# Verification Example for Adsorption of PFAS Adsorption on Air-Water Interface in the Unsaturated Zone

This example problem discusses one dimensional advective transport of PFAS in the vadose zone. The experiments conducted by Lyu (2018) are simulated here to evaluate the accuracy of the model in their validation. These experiments were also simulated by Silva et al. (2020) using a modified Hydrus model.

The setup simulated here consists of a 1-dimensional vertical soil column of 0.35 mm sand, 15 cm long, with a steady-state recharge from the top that gives a pore velocity of 37 cm/hr. For a porosity value of 0.33, the recharge rate is 12.21 cm/hr, and one pore volume (PV) is equal to 0.405 hours. Once the flow field was stabilized, PFOA solution was injected with the recharge water. The experiment was conducted with different soil water saturations, and different injection concentrations of PFOA. The simulations conducted here are for saturated conditions, and for a water saturation (Sw) of 0.68, with PFOA concentrations of 1, 0.1, and 0.01 mg/L.

The soil column was discretized uniformly into 30 numerical layers of 0.5 cm thickness each with a bottom elevation of zero and a top elevation of 15 cm. Recharge was simulated from the top end at a rate of 12.21 cm/hr, with a prescribed head boundary condition at the bottom that can control the degree of saturation of the soil column. For the saturated case, the prescribed head condition was above the top of the soil column at 20 cm. For the case of Sw = 0.68, The bottom head was set to -1.8 cm with van Genuchten parameters a = 12.6 cm-1, b = 1.16, Sr = 0.22, and the Brooks Corey exponent = 4. The steady-state flow-fields thus generated were used for the transport simulations.

For the saturated case, there is no air-water interface, so the only adsorption that occurs is on the soil. Lyu (2018) provides a linear sorption coefficient kd = 0.08 cm3g-1 for the 0.35 mm sand. Simulations were conducted with and without adsorption on soil to evaluate the retardation that occurs due to soil. For the unsaturated case, adsorption also occurs on the air-water interface and is related to the specific area of the air-water interface (Aawi) as well as an air-water interface partition coefficient (kawi). Aawi is computed as Aawi = Amax (1-Sw) where Amax is given as 216 cm2/cm3 (Lyu, 2018 and Silva et al. 2020). The air-water interface adsorption coefficient was provided as linearized for the three source concentrations by Lyu (2018) as 0.0021, 0.0027, and 0.004 for PFOA concentrations of 1, 0.1, and 0.01 mg/L respectively. Silva et al. (2020) used the thermodynamic relationship with surface tension to estimate the air-water interface adsorption as a function of concentration; however, there is no change in kawi for concentration values less than 1 mg/L and thus they did not see a relationship of PFAS transport with respect to source concentration. Since the Langmuir isotherm is used for kawi in USG-Transport, the air-water adsorption isotherm A and B parameters can be provided as A = 0.0021, 0.0027, and 0.004 for PFOA concentrations of 1, 0.1, and 0.01 mg/L respectively, and B = 0.

For the unsaturated case, Silva et al. (2020) noted that the simulated breakthrough curves for the unsaturated cases match the laboratory study better with a dispersion coefficient of 0.7 cm. The same behavior was noted with simulations conducted with USG-Transport. Also, a diffusion coefficient of 0.01944 cm2/hr (5.4 x 10-6 cm2/s) was provided.

A comparison of simulated results versus the laboratory observations is shown for the different source concentrations in Figure AW1. The simulated results are superposed on the results of Figure 4 of Lyu (2018).

Chart, histogram

Description automatically generated

*Figure AW1 – Breakthrough of PFOA for different concentration cases compared to Lyu (2018) experimental results.*

For all cases, it is noted that the simulations compare very well with the experimental results. Figure AW2 shows a comparison of simulated results versus the laboratory observations for the different saturation conditions. Note that the case of saturation = 0.86 was not simulated, however, the simulation cases for both with and without dispersion are showin for the unsaturated case. Again, it is noted that the simulations compare very well with the experimental results. The simulation case without soil adsorption is also shown on Figure AW2, to note the impact of the various adsorption mechanisms on the movement of PFOA. Retardation due to soil adsorption slows down the breakthrough of PFOA by less than half a pore volume, however, adsorption on the air-water interface slows it down further by more than one pore volume.

Chart, histogram

Description automatically generated

*Figure AW2 – Breakthrough of PFOA for different saturation cases compared to Lyu (2018) experimental results.*