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Project Title: **Behavior of Dense, Immiscible Solvents in Fractured Clay-Rich Soils**

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Behavior of Dense, Immiscible Solvents in Fractured Clay-rich Soils

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Research Objective

This research program addresses the nature and distribution of chlorinated solvent DNAPL sources in fractured clays and weathered shales and the potential for natural attenuation of plumes derived from these sources. These investigations are needed to build the scientific framework for assessment of DNAPL fate in fractured clays and remediation or control options. Specific objectives include:

1. Determine whether chlorinated solvent DNAPLs are likely to enter fractures and/or fine matrix pores for a typical DNAPL spill scenario and determine how DNAPL will be distributed in the soil, using capillary pressure - saturation experiments in large undisturbed columns of fractured shale saprolite.
2. Determine whether values of fracture aperture and fracture porosity derived from the "cubic law" are useful indicators of DNAPL entry pressure and residual saturation.
3. Investigate the influence of "matrix diffusion" on the dissolution and apparent disappearance of residual DNAPL (this mechanism can cause more rapid dissolution and spreading of the DNAPL, but does not actually cause disappearance of the contaminant).
4. Investigate potential for biodegradation of chlorinated solvents in fractured and weathered shales at an existing contaminated field site and through the use of laboratory studies in microcosms and undisturbed columns of fractured shale saprolite.
5. Comparison of DNAPL behavior in different types of fractured clay-rich materials, primarily clay-rich shale saprolite in east Tennessee, and clay-rich tills in southwestern Ontario.

Research Progress and Implications

This report summarizes progress made during the first 2.5 years of a 4-year project (we are applying for a no-cost extension). The project investigates the behavior of chlorinated solvent DNAPLs (mainly TCE) in two fractured clay-rich materials: highly weathered shale saprolite at Oak Ridge National Laboratory in eastern Tennessee; and weathered glacial till in southwestern Ontario, Canada. The materials, although different in origin are similar in terms of fracturing, porosity, and hydraulic conductivity. As a result, it is expected that DNAPL behavior in the materials will be similar in some ways. This study will help us to evaluate whether findings from the extensive previous DNAPL studies in fractured tills can be applied to DNAPL behavior in shale saprolite. Results to date for the major sub-projects are briefly described below.

Weathered and Fractured Shale Saprolite Column Experiments

Air/water and DNAPL/water entry and pressure-saturation curves have been experimentally measured for an undisturbed column sample of fractured weathered shale from Oak Ridge

National Laboratory (ORNL). Preliminary evaluation of the results indicate that air/water data can be used, along with appropriate scaling factors based on the differences in fluid properties, to estimate DNAPL/water behavior. This is significant, because it raises the possibility that air/water curves (which are more commonly used in agricultural research) can also be used to estimate DNAPL/water behavior in these materials. The preliminary experiments showed that typical fractures in saprolite are sufficiently large to allow entry of DNAPL even for very small spills (capillary pressure head values of 5-8 cm). The experiments also show a relatively low matrix pore entry pressure (160-210 cm of head), indicating that at many sites DNAPL is likely to enter both the fractures and the matrix, where it would be virtually impossible to remove with DNAPL recovery wells. A series of experiments is currently underway to measure DNAPL distribution in the fractures and matrix for simulated large and small spills. This involves injecting DNAPL into a saprolite column under controlled capillary pressure conditions and then dismantling the column and measuring DNAPL distribution using a microcoring technique.

Matrix Porosity and Pore Size Investigations in Weathered Shale Saprolite

Investigations of porosity and pore size distribution have been carried out using gravimetric methods, mercury/helium porosimetry (described in previous annual report), and microscopy with resin-impregnated thin-sections. The studies indicate that there is a wide range of fracture and matrix pore types and sizes in the saprolite. Many of the most prominent fractures are infilled with pedogenic clays, so it is often the less prominent features that are most likely to be conductive. This was confirmed by examining thin-sections from a soil column through which fluorescent microspheres had been passed. The retained microspheres clearly showed that the secondary fractures were often very important for transport and hence are likely to be most readily invaded by DNAPLs. The thin-sections also showed that there is much greater variability in the matrix lithology and pore size distribution than previously expected. In some regions of a sample, matrix pores might be largely filled with pedogenic clays or Fe/Mn oxides, while only a few cm's away the pores were largely open. This is consistent with the low DNAPL matrix entry pressures observed in the experiments.

