Movement of Trichloroethylene into Caliche

B.A. Schumacher[a], K.E. Snyder[b], M.M. Minnich[b], J.H. Zimmerman[b], and K. Al-Khafaji[a]

[a]United States Environmental Protection Agency, Office of Research and Development, NERL, ESD, CMB, P.O. Box 93478, Las Vegas, Nevada, USA 89119
[b]Lockheed Martin Environmental Services, 980 Kelly Johnson Drive, Las Vegas, Nevada, USA 89119

Abstract

This study evaluated the premise that caliche would act as an effective barrier to the downward movement of trichloroethylene (TCE) should a surface spill occur. Dyed TCE was applied to a soil near Las Vegas, Nevada, having petrocalcic and cemented calcic horizons. Liquid TCE was traced as dye-stained soil after its application from a point source. Mean infiltration rates were 0.9 L h^{-1} in the first study plot and 0.2 L h^{-1} in the second study plot with the difference being attributed to elevated water contents in the soil following a storm event during the application of TCE at the second plot. The TCE infiltrated downward and outward from the application points in relatively compact, symmetrical patterns. There were irregularities in the dye pattern at the millimeter and centimeter scale along the advancing front, particularly within the platy structure of the cemented horizons. The dyed TCE moved first along plate surfaces, then into peds along preferential flow paths, and finally throughout the matrix by capillary flow. Subsurface vapor concentrations were measured below the first study plot to evaluate TCE vapor movement. The vapor moved readily through the cemented horizons, with the vapor sorbers intercepting an average of 6900 ng during the first 5 days after TCE was applied. The quantity sorbed decreased approximately 30%, 18%, 18%, and 58% per week after the TCE-contaminated soil was excavated.

Introduction

Caliche is "a general term for a prominent zone of secondary calcium carbonate accumulation in surficial materials .... Finely crystalline calcium carbonate forms a nearly continuous surface-coating and void-filling medium in geologic (parent) materials. Cementation ranges from weak ... to very strong .... Most petrocalcic and some calcic horizons are caliche" (Soil Survey Staff, 1997). In this poster, caliche is used as a synonym for petrocalcic horizons and cemented or indurated calcic horizons (Soil Survey Staff, 1998). Caliche is typically massive in structure, may be platy, and ranges in thickness from several centimeters to several meters. It may occur centimeters to many meters below the land surface. Its geographic extent is broad. A search of the USDA Natural Resources Conservation Service state soil geographic (STATSGO) database found 10 million ha of soils with petrocalcic horizons distributed throughout the southwestern and western United States.

Where well-cemented caliche is present between the land surface and groundwater, this physically restrictive material may impede the downward movement of non-aqueous phase liquids (NAPLs). Based on its gross morphology, caliche is frequently referred to as *nature's concrete* and is presumed to act as a monolithic restrictive layer in the vadose zone. Such casual references and presumptions led to questions about how spilled NAPLs move through caliche.

Further, certain state laws in the southwestern United States require that if a NAPL spill is suspected or has occurred, that a monitoring or sampling well must be drilled to a given depth below the soil surface regardless of the presence or lack of caliche. These laws led to concerns that if the caliche acts as an effective barrier to the downward flow of spilled NAPLs but the law requires a hole be drilled through the caliche to reach the required depth, the sampler has just opened an effective drain hole that will lead to accelerated NAPL movement toward the underlying ground water.

Objectives

The objectives of this study were: (1) to determine if caliche acts as an effective barrier to the downward movement of trichloroethylene (TCE) and (2) to monitor the movement of the dyed liquid TCE, and its associated gaseous phase, through the soil and caliche.

Materials & Methods

Site Description

Experiments were conducted from late July through September 1998 at the U.S. Department of Energy's Nevada Test Site, 140 km northwest of Las Vegas, Nevada. Soils (loamy-skeletal, mixed, thermic, shallow Argic Petrocalcids) at the site have developed in alluvium and an overlying 10- to 15-cm thick eolian mantle. The alluvium is derived from local tuff and clastic rocks, while the eolian sediment results from aggradation of dust blown from playas in the region. A 30 m long, 1.5 m deep trench at the study site provided a very good exposure for studying the soil and caliche (Figure 1). Throughout the trench, the caliche had a carbonate morphology indicative of substantial pedogenic carbonate accumulation. All but the finest pores in the matrix were plugged and cemented (stage III) with carbonates and in many places, a laminae of pure carbonate overlies the plugged zone (stage IV) (Gile et al., 1966; Nettleton and Peterson, 1983).

