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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 highly weathered shales, and the potential for natural attenuation of plumes derived from these sources.

Specific objectives include:

1. 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.
2. Investigate the factors controlling migration of chlorinated solvent DNAPLs in fine-grained, highly structured soils and weathered shale bedrock.
3. Investigate the influence of "matrix diffusion" on the dissolution and apparent disappearance of residual DNAPL.
4. Comparison of DNAPL behavior in different types of fractured clay-rich materials.

Research Progress and Implications

This report summarizes progress made during the 4-year project (now complete). 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 (ORNL) in eastern Tennessee; and weathered glacial till in southwestern Ontario, Canada.

DNAPL Natural Attenuation in Fractured and Weathered Shale

An existing plume of TCE-contaminated groundwater in fractured and weathered shale adjacent to an old waste trench in Waste Area Grouping 5 (WAG-5) at ORNL was investigated using a combination of geochemical and microbial methods to determine if natural attenuation of the TCE was occurring. The study clearly indicates that anaerobic degradation of TCE and its daughter products is occurring in the upper portion of the bedrock, and possibly in the overlying saprolite. This is the first documented example of biodegradation of chlorinated solvents in a fine-grained soil or rock, and suggests that

natural attenuation may be a viable option for organic contaminants at ORNL and at other DOE sites in similar geologic settings. Evidence for TCE biodegradation at the site include: declining TCE concentrations with distance from the waste trench; appearance of the daughter products 1,2 DCE, vinyl chloride, ethylene and methane; the occurrence of redox conditions (iron reduction, sulfate reduction and possibly methanogenesis) that are favorable for anaerobic biodegradation; and the appearance of microbial communities that are very similar to communities previously implicated in degradation of chlorinated solvents. The plume of organic contamination disappears just before the groundwater discharges as a spring approximately 50 m from the waste trench, and we hypothesize that aerobic degradation is occurring in the very shallow groundwater near the spring. The potential for natural attenuation of chlorinated solvents in the groundwater was also evaluated using data from 5 wells and the Air Force Center for Environmental Excellence (AFCEE) protocol. Scores ranged from 11 to 22, indicating anywhere from limited potential to strong potential for natural attenuation. The scores also indicated a strong seasonal trend, with much greater potential for natural attenuation occurring during the winter, when the elevation of the groundwater table, which influences redox conditions, tends to be much higher. The partial agreement between the AFCEE protocol and the much more extensive evaluation carried out by the investigators indicates that the protocol can be useful, but evaluations should be carried out a several different times of the year.

A series of laboratory experiments were carried out in undisturbed columns of saprolite from a nearby, uncontaminated site to investigate biodegradation processes. The study involved continuously pumping groundwater spiked with approximately 1800 ppb of TCE through two saprolite columns for a period of approximately one year. The influent water for one of the columns also contained an agent (sodium azide) to inhibit microbial growth. Effluent from the inhibited column showed no evidence of TCE degradation (as expected). However in the “biotic” column strong evidence of biodegradation appeared within 1-6 months of the start of the injection. This evidence included declining TCE concentration, appearance of cDCE and vinyl chloride, changing redox conditions, and shifts in the microbial community to a structure which resembled that of the contaminated field site. This experiment confirms that the TCE degradation is microbially mediated, and that microbial communities can rapidly shift to facilitate biodegradation. The AFCEE protocol was applied to effluent from the biotic column and produced a score indicative of strong natural attenuation, further indicating that this protocol is useful in fractured clay-rich materials.

Shale Saprolite Column Experiments

Laboratory experiments to simulate spills of DNAPL in shale saprolite (highly weathered rock) from Oak Ridge National Laboratory (ORNL) show that even small spills of typical DNAPLs are likely to result in significant infiltration and spreading of contaminants. The experiments, carried out in undisturbed columns of fractured saprolite, showed that entry pressures needed for TCE or Fluorinert (a low solubility DNAPL) to enter fractures and macropores are typically less than 10 cm of equivalent water head. The experiments also show a relatively low matrix pore entry pressure (160-210 cm of head for Fluorinert), 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 ivestigate dissolution of DNAPL once it has entered a fractured saprolite. The experiment involved injecting TCE containing a water-insoluble fluorescent dye into columns of undisturbed shale saprolite. The samples were allowed to sit for a few weeks and then dismantled. The initial distribution of immiscible TCE was mapped based on the fluorescent dye, and the final distribution of TCE was mapped using a micro-coring and extraction technique. The study shows that after only 2-3 weeks, almost all of the TCE has dissolved and spread

into the fine-grained matrix pores adjacent to the fractures and other macropores. This rapid dissolution occurs because of the very high surface area to volume ratio of the immiscible TCE after the initial injection. Once in the matrix it is extremely difficult to remove the dissolved TCE, indicating that it would not be feasible to use methods such as pump and treat to remove DNAPL contaminants from this type of material.

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 in-filled 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.

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".

Information Access

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, in press.

M. Lenczewski, P.M. Jardine, L.D. McKay, and A. Layton, Field evidence of biodegradation of chlorinated organic solvents in fractured and weathered shales, In review, J. of Contaminant Hydrology.

M. Lenczewski, L.D. McKay and A. Layton, Biodegradation of TCE in undisturbed columns of fractured saprolite, Manuscript in preparation for submittal to Environmental Science and Technology.

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.

McKay, L.D., A. Pitner, and S. Driese, Influence of pore structure on transport and dissolution of TCE in 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.

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

Lenczewski, M.E., Biodegradation of TCE in fractured shale and saprolite, PhD thesis, Univ. of Tennessee, Knoxville, TN, 2000.

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/