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Project Title: **Partitioning Tracers for In Situ Detection and Quantification of Dense Nonaqueous Phase Liquids in Groundwater Systems**

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Research Objective

The overall goal of the project is to explore the use of an innovative in-situ method (partitioning tracer tests) for detection and quantification of dense nonaqueous phase liquids (DNAPLs) in subsurface systems. DNAPLs occur in the subsurface at numerous contaminated sites and can act as long-term sources of groundwater contamination. Both effective risk assessment and remediation of DNAPL-contaminated sites is limited by current site characterization techniques. A major limitation of the current methods is that they provide data at discrete points, such that the probability of sampling a zone of localized DNAPL is quite small. The results of this research will lead to an improved method for characterizing DNAPL-contaminated sites and will enhance our understanding of the distribution of immiscible liquids in the subsurface. The use of this method will help reduce the uncertainty associated with risk assessments and remediation planning.

Research Progress and Implications

This report summarizes work completed mid-way through year three of this project. During the past year, we have: (1) conducted a set of experiments in an intermediate-scale flow cell to examine the impact of heterogeneity and sampling method on the performance of the partitioning tracer method; (2) conducted a set of preliminary experiments in an intermediate-scale weighing lysimeter to evaluate the efficacy of a gas-phase partitioning tracer method for measuring soil-water content; (3) conducted several sets of experiments in the laboratory to continue to search for viable partitioning tracers; and (4) critically reviewed and summarized published applications of the partitioning tracer method. The results of these efforts are summarized below, with a focus on the first two items.

The purpose of this set of experiments was to examine the effect of porous-media heterogeneity, nonuniform distribution of DNAPL, and sampling method on the performance of the partitioning tracer method for measuring DNAPL saturation in water-saturated subsurface systems. Experiments were conducted in an intermediate-scale flow cell (2m x 1m x 0.06m) containing two discrete zones of trichloroethene (TCE) at residual saturation. One zone (Zone 2) consisted of ~10% saturation formed in the same sand as used for the flow-cell matrix. The other zone (Zone 1) consisted of ~10% saturation in a finer sand emplaced within the coarser matrix. Aqueous samples were collected using depth-specific sampling, vertically integrated sampling, and at the extraction
well. A dual-energy gamma radiation system was used to measure TCE saturation before and after the tracer experiment, allowing the measurements obtained from the tracer experiment to be compared to a previously tested method. The saturations estimated using the data collected at point-sampling ports located downgradient of Zones 1 and 2 were approximately 7% and 50% of the true values, respectively. The saturations estimated using the data obtained from the vertically-integrated ports were 2% and 0% of the true values, respectively. Finally, the saturation estimated using the extraction-well data was 30% of the cell-wide averaged value. These results indicate that the presence of porous-media heterogeneity and a variable distribution of DNAPL saturation can lead to reduced accuracy of the partitioning tracer test. The reduced performance can be improved, in part, by using depth-specific sampling.

The purpose of this set of experiments was to evaluate a gas-phase partitioning tracer method for the in-situ measurement of soil-water content in water-unsaturated systems. The method is based on the use of a tracer test with non-partitioning and partitioning tracers introduced into the system in the gas phase. Experiments were conducted in the laboratory and in a large weighing lysimeter (2.5m x 4m) to test the performance of the gas-phase partitioning tracer method. Soil-water contents estimated from the tracer tests were reasonably close to values obtained using gravimetric and time domain reflectometry measurements, indicating the gas-phase tracer method has the potential to provide accurate measurements of soil-water content at the field scale.

**Planned Activities**

We are currently conducting a second set of experiments with the intermediate-scale flow cell mentioned above. One objective of this new work is to examine the impact of a DNAPL pool on the performance of the partitioning tracer method. Another objective is to examine the impact of temporal variability of DNAPL saturation (e.g., due to dissolution) on the performance of the partitioning tracer method.

**Information Access**