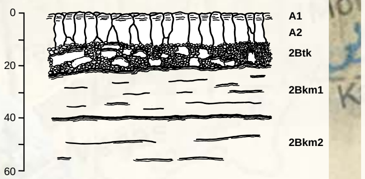

Figure 1. *Soil morphology along the exposed trench face.*

The Study Plots

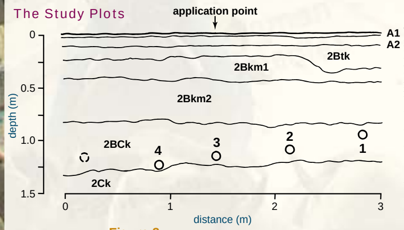

Figure 2. *Location of boreholes beneath Study Plot 1.*

The first study plot was about 1 m on a side, having blackbrush shrubs on three sides and the trench on the fourth side. Four vapor monitoring holes were drilled horizontally into the 2BCk horizon underneath the plot from the trench (Figure 2). Borehole 3 was directly below the center of the plot. A fifth borehole (not shown) was located 20 m to the right of Borehole 1 and served as a control. Each borehole was 2.25 m long, 3 cm in diameter, and approximately 1 m below the ground surface.

At the plot center, a 2-L Teflon™ separatory funnel was suspended from a ring stand. One end of a short length of Tygon tubing was attached to the funnel stopcock and the other end of the tubing was placed in a small hole (approximately 4 cm deep and 4 cm in diameter) excavated in the soil below the funnel. The small hole served as the reservoir from which TCE infiltrated into the soil.

Before applying TCE to the soil, an EMFLUX passive vapor sorber (Quadrel Services, Clarksburg, MD) was placed in each borehole using a 2.5 m long length of Teflon™ tubing (6.35-mm o.d. and 4.76-mm i.d.). One meter of the tubing at the end containing the sorber was perforated at 2.5-cm intervals with four, 2-mm diameter holes. No sorbers were placed directly below the application reservoir. Sorbers were positioned vertically below the application reservoir but about 0.5 m laterally back from the trench face from the TCE spill point. The boreholes were sealed with a fast-setting cement that contained no organic compounds. After TCE was applied to the plot, the sorbers and tubing were replaced every 5 to 8 days for 5 weeks. Sorbers were transported for analysis in 20-mL, crimp-sealed glass vials and analyzed using a SRI GC with a thermal desorber and dry electrolytic conductivity detector. Quantitation limits were approximately 30 ng TCE.

The First Spill

Approximately 6 L of reagent-grade TCE dyed with Oil Red O were applied to the soil in 2 days (Table 1). Liters 2 through 6 were added consecutively. During the addition of each liter, TCE was maintained in the reservoir at a height of 3 to 4 cm. Excavation of the study plot began 4 days after the last liter was added and took 2 days to complete. The plot was excavated in 1- to 5-cm thick lifts until no dyed soil was visible. In order to document the pattern of red dye, photographs and cross-sectional measurements were made at the top of each soil horizon and in the thicker horizons.

The Second Spill

A second study plot (slightly smaller than 1 m by 1 m) was established 2.5 m from the first plot. The setup for applying TCE to the soil (i.e., funnel, tubing, reservoir, etc.) was identical to that used for the first plot. Six liters of dyed TCE were added intermittently throughout a 7-day interval (Table 1). The first two liters and the fourth and fifth liters were added consecutively. During all additions, the TCE was maintained in the reservoir at a height of 3 to 4 cm. Excavation of the study plot began 7 days after the last liter was added and followed the same system used at the first plot.

Liter	Date	Infiltration period (h)	Infiltration rate (L h^{-1})
STUDY PLOT 1			
1	29 July	1710-1920	0.4
2	30 July	0922-1005	1.4
3	30 July	1006-1054	1.2
4	30 July	1055-1154	1.0
5	30 July	1156-1321	0.7
6	30 July	1322-1450	0.7
STUDY PLOT 2			
1&2	9-10 Sept.	1725-0625	0.1
3	11 Sept.	1039-1658	0.2
4&5	14 Sept.	1111-1755	0.3
6	15 Sept.	1020-1316	0.3

Table 1.
TCE application dates, infiltration periods, and infiltration rates.

