BEHAVIOR OF DENSE, IMMISCIBLE SOLVENTS IN FRACTURED CLAY-RICH SOILS

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Larry D. McKay, Melissa Lenczewski, and Andrew H. Pitner, University of Tennessee, Department of Geological Sciences
Alice Layton, University of Tennessee, Center for Environmental Biotechnology
Phillip M. Jardine, Oak Ridge National Laboratory, Environmental Sciences Division

Introduction

Fractured clay-rich soils are widespread in the eastern US and include soils developed on saprolite or highly weathered rock, glacial tills, and lake or marine deposits. Many DOE facilities, including those at Oak Ridge, TN, Fernald, OH, and West Valley, NY, are located on fractured clay-rich soils.

Dense, non-aqueous phase liquids (DNAPLs) can enter small aperture fractures or biopores in clay-rich soils, causing significant contamination of the soil, nearby streams or underlying aquifers. Contamination tends to be highly erratic, with much of the DNAPL mass residing in the fine-grained matrix, which can act as a long term source. Conventional monitoring and remediation methods are often ineffective in these materials.

Goals and Objectives

This research program addresses the nature and distribution of chlorinated solvents DNAPL sources in fractured clays and weathered shales, and the potential for natural attenuation of plumes derived from these sources. Specific objectives include:

- Investigate factors controlling migration and distribution of immiscible phase.
- Investigate dissolution of DNAPL and diffusion into matrix.
- Assess potential for natural attenuation.
- Address the relevance for DOE and other federal agencies.
  - - implications for monitoring & site characterization
  - - limitations for conventional remediation methods
  - - potential for natural attenuation

Background

The focus of this research has been sites at the Oak Ridge National Laboratory (ORNL), where mixed waste, including DNAPLs, was dumped into shallow unlined trenches (figure 1). The geologic material involved in both the field study and the laboratory experiment described here is a very heterogeneous, highly weathered and fractured saprolite derived from the Cambrian-aged Dismal Gap Formation. Table 1 lists common physical properties of the material. Despite intense weathering of this carbonate shale, characteristic structures, including bedding and three sets of orthogonal fractures are preserved. A conceptual model (figure 2) for DNAPL transport has been developed and the research presented here addresses how contamination spreads in this material and how natural attenuation eliminates the off-site transport.

Figure 1. Mixed waste dumped in unlined trenches. Note visible structure and heterogeneity of saprolite.

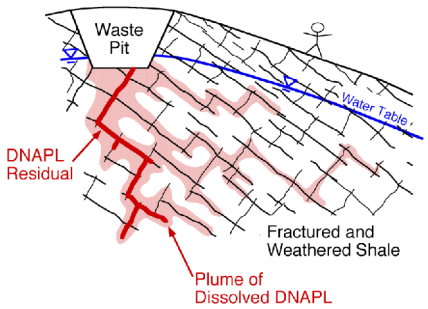


Figure 2. Conceptual model of DNAPL distribution in fractured clay-rich soils.

Table 1. Physical properties of the saprolite.

Hydraulic Conductivity: 1.5 x 10^{-5} to 1.1 x 10^{-7} m/s
Hydraulic Gradient: 0.06 to 0.1
Porosity: 10 to 53%
Fracture Aperture: 19 to 10 μm
Fracture Density: 5 to 200 per m

Laboratory Investigation of the Spread of TCE Contamination in Large Columns of Fractured Shale Saprolite

Objectives

The objectives of this study were to:

1. Experimentally determine whether "cubic law" derived fracture aperture are useful indicators of DNAPL entry in shale saprolite.
2. Experimentally determine whether dissolution and diffusion of TCE is sufficient to cause significant spreading of contamination through the matrix and possibly cause disappearance of the immiscible phase over a short time period.
3. Map the distribution of contamination resulting from a simulated spill using physical and chemical methods.
4. Determine if saprolite lithology exerts control over the flow or final distribution of contamination.

Experiments

TCE spills were simulated using two columns that were carefully excavated and transported back to the lab. TCE was injected with a system that primarily consisted of a high-precision digital screw pump attached to a computer controller and a data logger. Prior to injection, the TCE was dyed with Nile Red, a fluorescent dye that is soluble in TCE but insoluble in water. Injections continued until the dyed TCE was seen in the effluent. At this point the columns sat for a period of time (28 and 10 days) to allow for dissolution and diffusion of the contamination. The columns were then dismantled by taking horizontal slices spaced 9 cm apart. During the dismantling process, photographs were taken under both natural light and short-wave ultraviolet light to detect the dye. A sampling technique, known as microcoring (figures 3 & 4), was used to chemically analyze the spread of contamination with a gas chromatograph. In addition to these techniques, lithology mapping was performed at a later date after the contamination had a chance to volatilize.

