

# Environmental Management Science Program

**Project ID Number 54908**

## **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 proposed project is to explore the use of an innovative in-situ method for the detection and quantification of dense nonaqueous phase liquids (DNAPLs) in water-saturated and unsaturated heterogeneous media. Effective risk assessment and remediation of DNAPL contaminated sites is constrained by the limitations of current site characterization techniques. A major weakness 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 the proposed research will lead to improved techniques for characterizing DNAPL contaminated sites and will enhance our understanding of the distribution of DNAPLs in the subsurface. The use of this methods will reduce the uncertainty associated with risk assessments and remediation planning. The project objectives include exploring partitioning tracers for the detection and quantification of DNAPLs in saturated systems using aqueous tracers and in unsaturated systems using gas-phase tracers.

### Research Progress and Implications

This report summarizes work completed mid-way through year 2 of a 3-year project. Batch experiments have been conducted for a suite of bulk-phase partitioning tracers to determine water-trichloroethene (TCE) partitioning coefficients. Interfacial tension measurements have been made between TCE and solutions of several potential interface partitioning tracers. Preliminary column experiments have been conducted for the aqueous bulk-phase partitioning tracers using columns packed with a homogeneous sand and containing a residual saturation of TCE. These preliminary sets of experiments have enabled selection of suitable tracers for the water-saturated experiments and have lead to improved experimental designs and methods.

To conduct detailed, quantitative tracer studies at the intermediate scale, we've designed and constructed a new flow cell. The inside dimensions are 1.8 x 1 x 0.05 m. The flow cell is designed to be fully compatible with our dual-energy gamma radiation system. With that system, we intend to measure water and residual NAPL saturation simultaneously. One side of the flow cell is made of glass, to allow flow and transport visualization. The other wall is made of Kynar, a DNAPL resistant plastic. The Kynar wall has been machined to allow for the installation of twenty-four point-sampling ports consisting of laser drilled stainless steel tubing. Depth integrated sampling ports have also been installed. An automated sampling system has been designed and will soon be installed. Preparations have been made for packing the flow cell. Arrangements have been made with EMSL (Environmental Molecular Sciences Laboratory) for the analysis of TCE and our four tracers TCE using GC-MS, LC-MS, and an Ion Chromatograph.

Batch experiments have also been conducted for a suite of gas-phase partitioning tracers to determine their Henry's Constants and air-NAPL partition coefficients. Preliminary gas transport experiments have been conducted for the gas-phase partitioning tracers using columns packed with a homogeneous sand and containing a residual saturation of water. Results from these preliminary

sets of experiments will be used to help in the selection of suitable tracers for the unsaturated experiments and have improved experimental designs and methods.

We have tested the gas-phase partitioning tracer method in a controlled field-scale experiment conducted in a large weighing lysimeter located at the University of Arizona's Karsten Center for Research. The lysimeter is 4.0 m deep, 2.5 m in diameter, and is equipped with tensiometers, TDR probes, a neutron-probe access tube, and 48 porous stainless steel cups for gas injection and sampling. The weighing scales have a capacity of 45 Mg and can detect a 200-g mass change, equivalent to  $\pm 0.04$  mm of water on the surface. The instrumentation allows the values of water content estimated from the partitioning tracer experiment to be compared to known values obtained with the neutron probe. Pressure transducers (model 136PC15G2, Microswitch, Freeport, IL) installed at 50 cm increments from the inlet allow pressure to be monitored during the tracer experiments. The lysimeter was filled homogeneously with Vinton fine sand (sandy, mixed thermic Typic Torrifluent). To date, we have tested the method for measuring water content. In the future, we will inject TCE-NAPL in the lysimeter and test the gas-phase partitioning tracer method for measuring TCE-NAPL in an unsaturated system.

Our results to date demonstrate that the lysimeter provides a well-controlled setting for exploring the use of gas-phase tracer tests for measuring immiscible liquid saturations. Our results indicate that tracer tests have the potential to accurately measure water contents at the field scale. This method would complement both the traditional, small-scale methods and the regional [watershed] scale methods of measuring water content.

The performance of the STOMP simulator to compute multiple-phase flow through subsurface environments was improved for conditions of nonwetting fluid entrapment. The original version of the STOMP simulator modeled nonwetting fluid entrapment and scanning path hysteresis using the relative permeability-saturation-capillary pressure (k-s-p) theory developed by Lenhard and Parker (1987 Water Resources Research). This simplified model of Kaluarachichi and Parker, including air entrapment for three-phase cases, has been incorporated into the Water-Air and Water-Oil-Air operational modes of the STOMP simulator and is currently being verified for proper execution.

## Planned Activities

**Summer 1998:** Bulk-phase partitioning tracer experiments will be conducted in saturated columns containing TCE-NAPL at different pore-water velocities to test the effect of rate-limited mass transfer. Also the form and quantity of NAPL will be varied. In addition, experiments will be conducted in the intermediate-scale flow cell. The STOMP simulator will continue to be modified and tested.

**Fall 1998:** Experiments will be conducted to examine the transport of interface partitioning tracers in saturated systems containing NAPL. Gas transport experiments will be conducted in the weighing lysimeter to measure NAPL saturation. Data collected from experiments conducted in the flow cell during the summer will be analyzed. The STOMP simulator will continue to be modified and tested.

**Spring 1999:** The STOMP simulator will be used to simulate data collected from experiments conducted in the flow cell. These results will be compared to other models.