Water-Resources Investigations Report 97-4097

Preliminary Conceptual Models of the Occurrence, Fate, and Transport of Chlorinated Solvents in Karst Regions of Tennessee

Prepared by the
U.S. GEOLOGICAL SURVEY

in cooperation with the
TENNESSEE DEPARTMENT OF ENVIRONMENT
AND CONSERVATION, DIVISION OF SUPERFUND

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By WILLIAM J. WOLFE, CONNOR J. HAUGH, ANK WEBBERS,
and TIMOTHY H. DIEHL

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Nashville, Tennessee

1997

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

For additional information write to:

District Chief
U.S. Geological Survey
810 Broadway, Suite 500
Nashville, Tennessee 37203

Copies of this report may be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, Colorado 80225-0286

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CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
micron (µ)	0.00003937	inch
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square kilometer (km^2)	0.3861	square mile
hectare (ha)	2.471	acre
liter (L)	0.2642	gallon
cubic meter (m^3)	35.31	cubic foot
kilogram (kg)	2.205	pounds
grams per cubic centimeter (g/cm^3)	62.43	pounds per cubic foot
liter per second (L/s)	15.85	gallon per minute
cubic meter per day (m^3/d)	264.2	gallon per day
centimeter per second (cm/s)	2,835	foot per day
meter per day (m/d)	3.281	foot per day
meter squared per day (m^2/d)*	10.76	foot squared per day

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:
°F = 1.8 x °C + 32

Sea level: In this report “sea level” refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

*Transmissivity: In this report transmissivity is expressed as meter squared per day (m^2/d)—The standard unit for transmissivity (T) is cubic meter per day per square meter times meter of aquifer thickness “$[(m^3/d)/m^2]m$” or cubic foot per day per square foot times foot of aquifer thickness “$[(ft^3/d)/ft^2]ft$.” These mathematical expressions reduce to meter squared per day “(m^2/d)” or foot squared per day “(ft^2/d).”

ABBREVIATIONS AND ACRONYMS

DNAPL	Dense Non-Aqueous Phase Liquid
DCE	Dichloroethylene
MCL	Maximum Contaminant Level
PCE	Perchloroethylene or Tetrachloroethylene
1,1,1-TCA	1,1,1-Trichloroethane
TCE	Trichloroethylene
U.S. EPA	United States Environmental Protection Agency
USGS	United States Geological Survey

GLOSSARY

Capillary pressure. Difference in pressure across the interface between two fluids.

Conduit flow. Water movement through *discrete* passages that are large enough for turbulent flow to occur—typically greater than 5 millimeters across.

Diffuse flow. Laminar water movement in granular or fractured media through *networks* of small, interconnected openings.

DNAPL. An acronym for denser-than-water nonaqueous-phase liquids.

DNAPL pool. A contiguous accumulation of DNAPL with a hydrostatically level upper surface. In the absence of capillary forces, the upper surface of a pool is typically flat and horizontal. DNAPL pools are typically greater than a few millimeters in depth.

Karst. Landscape in which chemical dissolution has enlarged joints, fractures, bedding planes, or other openings in soluble, underlying bedrock; may be characterized by sinkholes, caves, and disappearing streams.

Macropore. A crack, pipe, fissure, or other opening in soil or regolith greater than 1 millimeter across; formed by plant growth, animal activity, shrinking or swelling due to changing temperature or moisture content, mass movement, and numerous other processes; macropores form preferential flow paths for water and other fluids.

Matrix diffusion. Molecular diffusion of a dissolved chemical from a fracture into pores within adjacent rock or soil.

Regolith. Unconsolidated earth material including soil, residuum from weathered bedrock, and sediments.

Residual DNAPL. Isolated blobs or ganglia of DNAPL held in porous or fractured media following free drainage. Residual DNAPL masses are distinguished from pools by (1) their discontinuous nature; (2) their relatively small size—typically less than a few millimeters in any dimension; and (3) the dominance of capillary, rather than hydrostatic, forces in determining the shape and location of their free surfaces.

Residual saturation. Fraction of the pore space in a porous granular or fractured medium that retains residual DNAPL immediately after free drainage has occurred.

Preliminary Conceptual Models of the Occurrence, Fate, and Transport of Chlorinated Solvents in Karst Regions of Tennessee

By William J. Wolfe, Connor J. Haugh, Ank Webbers, *and* Timothy H. Diehl

Abstract

Published and unpublished reports and data from 22 contaminated sites in Tennessee were reviewed to develop preliminary conceptual models of the behavior of chlorinated solvents in karst aquifers. Chlorinated solvents are widely used in many industrial operations. High density and volatility, low viscosity, and solubilities that are low in absolute terms but high relative to drinking-water standards make chlorinated solvents mobile and persistent contaminants that are difficult to find or remove when released into the ground-water system. The major obstacle to the downward migration of chlorinated solvents in the subsurface is the capillary pressure of small openings. In karst aquifers, chemical dissolution has enlarged joints, bedding planes, and other openings that transmit water. Because the resulting karst conduits are commonly too large to develop significant capillary pressures, chlorinated solvents can migrate to considerable depth in karst aquifers as dense nonaqueous-phase liquids (DNAPL's). Once chlorinated DNAPL accumulates in a karst aquifer, it becomes a source for dissolved-phase contamination of ground water. A relatively small amount of chlorinated DNAPL has the potential to contaminate ground water over a significant area for decades or longer.

Conceptual models are needed to assist regulators and site managers in characterizing chlorinated-solvent contamination in karst settings and in evaluating clean-up alternatives. Five preliminary conceptual models were developed, emphasizing accumulation sites for chlorinated DNAPL in karst aquifers. The models were developed for the karst regions of Tennessee, but are intended to be transferable to similar karst settings elsewhere. The five models of DNAPL accumulation in karst settings are (1) trapping in regolith, (2) pooling at the top of bedrock, (3) pooling in bedrock diffuse-flow zones, (4) pooling in karst conduits, and (5) pooling in isolation from active ground-water flow.

More than one conceptual model of DNAPL accumulation may be applicable to a given site, depending on details of the contaminant release and geologic setting. Trapping in regolith is most likely to occur where the regolith is thick and relatively impermeable with few large cracks, fissures, or macropores. Accumulation at the top of rock is favored by flat-lying strata with few fractures or karst features near the bedrock surface. Fractures or karst features near the bedrock surface encourage migration of chlorinated DNAPL into karst conduits or diffuse-flow zones in bedrock. DNAPL can migrate through one bedrock flow regime into an underlying flow regime with different characteristics or into openings that are isolated from significant ground-water flow.

As a general rule, the difficulty of finding and removing DNAPL increases with depth, lateral distance from the source, and complexity of the ground-water flow system. The prospects for mitigation are generally best for DNAPL accumulation in the regolith or at the bedrock surface. However, many such accumulations are likely to be difficult to find or remove. Accumulations in bedrock diffuse-flow zones or in fractures isolated from flow may be possible to find and partially mitigate, but will likely leave significant amounts of contaminant in small fractures or as solute diffused into primary pores.

INTRODUCTION

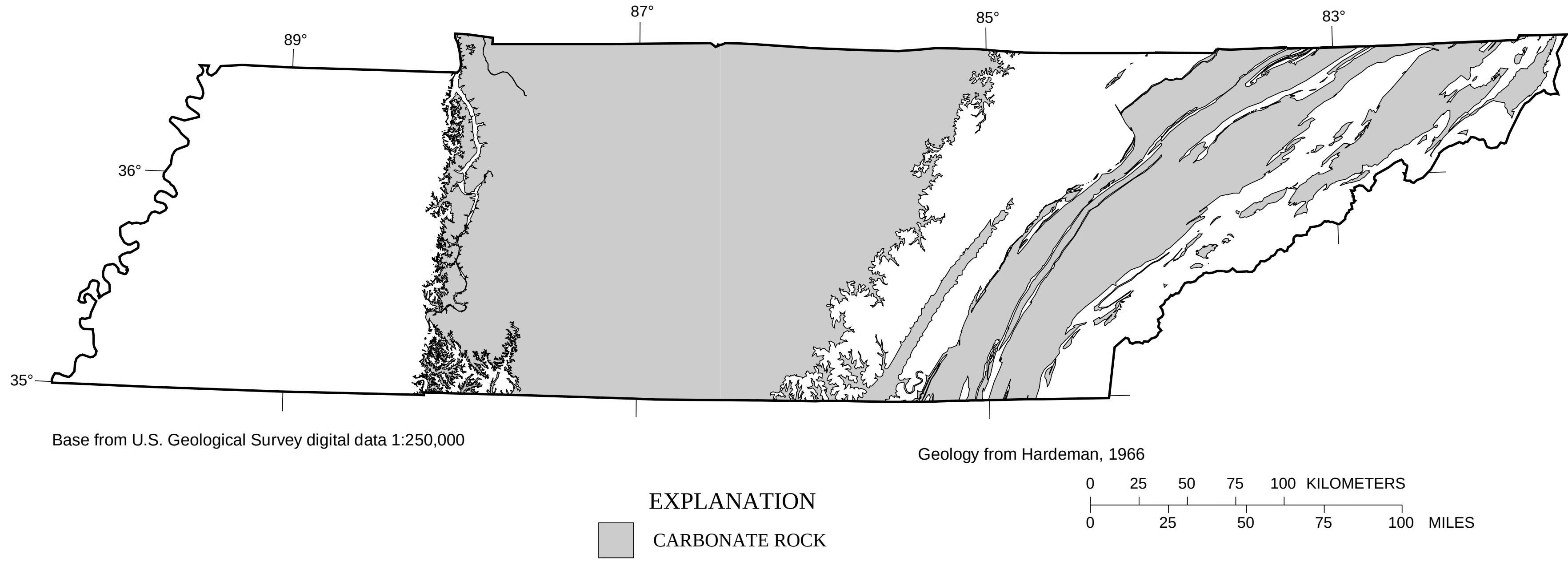
Two of the most problematic topics in contaminant hydrogeology are chlorinated solvents and **karst** (bold terms can be found in Glossary) aquifers. Chlorinated solvents are one of the most widespread classes of ground-water contaminants in the United States (Pankow and Cherry, 1996). The physical and chemical properties of these organic chemicals make them difficult to find or remove once they have entered the subsurface (Schwille, 1988; Cohen and Mercer, 1993; Pankow and Cherry, 1996). Karst aquifers are units of water-soluble rocks, such as limestone, in which chemical dissolution has enlarged joints, bedding planes, and other water-transmitting openings (White, 1988; Ford and Williams, 1989; Quinlan and others, 1992). Chemical dissolution of water-transmitting openings gives karst aquifers hydraulic properties that differ radically from those of other aquifers (Ford and Williams, 1989; Quinlan, 1989; Field, 1993). The presence of either chlorinated solvents or karst development at a contaminated site increases the complexity, difficulty, and expense of site characterization and mitigation (Quinlan, 1989; Cohen and Mercer, 1993; Field, 1993; Pankow and Cherry, 1996), but the combination of these two factors is especially problematic. Because chlorinated **DNAPL's** are denser and less viscous than water, they migrate readily through subsurface openings, both above and below the water table (Cohen and Mercer, 1993). Karst aquifers are distinguished by an abundance of large subsurface openings and are therefore especially vulnerable to chlorinated-solvent contamination. The release of chlorinated solvents into karst aquifers presents a difficult challenge to environmental scientists, managers, and regulators.

Chlorinated solvents, such as perchloroethylene (PCE) and trichloroethylene (TCE), are widely used in manufacturing, cleaning and degreasing, and other industrial operations (Schwille, 1988; Pankow and Cherry, 1996). These compounds are generally produced and used as organic liquids but, when released into the environment, can also exist in other phases. Chlorinated solvents can sorb to organic matter or mineral surfaces, volatilize into vapor, or dissolve into aqueous solution. In aqueous solution, chlorinated solvents can enter drinking-water supplies and threaten human health. Drinking-water standards for chlorinated solvents are typically three to six orders of magnitude lower than their solubilities in water (Pankow and Cherry, p. 14, 1996). A relatively small amount of chlorinated solvent has the potential to contaminate ground water over a large area for decades or longer (Cohen and Mercer, 1993; Pankow and Cherry, 1996).

