



Recent Advancements in Mechanistic Understandings of PFAS Fate & Transport in the Vadose Zone

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Background/Objectives: Per- and Polyfluoroalkyl substances (PFASs) are a group of highly recalcitrant, bioaccumulative, and toxic chemicals that are frequently introduced to groundwater through land surface exposure. As a result, the vadose zone has been identified as a significant long-term source zone for PFAS leaching into groundwater. This talk summarizes critical findings regarding PFAS transport in the vadose zone and introduces several emerging topics expected to develop over the next several years.

Approaches/Activities: Early efforts in understanding PFAS Fate & Transport processes focused on their multi-phase retention processes. Specifically, understanding the degree of equilibrium partitioning to the solid phase and the air-water interface have been intensely studied topics. Equilibrium partitioning to solid and air-water interfaces generally increases with increasing molecular volume, with exceptions for very long chain perfluoroalkyl acids (PFAAs), cationic and zwitterionic PFASs, perfluoroalkyl ethers, and PFASs with very large headgroups. Recent research and emerging field data suggest many sites are impacted by non-ideal, non-equilibrium processes. Evidence of PFAA generation from precursor transformation, physically driven non-ideal transport, and chemically driven non-idealities have emerged as environmentally relevant topics. A specific list of topics for discussion is presented below:

- **Precursor Transformation:** Despite the name “forever chemicals”, there are many PFASs known as PFAA precursors. Precursors transform into PFAAs, which are more mobile and can serve as a centennial source of PFAS contamination to underlying aquifers.
- **Non-Ideal Transport Mechanisms Can Accelerate PFAS Leaching:** Non-Ideal transport can be caused by physically driven non-equilibrium processes. Examples include flow path channelization, immobile water formation, sheet flow, and reduced accessibility of air-water interfaces. It is likely that these mechanisms drive rate-limited desorption from solid-phase materials. Non-Ideal transport appears to be more prevalent at lower saturations.
- **Additional Transport Processes:** PFAS retention and retardation by the presence of other co-contaminants such as non-aqueous phase liquids (NAPLs) in media are starting to receive more research attention.
- **Evidence of Self-Assembly and Chemically Driven Rate-Limited Desorption:** Molecular self-

assembly refers to the potential of PFASs and other surfactants to form discrete microstructures at liquid interfaces. These thermodynamically stable microstructures may contribute to the consistently elevated PFAS concentrations observed in source zones.

Results/Conclusions: Many considerations are needed when assessing the fate & transport risks for PFASs at a given site. While there is early evidence that equilibrium models can predict long-term mass flux in some locations, these models may not predict large discharges from discrete storm events. Terminal PFAA discharge to groundwater from precursor transformation is of critical importance to understanding the long-term behavior of PFASs in the subsurface. The potential for Non-Ideal transport to accelerate PFAS transport may explain the conundrum of why some long chain PFAAs are found in groundwater systems despite their strong equilibrium retention properties. Another explanation for accelerated transport is the potential for competitive adsorption of mixtures to reduce the equilibrium partitioning potential of substances in mixtures. Additional retention (i.e., adsorption to NAPLs) requires additional study to determine appropriate partitioning parameters. Finally, PFASs may have unique transport and retention mechanisms which may be enhanced by their surfactant properties.