Figures 3 and 4. Collection of microcore samples and final sampling pattern. Each sampling point was 1.25 cm apart and each sample was roughly 0.6 cm in diameter and 1.25 to 2 cm deep. Each sample was dropped into a vial of of methanol to extract the TCE from the soil and subsequently diluted with pentane prior to analysis with a Shimadzu GC-14A gas chromatograph equipped with an ECD detector.

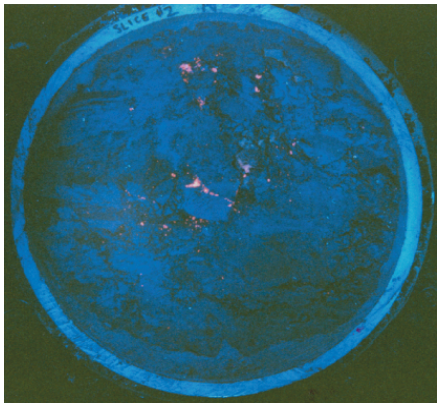


Figure 5. Column 2, slice 2 under uv light. Note fluorescence along fracture at center.

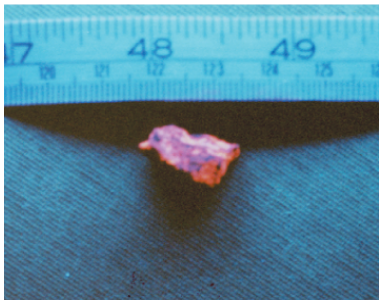


Figure 6. Small ped under UV light showing surface stains from fracture flow of dyed TCE.

Conclusions and Implications

The results of the experiments shed light on the processes that control the distribution and fate of a typical DNAPL spill in fractured clay-rich material.

1. Cubic law derived values for fracture aperture can yield misleading entry pressure values for DNAPLs, both over- and underestimating the entry aperture.

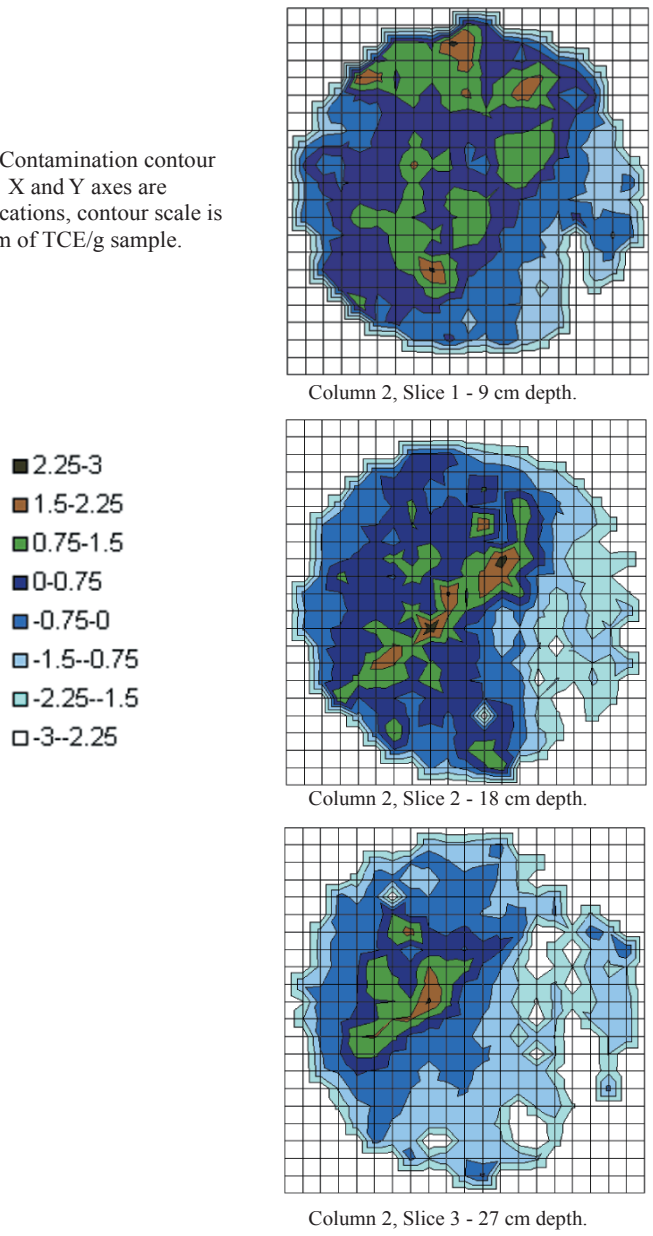
2. Immiscible phase TCE "disappeared" during the short period allowed for dissolution and diffusion and contamination spread throughout much of the available porosity of the saprolite.