Until the 1970's, disposal of chlorinated solvents was routinely carried out by pouring the solvents onto the land surface in the expectation that they would quickly evaporate. Such practices resulted in large quantities of chlorinated solvents being introduced to the ground-water system. Since scientists first became aware of ground-water contamination from chlorinated solvents (Schwille, 1988), these compounds have been documented at hundreds of sites in the United States (Pankow and Cherry, 1996). Restoring ground-water quality in and around sites where chlorinated solvents have been released requires an understanding of how these contaminants behave in the subsurface. To date, the vast majority of research on the subsurface behavior of chlorinated solvents has focused on nonkarst settings (Cohen and Mercer, 1993).

The term "karst" has been defined many ways (Cvijic, 1893; Sweeting, 1972; Quinlan, 1978; Jennings, 1985; Quinlan and others, 1992). In this report, "karst" refers to a landscape underlain by rocks in which chemical dissolution has enlarged joints, fractures, bedding planes, or other openings through which water flows (Quinlan and others, 1992). In Tennessee, this definition applies to areas underlain by carbonate rocks—more than two thirds of the State (fig. 1). The carbonate rocks of Tennessee are generally of Paleozoic age—about 230 to 600 million years old (Miller, 1974). These rocks vary considerably in lithology and hydraulic characteristics, but in comparison with many younger carbonate rocks, they have high bulk density and low primary porosity (Brahana and others, 1988). Because primary pores, the spaces between the original sediment grains, have been filled through compaction and cementation during geologic time, the major flow paths for water and other fluids within these dense carbonate rocks are secondary openings such as fractures, joints, and bedding-plane partings. The frequency of such openings and the degree to which they have been enlarged by chemical dissolution are the major factors determining the hydraulic characteristics of dense carbonate rocks in Tennessee and in similar geologic settings elsewhere.

Karst aquifers within carbonate-rock units are important sources of water supply across most of Middle Tennessee and large areas of East Tennessee. In 1990, karst aquifers provided an average 1.84 x 10^5 cubic meters (48.6 million gallons) per day of water to Tennessee public water supplies—about 18 percent of



Base from U.S. Geological Survey digital data 1:250,000

Geology from Hardeman, 1966

Figure 1. Distribution of carbonate rocks in Tennessee.

ground-water withdrawals for public supply statewide and 87 percent of public-supply withdrawals in Middle and East Tennessee (Hutson, 1995). Approximately 15 percent of households in carbonate-rock areas of Tennessee, about half a million people, rely on private wells and springs for their water supply (estimate based on data from U.S. Bureau of Census, 1996). The importance of karst aquifers to water supply and their vulnerability to contamination by chlorinated solvents are reasons to seek improved understanding of how chlorinated solvents behave in karst aquifers.

The U.S. Geological Survey (USGS), in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund, is conducting a study of the occurrence, fate, and transport of chlorinated solvents in karst regions in Tennessee. One objective of this study is to develop conceptual models that describe the occurrence, fate, and transport of chlorinated solvents in karst aquifers of Tennessee.

This report presents preliminary results of the conceptual-model study of chlorinated solvents in karst settings. The scope of the report encompasses review and synthesis of relevant literature, examination and summary of data from 22 sites in Tennessee where chlorinated-solvent releases have occurred, and the development of conceptual models of chlorinated-solvent behavior in karst aquifers. The objectives of the report are to:

1. Summarize current understanding of:
    a. subsurface behavior of chlorinated solvents,
    b. water and contaminant movement in karst aquifers, and
    c. the geographic distribution and variability of karst aquifers in Tennessee.
2. Develop and present preliminary conceptual models of how chlorinated solvents behave in karst aquifers.
3. Document occurrence and characterization of chlorinated-solvent contamination at selected sites in Tennessee.

The body of the report is divided into five sections. The first section is a general overview of previous studies dealing with chlorinated-solvent contamination, contamination of karst aquifers, and the relatively few published studies of chlorinated-solvent contamination in karst. The second section provides a more detailed treatment of the physical and chemical properties of chlorinated solvents and how these properties affect the phase transformations and movement of chlorinated solvents in the subsurface. The third section reviews the characteristics of karst aquifers and their geological controls and presents a regionalization of karst settings in Tennessee with a description of each karst region. The fourth section integrates material from the previous sections to present five conceptual models of the accumulation of chlorinated solvents in different parts of karst aquifers and the implications of such accumulation for contaminant residence time, mitigation, and delivery to water supplies. Finally, the fifth section describes specific instances of chlorinated-solvent contamination in karst regions of Tennessee, with emphasis on characterization of site hydrogeology, contaminant-source-mass distribution, and the movement of dissolved contaminants into surrounding ground water.

The conceptual models presented in this report are preliminary in nature and are intended to serve as starting points in the site-specific analysis of chlorinated-solvent contamination in karst settings. Nothing in this report in any way reduces the critical importance of careful characterization of the environmental settings and contaminant distributions at specific sites. The geographic focus of this report is the karst regions of Tennessee. However, the concepts developed in the following sections are intended to be transferable to similar karst settings in dense carbonate rocks elsewhere.

PREVIOUS STUDIES

Few comprehensive studies of contamination of karst by chlorinated solvents have been published (Barner and Uhlman, 1995; Cary McConnell, University of Missouri, written commun., 1996; Robert Westly, SCS Engineers, written commun., 1996). Most articles relevant to this topic fall into the following categories:

- studies of chlorinated-solvent properties that consider karst briefly or not at all
- studies of karst properties and karst hydrogeology
- studies of contamination of karst that devote little or no attention to nonaqueous contaminants.

Published case studies of chlorinated-solvent contamination in karst are few. None meet current standards for definitive characterization of contaminated karst sites, nor the more stringent standards applicable to dense nonaqueous-phase liquid (DNAPL) contamination at such sites (Field, 1988a; Quinlan, 1989, 1994; Barner and Uhlman, 1995; Quinlan and others, 1995). A few case studies of DNAPL contamination in fractured rock are relevant to the potential for DNAPL movement in carbonate rocks with little dissolutional enlargement of fractures.

Studies of Chlorinated Solvents, with Emphasis on DNAPL

Chlorinated solvents present unique contamination problems when released onto or into the ground. A number of reports provide comprehensive descriptions of chlorinated-solvent contamination (Schwille, 1988; Mercer and Cohen, 1990; Wilson and others, 1990; Cohen and Mercer, 1993; Pankow and Cherry, 1996). A few of these reports discuss the movement and dissolution of DNAPL in fractured rock, but none treat karst as a separate type of setting. Several other reports discuss volatilization of DNAPL (Marrin and Thompson, 1987; Nitao and others, 1991), DNAPL movement in porous media (Kueper and others, 1989, 1993; Poulsen and Kueper, 1992; Michalski and others, 1995; Tuck and Iversen, 1995) and in fractures (Helton, 1987; Cherry, 1989; Quigley and Fernandez, 1989; Kueper and McWhorter, 1991; Ford, 1993), the dissolution of **DNAPL pools** (Johnson, 1987; Feenstra, 1990; Anderson and others, 1992; Johnson and Pankow, 1992; Uhlman, 1992), and the dissolution and diffusion of DNAPL from cracks into the rock or clay matrix (Vogel and Giesel, 1989; Watts and Cooper, 1989; Parker and others, 1994; Parker and Cherry, 1995; VanderKwaak and Sudicky, 1996).

Karst Studies

Many previous studies of karst exist. Comprehensive works include general texts on karst (Herak and Stringfield, 1972; Sweeting, 1972; Milanovic, 1981; White, 1988; Ford and Williams, 1989; Higgins and Coates, 1990), and discussions of carbonates, dissolution, and conduits (Bebout and others, 1979; Brahana and Hollyday, 1988; Brahana and others, 1988; White and White, 1989). Other studies particularly relevant to chlorinated-solvent contamination focus on properties of karst that control DNAPL movement and on the potential for contamination of karst ground water.

Studies of Karst Properties Affecting DNAPL Movement

Karst soils and subsoils typically have sufficient secondary porosity to allow infiltration of low-viscosity DNAPL (Thomas and Phillips, 1979; Watson and Luxmoore, 1986; Quinlan and Aley, 1987; Wilson and others, 1991a, 1991b). Other studies have reached the same conclusion for clays and clayey soils in general (Cherry, 1989; Everts and others, 1989; Wells and Krothe, 1989).

Sinkhole development creates opportunities for the direct introduction of contaminants into karst aquifers, and is controlled by a variety of geologic factors (Kemmerly, 1980, 1981; Magdalene and Alexander, 1995; White and White, 1995). Human activities, including the disposal of storm water and liquid and solid wastes, can contribute to karst subrosion and sinkhole development (Royster, 1984; Newton, 1987; Field, 1993).

Epikarst, the hydraulically important transition zone including the base of the **regolith** and the irregular and dissected bedrock surface, is the focus of only a few articles (Julian and Young, 1995). Epikarst is discussed (with or without the use of the term “epikarst”) in several more general reports (Field, 1988a, 1989, 1993; Ford and others, 1988; White, 1988; Quinlan and others, 1992) and in a few site studies (Chieruzzi and others, 1995; Glover and others, 1995).

Studies of Karst Contamination

Karst is more vulnerable to ground-water contamination than are many other hydrogeologic settings (Quinlan and others, 1992; Fetter, 1993; Field, 1993). Adequate characterization of contaminant movement in karst is difficult, and the use of approaches well-suited for other settings may produce ambiguous or misleading results (Field, 1988b; Alexander, 1989; Rubin, 1992; Quinlan, 1994; Barner and Uhlman, 1995). Dense immiscible contaminants may become isolated in or under sediment deposits commonly found in conduit systems (Gale, 1984; Palmer, 1986). The movement of the dissolved contaminant can be complex and unpredictable (Becher, 1989; Seiler and others, 1989; Sudicky and MacQuarrie, 1989; Jancin and Ewart, 1995). Various other authors have investigated specific cases of contamination (Harvey and Skelton, 1968; Alexander, 1989; Hannah and others, 1989; Waite and Thomson, 1993; Currens, 1995; Sasowsky and others, 1995).

Numerical models of multiphase flow have been developed for application to porous media in the laboratory setting (Guarnaccia and Pinder, 1992; Zhan, 1992; Al-Sheriadeh and Illangasekare, 1993), and have been applied also to karst field sites (Faust, 1985; Guswa, 1985; Faust and others, 1989). The difficulties of modeling aqueous flow in karst are well known (Quinlan and others, 1995). The necessity to model multiple-phase, density-driven flow greatly complicates the modeling task, particularly in extremely heterogenous, anisotropic karst settings. The extent to which digital modeling adds to the understanding of chlorinated-solvent contamination is debatable (Schmelling and Ross, 1989; Huling and Weaver, 1991; Cary McConnell, University of Missouri, written commun., 1996).

Site Studies of DNAPL Contamination in Karst and Fractured Rock

The movement of DNAPL's in karst landscapes has been studied in several locations, but only a few of these investigations have resulted in published reports (Cary McConnell, University of Missouri, written commun., 1996; Robert Westly, SCS Engineers, written commun., 1996). Near Ville Mercier, Quebec, chlorinated solvents penetrated 30 meters (m) of sandy glaciofluvial deposits, bypassed 3 m of clayey till, and entered the fractured sandy dolomite underlying the site (Martel, 1988). At the Bear Creek Burial Grounds at Oak Ridge National Laboratories in Tennessee, investigators reported DNAPL moving down the dip of steeply dipping shale and limestone (Doll, 1992; Kueper and others, 1992; Shevenell and others, 1992). At Pinto, West Virginia, TCE descended through the alluvium of the North Branch Potomac River and deep into karst bedrock, making complete remediation infeasible (Ford, 1993). Chieruzzi and others (1995) used well tests to demonstrate the dominance of **diffuse** over **conduit flow** in a southwestern Kentucky karst setting contaminated with DNAPL.

