higgins & Luthy, 2006; Wei et al., 2017)

$$C_s = K_f C^N, \tag{9}$$

where K_f and N are fitting parameters found based on experimental data.

In addition to the adsorption terms, advection and diffusion are mechanisms of PFAS flow that need to be considered when simulating the transport of PFAS. Advection consists of the bulk movement of solutes carried by flowing solvent, and diffusion is the spreading of the contaminant plume from a high concentrated zone to a less concentrated zone (Freeze and Cherry, 1979). Both factors combined, form an advection-diffusion equation as shown by Equation (10).

$$\frac{\partial c}{\partial t} = -v_s\frac{\partial c}{\partial x} + D^*\frac{\partial^2 c}{\partial x^2}, \tag{10}$$

where D^*, the effective diffusion coefficient (cm^2/s), is given by Fick's Second Law and combines the longitudinal mechanical dispersion, D_L with molecular diffusion, D_0; v_s is the seepage velocity (cm/s); and C is the aqueous concentration of the contaminant ($\mu mol/cm^3$)

Therefore, the transport of PFAS is governed using the combined processes of seepage, advection, dispersion, and adsorption to the fluid-fluid and solid-fluid interfaces. Researchers have described it by an advection-dispersion equation with adsorption terms (Guo et al., 2020; Brusseau et al., 2019; Kim et al., 1997).

$$\frac{\partial(\theta C)}{\partial t} + \rho_b\frac{\partial}{\partial t}k_f C^N + \frac{\partial}{\partial t}(A_{aw}k_{a\omega}C) + \frac{\partial}{\partial z}(\theta v C) - \frac{\partial}{\partial z}\left(\theta D\frac{\partial C}{\partial z}\right) = 0 \tag{11}$$

where ρ_b is the bulk density of the porous medium (g/cm^3); $V = q/\theta$ is the interstitial pore-water velocity (cm/s); q is the Darcy flux; and D is the dispersion/diffusion Coefficient (cm^2/s).

Using the forward and central difference methods to solve the PDEs of Transport, Equation (11) can be discretized as follows.

$$C_{i+1}^{t+1}\left(-\frac{\theta_i^{t+1}v_i^{t+1}}{dz} + \frac{D_i^{t+1}\theta_{i+1}^{t+1}}{dz^2} + \frac{\theta_i^{t+1}D_{i+1}^{t+1}}{dz^2}\right) + C_i^{t+1}\left(3\frac{\theta_i^{t+1}v_i^{t+1}}{dz} - \frac{\theta_i^{t+1}v_{i+1}^{t+1}}{dz} - \frac{v_i^{t+1}\theta_{i+1}^{t+1}}{dz} -\right.$$
$$\left.\frac{D_i^{t+1}\theta_{i+1}^{t+1}}{dz^2} + \frac{D_{i+1}^{t+1}\theta_i^{t+1}}{dz^2} + \frac{D_i^{t+1}\theta_i^{t+1}}{dz^2} - \frac{\theta_i^{t+1}}{dt} - \frac{F_i^{t+1}}{2dt} - \frac{F_i^t}{2dt} - A_{aw}\frac{k_{a\omega i}^{t+1}}{dt}\right) + C_{i-1}^{t+1}\left(\frac{D_i^{t+1}\theta_i^{t+1}}{dz^2}\right) = \tag{12}$$
$$C_i^t(-\frac{\theta_i^{t+1}}{dt} - \frac{F_i^{t+1}}{2dt} - \frac{F_i^t}{2dt} - A_{aw}\frac{k_{a\omega i}^t}{dt},$$

where:

$$\frac{dc}{dt} = \frac{c_i^{t+1} - c_i^t}{dt}$$

$$\frac{d^2}{dz^2}C = \frac{C_{i+1} - 2C_i + C_{i-1}}{dz^2}$$

$$\frac{dc}{dz} = \frac{c_{i+1} - c_{i-1}}{2\,dz}$$

$$\frac{d}{dt}C^N = NC^{N-1}\frac{dC}{dt}$$

$$F = k_f\rho_b NC^{N-1}$$

Using MATLAB, Equation (12) was then used to numerically simulate several scenarios. Below, the results of simulating those scenarios are discussed where the domain, z is 5 cm thick and dz and dt are 0.5 and 10 respectively.