DNAPL Natural Attenuation in Fractured and Weathered Shale

A field facility at the Oak Ridge National Laboratory is serving as an extraordinary example of how natural attenuation processes are eliminating the off-site transport of chlorinated organics in a fractured shale bedrock. The field facility consist of a 35 m long transect of multilevel sampling wells that follow strike parallel geology and extend from a waste burial trench containing organic solvents to a seep exiting into a perennial stream. Preliminary data suggests that anaerobic degradation of TCE is occurring in the saprolite and the upper portion of the bedrock. TCE concentrations are highest in the portion of the plume closest to the waste trench and TCE daughter products 1,2 DCE and vinyl chloride are dominant further downgradient. Geochemical indicators are also consistent with biodegradation, and preliminary microbiological data indicates the presence of anaerobic heterotrophs, methanotrophs and sulfate-reducing bacteria which again suggest biodegradation. The microbial communities present at the field site have been characterized with molecular microbiological methods and indicate several types of potentially biodegrading organisms. A series of laboratory experiments using TCE in microcosms and columns of undisturbed saprolite are currently underway to determine whether biodegradation can be reproduced and quantitatively evaluated in the laboratory.

Fractured Till Column Experiments

One set of TCE entry experiments in a large undisturbed sample of clay till has been completed and a manuscript is currently in press. The study shows that TCE can enter very small fractures (5 to 6 µm) at relatively low pressure heads (a few m's or less). The study also confirmed the importance of matrix diffusion, by dismantling the column approximately a month after the injection and observing the existence of TCE "haloes" around the conductive fractures. Determination of the TCE distribution in the column was done with a micro-coring technique developed at University of Waterloo and currently being applied to experiments in the fractured shale saprolite, as described previously. A new series of column experiment(s) in fractured till is underway using mixtures of organic solvent DNAPLs. Because each solvent has a different solubility this results in retardation of the more soluble component relative to the less soluble component and can be used to assess channeling and transport rates in the soil.

Planned Activities

The planned activities for 1999-2000 include:

1. Continue and complete laboratory scale studies of DNAPL entry pressure, residual concentration and diffusive disappearance in weathered shale saprolite and glacial tills.
2. Continue and complete field and laboratory scale studies of biodegradation of organic solvents in fractured shale saprolite.
3. Continue and complete microbial characterization of contaminated and uncontaminated field/lab samples using conventional and molecular techniques to determine influence of contamination on microbial communities and to identify organisms capable of solvent biodegradation.
4. Completion of graduate theses, preparation and submission of manuscripts to peer-reviewed journals, presentation at conferences and technical meetings, preparation of new research or technical application funding proposals.

Publications, Theses and Abstracts

Peer-reviewed Manuscripts

O'Hara, S.K., B.L. Parker, P.R. Jorgensen and J.A. Cherry. Trichloroethene DNAPL flow and mass distribution in naturally fractured clay 1: Evidence of aperture variability. Water Resources Research, accepted with minor revisions.

O'Hara, S.K. and B.L. Parker. Trichloroethene DNAPL flow and mass distribution in naturally fractured clay: 2. Matrix diffusion effects and NAPL phase disappearance. Submitted to Water Resources Research, January 1999.

Jardine, P.M., M. Lenczewski, L. McKay, et al., Field evidence of biodegradation of chlorinated organic solvents in fractured and weathered shales, Manuscript in preparation for submittal to J. of Contaminant Hydrology.