Studies have been performed at several sites above the Niagara Escarpment in and near Niagara Falls. Mercer and others (1983) studied the Love Canal landfill at Niagara Falls, New York. At the S-area landfill in Niagara Falls, the glaciolacustrine clay confining layer over the dolomite prevented descent of DNAPL; at the Hyde Park landfill, DNAPL is present near the base of the dolomite aquifer (Faust and others, 1989). McIelwain and others (1989) characterized a site near Smithville, Ontario, where a solution of oil, polychlorinated biphenyls, chlorinated solvents, and other organic compounds penetrated through 5 to 10 m of weathered glaciolacustrine silty clay, then moved downward along joints and horizontally along bedding planes through limestones and dolostones of the Niagara Escarpment.

Studies of DNAPL contamination at sites underlain by fractured noncarbonate rocks demonstrate that many such rocks contain sufficient small openings to allow penetration by DNAPL (Kraus and Dunn, 1983; Nichols and Gibbons, 1988; Holmes and Campbell, 1990; Kueper and others, 1992; U.S. Environmental Protection Agency, 1992a; National Research Council, 1994). These results are relevant to carbonate rocks in which little dissolutional enlargement has occurred. In most cases, field data show that DNAPL descended until the fracture system pinched out. In other cases, confining units stopped or deflected DNAPL movement (Becher, 1989; Lindhult and others, 1990).

PROPERTIES AND PROCESSES

The physical and chemical properties of chlorinated solvents govern their behavior in the environment. Important fluid properties include density, viscosity, solubility, and volatility. Important properties governing fluid-fluid and fluid-solid interactions include interfacial tension, wettability, **capillary pressure**, **residual saturation**, and relative permeability. Comprehensive descriptions of these properties and the physics of DNAPL movement are in Mercer and Cohen (1990), Cohen and Mercer (1993), and Pankow and Cherry (1996). The effects of these properties on the occurrence, fate, and transport of chlorinated DNAPL are summarized in this section. As the scope of this report is limited to chlorinated solvents, within the context of this report, the term DNAPL is used to describe the immiscible or nonaqueous phase of chlorinated solvents. As such, discussions of DNAPL within this report only apply to liquids with high density and low viscosity. Liquids with high density and high viscosity such as creosote and PCB oils are also DNAPL's, but because they are much less mobile in the subsurface, they behave differently and are not addressed in this report.

Pankow and Cherry (1988, 1996) recognized that chlorinated solvents have physical, chemical, and biological properties that make this class of compounds particularly likely to cause ground-water contamination (table 1). Properties for selected chlorinated solvents are listed in table .

The high densities and low viscosities of chlorinated solvents relative to water allow them to move readily downward as DNAPL through the subsurface under the influence of gravity. The exact pathway of downward migration is influenced by such factors as interfacial tension, capillary pressure, hydraulic gradients, structural controls, and the type and nature of openings in an aquifer.

Liquid interfacial tension between DNAPL and water develops because of the difference between the greater mutual attraction or cohesive forces of like molecules within each fluid and the lesser attraction of dissimilar molecules across the immiscible fluid interface (Cohen and Mercer, 1993). Completely miscible liquids have an interfacial tension of zero.

Wettability refers to the preferential spreading of one fluid over solid surfaces in a two-fluid system and depends on interfacial tension. The interaction of adhesive forces between the two fluids and the solid surface and cohesive forces within the fluids will usually result in one fluid having a greater affinity for the solid. The fluid with the greater affinity for the solid surface is the wetting fluid. In a DNAPL/water system, water is usually the wetting fluid and will preferentially coat the aquifer solids (fig. 2). Wettability is controlled by the properties of the two fluids and the composition of the solid surface.

The difference between the wetting fluid pressure and nonwetting fluid pressure is the capillary pressure. Capillary pressure depends on interfacial tension, wettability, and pore size or fracture aperture. Effects of capillary pressure explain much of the distribution and movement of subsurface DNAPL (Cohen

Table 1. Physical, chemical, and biological properties of the chlorinated-solvent compounds which have helped lead to extensive ground-water contamination by this compound class (From Pankow and Cherry, 1996)

[g/cm^3, grams per cubic centimeter; mg/L, milligrams per liter]

1. The high volatilities of the chlorinated solvents led to a false sense of security regarding how these chemicals must be handled. Historically, it was believed that chlorinated solvent released to the unsaturated zone would easily volatilize to the atmosphere. Thus, when poured on dry ground, although a chlorinated solvent may *appear* to be lost entirely to the atmosphere, some will be transported into the subsurface by gaseous diffusion, by infiltration of contaminated water, and as a moving DNAPL phase. And, once contamination reaches the saturated zone (including direct releases to the saturated zone), high volatility is of little assistance in removing the solvents: transport across the capillary fringe can be exceedingly slow (McCarthy and Johnson, 1993).
2. The high densities of the chlorinated solvents (1.2 to 1.7 g/cm^3) relative to that of water (1 g/cm^3) mean that if a sufficient volume of a typical chlorinated solvent is spilled, then liquid solvent may be able to penetrate the water table. In the saturated zone, the unstable nature of the solvent flow causes the solvent to form thin “fingers” which can lead to the collection of large amounts of solvent in one or more “pools” on top of less permeable layers. Since a pool presents a very low cross section to on-coming ground-water flow, absolute removal rates of dissolved solvent from the pool will usually be very low (Johnson and Pankow, 1992).
3. The relatively low viscosities of the chlorinated solvents allow relatively rapid downward movement in the subsurface. Chlorinated-solvent mobility in the subsurface increases with increasing density/viscosity ratios (Cohen and Mercer, 1993).
4. The low interfacial tension between a liquid chlorinated-solvent phase and water allows a liquid chlorinated solvent to enter easily into small fractures and pore spaces, facilitating deep penetration into the subsurface. Low interfacial tension also contributes to the low retention capacities of soils for chlorinated solvents.
5. The low *absolute* solubilities of the chlorinated solvents (typically on the order of hundreds of mg/L) mean that when a significant quantity of such a compound is spilled on the ground surface, liquid solvent will be able to migrate as a DNAPL phase in the subsurface, potentially accumulating as one or more pools on the tops of low permeability layers. The low solubility will then permit such pools to persist for decades to centuries (Johnson and Pankow, 1992).
6. The high *relative* solubilities of the chlorinated solvents mean that a solvent spill can cause ground-water contamination at levels which are high *relative* to concentrations which appear harmful to human health.
7. The low partitioning to soil materials exhibited by the chlorinated solvents means that soil and rock materials will bind these compounds only weakly. This applies to both the unsaturated and saturated zones. Thus, sorption to soils will not significantly retard the movement of a chlorinated solvent, and zones of contamination can grow essentially as quickly as the ground water can move.
8. The low degradabilities of the chlorinated-solvent compounds, either by biological means, or by abiotic-chemical reactions, mean that subsurface lifetimes of these chemicals can be very long.

and Mercer, 1993). Because the adhesive forces between the wetting fluid and the solid surface are greater than the adhesive forces between the wetting and nonwetting fluid, the resulting capillary pressure draws the wetting fluid into smaller openings in porous media and smaller aperture spaces in fractures. The nonwetting fluid is repelled from the smaller spaces. The pressure head in the nonwetting fluid must exceed the capillary force to displace the wetting fluid and enter an opening.

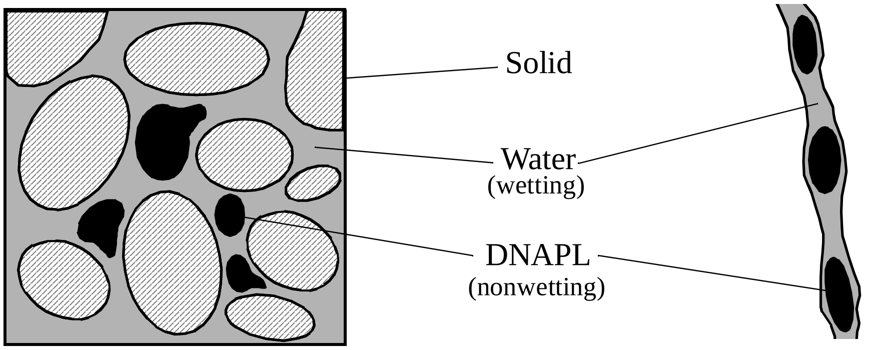
Capillary pressure increases as the size of the opening decreases. Fine-grained layers with small pore openings and fractures with small apertures have higher capillary pressures and can restrict DNAPL movement. The entry pressure for a nonwetting DNAPL to penetrate a layer in porous media is equal to the capillary pressure that must be overcome to enter the pores of the layer. Similarly, the entry pressure for a DNAPL to penetrate a fracture is equal to the capillary pressure that must be overcome to enter the largest aperture of the fracture. This entry pressure can be directly related to the height or thickness of DNAPL which must accumulate above a layer or fracture to penetrate the capillary barrier. Therefore,

Table 2. Properties of selected chlorinated organic compounds

[values are at 20° Celsius; mg/L, milligrams per liter; g/cm^3, grams per cubic centimeter; cP, centipoise; mm Hg, millimeters of mercury; NA, not applicable; data from Cohen and Mercer, 1993, and Lucius and others, 1992]

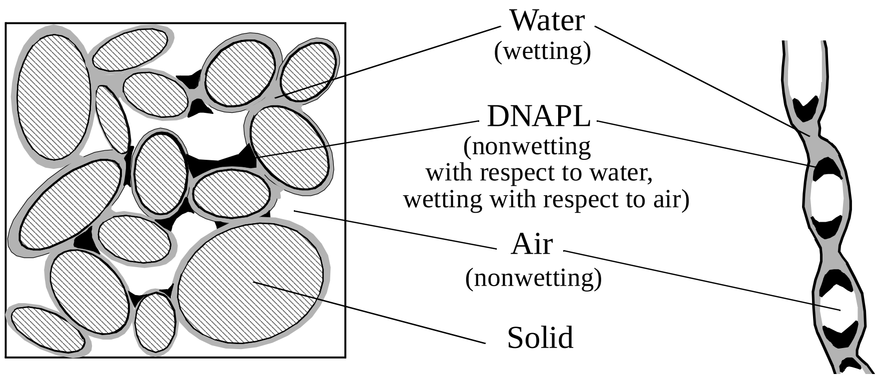
Compound	Molecular weight (grams)	Solubility in water (mg/L)	Density (g/cm^3)	Absolute viscosity (cP)	Vapor pressure (mm Hg)	Relative vapor density[1]
Tetrachloroethylene (PCE)	165.8	200	1.62	0.89	14	1.09
Trichloroethylene (TCE)	131.4	1,100	1.46	0.57	58	1.27
cis-1,2-dichloroethylene (cis-DCE)	96.9	3,500	1.28	0.48	160	1.63
trans-1,2-dichloroethylene (trans-DCE)	96.9	6,300	1.26	0.40	260	1.83
1,1-dichloroethylene (1,1-DCE)	96.9	400	1.22	0.36	490	2.54
1,1,2,2-tetrachloroethane	167.8	2,900	1.60	1.75	5.0	1.03
1,1,1-trichloroethane (1,1,1-TCA)	133.4	1,300	1.34	1.20	100	1.48
1,1,2-trichloroethane (1,1,2-TCA)	133.4	4,400	1.44	0.12	19	1.09
1,1-Dichloroethane (1,1-DCA)	99.0	5,500	1.17	0.44	180	1.58
1,2-Dichloroethane (1,2-DCA)	99.0	8,700	1.25	0.80	64	1.21
Carbon tetrachloride (CTET)	153.8	800	1.59	0.97	90	1.52
Trichlorofluoromethane (TCFM)	137.4	1,100	1.49	0.42	690	4.91
Dichloromethane (DCM)	84.9	20,000	1.33	0.44	340	1.90
Water	18.0	NA	1.00	1.00	17.5	1.0

[1] Relative vapor density is calculated as the weighted mean formula weight of compound-saturated air relative to the mean formula weight of moist air (Schwille, 1988).



a. In saturated porous media

b. In saturated fracture



c. In partly saturated porous media

d. In partly saturated fracture

Figure 2. Wetting and nonwetting fluids in various media.

macropores, large-aperture fractures, and coarse-grained layers with relatively large openings are preferential pathways for DNAPL movement.