III. Results and Discussion

The following only show a one-way coupling for now, even though the code is capable of simulating a two-way coupling. In this case, the seepage model simulates the transient groundwater flow before PFAS is introduced into the soil. As shown in Figure 3, the groundwater moves from areas of higher hydraulic head toward those of lower hydraulic head, which was qualitatively validated against and was consistent with results by Freeze and Cherry (1979) in the literature. Then in the next step, the transport of PFAS in the same domain is simulated using the above-mentioned parameters and equations. Different initial scenarios were simulated in order to confirm that the model works properly. The advection part of the simulation is not considered here to simplify the evaluation of the results for validation purposes. Following scenarios were simulated, accounting for diffusion, and adsorption onto the air-water and solid-phase interfaces at various different degrees of water saturation. As seen in Figure 4, the PFAS concentration moves from a highly concentrated zone to a less concentrated zone, due to diffusion and adsorption terms. The change in the degree of water saturation retards the PFAS transport as expected. As shown in Figure 4, higher degrees of air-saturation (i.e., lower degrees of water-saturation) result in a retardation of PFAS transport through the vadose zone. The simulations for PFAS transport were done in increments of 15*dt over a period of 1000 seconds therefore figure 4 represent every 15th curve in time.
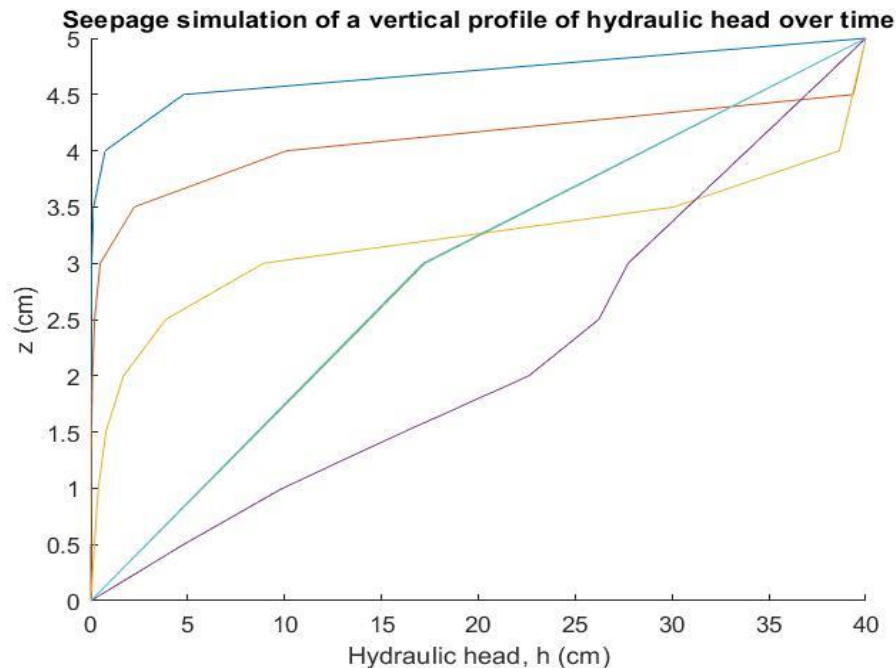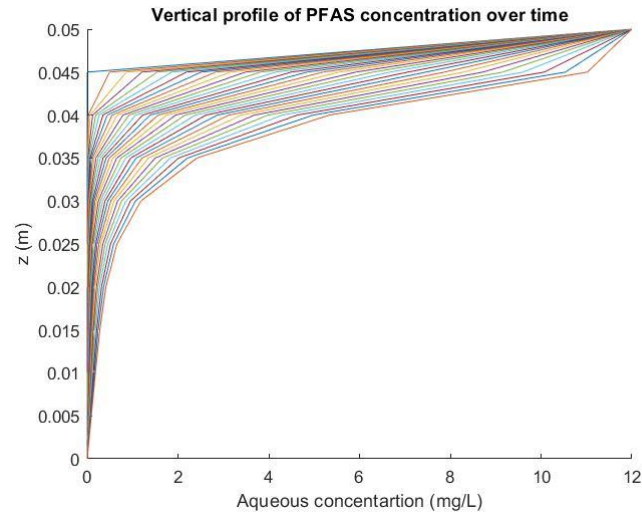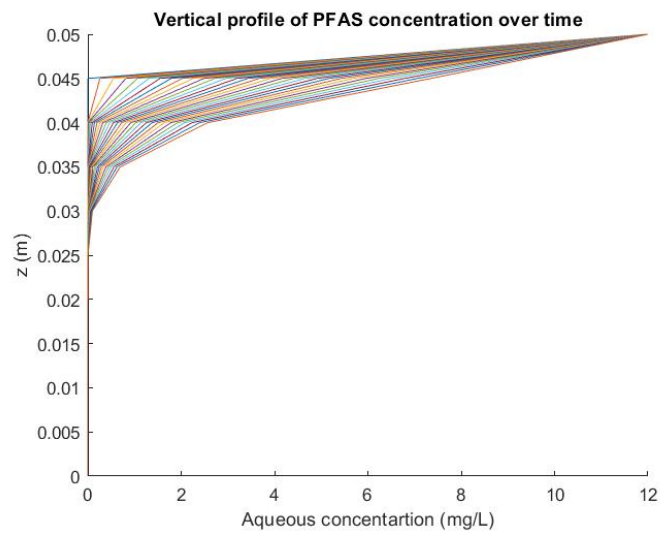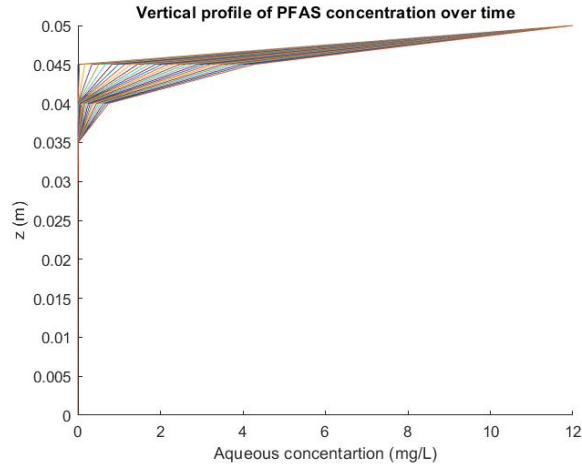