Results

Study Plot 1

At the ground surface, the dye extended radially about 18 cm from the center of the reservoir (Figure 3). The edge of the circle was wavy, having an outline interwoven around pebbles of the desert pavement. Four centimeters below the ground surface, in the upper part of the A2 horizon, the dye formed a circle 44 cm in diameter. Near the bottom of the A2 horizon, the dye circle expanded to about 53 cm in diameter. The dye maintained this same shape and size for about 20 cm into the caliche, where it abruptly tapered and ended 36 cm below the ground surface (Figure 4). Both A horizons and the central part of the caliche were darkly strained. Throughout the excavation, the lateral dye front was observed to be undulose, but abrupt, with crenulations up to several centimeters.

Sorbers retrieved 5 days after the TCE was applied had very high concentrations of TCE (Figure 5), ranging from 6000 ng in Borehole 4 to 7600 ng in Borehole 2. The remaining four sampling intervals were sampled after source removal via excavation of the dyed, TCE-contaminated soil. The mean concentration of the second set of sorbers (4825 ng per sorber) was 30% less than that of the first set. Mean TCE concentrations declined in the following two sampling intervals by about 18% per period. Sorbers from the fifth set had a mean concentration less than the fourth set, and like the change between the first and second set of sorbers, the decline was substantial, 58%. No TCE was detected in the background borehole 20 m away.

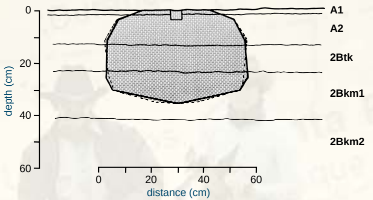

Figure 3. *Cross-section of the dyed soil at Study Plot 1. Solid lines indicate measurements made north-south and broken lines indicate measurements made east-west through the dye pattern.*

Figure 4.
Clod from the 2Bkm1 horizon (from Study Plot 1) showing the abrupt dye front at the bottom of the dye pattern. The lens cap is 5.5 cm in diameter.

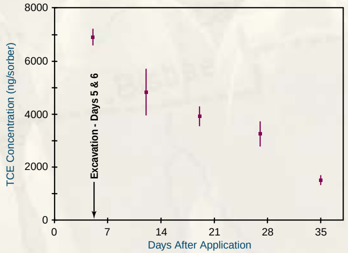

Figure 5. *Change in the mean TCE concentration with time. Error bars are ± 1 standard deviation (n = 4 for the first three sampling periods, n = 3 for the fourth period, and n = 7 for the fifth period).*

Study Plot 2

At the ground surface, the dye extended radially about 15 cm from the center of the reservoir (Figure 6). As at the first study plot, the edge of this circle was wavy and interwoven with pebbles of the desert pavement. At the A1-A2 horizon boundary (1 cm below the ground surface), the dye formed a circle 40 cm in diameter (Figure 7a) and at the A2-2Btk horizon boundary (top of the caliche), the dye expanded to 55 cm in diameter. The A horizons were dark red and uniformly stained throughout. The coarse prismatic structure of the A2 horizon had limited effect on the lateral movement of dyed TCE. The dyed TCE expanded throughout the 2Btk horizon and reached a maximum of 69 cm in diameter at the top of the 2Bkm1 horizon (Figure 7b). The dyed area tapered slightly throughout the next 6 cm. The dye front was undulose with crenulations of up to several centimeters. The stain was darkest and most uniform at the center (beneath the reservoir), with a lighter red halo 5 to 10 cm wide along the dye front.

As in the first plot, the dye front stopped abruptly, yet it was evident that the caliche behind the dye front was not uniformly stained. The caliche behind the dye front was darkly stained on the top, bottom and side (or end), however, the interior was variegated with colors ranging from white (unstained areas) to red (Figures 8a and 8b). Contrasting colors are often juxtaposed centimeters to millimeters from each other. In certain locations, the darker colors can be visually associated with fractures and macropores (Figure 8a) while in other locations, no such association can be made.