Porous Media

In the vadose zone, capillary phenomena are the dominant mechanisms controlling the movement and distribution of DNAPL. In this situation, DNAPL can be either the wetting or nonwetting fluid, depending on the moisture content of the media. In dry media where DNAPL and air occupy the pore spaces, the DNAPL is usually the wetting fluid and will coat the geologic media and preferentially occupy the smaller pore spaces. Where DNAPL is the wetting fluid, capillary forces enhance DNAPL entry into fine-grained media.

More typically, the vadose zone is partly saturated or water-wet, resulting in DNAPL, water, and air occupying the pore spaces. Water will usually be the wetting fluid with respect to DNAPL and will coat the geologic media and preferentially occupy the smaller pore spaces (fig. 2). DNAPL will be wetting with respect to air and will coat the water, situating itself between the water and air phases. In this situation, capillary forces will act as a barrier to DNAPL entry into fine-grained media. When a dry medium with DNAPL as the wetting fluid is invaded by water, DNAPL is displaced from the solid surfaces by the water.

After a DNAPL mass has moved through the vadose zone, a part of the DNAPL will be retained by capillary forces as **residual DNAPL**. Values of residual saturation of chlorinated solvents in the vadose zone typically range from 0.01 to 0.10 for dry sands and 0.02 to 0.20 for moist sands (Schwille, 1988; Poulsen and Kueper, 1992; and Cohen and Mercer, 1993). DNAPL may be retained as films, wetting pendular rings, wedges surrounding aqueous pendular rings, and as nonwetting blobs in pore throats and bodies (Cohen and Mercer, 1993).

Two processes in the vadose zone work to deplete a DNAPL mass: volatilization into the air phase and dissolution into water. Direct volatilization of DNAPL into the soil gas is generally the most significant mechanism for depletion of chlorinated DNAPL’s from the vadose zone (Pankow and Cherry, 1996). The higher the vapor pressure of a compound, the more readily it will volatilize (table). Additionally, DNAPL that dissolves into water in the vadose zone would also be available to volatilize into the soil gas or sorb to solid surfaces. Subsequently, sorbed contaminant may be remobilized through volatilization or dissolution.

Vapor-phase contamination, whether from direct volatilization or dissolution and then volatilization, is a source for a dissolved-phase plume in the ground water, either from dissolution into infiltrating recharge water or diffusion at the water-table surface. The vapor-phase contamination will move by diffusion and sink by density-driven advection. The higher the relative vapor density, the greater the tendency for the vapor-phase contamination to sink (table). These processes will spread the source for the dissolved groundwater plume over a larger area. Diffusive loss of vapors to the atmosphere can occur, but will be limited if the ground surface is covered with vegetation or finer-grained layers which will restrict vapor movement (Pankow and Cherry, 1996).

Below the water table, where DNAPL and water occupy pore space, DNAPL is usually the nonwetting fluid and must overcome capillary forces to enter the smaller pore spaces occupied by the water. DNAPL will continue to move downward under the force of gravity until a finer-grained layer presents a capillary barrier. The DNAPL will then be diverted laterally, seeking a path downward, or will pool at the barrier until significant pressure builds to penetrate the capillary barrier.

DNAPL pools in porous media typically are wide and shallow. Compared with residual DNAPL, pools of DNAPL have less surface area per volume in contact with ground water. DNAPL pools can persist for long periods of time. The rate of dissolution from a DNAPL pool is controlled by the vertical dispersion and subsequent removal of the dissolved phase by the moving ground water. Johnson and Pankow (1992) concluded that because the vertical mixing process is quite weak, the lifetime of chlorinated DNAPL pools will typically be on the order of decades to centuries.

As in the vadose zone, the trailing edge of the DNAPL mass will leave residual DNAPL trapped by capillary forces as isolated blobs and ganglia. Values of residual saturation of chlorinated solvents in porous media in the ground-water zone have been measured in the range from 0.15 to 0.40 (Anderson, 1988). Residual saturation values in the ground-water zone are normally greater than the values in the vadose zone because the fluid density ratio (DNAPL to air as compared to DNAPL to water) favors greater drainage in the vadose zone and, as the nonwetting fluid in the ground-water zone, DNAPL is held in the larger pore spaces (Cohen and Mercer, 1993). The dominant natural process to remove residual DNAPL below the water table is dissolution into ground water. The residual DNAPL provides a source for dissolved-phase ground-water plumes.

Fractured Media

DNAPL movement in fractures is controlled by the same properties and processes as in granular material. The concepts of wettability and capillary pressure apply to DNAPL movement in a fracture as they do in a granular material. If the capillary pressure at the leading edge of the DNAPL exceeds the entry pressure of a water-saturated fracture, the DNAPL will displace the water and enter the fracture. In most cases, water will be the wetting fluid and will coat the fracture walls, and DNAPL will be the nonwetting fluid and will fill the larger aperture spaces. The minimum pool height required to overcome the entry pressure is proportional to the DNAPL-to-water interfacial tension and inversely proportional to the difference in fluid densities and fracture aperture (Kueper and McWhorter, 1991). Using values of density and interfacial tension typical of chlorinated solvents, fracture apertures on the order of 2 to 100 microns (μ) can be invaded with DNAPL pool heights in the range of 0.15 to 1.0 m (Kueper and McWhorter, 1991; Kueper and others, 1992; Pankow and Cherry, 1996). Fractures in this aperture range have been measured in fractured, unlithified clay deposits (McKay and others, 1993). Dissolution-enlarged fractures in carbonate aquifers have apertures of a scale significantly larger than this, commonly on the order of a millimeter to tens of centimeters. Therefore, the entry pressure for dissolution-enlarged fractures in carbonate rocks will be easily overcome by even a thin pool of DNAPL. In large open fractures [greater than 1 centimeter (cm)], capillary forces will be insignificant and DNAPL will drain freely under the influence of gravity. In fractures filled with residuum, DNAPL entry and movement is controlled by the pore size of the material filling the fracture.

Migrating DNAPL will not uniformly fill a fracture but will preferentially migrate along the larger aperture pathways that present the least capillary resistance. Progressively smaller aperture fractures will be invaded due to the increased fluid pressure at the base of the DNAPL accumulation if the DNAPL extends vertically as a continuous phase (Pankow and Cherry, 1996).

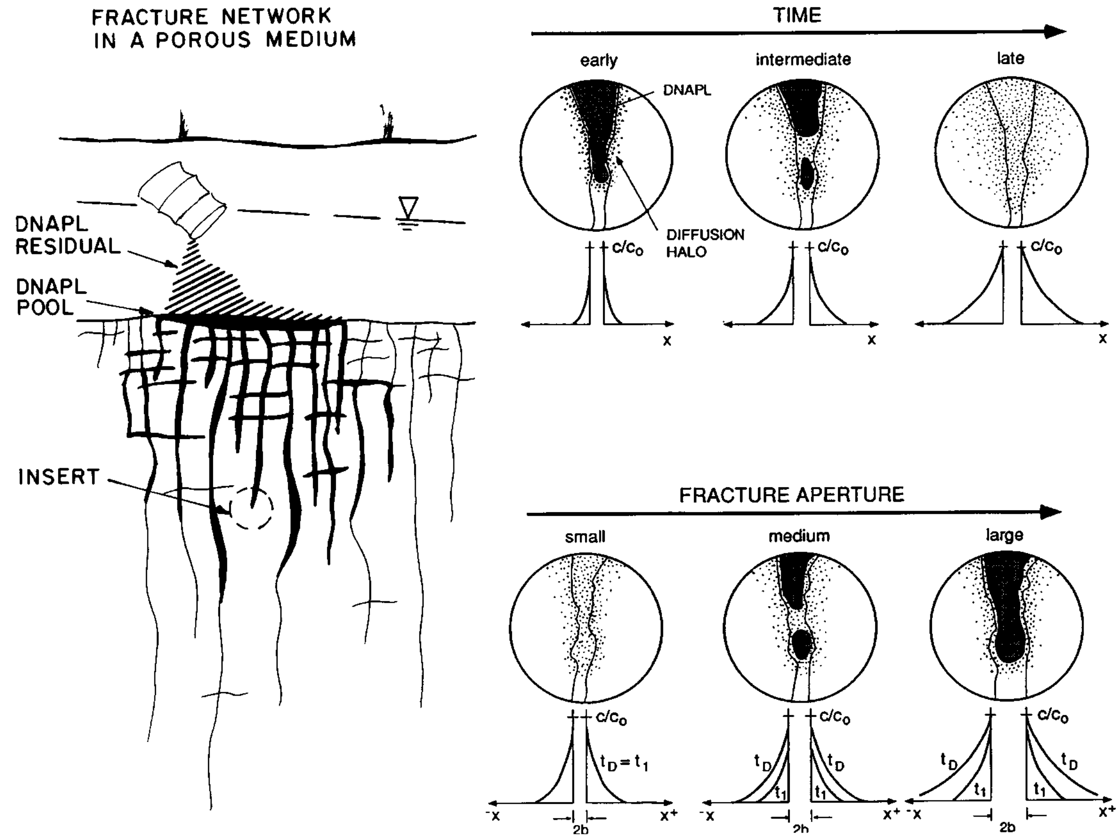
Large vertical accumulation of DNAPL will most likely occur in settings with small fracture apertures and may be less common in settings with dissolution-enlarged fractures. Once a DNAPL has entered a fracture network, it will most likely continue to drain into the network until the DNAPL source is depleted. DNAPL will move into an intersecting fracture if the local capillary pressure at the advancing front exceeds the entry pressure of the intersecting fracture.

DNAPL migration will be predominantly downward due to gravity, but significant lateral flow can occur along horizontal bedding planes or fractures in response to the closing of fractures with depth. Local structure, including degree of fracture interconnection and distribution of fracture apertures within individual fracture planes, will control DNAPL migration (Kueper and others, 1992). The preferential pathways for DNAPL migration will not necessarily be the same as for ground-water flow. Numerical models and laboratory studies (Schwille, 1988; Pruess and Tsang, 1990; Kueper and McWhorter, 1991; Murphy and Thomson, 1993) have indicated that rates of DNAPL movement in single, small-aperture [less than 1 millimeter (mm)], rough-walled fractures range from minutes to hours per 1 m length of fracture (Pankow and Cherry, 1996). If these rates are applied to field conditions, DNAPL could sink through hundreds of meters of fractured rock in a matter of days to weeks, depending on fracture openings and interconnection. Rates in dissolution-enlarged fractures would be even faster.

Once the supply of the DNAPL to a fracture has been depleted, the DNAPL will redistribute itself as residual DNAPL and pools. In laboratory experiments, Schwille (1988) showed increased solvent retention in fractures when the aperture was reduced. Pools are distinct from residual DNAPL in that they are formed when the leading edge of the migrating DNAPL can no longer overcome capillary resistance (Pankow and Cherry, 1996). This situation can occur where a fracture pinches down to a smaller aperture or where the fracture is filled with fine-grained material. Substantial amounts of DNAPL can be retained as pools in fractures. These pools could be remobilized if the balance of forces holding them static changes. In large conduits and dissolution-enlarged fractures where DNAPL would be expected to drain freely, large amounts of DNAPL can pool in depressions, particularly in horizontal to gently dipping fractures or bedding-plane openings. DNAPL pools in fractured media can be a network of small interconnected fractures filled with solvent or DNAPL accumulations in depressions of dissolution-enlarged fractures.