Figure 3. Seepage simulation: vertical profile of hydraulic head over time (every 250 seconds up to 15000 seconds) for unsaturated flow

(a) Sw=100%

(b) Sw=73%

(c) Sw=47%

Figure 4. Progression of vertical profile of PFAS' aqueous concentration over time (curves are 150 seconds (every 15th dt) apart up to 4500 seconds); Results are for the case of diffusion, dispersion, soil-phase adsorption, and micelles formed at air-water interface for various degrees of water saturation: (a) 100%, (b) 73%, and (c) 47%.

The retention of PFAS in the vadose zone is dependent on the soil matrix as well as the moisture content. Higher the moisture contents result in lower retention due to the low availability of air-water interfacial areas (Silva et al., 2020; Lyu et al., 2018). Figure 5 shows how the concentration passing through a specific point (X cm below the top boundary) at a specific time (Y seconds after the PFAS is introduced into the sample) changes with the degree of saturation. As expected, at lower degrees of water-saturation, the transport of PFAS is retarded (i.e., is slower), which demonstrates the increase in retardation due to low degrees of saturation.
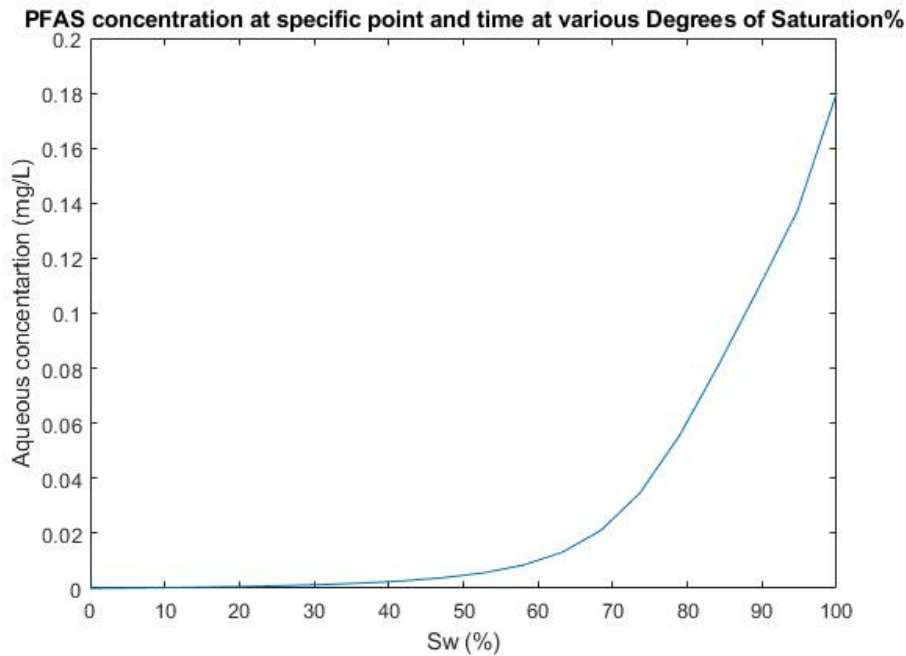

Figure 5. PFAS aqueous concentration at node 2 in space and node 5 in time (i.e., z=0.05-dz and t=5*dt) at various Degrees of Saturations

IV. Conclusion

In this paper, a coupled one dimensional (1D) numerical model was introduced to simulate the groundwater seepage and transport of PFAS. The model details were discussed, and a series of results for various scenarios was shown, which are consistent with the literature. However, the model is still being improved to account for more complex scenarios, and those improvements do not fit within the scope of this paper. The next steps will consist of testing advection impact and the two-way coupling of seepage and PFAS transport where the effect of PFAS transport on the seepage by changing the properties of the flowing water (e.g., change in the hydraulic conductivity due to a change in the viscosity of water by the dissolved PFAS) will be simulated and analyzed.

V. Reference

Ahrens, L., (2011). "Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate." *J. Environ. Monit*, 13, 20−31.

Anwar, A. H. M. F., (2001). "Experimental determination of air−water interfacial area in unsaturated sand medium. New Approaches Characterizing Groundwater Flow." Proceedings of *the XXXI IAH Congress*, Munich, Germany, Sept 10−14, Vol. 2, pp 821−825.

Araujo, J.B., Mainhagu, J., and Brusseau, M. L. (2015). "Measuring air-water interfacial area for soils using the mass balance surfactant-tracer method." *Chemosphere*, 134, 199–202

Barzen-Hanson, K.A., Roberts, S.C., Choyke, S., Oetjen, K., McAlees, A., Riddell, N., McCrindle, R., Ferguson, P.L., Higgins, C.P., Field, J.A., (2017). "Discovery of 40 classes of per- and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFF) and AFFF-impacted groundwater." *Environ. Sci. Technol*. 51,2047-2057.

Brusseau, M. L. (2019a). "Estimating the relative magnitudes of adsorption to solid-water and air/oil-water interfaces for per- and poly-fluoroalkyl substances." *Environmental Pollution*, *254*, 113102.

Brusseau, M. L. (2019b). "The influence of molecular structure on the adsorption of PFAS to fluid-fluid interfaces: Using QSPR to predict interfacial adsorption coefficients." *Water Research*, *152*, 148–158.

Brusseau, Mark L. (2020). "Simulating PFAS transport influenced by rate-limited multi-process retention." *Water Research*, Volume 168,115179.

