1.1: ABSTRACT

1. Proposal Number: ER20-C4-1203

2. Proposal Title: Quantifying the Distribution of Biotic & Abiotic Transformation Rate Constants in Low Permeability Clay Zones for Improved Assessment of TCE Impacts to Groundwater at DoD Field Sites

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5. Objective: Back diffusion of trichloroethylene (TCE) and daughter products from low permeability zones (LPZs) such as clay aquitards is one of the biggest challenges facing attainment of groundwater cleanup goals at DoD sites. These pollutants are slowly released from LPZs to more permeable stratigraphic units at mass discharge rates that often result in extracted groundwater exceeding MCLs. At issue is whether these discharge rates will significantly decrease over time due to natural attenuation, or whether some interim remedial measure is needed to more quickly bring these rates down to acceptable levels. Chief among factors confounding the prediction of future discharge rates is poor knowledge of long-term transformation rates of TCE and associated reaction products. The overall goal of the proposed work is to quantify representative rate constants that characterize naturally occurring long-term biotic and abiotic transformation of trichloroethylene (TCE) and associated transformation products in LPZ clays, the mechanisms that contribute to rate constant variability, and the impact of these rate constants on site remediation and long-term natural attenuation. Based on our prior work, **we hypothesize that (1)** vertical concentration profiles of key reactants and products in LPZ clay cores, coupled with reactive transport modeling, can be used to quantify apparent rate constants, **(2)** rate constant variability can be captured by evaluating many such profiles in LPZ cores subject to different boundary conditions, and **(3)** reaction pathways that dominate TCE transformation are controlled by vertical profiles of solute concentrations and mineral types, which together determine redox conditions and reactive secondary mineral formation.

6. Technical Approach: Two novelties of our effort are preserving solute and mineral distributions in LPZ clay cores via cryogenic treatment, and quantifying the distribution of biotic and abiotic transformation rate constants by simulating vertical transects of TCE associated reactants and products in field-based and laboratory-perturbed LPZ clay cores. Cryogenic LPZ cores will be collected at a TCE contaminated site on Pease AFB, sectioned, thawed, and analyzed for vertical concentrations of solutes and mineralogy. Similar LPZ cores from an adjacent "clean" site will be collected, placed into columns, and subject to varying boundary conditions in the laboratory to promote selected TCE reaction pathways. They too will be frozen after reaction pathway development is apparent, and then sectioned, thawed, and analyzed. Complementary batch experiments will be performed to explore a larger suite of conditions that promotes reactive mineral formation near the LPZ-HPZ interface. A mechanistically-based reactive transport model will be coupled with a geochemical speciation model to simulate vertical profiles of solutes and minerals measured in the aforementioned cores. Alternative conceptual models of reaction processes will then be evaluated using a fully Bayesian approach to estimate the probability distribution of biotic and abiotic kinetic parameters, and these parameter distributions will be applied at the field-scale to evaluate the impact of different management decisions on groundwater cleanup goals.

7. Benefits: This project will demonstrate whether cryogenic methods can be used to preserve vertical concentration profiles of TCE associated volatiles at field sites, and in cores brought to the laboratory and subject to different boundary conditions. It will demonstrate how these and other (e.g., mineralogy) vertical concentration profiles can be simulated to obtain distributions of reaction rate constants for biotic and abiotic TCE transformation pathways, and how these distributions can be used to select the appropriate conceptual model for TCE reaction modeling. This project will also produce a set of stochastic reaction models that will demonstrate how uncertainty in rate constants leads to the uncertainty in contaminant flux exiting an LPZ-HPZ system, and how this uncertainty can be used to make management decisions regarding cleanup at Pease AFB and other relevant DoD sites, including when to transition from more active to more passive remedial measures. Last, this project will result in peer-reviewed papers, presentations at national meetings, and the development of accessible and field-relevant guidelines for development and use of chlorinated ethene reaction rate constants in the field.