DNAPL pools can persist for long periods of time. Pools that fill interconnected fractures have limited surface area in contact with moving ground water. The rate of dissolution from a DNAPL pool is controlled by vertical dispersion or diffusion (depending on the location of the pool), the solubility of the DNAPL, and subsequent removal of the dissolved phase by the moving ground water (Hunt and others, 1988). Because both dispersion and diffusion are quite slow, the lifetime of chlorinated DNAPL pools will typically be on the order of decades to centuries. DNAPL pools in depressions of dissolution-enlarged fractures present more surface area to moving ground water than do pools filling interconnected fractures, but DNAPL removal is still limited by vertical mixing. Ground-water flow in dissolution-enlarged fractures may be turbulent, enhancing mixing with DNAPL pools and decreasing the DNAPL pool lifetime.

Matrix diffusion is an important mechanism in DNAPL depletion where DNAPL is pooled in interconnected fractures and the matrix porosity is high (as is typical in fractured clays, shales, and some sedimentary rocks) (VanderKwaak and Sudicky, 1996). In matrix diffusion, DNAPL slowly dissolves into the adjacent water wetting the fracture and then diffuses into the porous matrix (fig. 3). Diffusion of DNAPL into water held in matrix porosity decreases the DNAPL mass held in fractures (Parker and others, 1994) and slows the movement of the concentration front in fractured aquifers (Vogel and Giesel, 1989). Pankow and Cherry (1996) show that in media with small fracture apertures (less than 1 mm) and significant matrix porosity (greater than 5 percent) the total void space in the matrix of fractured porous media is commonly orders of magnitude larger than the void space provided by the fracture network, and matrix diffusion can account for the complete disappearance of DNAPL from fractures. They further show that for a clay with matrix porosity of 37 percent and typical fracture apertures of 1 to 100 μ, TCE would disappear into the clay matrix on the order of days to a few years; for sedimentary rocks with matrix porosity of 10 percent and fracture apertures of 10 to 100 μ, years or decades would be required. Given the same matrix porosity, time for complete removal increases as



Conceptualization of DNAPL persistence and distribution with DNAPL mass loss due to diffusion in water-saturated fractures in a porous medium (such as a fractured clay till or sedimentary rock) as a function of: a) time; and b) fracture size (aperture). Diffusion halos around fractures containing DNAPL become large (more developed) with increases in time, as shown with the concentration *vs.* distance plots for the three relative time periods in part a. At any particular time t_1, the DNAPL mass distribution will vary in different size fractures, with DNAPL disappearance occurring most rapidly in the samllest fractures; residual or disconnected DNAPL will be present in medium-sized fractures, and free DNAPL will be present in the largest fractures that are connected to overlying DNAPL pools. DNAPL disappearance times (t_D) increase with an increase with fracture aperture.

Figure 3. Matrix diffusion as explained by Pankow and Cherry, 1996.

fracture aperture increases due to higher DNAPL volume in relation to surface area. In karst formations with larger dissolution-enlarged fractures (greater than 1 mm), removal of DNAPL by matrix diffusion will be even slower. The dense Paleozoic carbonate rocks that occur in Tennessee have limited matrix porosity, typically less than 3 percent (Brahana and others, 1988). Higher matrix porosity occurs locally in weathered halos surrounding dissolution-enlarged fractures. In Tennessee karst, the regolith, fractured shaley limestones, and residual fill of conduits may contain very small fractures (1 to 100 μ) and have enough matrix porosity so that matrix diffusion can be important.

In formations with large fracture porosities where the matrix/fracture mass-storage capacity ratio is less than one, complete removal of DNAPL cannot occur by diffusion into the matrix alone because the pore-water volume is insufficient (Pankow and Cherry, 1996). Although matrix diffusion may be more effective in removing DNAPL mass in fractures than dissolution into ground water, once the DNAPL mass is depleted, the mass diffused into the matrix will provide a continuing source for a dissolved ground-water plume as it diffuses back out of the matrix.

The properties and processes discussed here control how chlorinated solvents behave in the subsurface. Various processes, such as volatilization, dissolution, and matrix diffusion, serve to deplete the DNAPL through mass transfer to other phases. In most cases, these processes do not remove any of the contaminant mass from the subsurface environment; the ultimate fate of the DNAPL is to be a persistent source of dissolved-phase contamination (fig. 4). As the dissolved-phase contamination migrates, dispersion and sorbtion reduce contaminant concentrations. Under the right conditions, chemical and microbial transformations of chlorinated solvents can result in natural or enhanced attenuation of dissolved-phase plumes. Various reactions including hydrolysis, reductive dechlorination, co-metabolism, and nucleophilic substitution are currently the subject of field research (Vogel and McCarty, 1985; Henry and Grbic-Galic, 1994; Campbell and others, 1997).

CHARACTERISTICS OF KARST AQUIFERS IN TENNESSEE

Karst aquifers contain a variety of flow regimes, ranging from rapid turbulent flow in freely draining conduits to slow laminar flow through bedrock-fracture networks, cave and fracture sediments, or regolith. The relative importance of different types of flow varies with depth, horizontal location, short-term changes in hydrologic conditions, and long-term geologic evolution of the aquifer. The spatial and temporal distribution of different flow regimes largely defines the overall hydraulic character of a karst aquifer.

Under the best of circumstances, chlorinated solvents are difficult to find and recover once they have entered the subsurface (Cherry, 1996). The distinctive hydraulic characteristics of karst aquifers compound this difficulty. Sampling strategies, analytical techniques, and approaches to monitoring that work in unconsolidated granular or fractured rock aquifers commonly give erroneous results in karst (Quinlan, 1989, 1994; Barner and Uhlman, 1995).

Karst conduits provide pathways for the rapid transport of water and contaminants. The presence of conduits, natural openings formed by the chemical dissolution of limestone or other soluble rock, often confounds efforts to understand or model karst aquifers through standard analytical techniques based on Darcy’s Law (White, 1988; Ford and Williams, 1989). The most familiar examples of karst conduits are large explorable caves with diameters on the order of meters to tens or hundreds of meters (Barr, 1961; Matthews, 1971; White and White, 1989). Most karst conduits are much smaller than explorable caves, with widths ranging down to about a few millimeters (White, 1988; Ford and Williams, 1989). Conduit shape and orientation are extremely variable. Some conduits are nearly circular in cross section, but most are long and thin, following the orientations of bedding planes, joints, and similar sheet-like openings. Conduits a few centimeters across can dominate ground-water flow in an aquifer, even though they account for only a small part of water-bearing pore space (Quinlan and Ewers, 1985; Smart and Hobbs, 1986).

Diffuse-flow networks in karst aquifers include integrated fracture systems in bedrock and intergranular pores in regolith and unconsolidated cave fill. The size, distribution, tortuosity, and interconnection of voids in fractured rock or unconsolidated material determine how readily water will move through diffuse-flow systems. Fractured rock and unconsolidated materials transmit water much more slowly than conduits but may store large quantities of water. Fracture networks and unconsolidated materials typically represent a much greater proportion of aquifer volume than do large conduits. Much of the flow carried by conduits first passes

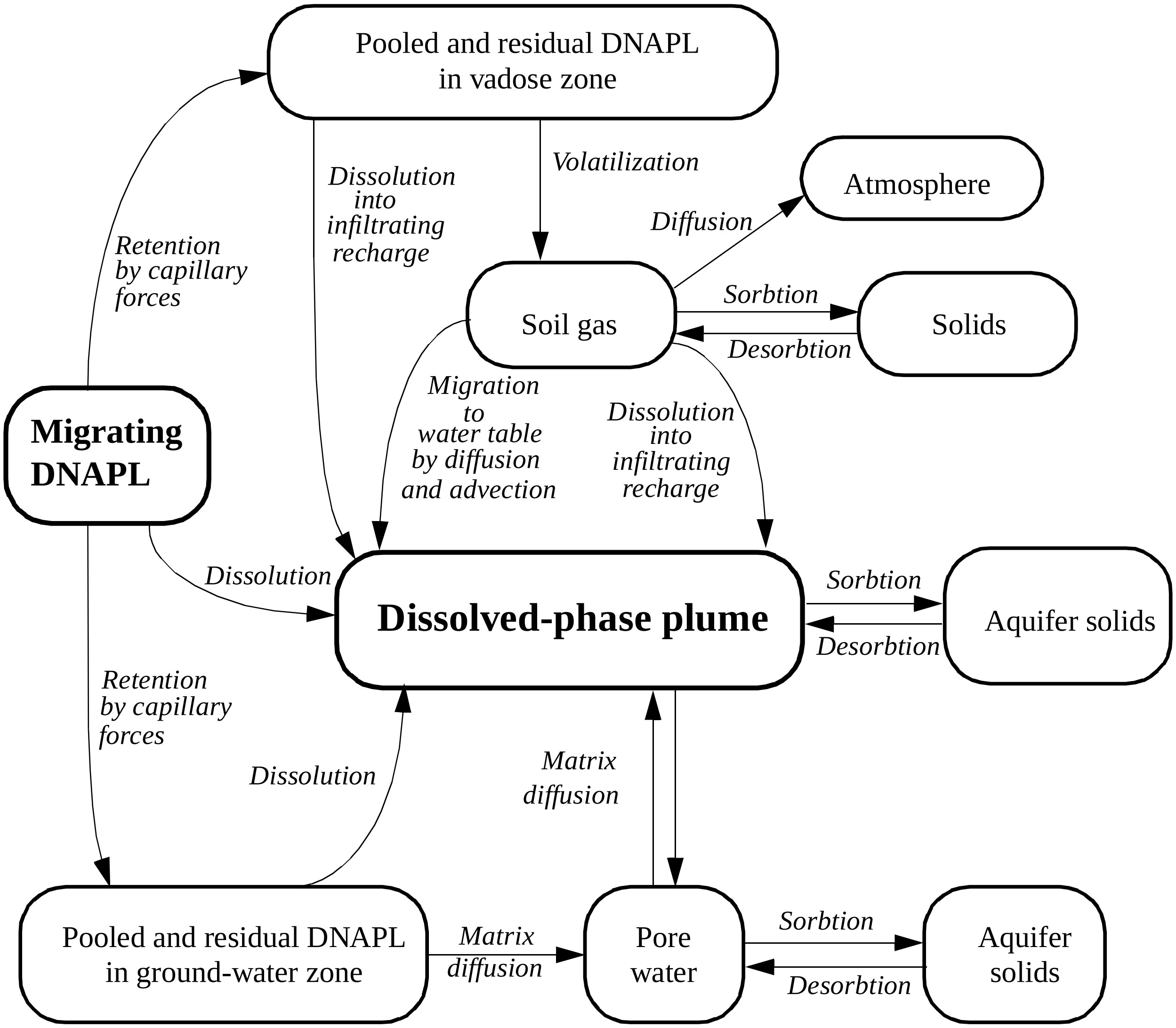


Figure 4. Processes controlling DNAPL distribution and fate in the subsurface.

through diffuse-flow networks. Chemical and isotopic analyses of water seeping into a cave in Israel showed that water was stored in the regolith and small fractures for periods ranging from days to decades before entering the karst-conduit system (Even and others, 1986). Bedrock fractures, regolith macropores, and intergranular pores of unconsolidated material also provide potential storage for contaminants.

The behavior and ultimate fate of a given contaminant mass in a karst setting will reflect the relative importance and detailed geometry of the conduits and diffuse-flow zones into which the contaminant has been introduced and the degree of hydraulic coupling between the flow systems. Contaminants introduced into sinkholes may move directly into connected conduits. More typically, contaminants accumulate in diffuse-flow zones within karst aquifers. In such cases, the hydraulic efficiency of the diffuse-flow network and the degree of integration between the diffuse-flow and conduit components of the aquifer exert a major influence on the residence time and delivery of dissolved-phase contamination into the conduit system and, eventually, to a discharge point.

Geologic Controls of Karst Aquifers

The concepts presented by White (1969, 1977), Quinlan (1978), Stringfield and others (1979), Chen

(1988), Gunn (1992), and Quinlan and others (1992) provide a basis for identifying major factors that control the recharge, flow, and discharge characteristics of karst aquifers in a given climatic setting. These factors include geologic factors such as lithology, geologic structure, and stratigraphy, and geomorphic factors such as topographic relief, landforms such as sinkholes and caves, and the thickness and properties of the regolith.

