

ABSTRACT:

1. Objective: It is widely recognized that the most challenging hazardous waste sites for groundwater remediation are those with DNAPL sources in highly heterogeneous aquifers. At DoD sites with a history of contamination, DNAPL has slowly dissolved from trapped ganglia or pools resulting in groundwater plumes with high levels of contamination. Dissolved contaminants in high permeability zones (HPZs) within these plumes can diffuse over long time periods into low permeability zones (LPZs) such as rock matrices, clay aquitards and lenses, i.e., “matrix diffusion.” When contaminant mass in the HPZ is depleted through natural attenuation or active remediation, back-diffusion of contaminants from LPZs into groundwater flowing through HPZs can occur for decades. The overall objectives of our SERDP proposal are to quantify the biotic and abiotic attenuation mechanisms that impact the fate of trichloroethylene (TCE) within and at the boundaries of LPZs comprised of clays and silts, and to incorporate these processes into a computationally efficient model that can be used to directly address key questions regarding natural attenuation time scales and cleanup at TCE-impacted sites. We hypothesize that a suite of naturally occurring biotic and abiotic mechanisms may serve to significantly attenuate diffusive flux of TCE and TCE degradation products from LPZs over long time periods, resulting in decreased impacts (both magnitude and timeframe) of back-diffusion on groundwater quality. These mechanisms may occur within the LPZ itself, or at the LPZ-HPZ interface. Furthermore, we hypothesize that biogeochemical conditions (e.g., reducing, aerobic, Fe minerals, organic carbon) will impact these naturally occurring mechanisms.

2. Technical Approach: The proposed work will elucidate the critical physical, chemical and biological processes that control natural attenuation of chlorinated ethenes in LPZs, and result in the development of a computationally efficient model that can be used to assess the impact of natural attenuation mechanisms on back diffusion from LPZs. Toward these efforts, core samples will be collected at two DoD field sites in Task 1 where co-PI Schaefer is involved with site cleanup activities, and where back diffusion is suspected of prolonging site cleanup. We will sample both LPZs and HPZs, and characterize contaminant concentrations, mineralogy, aqueous species, and microbial populations to help interpret batch and flow cell experimental results. In Task 2, natural attenuation reaction mechanisms will be evaluated in well-mixed batch studies, where mass transfer limitations are minimized. We will use ¹⁴C-TCE and stable isotope probing to unambiguously quantify reaction mechanisms and pathways, and will use this information to help guide flow cell experiments and numerical model development. In Tasks 3 and 4, we will evaluate natural attenuation mechanisms in flow cells, where diffusion controls mass transport in LPZs. The effects of pore size, mineralogy, microbiology, and electron shuttling will be evaluated along the redox gradient in LPZs. As necessary, radio-labeled TCE and stable isotope probing will help quantify the effects of diffusion limitations on coupled reaction mechanisms, and LPZ high resolution sectioning and analysis of spatially distributed mineralogy, microbiology, and contaminant concentrations will contribute to this forensic effort. In Task 5, we will develop a computationally efficient numerical model to simulate flow cell experiments, and use this to probe important reaction mechanisms in the field.

3. Benefits: The project objectives and tasks will result in a more clear understanding and quantification of reaction mechanisms that contribute to natural attenuation in LPZs, and the corresponding effects of biogeochemical parameters, i.e., grain/pore size, microbial population, mineralogy, redox potential, and mass transfer limitations. For example, a clear understanding of the role of oxidation versus reductive transformation processes for TCE degradation is lacking, which will impact TCE fate and potentially any cleanup technology chosen for partial or full-site remediation. The project objectives and tasks will also result in a computationally efficient and accessible model that will allow scientists and engineers to interpret controlling mechanisms at field sites, and provide recommendations for what data is needed to parameterize the model, determine the controlling mechanisms, and predicting plume longevity under different site management scenarios. These outcomes will not only provide for improved management of chlorinated solvent plumes and refined tools for selecting how and where remediation resources should be allocated, but will also provide for improved justification of monitored natural attenuation (MNA) due to better insight into the naturally occurring degradation mechanisms present in LPZs.