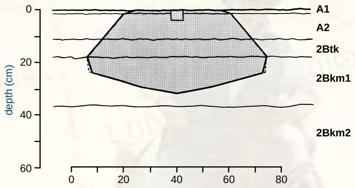

Figure 6. *Cross-section of the dyed soil at Study Plot 2. Solid lines indicate measurements made north-south and broken lines indicate measurements made east-west through the dye pattern.*

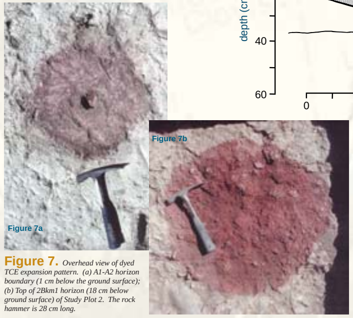

Figure 7. *Overhead view of dyed TCE expansion pattern. (a) A1-A2 horizon boundary (1 cm below the ground surface); (b) Top of 2Bkm1 horizon (18 cm below ground surface) of Study Plot 2. The rock hammer is 28 cm long.*

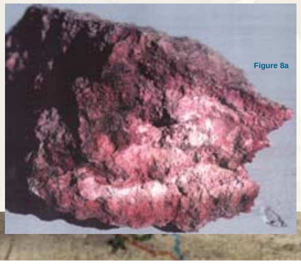

Figure 8. *Dye distribution patterns within caliche. (a) sample (3.5 cm thick) taken part way between the center and edge of the dye front in the 2Bkm1 horizon of Study Plot 2; (b) sample (3 cm thick) taken from the lateral edge of the dye front in the 2Bkm1 horizon of Study Plot 2.*

Discussion

The dye pattern at each study plot was remarkably symmetric, showing no erratic changes in direction or shape as the dyed TCE moved down through the soil. The 3-dimensional dye pattern at the first plot was cylindrical and that at the second plot was shaped like a top.

During excavation of Study Plot 2, the dyed soil was examined for clues that would explain how the liquid TCE moved into and in the caliche. While the A horizons and most of the caliche were intensely stained red, the caliche at and near the dye front was unevenly stained. This uneven staining is interpreted as evidence of preferential flow and occurred at the millimeter and centimeter scale. Apparently, TCE moved first along plate boundaries (pedal flow). Plates at the dye front were stained on the tops, sides, and bottoms, and had variegated interiors, the later demonstrating that even within the plates, TCE movement was not uniform (Figures 8a and 8b). Smaller-scale preferential flow was documented by staining along matrix irregularities, such as fractures and biopores. A little closer to the central axis of the dye pattern (i.e., beneath the reservoir) the entire caliche matrix was stained, probably by capillary flow.

TCE vapors moved readily through the caliche. While liquid TCE was present in the soil (the first 5 days), the mean quantity of TCE intercepted for the 5-day period was 6900 ng TCE. Upon removal of the dyed soil, vapor concentrations in the boreholes declined, except at Borehole 1 where the concentration increased slightly from the first sampling period to the second sampling period. The concentration increase may represent measurement error or it may reflect a delay in the arrival of the advancing vapor front at Borehole 1 which was the borehole farthest from the source (approximately 2 m from the application reservoir). The quantity of vapors collected showed a linear decline from Day 14 through Day 35.

Conclusions

The caliche found in the soils at the Nevada Test Site were not effective barriers to the downward flow of TCE. Liquid TCE moved slowly and essentially vertically through caliche in a relatively compact, symmetrical pattern, except where macropores allowed more rapid preferential flow ahead of a capillary wetting front.

TCE vapors also moved readily through the caliche. After the liquid TCE-contaminated soil was removed, vapors continued to permeate downward through the soil and caliche with mean residual soil vapor concentrations declining approximately 30%, 18%, 18%, and 58% per week.

References

Gile, L.H., Peterson, F.F. and Grossman, R.B., 1966. Morphological and genetic sequences of carbonate accumulation in desert soils. Soil Science 101: 347-360.

Nettleton, W.D. and Peterson, F.F., 1983. Aridisols. In: Wilding, L.P., Smeck, N.E., Hall, G.F. (Editors), Pedogenesis and Soil Taxonomy. II. The Soil Orders. Elsevier, Amsterdam, pp. 165-215.

Soil Survey Staff, 1997. National Soil Survey Handbook (Title 430-VI). Part 629 - Glossary of Landforms and Geologic Terms. U.S. Department of Agriculture, Natural Resources Conservation Service, Washington, DC.

Soil Survey Staff, 1998. Keys to Soil Taxonomy. U.S. Department of Agriculture, Natural Resources Conservation Service, Washington, DC.

022CMB01