Lithology is probably the single most important determinant of whether karstification occurs in a given climatic and tectonic setting. In the Eastern United States, some degree of karst development can be assumed in any rocks that contain a significant proportion of carbonate minerals (Quinlan, 1978; Quinlan and others, 1992). Karst development is generally proportional to carbonate or other soluble mineral content, mechanical strength, and absence of primary porosity (Sweeting, 1972; White, 1988; Ford and Williams, 1989). Carbonate rocks with high primary porosity or high proportions of insoluble minerals will generally have lower levels of karst development. However, such rocks are likely to have some degree of dissolution enlargement of joints, bedding planes, and other voids and may include areas with considerable karst development (Brahana and others, 1988; Wolfe, 1996a, b).

Geologic structure and stratigraphy determine the spatial arrangement of karst and nonkarst rocks. Regional fold systems, such as that in the Valley and Ridge Physiographic Province (Fenneman, 1938), tend to constrain the direction of ground-water flow, typically down-dip or along strike (Bailey and Lee, 1991). The numerous faults that commonly accompany regional folding may offset confining units and allow hydraulic connection between stratigraphically separate karst aquifers.

In flat-lying or gently dipping strata, the thicknesses and relative positions of karst and nonkarst rocks are major controls of the overall ground-water flow regime and of the movement and storage of contaminants. The gently dipping carbonate strata of Middle Tennessee form a series of alternating karst aquifers and clay-rich leaky carbonate confining units. Thick karst aquifers are important sources of ground water. These aquifers may represent high potential for deep infiltration of low-viscosity DNAPL’s such as chlorinated solvents.

Topographic relief commonly reflects lithology and geologic structure, but its effects on karst development and the hydraulic response of karst aquifers can be considered independently. The difference in elevation between the top of a karst aquifer and regional base level is the maximum hydraulic head driving water through the aquifer (White, 1977). The greater that driving force, the greater the potential for karst development, when geologic and climatic factors are equal. White (1977) explicitly incorporated topographic relief relative to base level into his karst classification. Similarly, Quinlan and others (1992) recognize that the distribution of dissolution porosity relative to regional base level is a critical determinant of the volume of water that remains in long-term storage in a karst aquifer. If most of the dissolution porosity in a karst aquifer lies above regional base level, flow through the aquifer will be relatively rapid and storage minimal (White, 1977; Quinlan and others, 1992). A karst aquifer with most of its dissolution porosity below regional base level will have a correspondingly higher volume of long-term storage and, for a given conduit geometry, slower flow rates. Regional base level can rise or fall relative to the location of secondary porosity during the geologic lifespan of a karst aquifer, causing adjustments in flow and storage characteristics.

Karst landforms are critical factors in routing surface runoff and recharge. Surficial karst landforms in the humid, unglaciated parts of the United States include simple and compound sinkholes (uvalas), residual hills (knobs), blind valleys, disappearing streams, vertical shafts, cave openings, springs, and seeps (White and others, 1970; White, 1988, 1990). With a few exceptions, most of these landforms were formed by, and continue to mediate, hydraulic connections between the surface and subsurface; they are points of ground-water recharge, discharge, or, intermittently, both. The distribution of sinkholes, shafts, disappearing streams, and related karst depressions is a critical determinant of the rapidity of ground-water recharge and the hydraulic response of an aquifer to rainfall events. Such depressions also provide efficient pathways for contaminants to enter karst aquifers.

Regolith and landforms are important components of karst aquifers because they largely control the rate, depth, and distribution of recharge (White, 1977, 1988; Quinlan and others, 1992). These factors also influence movement of contaminants from the surface to underlying karst aquifers. Regolith includes soil, residuum, colluvium, and alluvium. In humid areas, such as Tennessee, where bedrock outcrops compose a small part of the land surface, contaminants released at the surface must pass through the regolith to reach an underlying karst aquifer.

One important control on the movement of fluids through regolith is macro-porosity. Macropores include cracks, pipes, root channels, animal burrows, and other visually discernible openings with dimensions on the order of 0.1 cm to several centimeters or larger (Germann and Beven, 1981). Such openings are present in all soils and in most natural unconsolidated materials. A wide variety of processes including plant growth, animal activity, and shrinking and swelling in response to changes in temperature or moisture content form macropores (Germann and Beven, 1981).

Karst processes greatly increase the likelihood of macropore formation in several ways. The gradual dissolution and lowering of the bedrock surface generally occurs unevenly (White, 1988; Ford and Williams, 1989) so that the regolith is subjected to slowly but constantly changing stresses. More episodic karst processes such as sinkhole collapse leave large voids in the soil surface that are directly connected to karst conduits (White, 1988). Once a collapse occurs, tension or shear cracks may develop as the surrounding soil adjusts to the collapse through mass movements (Kemmerly, 1981). Dissolution openings may be retained as relict soil structures in carbonate-rock residuum. Numerous studies in Tennessee and adjacent states have documented rapid, preferential infiltration and routing of water through soil macropores (Thomas and Phillips, 1979; Watson and Luxmoore, 1986; Quinlan and Aley, 1987; Wolfe, 1996a, b).

The interface between bedrock and regolith commonly is highly irregular in karst settings. Lithologic and structural variation and numerous other factors typically produce a complex top-of-rock topography characterized by bedrock pinnacles, pits, channels, and weathered rock fragments mixed with finer grained regolith. This complicated mixture of consolidated and unconsolidated material, known as epikarst or the subcutaneous zone (Williams, 1985), is one of the least understood aspects of karst. Epikarst can store infiltrating ground water (or contaminants) or provide a direct route to the underlying aquifer (White, 1988; Ford and Williams, 1989). In some settings, epikarst forms an important, even locally dominant, aquifer (Haugh and Mahoney, 1994; Julian and Young, 1995). Quinlan and others (1992) regard the presence of epikarst as a given in carbonate settings unless evidence is provided for its absence.

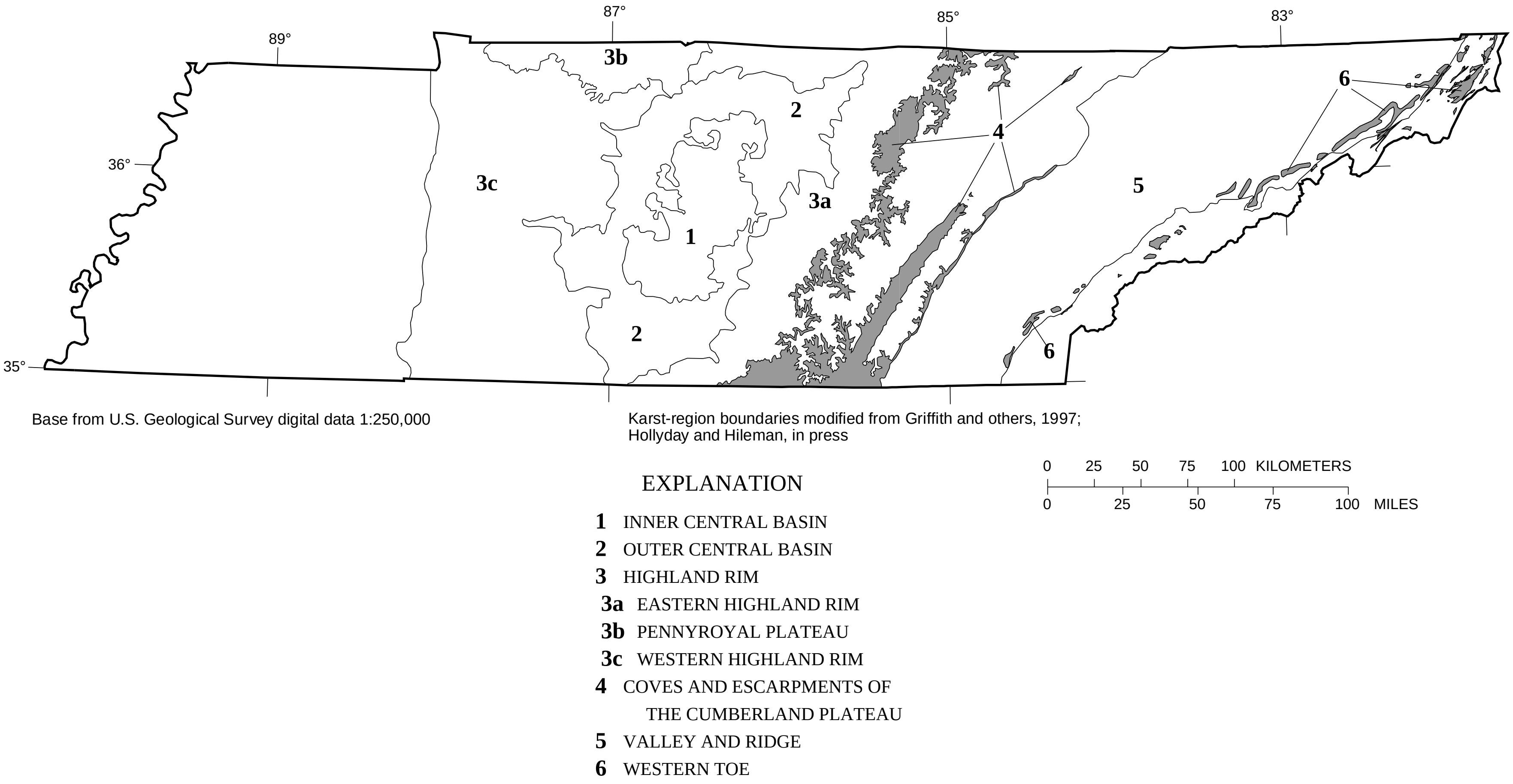
Unconsolidated materials affect the movement of water and contaminants within karst aquifers below the epikarst zone (Gale, 1984). Dissolution enlargement of voids commonly leaves insoluble residue from the carbonate rock in caves, joints, and bedding planes. Such residual fill can remain in place, where it interferes with flow, or it can be mobilized as cave sediment. Infiltrating rainwater can carry the finer fraction of unconsolidated material from the regolith downward into karst openings in the bedrock. Disappearing surface streams also transport sediment into karst aquifers (White, 1988; Ford and Williams, 1989).

Karst Aquifers of Tennessee

Carbonate rocks underlie most of Middle Tennessee and large areas of East Tennessee. The carbonate areas of Tennessee can be divided into regions based on geologic structure, stratigraphy, relief, regolith thickness, and karst landforms. Six karst regions will be considered in this report: (1) the inner Central Basin, (2) the outer Central Basin, (3) the Highland Rim, (4) coves and escarpments of the Cumberland Plateau, (5) the Valley and Ridge, and (6) the western toe of the Blue Ridge (fig. 5). The delineation of the six karst regions was based on their general physiographic and hydrogeologic characteristics (table 3) and selected geomorphic criteria such as depth to bedrock, land-surface slope, streamflow recession characteristics, and sinkhole density (table 4).

Inner and Outer Central Basin

The Central Basin (“Nashville Basin,” Fenneman, 1938) is an elliptical topographic basin trending northeast to southwest through the middle of Tennessee (fig. 5). Most of the basin is underlain by carbonate rocks of Ordovician age that were exposed by weathering and erosion of the central part of the Nashville (structural) Dome (Fenneman, 1938; Wilson, 1962; Miller, 1974). These carbonate rocks include several relatively pure limestones with well-developed karst conduit systems. The relatively pure limestones are separated by shaley confining units (Newcome, 1958). At the base of the Ordovician carbonate sequence is the Cambrian-Ordovician Knox Group (Newcome, 1958). In the Central Basin, the upper contact of the Knox Group is an erosional unconformity, generally 100 to 300 m below land surface. The base of the Knox Group is approximately 1,600 to 2,000 m below land surface (Newcome, 1958; Newcome and Smith,



Base from U.S. Geological Survey digital data 1:250,000

Karst-region boundaries modified from Griffith and others, 1997; Hollyday and Hileman, in press

Figure 5. Location of karst regions of Tennessee.

Table 3. General physiographic and hydrogeologic characteristics of karst regions of Tennessee

[<, less than; Lithologic units listed here are representative of the different regions. This list is neither comprehensive nor restrictive.]