3. Dye stained fractures and root holes reveal discrete and erratic flow paths for a typical DNAPL.

4. Clay-rich limestone saprolite contained the highest TCE concentrations, but preferential flow paths along fractures were most prevalent in the blocky siltstone/shale saprolite.

This study shows that even small DNAPL spills have the potential to contaminate large amounts of fractured material. Spreading of DNAPLs from fractures, due to both immiscible phase matrix entry and dissolution and diffusion, has the ability to limit the extent of contamination by "soaking up" the spill. However, while these processes may help to localize the contamination, they also make it very difficult to remove DNAPL contamination using conventional pump-and-treat remediation strategies and they can lead to long-term contamination problems.

Figure 7. Contamination contour mapping. X and Y axes are sample locations, contour scale is log of ppm of TCE/g sample.



Column 2, Slice 1 - 9 cm depth.

Column 2, Slice 2 - 18 cm depth.

Column 2, Slice 3 - 27 cm depth.

Natural Attenuation of TCE in Fractured and Weathered Shale at the Oak Ridge Reservation, Oak Ridge, TN

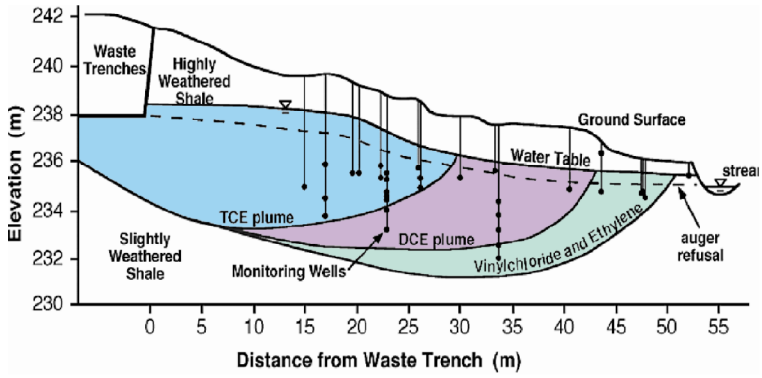
Objectives:

The objectives of this study were to:

1. Evaluate natural attenuation of TCE at a site of fractured weathered shales
2. Describe the distribution of volatile organic carbons (VOC) and electron acceptors/donors
3. Describe the microbial community structure and identify potential microorganisms involved in biodegradation of TCE

Introduction:

A field example of suspected biodegradation of chlorinated solvents in fractured shale is at a former disposal site in WAG5 at the Oak Ridge Reservation. A 50 m long contaminant plume has been detected in the fractured shale adjacent to buried waste trenches. The monitoring site is located in the southwest portion of WAG5 (figure 8) and consists of multilevel sampling wells along discharge zone adjacent to the trenches.



Figures 8 and 9. The field site at WAG5 consists of a transect of wells running from the waste storage trench downslope towards a small stream. The contamination plume exhibits a zonation of TCE and its daughter products with distance from the trench.

Results:

VOC Results:

- TCE and its anaerobic daughter products are located at a site of fractured and weathered shale (figure 9)
- Concentration of VOC are highest near the trenches with decreasing concentration away from trenches
- No VOC are present at the seep indicating potential aerobic cometabolism with methane for complete degradation of TCE
- Plume configuration changes (figure 10) during wet and during season with continuous source of TCE located in the matrix zone

