Diffusion in Clay Layers & Groundwater Remediation

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The DOD's Strategic Environmental Research and Development Program (SERDP) estimates that over 3,000 DOD sites have groundwater contaminated with some type of chlorinated aliphatic hydrocarbon (CAH). Commonly used by the DOD as solvents, nonpolar CAHs such as tetrachloroethylene, trichloroethylene, and carbon tetrachloride are of particular concern to the DOD. Past use and disposal of these CAHs have led to extensive subsurface soil and groundwater contamination. CAHs persist in the groundwater environment and are difficult to remove with current remediation technologies.

Undissolved CAHs are sometimes referred to as dense non-aqueous phase liquids (DNAPLs) — hydrocarbons or hydrocarbon mixtures that are heavier than and only slightly soluble in water. When released to the subsurface, DNAPLs migrate downward until they encounter low-permeability clay layers where they may pool (see Figure 1).

Based upon research sponsored by AFCEE, it is believed that pooled DNAPL sitting atop the low-permeability clay layers dissolves into the surrounding groundwater, and the dissolved CAH molecules diffuse into the clay layers. Upon removal of the DNAPL pool, the dissolved CAHs in the low-permeability clay layers remain and serve as a long-term source of contamination through "back diffusion" into the relatively clean groundwater flowing past.

The current paradigm is that CAHs move into and out of the low-permeability clay layers primarily through diffusion. However, based upon reports of CAH concentrations greater than that expected from simple diffusion, there is evidence other transport processes are important. "Enhanced" diffusion may result from cracks in the clay layers, perhaps pre-existing or formed by the interaction between the DNAPL and clay. It has been shown that clay particles flocculate in contact with nonpolar organic solvents, resulting in the formation of cracks. Not accounting for this enhanced diffusion could lead to significantly erroneous predictions of the amount of CAHs in low permeability zones and their release rates from these zones.

In a collaborative SERDP-funded study, researchers from the Air Force Institute of Technology, the U.S. Environmental Protection Agency, and the University of Michigan developed a numerical model that simulates the enhanced transport of CAHs into and out of low permeability clay layers due to the presence of cracks. Using DOD's Groundwater Modeling System (GMS), three different groundwater contamination scenarios using trichloroethylene (TCE) are modeled:

Scenario 1 is a sand aquifer (with no clay layer present) that initially contains a constant 110 mg/L TCE source for 10 years, after which the aquifer is flushed with clean uncontaminated water for 20 years.

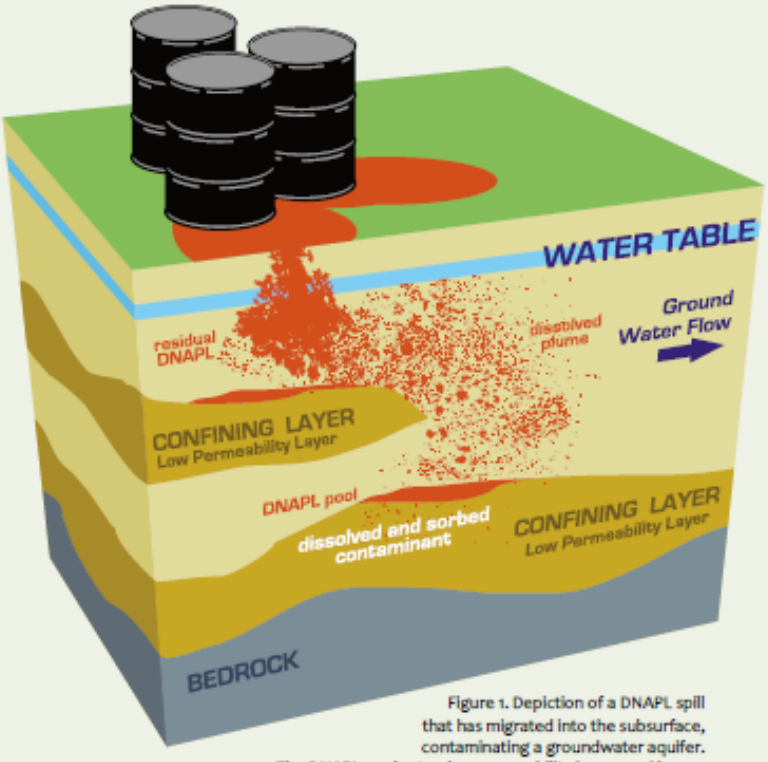

Figure 1. Depiction of a DNAPL spill that has migrated into the subsurface, contaminating a groundwater aquifer. The DNAPL pools atop low permeability lenses and layers.