Brusseau, M. L., Peng, S., Schnaar, G., and Murao, A. (2007). "Measuring air-water interfacial areas with X-ray microtomography and interfacial partitioning tracer tests." *Environmental Science & Technology*, 41(6), 1956–1961

Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, Jensen AA, Kannan K, Mabury, SA, and Van Leeuwen SP (2011). " Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." *Integrated environmental assessment and management*. 7:4:513. [PubMed: 21793199]

Freeze, A., and Cherry, J., (1979). "Groundwater." Prentice-Hall, Englewood Cliffs, New Jersey, 604 pages.

Fredlund, D. G., (1997). "Soil Mechanics for unsaturated soils." *China Architecture & Building Press*, Beijing Shi, China.

Guo, Bo & Zeng, Jicai and Brusseau, Mark. (2020). "A Mathematical Model for the Release, Transport, and Retention of Per- and Polyfluoroalkyl Substances (PFAS) in the Vadose Zone." *Water Resources Research*. 56. 10.1029/2019WR026667.

Higgins, C. P., and Luthy, R. G. (2006). "Sorption of perfluorinated surfactants on sediments." *Environmental Science & Technology*, 40(23),7251–7256.

Huang, Feng, Lyu, Jianguo, Wang, Guihe, and Liu, Hongyan (2017). "One-Dimensional vacuum steady seepage Model of Unsaturated soil and finite difference solution." Mathematical Problems in Engineering, Article ID 9589638.

Krafft, M. P.; Riess, J. G. (2015). "Per- and polyfluorinated substances (PFAS): environmental challenges." Curr. Opin. Colloid Interface Sci. 20, 192−212

Kim, H., Rao, P. S. C., and Annable, M. D. (1997). "Determination of effective air-water interfacial area in partially saturated porous media using surfactant adsorption." *Water Resources Research*, *33*(12), 2705–2711.

Lyu Y., Brusseau M.L., Chen, W., Yan, N., Fu, X., and Lin, X. (2018). "Adsorption of PFOA at the Air-Water Interface during Transport in Unsaturated Porous Media." *Environ Sci Technol*. 2018 Jul 17 ;52(14) :7745-7753. DOI : 10.1021/acs.est.8b02348. E-pub, Jun 26. PMID: 29944343; PMCID: PMC6312111.

Rayne, S.; Forest, K. (2009). "Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods." *J. Environ. Sci. Health*, Part A: Toxic/Hazard. Subst. Environ. Eng., 44, 1145−1199.

Schaefer, C., Drennan, D. M., Tran, D. N., Garcia, R., Christie, E., Higgins, C. P., and Field, J. A. (2019). "Measurement of aqueous diffusivities for perfluoroalkyl acids." *Journal of Environmental Engineering*, 145(11), 06019006.

Sharifan, H., Bagheri, M., Wang, D., Burken, J.G., Higgins, C. P., Liang, Y., Liu, J., Schaefer, C.E., and Blotevogel, J., (2021). "Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone." *Science of The Total Environment*, Volume 771, 145427.

Shin, H.M., Vieira, V.M., Ryan, P.B., Detwiler, R., Sanders, B., Steenland, K., and Bartell, S.M., (2011). "Environmental fate and transport modeling for perfluorooctanoic acid emitted from the Washington works facility in West Virginia." *Environ. Sci. Technol.,* 45 (4) (2011), pp. 1435-1442

Silva, J.A.K., McCray, J.E., Martin, W.A., (2020). "Final report: baseline data acquisition and numerical modeling to evaluate the fate and transport of PFAS within the vadose zone." SERDP project ER18-1389.

Wang, Zhanyun, DeWitt, Jamie C., Higgins, Christopher P., and Cousins, Ian T., (2017)." A never-ending story of per-and polyfluoroalkyl substances (PFAS)." *Environ. Sci. Technol*. 51,2508-6623.

Wei, C., Song, X., Wang, Q., and Hu, Z. (2017). "Sorption kinetics, isotherms, and mechanisms of PFOS on soils with different physicochemical properties." Ecotoxicology and Environmental Safety 142, 40–50.

Xu, M., & Eckstein, Y. (1995). "Use of weighted least-squares method in the evaluation of the relationship between dispersity and field scale." Groundwater, 33(6), 905–908.