Region name	Physiography	Aquifer characteristics	Typical lithologic units
Inner Central Basin	High sinkhole density; thin soil cover; low relief and few hills.	Relatively pure limestone, <30 meters thick, separated by shaley limestones; minor confinement throughout.	Carters Limestone, Lebanon Limestone, Ridley Limestone, Pierce Limestone, Murfreesboro Limestone; Knox Group (paleokarst).
Outer Central Basin	Moderate sinkhole density and fluvial drainage, variable soil thickness; numerous hills (knobs).	Relatively pure limestones, <30 meters thick, overlain and underlain by shaley limestone; major confinement at base (Hermitage Formation).	Leipers and Catheys Formations, Bigby and Cannon Limestones, Hermitage Formation.
Highland Rim	Sinkholes and caves well developed in upper units, decreasing down section; thick soils; relief extremely variable—well dissected over much of Western and parts of Eastern Highland Rim but nearly flat elsewhere on the Eastern Highland Rim and Pennyroyal Plateau.	Upper units thick, relatively pure limestone with many large openings, lower units increasingly impure limestones grading to chert and shale with relatively weak dissolution porosity; major confinement at base (Chattanooga Shale; locally Fort Payne Formation).	Ste. Genevieve Limestone (Pennyroyal Plateau), Monteagle Limestone (Eastern Highland Rim), St. Louis Limestone, Warsaw Limestone, Fort Payne Formation; Chattanooga Shale.
Coves and escarpments of the Cumberland Plateau.	Sandstone caprock over cavernous limestone; steep-sided coves and escarpments; thick, coarse-grained colluvium at base of slopes.	Relatively thick, pure limestones interbedded with minor shale, sandstone, and chert, large springs and cave streams; minor confinement throughout.	Bangor Limestone, Hartselle Sandstone, Monteagle Limestone, St. Louis Limestone, Knox Dolomite in Sequatchie Valley east of Sequatchie Fault.
Valley and Ridge	Parallel, structurally controlled valleys and intervening ridges; significant cavern development.	Dolomites and dolomitic limestones of varying thickness, porosity, and composition; many large springs; major confinement at several stratigraphic horizons (Pumpkin Valley Shale, Nolichucky Shale, Athens Shale, Ottosee Shale, Bays Formation, and Martinsburg Shale).	Conasauga Group, Knox Group, Chickamauga Group, Jonesboro Limestone, Newman Limestone.
Western toe of the Blue Ridge.	Coalesced alluvial and colluvial fans over carbonate rocks.	Fractured, cavernous carbonates between overlying alluvial/colluvial deposits and low-permeability, underlying shale and quartzites; large springs; major confinement at base (Chilhowee Group).	Shady Dolomite, Honaker Dolomite.

Table 4. Distributions of selected geomorphic variables among karst regions of Tennessee

[p10, 10th percentile; p50, median; p90, 90th percentile; p100, maximum; %, percent; <, less than; >, greater than]

Region	Depth to bedrock, in meters[1]				Land-surface slope, in degrees[2]				Streamflow recession index, in days per log cycle[3]			Percent of region in various sinkhole-density classes[4]			Reported cave entrances per 1,000 square kilometers[5]
	p10	p50	p90	Number of wells	p10	p50	p90	p100	p10	p50	p90	<1% sinkholes	1-10% sinkholes	>10% sinkholes	
Inner Central Basin	0.9	2.4	7.3	2,544	0	0	2	14	32	32	32	50.2	46.1	3.7	10
Outer Central Basin	1.5	3.7	13.7	3,920	0	2	7	26	35	35	50	94.1	5.9	0	18
Eastern Highland Rim	3.7	14.6	25.0	3,347	0	0	5	22	50	65	140	70.2	23.3	6.5	20
Pennyroyal Plateau	4.9	11.0	18.3	529	0	0	1	9	50	80	80	31.8	52.0	16.2	10
Western Highland Rim.	3.0	15.2	35.1	4,703	0	1	4	13	50	120	140	97.4	2.5	0.1	6
Coves and escarpments of the Cumberland Plateau.	.9	8.2	25.9	745	1	8	14	34	32	50	100	87.8	7.8	4.4	63
Valley and Ridge	3.4	12.8	38.4	8,925	0	2	8	36	50	80	120	62.1	34.9	3.0	9
Western toe of the Blue Ridge.	5.2	19.2	42.7	357	0	3	11	28	75	109	120	73.9	25.1	1.0	30

[1] Data from private-well logs maintained by Tennessee Department of Environment and Conservation, Division of Water Supply.

[2] U.S. Geological Survey digital elevation model, scale 1:250,000.

[3] Distribution based on streamflow recession areas delineated by Bingham (1986) subdivided into 500 x 500 meter cells distributed among karst regions.

[4] Crawford and Veni, 1986; based on U.S. Geological Survey topographic quadrangle maps, scale 1:24,000.

[5] Cave-entrance locations from Barr (1961) and Matthews (1971).

1962). Newcome (1958) considered the paleokarst of the upper 30 m of the Knox Group to be a reliable aquifer in the Central Basin but noted variable water quality and generally low well yields.

The Central Basin can be subdivided into two concentric zones: a relatively flat inner basin and a more hilly outer basin. For this report, the boundary between the inner and outer Central Basin (fig. 5) corresponds roughly with the outcrop of the contact between the Hermitage Formation and the Carters Limestone. In comparison with the outer Central Basin, the inner Central Basin has thinner soils, higher sinkhole density, lower cave density, and lower land-surface slope (tables 3 and 4). The difference in cave density reflects the greater topographic relief of the outer Basin rather than a difference in karst development. Large (greater than 1 m) conduits are more likely to be explored and designated as caves when they drain freely and have readily accessible openings. Both of these conditions require a certain amount of topographic relief and are more commonly met in the hillier outer Central Basin than in the flatter inner Basin.

The most productive aquifers in the inner Central Basin are zones of conduit flow in the Carters, Ridley, and Murfreesboro Limestones (fig. 6), of which the Ridley Limestone is the most reliable (Newcome, 1958). Dissolution-enlarged conduits in these units typically are concentrated within 50 m of the land surface (E.F. Hollyday, U.S. Geological Survey, oral commun., 1996). Large explorable caves, such as Snail Shell Cave developed in the Ridley Limestone (Barr, 1961), are present, but most karst conduits are a few centimeters or smaller in width (J.V. Brahana, U.S. Geological Survey, oral commun., 1996). Important potential confining units include the Lebanon and Pierce Limestones (Newcome, 1958).

The capacity of a geologic unit to develop and maintain open conduits is inversely related to its insoluble mineral content (Ford and Williams, 1989, p. 30). White (1974) reports chemical analyses from three rock cores from the Central Basin. Fourteen samples of the Carters Limestone, 14 samples of the Ridley Limestone, and 55 samples of the Murfreesboro Limestone had average insoluble residue contents of 9 to 10 percent. In contrast, 16 samples of the Lebanon Limestone and 3 samples of the Pierce Limestone had average insoluble residue contents of 24 and 14 percent, respectively (White, 1974).

The outer Central Basin has hillier topography than the inner Basin, reflected in a median land-surface slope of 2 degrees compared with 0 degrees for the inner Basin (table 4). Major rock units include the Leipers and Catheys Formations, the Bigby and Cannon Limestones, and the Hermitage Formation, all of Ordovician age (Newcome, 1958; Wilson, 1962). Dissolution-enlarged conduits in the Bigby and Cannon Limestones compose the most important aquifer in the outer Central Basin (Newcome, 1958). Zones of well-developed conduits in the Bigby and Cannon Limestones are typically concentrated within 30 m of the land surface (E.F. Hollyday, U.S. Geological Survey, oral commun., 1996; fig. 7). Reported values for insoluble residue in the Bigby and Cannon Limestones average less than 10 percent (Sprinkle, 1973; White, 1974). The Hermitage Formation is an important confining unit across much of the outer Central Basin (Newcome, 1958). Six samples from the Hermitage Formation analyzed by White (1974) had insoluble-mineral contents ranging between 14 and 82 percent and averaging 48 percent. The Leipers and Catheys Formations are less effective confining units than the Hermitage Formation and function locally as relatively low-yielding aquifers (Newcome, 1958). Insoluble residue contents in the Leipers and Catheys Formations are intermediate between those reported for the Bigby and Cannon Limestones and the Hermitage Formation (Smith, 1972; Sprinkle, 1973; White, 1974).

The carbonate sequence that underlies the Central Basin is more than 1,600 m thick (Newcome, 1958; Newcome and Smith, 1962). Karst development in many of these rocks provides substantial potential for the downward movement of low-viscosity DNAPL's such as chlorinated solvents. The high density of sinkholes, especially in the inner Basin, means that contaminants have efficient pathways to the subsurface. Even where sinkholes are absent, the thin soils of the Central Basin offer little or no resistance to infiltration of contaminants above the bedrock surface.

The numerous confining units in the Ordovician sequence have often frustrated developers, home owners, and well drillers by their ability to interfere with the vertical movement of economically significant quantities of water. However, the effectiveness of these confining units with respect to water is highly variable—both between units and within a given unit at different locations (Piper, 1932; Newcome, 1958). Even relatively effective confining units such as the Hermitage Formation transmit water freely at some locations because of fractures or lithologic variation (E.F. Hollyday, U.S. Geological Survey, oral

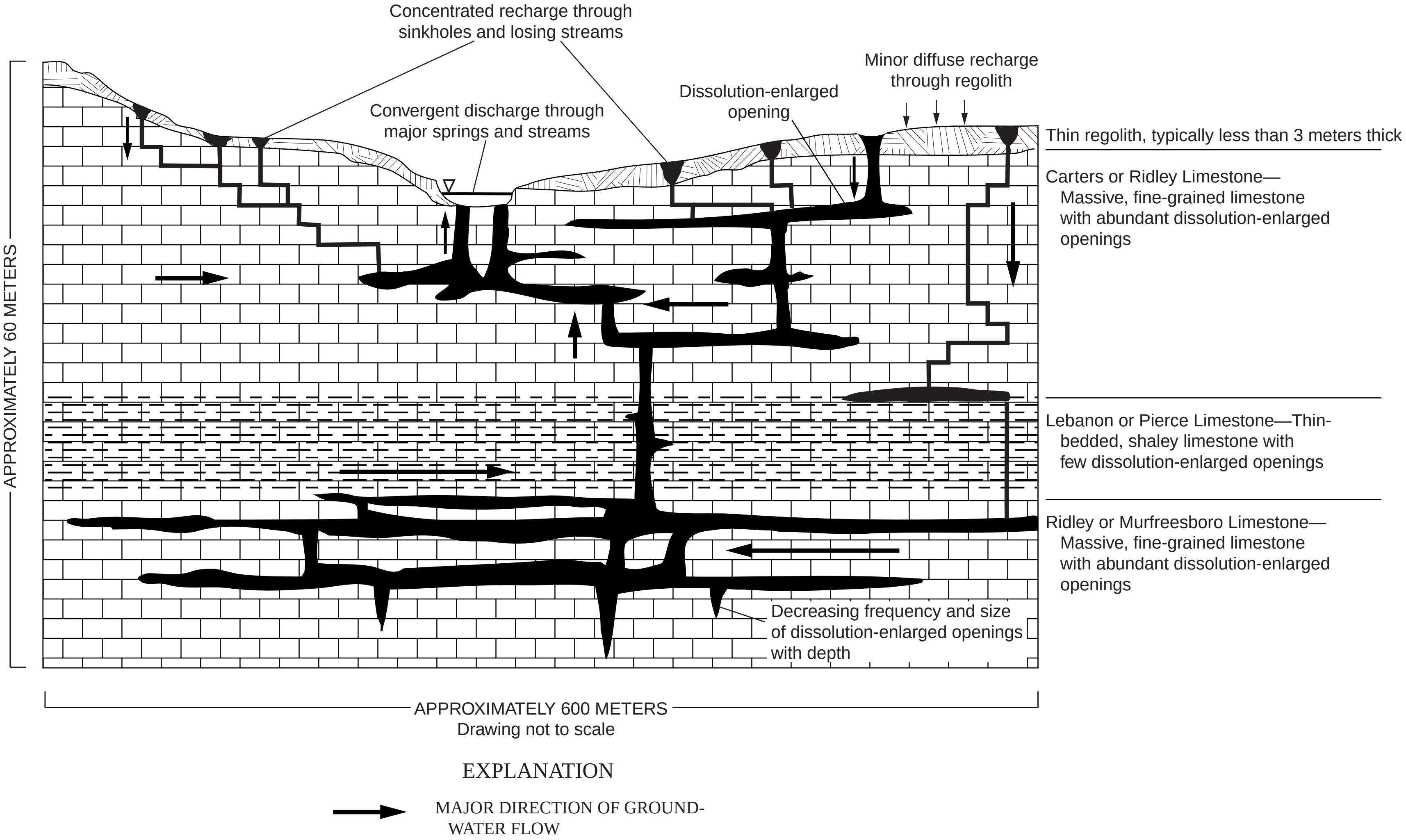


Figure 6. Generalized hydrogeologic section of the inner Central Basin of Tennessee. (Modified from Zurawski, 1978.)

