Project Number: 86804

Project Title: Resolving the Impact of Biological Processes on DNAPL Transport in Unsaturated Porous Media through Nuclear Magnetic Resonance Relaxation Time Measurements

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Research Objectives:
This research leads to a better understanding of how physical and biological properties of porous media influence water and dense non-aqueous phase liquid (DNAPL) distribution under saturated and unsaturated conditions. This project exploits the capability of low-field nuclear magnetic resonance (NMR) proton relaxation decay-rate measurements for determining environmental properties affecting DNAPL solvent flow in the subsurface, including determining if DNAPL exist in water-wet or solvent-wet environments, the pore-size distribution of the soils containing DNAPLs, and the impact of biological processes on their transport mechanisms in porous media. Knowledge of the in-situ flow properties and pore distributions of organic contaminants are critical to understanding where and when these fluids will enter subsurface aquifers.

Research Progress and Implications:
As of June 30, 2004, this report summarizes the work in months 10-22 of a 3-year project. Work in the initial 9 months of the project consisted of initial key experiments, development of soil column packing procedures, and development of robust and repeatable data processing and analysis algorithms. Subsequent work built upon the initial experiments to demonstrate differentiation of water- and TCE-saturated soils, using NMR measurements to quantify the T_2 relaxation time of TCE, and demonstrate the change in relaxation time as biofilm accumulates in a porous medium.

Discrimination between water-wet and TCE-wet soils: The first objective of this project is to quantify the differences in contaminant detectability in representative native soils from the INEEL and PNNL. Sample native soils from each major inter-bed sediments layer were obtained from the USGS core laboratory at INEEL. Preliminary experiments used columns of engineered soils to preserve the limited amount of native soil available. All experiments are repeated with the native soil samples throughout the project to validate results obtained with engineered soils.

In the initial engineered-soil experiments, the columns were packed with a mixture of fine sand (~75-300μm grain size) and 3% Ca-Montmorillonite clay (by weight). Water-retention curves were measured by draining the saturated columns for a constant time at different vacuum levels. The relation between the water-retention data and T_2 distributions at different residual-water content is shown in figure 1. In the porous medium, the relaxation time is decreased as the protons exchange energy with the surface of the pores. The subsequent decay-rate distributions reflect

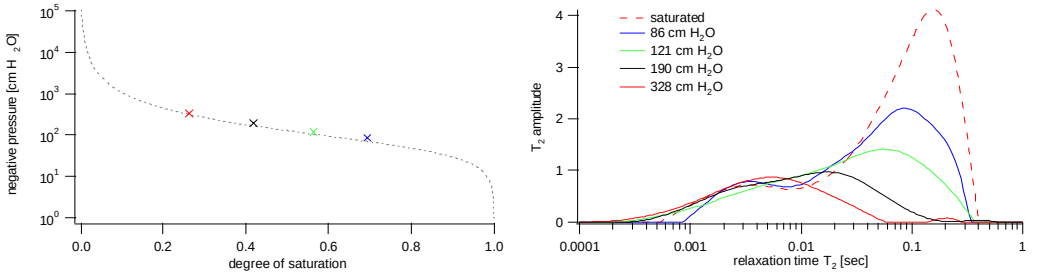

Figure 1: Water-retention curve (left) and a family of relaxation-time (T_2) distributions (right). The T_2 distributions are for different amounts of residual-water content. Each "x" mark on the water-retention curve corresponds to a different T_2 distribution. Water is drained from the larger pores first – moving from right to left on the water-retention curve corresponds to an "erosion" of the T_2 distribution toward faster relaxation times.

pore-size distributions—the large T_2 values are associated with the larger pores. Correlating the water-retention curve with distributions of relaxation times at different draining points shows that larger pores drain first, and smaller pores and more tightly bound water are last to drain. Subsequent saturation with an immiscible fluid (relative to the initial fluid) will fill the vacated pore space and perhaps displace some bound fluid.

Discriminating TCE from water in water-wet sands is demonstrated in figure 2. The observed relaxation time for bulk water is about 2.3 sec in our spectrometer. The relaxation time for bulk TCE is slightly larger, and ranges from about 2.5 –13sec depending on the amount of oxygen in the sample (*reference 1*). In a water-wet column, which has been drained to residual water saturation and then resaturated with TCE, the response due to the TCE is well separated from the saturated water response, even though the TCE is in the same pore space previously occupied by water. Our hypothesis is that in water-wet environments, TCE is blocked or isolated from interacting with the pore surfaces by the bound water layer. The shape (narrowness) and shift of the TCE peak may be related to the amount of residual water and pore-size distribution. This correlation will be studied more fully. The integrated area under the TCE peak is equal to 10% of the area of the water removed from the large pores, which is consistent with the relative proton density in TCE compared to water. Note that for the TCE-wet, TCE-saturated sample, the large-pore T_2 peak is shifted to the left indicating that the TCE can readily interact with the pore surfaces in this case (*reference 2)*.

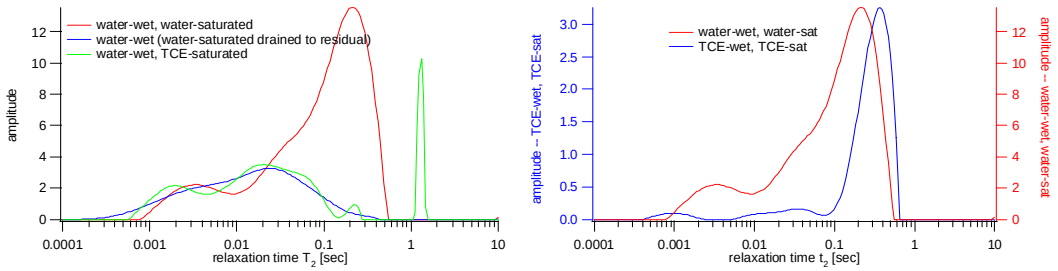

Figure 2: Discriminating water and TCE in water-wet soil columns. The curves on the left plot are for a water-wet case. Note that the TCE T_2-distribution peak (green) is shifted to the right and separate from the bound-water distribution (blue). The right plot compares water-wet, water-saturated soil column data (red) to TCE-wet, TCE-saturated column data (blue). Note that in this case, the TCE in the large pores is shifted toward shorter relaxation times because the TCE is allowed to interact with the pore surfaces.