Scenario 2 is the same sand aquifer with a constant 110 mg/L TCE source, but the TCE source now sits atop a non-cracked low-permeability clay layer.

Scenario 3 is the same as Scenario 2 except the low-permeability clay layer now contains cracks.

In the model, the cracked clay is represented using a dual-domain submodel; the cracks are represented as a domain of mobile water, while the clay matrix is represented as a domain of immobile water. (Figure 2)

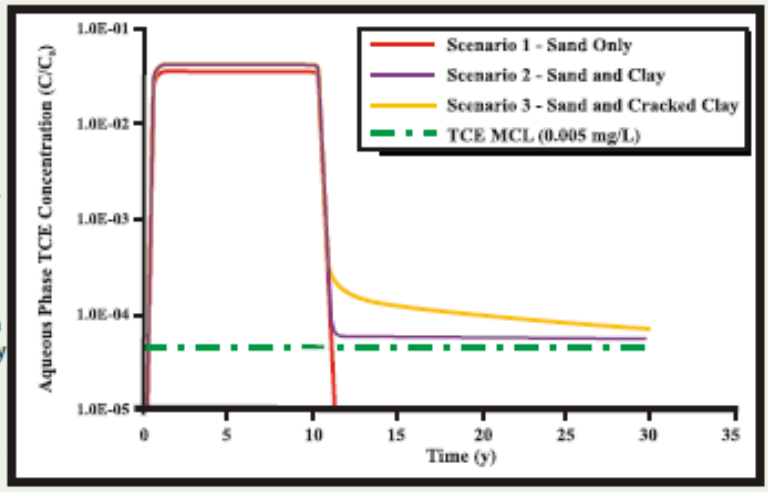

Figure 3. Concentration versus time breakthrough curves obtained from GMS for an observation point downgradient from a TCE source for three scenarios. The breakthrough curves suggest that enhanced diffusion and storage of groundwater contaminants in cracked low permeability clay layers lead to persistent downgradient contaminant concentrations even after the contaminant source is removed.

The GMS model output is the concentration calculated at an observation point 56 meters downgradient from the contaminant source as a function of time (Figure 3). For Scenario 1, after the TCE is removed, the concentration remaining is insignificant because there is no low-permeability clay layer that can act as a long-term contaminant source. For Scenarios 2 and 3, the downgradient concentration 20 years after the TCE source is removed is still above the maximum contaminant level for TCE of 0.005 mg/L. Higher downgradient concentrations are predicted in Scenario 3 than in Scenario 2 because the cracks in the low-permeability clay layer allow for more contaminant mass to enter the layer.

This research project is currently ongoing, as investigators attempt to determine the following: 1) how the interaction of DNAPLs and clay may lead to cracking, and 2) how the cracking might impact aquifer cleanup and downgradient risks.

Based on the model simulations performed to date, it appears enhanced diffusion due to cracks in low permeability clay layers may be an important transport process that should be taken into account by DOD site managers considering remediation strategies for groundwater contaminated with DNAPLs.

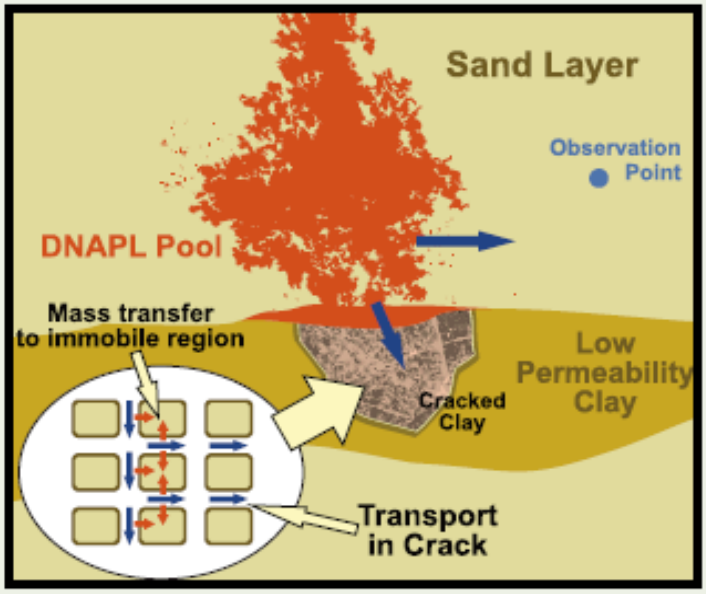

Figure 2. Conceptual depiction of a DNAPL pool atop a low permeability clay layer in a sand aquifer. Cracks in the clay, either naturally occurring or caused by the presence of the DNAPL pool, may allow for enhanced transport and storage of the DNAPL in the clay layer.

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