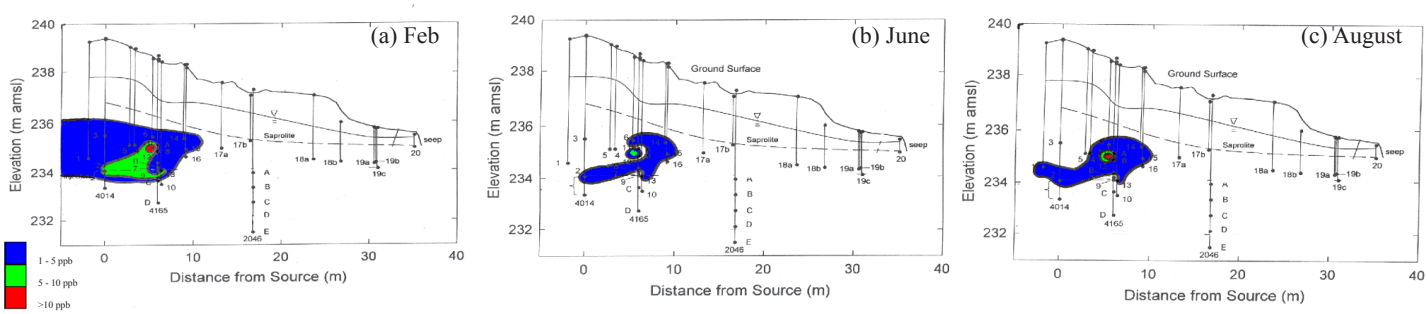


Figure 10. Concentration of dissolved TCE at WAG 5 during (a) February, (b) June, and (c) August of 1999.

Redox Potential:

- Site is general anaerobic throughout the year but aerobic at the seep
- Redox zonation previously describe in granular aquifers with iron, sulfate, and CO2 reduction was not evident at the site
- Methane is 1000x greater than any VOC and might be from other sources rather than being formed during reductive dechlorination of TCE

Microbial Community:
- Enrichments of wells at site (table 2) indicate present of iron-reducing bacteria, sulfate-reducing bacteria, methanogen, and methanotrophs in all wells
- Clone libraries (table 3) of two wells (10 and 11) indicate presents of a diverse community of microorganisms with some of the bacteria implicated in degradation of TCE
- Figure 11 shows the relationship of the Archaean clones to other known Archaean bacteria

Table 2. Most probable number of bacteria (CFU/ml).

Well Number	Methanogens	Iron Reducers	Anaerobic Heterotrophs	Sulfate Reducers	Methanotrophs
1	2.1	0.073	2400	0.03	210
2-4	>24	1.5	4600	4.6	39
2-5	>24	0.91	2400	>24	
2	2	0.036	4600	2.4	
10	>24	0.15	2400	0.15	>2400
11	4.3	0.036	11000	4.6	
14	11	0.091	>24000	0	
19c	2.4	0.091	11000	0.23	9.3

Table 3. Organisms of interest from clone libraries of wells 10 and 11.

- 4 unknown organisms similar to those from an aquifer undergoing intrinsic degradation of chlorinated solvents
- *Clostridium bifermentans* (PCE degrader)
- Sulfate and Iron reducing organisms
  - *Thermodesulfovibrio*
  - *Pelobacter*
  - *Desulfonema ishimotei*
  - *Geobacter sulferreducens* and *arculus*
- *Synthrophus* (propionate degrading)
- *Dechlorimonas* (chlorinated solvent degrader)
- 5 Methanogen strains

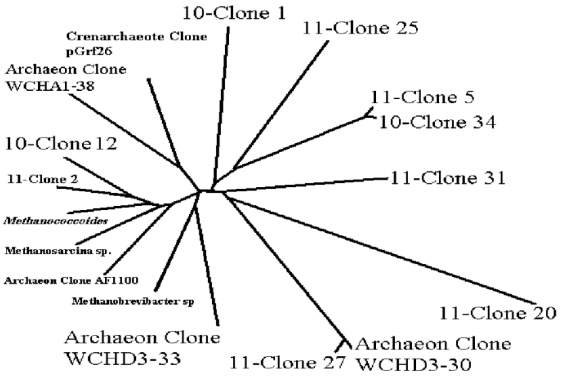


Figure 11. Phylogenetic tree of Archaean bacteria from wells 10 and 11.

Conclusions:

1. Biodegradation of chlorinated solvents can occur in fractured and weathered shale and is influenced by the structure of the shale
2. Data suggests a possible mechanism for natural attenuation of TCE being anaerobic biodegradation followed by aerobic biodegradation
3. Redox zonation that have been previously describe for granular aquifers is not evident at the field scale therefore iron reduction, sulfate reduction, and methanogenesis occurring at the same site.
4. A combination of monitoring of TCE and daughter products, redox potential, and microbial community structure aid in evaluation of contaminated site
5. This study refines the conceptual model of biodegradation in fractured shale

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