Development of a Quantitative Framework for Evaluating Natural Attenuation of 1,4-Dioxane, 1,1,1-TCA, 1,1-DCA, and 1,1-DCE

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Background/Objectives. Sites with a release of 1,1,1-trichloroethane (1,1,1-TCA) typically contain multiple degradation byproducts, and 1,4-dioxane is also frequently encountered at these sites because of its use as a stabilizer for 1,1,1-TCA. Existing protocols for the evaluation and implementation of MNA for chlorinated solvents are dated and provide little guidance for chlorinated ethanes; none address natural attenuation of 1,4-dioxane, which is increasingly recognized as a viable approach for managing this emerging contaminant. This presentation will discuss early results from an ESTCP project that aims to develop a standardized approach for demonstrating attenuation of 1,1,1-TCA, 1,1-DCA, 1,1-DCE and 1,4-dioxane. The decision tool generated by this project (BioPIC-TCA/Dioxane) will provide a stronger technical basis for RPMs to use in evaluating and selecting remediation strategies and likely increase the number of sites where MNA is selected.

Approach/Activities. The project is collecting data through a combination of field sampling, lab-based assays, desktop studies, and fate and transport modeling using methodologies that have been successfully applied on previous ESTCP projects. These efforts will be used to: (1) Modify the USEPA's BIOCHLOR model and develop decision matrices to analyze historical monitoring data to extract rate constants for natural degradation of 1,1,1-TCA, 1,1-DCA, 1,1-DCE, VC, and 1,4-dioxane so that RPMs can use the rate constants to support MNA as a remedy. The decision matrices will be coded into a modification of BioPIC, called BioPIC-TCA/Dioxane; (2) Develop and validate a protocol to directly measure rate constants for natural biodegradation of 1,4-Dioxane in groundwater using ^{14}C-labeled 1,4-Dioxane, and; (3) Validate existing DNA-based *q*PCR assays for organisms and enzymes involved in the biodegradation of 1,1,1-TCA, 1,1-DCA, 1,1-DCE, and 1,4-Dioxane by comparing the density of gene copies to the rate constants for removal of the contaminants at field scale as extracted from monitoring data or the rate constants for degradation as determined by a ^{14}C assay.

Results/Lessons Learned. Sampling of 1,4-dioxane plumes at seven different sites/operating units began in August 2018 and is expected to completed in early 2019. These sites include: (1) OU-11 at NAS North Island; (2) OU-20 at NAS North Island; (3) Site 9 at NAS North Island; (4) Camp Pendleton; (5) Ashumet Valley at Joint Base Cape Cod; (6) Former commercial/industrial site in the Midwest; and (7) Former commercial/industrial site in the Southeast. Each of the plumes at these sites also contain chlorinated solvent co-contaminants and have direct evidence and/or at least one favorable site characteristic for 1,4-dioxane co-oxidation. Rate constants for these sites, as well as at least 15 additional sites identified from published reports as part of a parallel desktop study, will be extracted by calibrating models to the field data. Samples from the seven field sites are also being analyzed using CSIA and qPCR assays to provide further lines of evidence for attenuation and potential correlations to rate constants. On-going lab-based studies using ^{14}C-labeled 1,4-dioxane are being performed to obtain independent estimates of 1,4-dioxane degradation rates for all samples from the field sites. An initial validation study using positive controls for 1,4-dioxane degradation (i.e., known metabolic and cometabolic 1,4-dioxane degrading strains and/or cultures) demonstrated that the

distribution of various radiolabeled fractions following degradation could be sufficiently quantified. Preliminary results indicate it will be possible to detect first-order rates of biodegradation as low as 9.0E-3 per year, corresponding to a half-life of 77 years.