Changes in T_2 relaxation time as biofilm accumulates: The second objective of this project confirms and shows how NMR T_2 relaxation measurements can be used to study and monitor the effects of bacterial accumulation in porous media on water and TCE fluid-pore distributions. Pseudomonas aerginosa produces an extra cellular polysaccharide (EPS), which we expect to coat the pore surfaces and, if allowed to grow fully, eventually plug the pore space. It was expected that a column in which the pore space is full of EPS would have a T_2 distribution that is biased toward shorter relaxation times since the bulk of the fluid will be trapped (or slightly bound) in the EPS and will relax more quickly. However, at the beginning of microbial growth, the effect may be the opposite – if the EPS accumulates on the pore boundaries then the fluid in the pore space will not be able to interact with the pore wall and the effective grain-relaxivity of the sample will be decreased allowing an increase in the relaxation time. Then as the volume of EPS grows, a component of the relaxation-time distribution will decrease and the longer components of the relaxation time will diminish.

Results from our first biological experiments using pseudomonas cultured in a very coarse gain sand samples are shown in figure 3. The pore space of the column was filled with a nutrient broth (T_2 relaxation time approximately equal to that of water). At 90 hours, the column was inoculated with microbes as the nutrient broth continued to pump

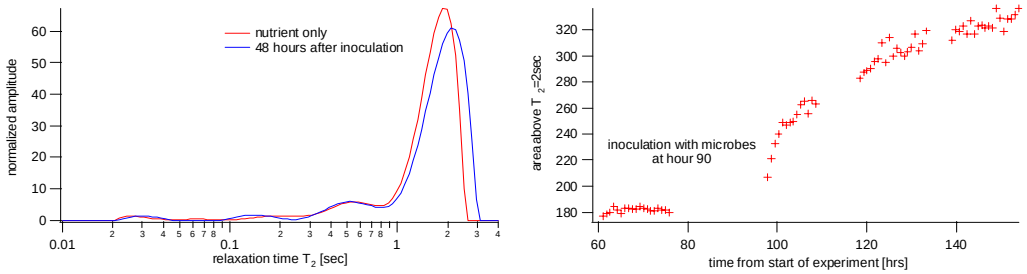

Figure 3: Left plot shows T_2 distributions from a coarse-grain soil column that is initially filled with nutrient broth (red) and then inoculated with microbes (blue). The T_2 distribution shifts to longer relaxation times as the microbe population increases. This shift-effect is shown quantitatively in the right plot, which shows the area under the T_2 distribution integrated from 2-10sec.

through the column. These data show that there was a shift toward the longer bulk relaxation time after the microbes were introduced. We did not see any shift toward shorter relaxation times, and destructive analysis of the column after the experiment showed that significant biomass had not accumulated. Succeeding results indicate that the while the bulk relaxation time of the nutrient broth is nearly equal to that of water (~2.5sec), the relaxation time of nutrient broth with inoculated with *pseudomonas* is larger (~3.5sec). This is an indication the change in the observed T_2 distribution may be sensitive directly to the growth of the microbes and not the coating of the grain boundaries as originally thought (*reference 3).*

Planned Activities:

The characteristics of other DNAPLs of interest to the EMSP project (dichloroethylene, dichloromethane, and chlorform) will be measured, both in bulk and in porous media. These are fundamental properties of chemicals that are of interest to other researcher investigating DOE contaminants. The water-wet, DNAPL saturated measurements with these DNAPLs will be repeated to verify that the response is similar to that for TCE. We will verify preliminary results that have been obtained with simple engineered soils with more complex engineered soils, and continue to compare results from engineered soils with results from actual soil samples obtained from core samples at the INEEL site. We will also engineer soils that are wettable with DNAPL in order to show the discrimination of DNAPL from water in a DNAPL-wet, water-saturated soil.

The biofilm experiments will continue in order to verify the hypothesis that the relaxation time will be reduced as biomass accumulates. We will quantify the capability to measure large biomass accumulation with NMR. We will investigate the change in T_2 distribution of water-wet, TCE saturated soil compared to "microbe-wet", TCE saturated soils. And a subset of all of these laboratory experiments will be repeated with a commercial field tool. A soil column that is larger than the field of view of the Schlumberger NMR tool will be developed and used in laboratory scale experiments to show that the tabletop results obtained with the relaxometer at the INEEL can be extrapolated to the field.

Information Access:

1. *T_2 Relaxation Times for DNAPLs in Bulk Fluids*, White, T.A., Hertzog, R.C., (*in preparation, to be submitted to* Environmental Science and Technology***).***
2. *Discrimination of DNAPL from Water Saturation in Water-Wet Porous Media*, Hertzog R.C., White T.A., Straley C., Baker, K.E., Schafer, A.L.(*in preparation, to be submitted to* Vadose Zone Journal.*).*
3. *Effects of Microbial Growth on NMR Relaxation Times),* White, T.A., Hertzog, R.C., Geesey, G.G. (*in preparation, to be submitted to* Enzyme and Microbial Technology*).*