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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.

Specific objectives include:

1. Investigate the factors controlling migration of chlorinated solvent DNAPLs in fine-grained, highly structured soils and weathered shale bedrock.
2. Investigate the influence of "matrix diffusion" on the dissolution and apparent disappearance of residual DNAPL.
3. 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.

Research Progress and Implications

This report summarizes progress made during the first 3.5 years of a 4-year project (now on 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.

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 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 second series of experiments was recently completed to measure DNAPL distribution in the fractures and matrix for lab-simulated spills. As a part of this study, the investigators developed and tested a new method for assessing DNAPL distribution and transport pathways in fractured clays. The method involves injecting a soil sample with a chlorinated solvent containing a water-insoluble fluorescent dye. The sample is allowed to sit for a few weeks and is then dismantled. The initial distribution of immiscible DNAPL can be mapped based on the fluorescent dye, and the final distribution of the dissolved DNAPL is measured using a micro-coring extraction technique. Comparison of the two resulting distributions was used to confirm the importance of matrix diffusion as a mechanism for redistributing DNAPLs after a spill occurs.

Matrix Porosity and Pore Size Investigations in Weathered Shale Saprolite
Investigations of porosity and pore size distribution have been carried out and they 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 conductive. 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 extend from a waste burial trench containing organic solvents to a seep exiting into a perennial stream. 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. 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
TCE entry experiments were carried out in years 1-3 of the project in a large undisturbed sample of clay till. The studies show that TCE can enter very small fractures (5 to 6 ìm) at relatively low pressure heads (a few m's or less). They also confirmed that matrix diffusion plays an important role in controlling the rate of dissolution of TCE residuals in fractures, which largely dissolve within a month or two of the initial contaminant "spill".

Planned Activities
The planned activities for the rest of 2000 include:
1. Continue and complete laboratory scale studies of biodegradation of organic solvents in fractured shale saprolite 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.
2. Complete writing of a series of 5 articles based on the DNAPL injections and biodegradation studies.

3. Preparation of funding proposals for related research (a proposal for EPA is in-prep.).

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, 36(1), 2000.

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. Water Resources Research, accepted with minor revisions.

Driese, S., L.D. McKay, and C. Penfield, Lithologic and pedogenic influences on porosity distribution and groundwater flow in fractured sedimentary saprolite: a new application of environmental sedimentology, J. Sedimentary Research, accepted pending minor modifications.

M. Lenczewski, P.M. Jardine, L.D. 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.

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.

Plus other manuscripts in preparation.

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.

Pitner, A.H., Experimental investigations of factors controlling DNAPL transport and dissolution in fractured saprolite, MS Thesis, Univ. of Tennessee, Knoxville, TN, 2000.

A PhD Thesis by M. Lenczewski is in progress and should be completed in fall/2000. Ms. Lenczewski has already accepted a tenure-track faculty position at Northern Illinois University, starting in January, 2001.

Abstracts and Conference Presentations

Approximately 25 presentations based on the research program have been made over the past 4 years. These include presentations at DOE/EMSP Workshops, national meetings of the Geol. Society of America, the National Ground Water Association, and the American Petroleum Institute, regional

meetings of the SE Division of GSA, and the TN Water Resources Association, and international workshops or meetings in Canada, Denmark and Great Britain (international travel was paid by other funding sources).

Solvents-Related Web Sites

L. McKay, Univ. of Tennessee
http://web.utk.edu/~hydro

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/