McKay, L.D., S. Driese and S. C. Cropper, Application of thin-section microscopy to interpretation of DNAPL/water capillary pressure - saturation behavior in a clay-rich saprolite, Technical note in preparation for submittal to Water Resources Research.

Cropper, S.C., and L.D. McKay, Comparison of air/water and DNAPL/water capillary pressure - saturation behavior in a fractured shale saprolite, Manuscript in preparation for submittal to J. Contaminant Hydrology.

Theses

O'Hara, S.K., Solvent DNAPL flow and matrix diffusion in natural fractured clay: A large column experiment, MS thesis, Univ. of Waterloo, Ontario, Canada, 1997.

Cropper, S.C., Experimental observations of capillary pressure - saturation drainage of air and DNAPL in fractured shale saprolite, MS Thesis, Univ. of Tennessee, Knoxville, TN, 1998.

Conference Abstracts and Papers (1998-99 only)

Lenczewski, M., L.D. McKay, J. Sanseverino, and C. Knight, Sorption and microbiological factors controlling the fate and transport of TCE in fractured shale saprolite, Conference on Mass Transport in Fractured Aquifers and Aquitards, Univ. of Copenhagen, Denmark, May 14-16, 1998.

Lenczewski, M., L.D. McKay, J. Sanseverino, and A. Layton, Biodegradation of TCE in fractured shale saprolite, Annual Meeting, Tennessee Water Resources Assoc., Nashville, TN, April 12-14, 1999.

Lenczewski, M., L.D. McKay, J. Sanseverino, and A. Layton, Biodegradation of TCE in fractured weathered shale in east Tennessee, Annual Meeting, American Soc. Microbiology, Chicago, IL, May 30-June 3, 1999.

McKay, L.D., Contaminant transport in highly weathered and fractured shales, Conference on Mass Transport in Fractured Aquifers and Aquitards, Univ. of Copenhagen, Denmark, May 14-16, 1998.

McKay, L., Cropper, S.C., et al., Behavior of dense, immiscible solvents in fractured clay-rich soils, Poster presented at DOE/EMSP Workshop, Chicago, IL, July 27-30, 1998.

McKay, L.D., Field and laboratory studies of DNAPL behavior in fractured and highly weathered shale, University Consortium Solvents-in-Groundwater Workshop, Queen's University, Kingston, Ontario, Canada, May 11-13, 1999.

O'Hara, S., Characterizing solvent DNAPL migration pathways in fractured clay using a large column laboratory experiment, University Consortium Solvents-in-Groundwater Workshop, Queen's University, Kingston, Ontario, Canada, May 11-13, 1999.

O'Hara, S.K., B.L. Parker, K.J. Slough and E. A Sudicky. Characterizing solvent DNAPL migration pathways in fractured clay using a numerical model and a large column laboratory experiment. American Geophysical Union (AGU) Fall Meeting, (December), San Francisco, CA, 1998.

Parker, B.L., Diffusion profiles for identifying DNAPL migration pathways in a glaciolacustrine fractured clay, Conference on Mass Transport in Fractured Aquifers and Aquitards, Univ. of Copenhagen, Denmark, May 14-16, 1998.

Parker, B.L., S.K. O'Hara, and G.A. Kirkpatrick. Solvent DNAPL flow in naturally fractured clay: Laboratory and field experiments. Presented at the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 18-21, 1998.

Pitner, A., L.D. McKay, and M. Lenczewski, DNAPL entry, dissolution and diffusion in fractured shale saprolite, Annual Meeting, Tennessee Water Resources Assoc., Nashville, TN, April 12-14, 1999.

Solvents-Related Web Sites

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http://web.utk.edu/~lmckay

P. Jardine, Oak Ridge National Laboratory
http://www.esd.ornl.gov/facilities/hydrology/WAG5/

J. Cherry & B. Parker, University of Waterloo
http://www.science.uwaterloo.ca/research_groups/ucsgrp/