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**Title:** Pore Scale Determination of the Rate of NAPL Dissolution or Volatilization  
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**Research Category:** Exploratory Research-Physics  
**Project Period:** January 1, 1998 - December 31, 1999

**Objectives of Research:**

To design a remediation scheme, it is important to understand the physicochemical processes that govern inter-phase mass transfer of NAPLs in the subsurface, both in the unsaturated and water-saturated regions. The rate at which NAPLs dissolve or volatilize in large part determines the time required to clean up a contaminated site. Non-equilibrium conditions are most important during remediation, when the rate of inter-phase mass transfer can significantly limit the effectiveness of any treatment scheme. The most important parameter for determining the rate of inter-phase mass transfer is the interfacial contact area, $a_c$, which up to now has proven impossible to measure experimentally. The existing empirical correlations available for calculating the inter-phase mass transfer coefficient, $k_p$, have used “surrogates” for the interfacial contact area.

The objective of this project is to experimentally observe the dissolution and volatilization processes at the pore scale as a function of saturation and pore space geometry for various NAPLs, and then to determine how $k_p$ is functionally related to the observed $a_c$ and how this correlates with NAPL saturation, $S_n$. The hypothesis is that the relationship between $a_c$ and $S_n$ varies with time, is non-linear, but can be expressed as a power function. A field-measurable value ($S_n$) can then be used to estimate $k_p$, for applications in a modeling framework.

**Approach:**

A micromodel setup is used to observe the mass transfer processes within a controlled pore scale geometry, with known fluid flow rates. The images are captured dynamically through a video camera for numerical processing of the digitized images to determine both NAPL saturation, $S_n$, and interfacial contact area, $a_c$, as a function of time. The outlet concentration of dissolved or volatilized NAPL in the flowing phase is measured using GC/MS. This information allows the experimental determination of the mass transfer coefficient, $k_p$, as a function of $a_c$ or $S_n$.

**Progress Summary:**

We have set up micromodel experiments to determine the rate of dissolution of various NAPLs. The micromodel is wetted initially with acetone to dissolve the air trapped in the pore spaces. Subsequently, the pores are flushed with water for at least 50 pore volumes. The liquid phases are introduced using a syringe under spring tension to ensure constant flow into the micromodel. Pressure in the system is monitored at the inlet using a digital manometer.

For the first experiments we introduced toluene into the pore spaces. The NAPL blobs can be seen in Figure 1. After toluene had moved through some of the pore spaces, the liquid phase was switched back to water. The sequence of images in Figure 1 (a-h) show how the NAPL blob shrinks over time. The rate of dissolution can then be calculated. Dissolution of toluene depends on the interfacial area exposed to the water phase. The interfacial area can be calculated using a variety of software tools. We have been exploring different options for the best results.
Figures 2a-f present a volatilization process, where toluene is been volatilized by an invading air phase. The sequence shows how air (light color) progressively enters the pore spaces, while the NAPL phase shrinks.

Publications: None to date.

Future Activities:
We will inject other NAPLs (e.g. tetrachloroethylene) into the aqueous phase of the micromodel and calculate $S_n$ and $a_c$ for each. The concentration of the NAPL in the water will be measured at the outlet of the micromodel. We will also determine saturated flow concentrations in the outlet of the micromodel after the phases have come into equilibrium using GC/MS. After completing our studies of dissolution in water, we will determine volatilization rates of NAPLs in the air-filled pore spaces of the micromodel. The concentration of NAPL in the air will be sampled using a gas-tight syringe and analyzed with a GC/MS. Mass transfer coefficients will be determined for all NAPLs tested.

We will test the use several fluorophores, such as fluorescein, 2,3-diaminonaphthalene, and naphthalene-2,3-dicarboxaldehyde, to highlight the NAPL/aqueous phase interface. We plan to determine NAPL concentrations as it dissolves in water using fluorescence and quenching as an index of concentration changes. The rate of dissolution will be related to the amount of fluorescence emitted from one of the phases and determined using image analysis software.

A mathematical model relating $a_c$ to $S_n$, and then to $k_p$, is currently under development. The conceptual model is initially based on simple pore geometries (circular spheres, sinusoidal pore spaces), and will progressively capture more of the natural variability in pore space geometries, to accurately represent the dissolution process.

As a part of this work we will setup a web page showing our micromodel images and calculations.

Supplemental Keywords: groundwater, chemical transport, mass transfer, NAPL, VOC, remediation, environmental chemistry and physics, engineering

Relevant Web site: http://www.bren.ucsb.edu/~keller/research/micromodel.htm