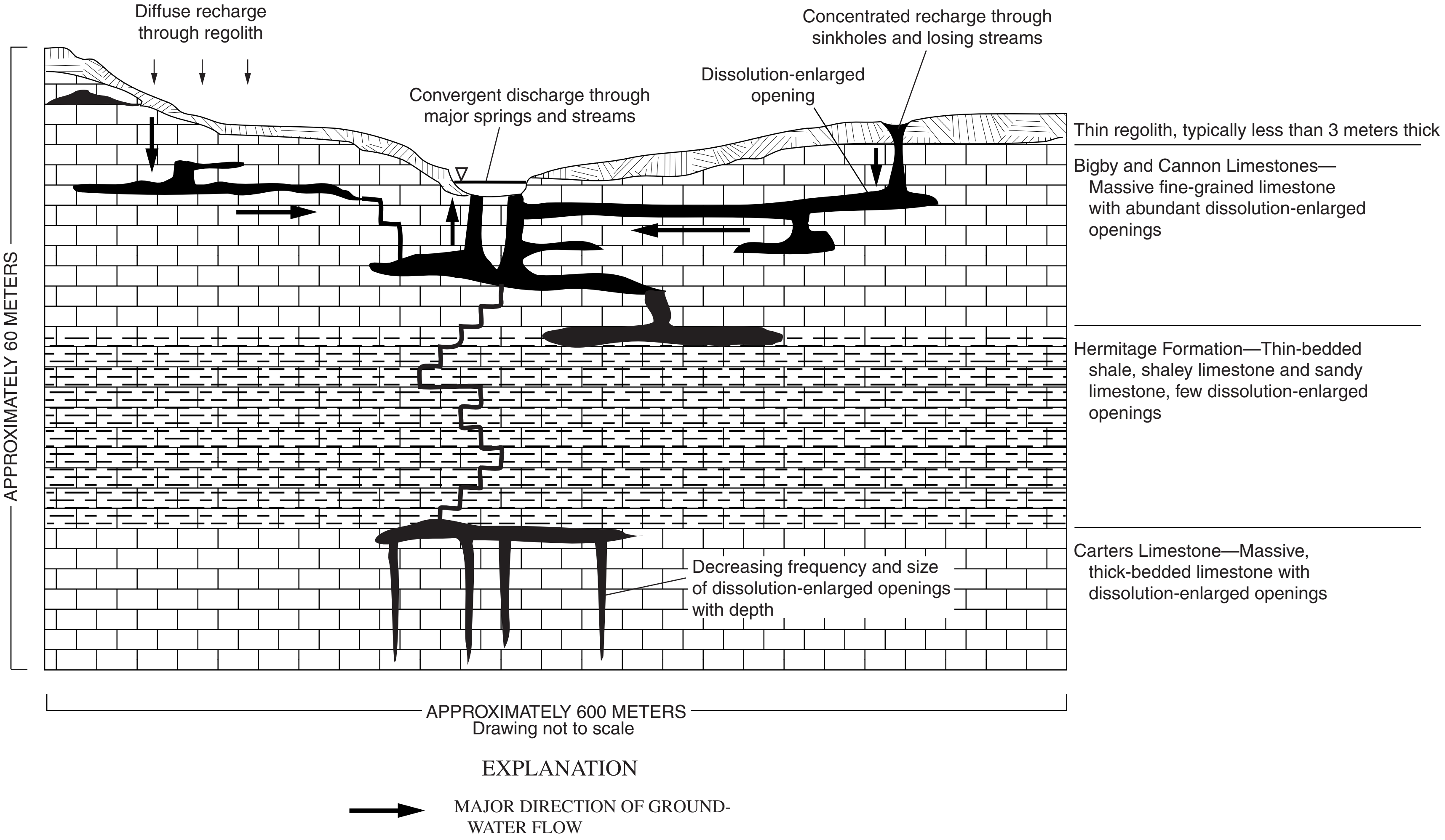


Figure 7. Generalized hydrogeologic section of the outer Central Basin of Tennessee. (Modified from Zurawski, 1978.)

commun., 1996). The confining units of the Central Basin are likely to be less effective as barriers to the downward movement of low-viscosity DNAPL's than to infiltration by water. Even where confining units stop or retard DNAPL movement, abandoned wells, commonly cased only a few feet near the surface, may provide localized but very efficient pathways for DNAPL to move from higher to lower stratigraphic units (Crawford and Ulmer, 1994, p. 46-48).

The Highland Rim

The Highland Rim is an undulating plateau that surrounds the Nashville Basin (fig. 5). The Rim is bounded on the east by the Cumberland Plateau, on the west by the Western Valley of the Tennessee River, and extends north and south into Kentucky and Alabama, respectively. Traditionally, the Highland Rim in Tennessee has been divided into eastern and western subdivisions (Miller, 1974). West of the Central Basin, the Highland Rim can be further subdivided into a smaller section (the Pennyroyal Plateau) north of the Cumberland River and a larger section south of the Cumberland River (Kemmerly, 1980; Smalley, 1980).

The entire Highland Rim in Tennessee is underlain by carbonate rocks of Mississippian age (Fenneman, 1938; Miller, 1974). From youngest to oldest, major rock units include the Ste. Genevieve Limestone (Pennyroyal Plateau only), the Monteagle Limestone (stratigraphic equivalent of Ste. Genevieve Limestone in the Eastern Highland Rim), the St. Louis Limestone, the Warsaw Limestone, and the Fort Payne Formation. The Ste. Genevieve, Monteagle, and St. Louis Limestones are relatively pure, mechanically strong limestones that develop extensive cave and sinkhole systems (Piper, 1932; Kemmerly, 1980; Mills and Starnes, 1983). The Warsaw Limestone is a variable unit consisting of thickly to thinly bedded limestone of variable purity with interbedded calcareous shales and sandstones (Piper, 1932). The Fort Payne Formation is even more variable, consisting of "an extremely heterogeneous and variable assemblage of siliceous and calcareous shale and sandy, cherty, and earthy limestone" (Piper, 1932). The base of the Mississippian sequence, and of the Highland Rim aquifer system, which encompasses this sequence (Brahana and Bradley, 1986), is the Upper Devonian to Mississippian Chattanooga Shale (Piper, 1932; Miller, 1974).

Three distinct topographic styles are characteristic of the Highland Rim as a whole and recur in varying proportions throughout the Rim's extent:

1. *Sinkhole plains* are areas of low to moderate relief with a high density of sinkholes and such related karst features as deep vertical shafts, blind valleys, and perennially flowing disappearing streams. Sinkhole plains are prominent in the Pennyroyal Plateau and at the base of the Cumberland Plateau escarpment. Ground-water flow systems include very responsive karst aquifers with point recharge, low storage, and efficient conduit systems as well as transitional aquifers with more diffuse flow regimes or higher storage.
2. *Barrens* are weakly dissected uplands of low relief that include broad, well-drained ridge-tops, poorly drained valley bottoms cut by weakly incised, intermittently flowing channels, perennially wet shallow pans, and short valley side-slopes. Weathering profiles are generally greater than 6 m thick, and thicknesses of greater than 30 m are common (Haugh and others, 1992). The largest area of barrens in Tennessee is The Barrens of the Eastern Highland Rim (Wolfe, 1996b). Other notable concentrations occur in southern Franklin County and the western Pennyroyal Plateau (Wolfe, 1996a). Recharge and ground-water flow are generally much more diffuse than in the sinkhole plains, though examples of concentrated recharge and conduit ground-water flow have been documented at some sites in The Barrens (Haugh and Mahoney, 1994; Wolfe 1996a, b).
3. *Fluvially dissected escarpments and valleys* are areas of high slope and relief that have been extensively cut by fluvial erosion. Fluvial dissection of the Eastern Highland Rim is strongest in the northeastern part where the Rim is cut by the Cumberland River and its tributaries (White and White, 1983) and along the escarpment that marks the Rim's transition to the Central Basin. A similar dissected escarpment leads from the Pennyroyal Plateau to the Cumberland River valley. Extensive areas of the Western Highland Rim are deeply incised by numerous large and small streams. Because fluvial dissection is an external process affecting both sinkhole plains and barrens areas, ground-water hydrology is somewhat more variable in dissected areas than in other topographic settings of the Highland Rim. Recharge and ground-water flow vary from concentrated to diffuse, depending on local lithology. Numerous springs and seeps discharge along the

dissected escarpments, notably at confining unit outcrops. In general, ground-water storage in areas within 1 kilometer of the escarpments is depleted each year (Piper, 1932; Smith, 1962; Burchett, 1977; Johnson, 1995).

Topography, especially the distribution of sinkholes and barrens, is strongly correlated with bedrock geology (fig. 8). Sinkholes are most common where the greatest thicknesses of relatively pure limestones such as the Ste. Genevieve and St. Louis Limestones crop out. Barrens are concentrated in areas underlain by the impure limestones, shales, and cherts of the Warsaw Limestone or Fort Payne Formation. The most extensive barrens areas are in the Eastern Highland Rim and Pennyroyal Plateau, but they occur throughout the Highland Rim (Wolfe, 1996a). In general, the Western Highland Rim is the most dissected of the three subdivisions, the Pennyroyal Plateau is the least dissected, and the Eastern Highland Rim is the most topographically variable (slope, table 4).

Coves and Escarpments of the Cumberland Plateau

The Cumberland Plateau is a broad upland with nearly flat topography locally broken by deeply incised stream valleys and low hills. The general elevation of the plateau is about 600 m and is bounded by prominent escarpments that descend roughly 300 m to the Valley and Ridge Physiographic Province (Fenneman, 1938) and the Highland Rim, respectively east and west of the Plateau. The main surface of the Cumberland Plateau is capped with a sequence of Pennsylvanian sandstones, shales, and conglomerates. These siliciclastic rocks are generally unaffected by karst processes and are typically on the order of 100 m thick. The siliciclastic caprock is underlain by a sequence of Upper Mississippian rocks consisting of a transition sequence of shales, sandstones, and impure limestones (the Pennington Formation). The Pennington Formation, in turn, overlies thick (greater than 30 m), relatively pure limestones (the Bangor, Monteagle, and St. Louis Limestones) separated by thinner confining units of sandstone, shale, or impure limestones (Miller, 1974; White and White, 1983; Crawford, 1987; fig. 9). The Mississippian limestones crop out along the escarpments that bound the Cumberland Plateau and in deeply incised valleys, locally known as “coves,” where stream erosion has cut through the caprock. By far the largest and most prominent stream valley incised into the plateau is that of the Sequatchie River (Milici, 1968; Miller, 1974; Crawford, 1989). Karst processes and features on the Cumberland Plateau are concentrated almost exclusively along the escarpments and coves.

The escarpments and coves along the edges of the Cumberland Plateau and along its transition to the Sequatchie Valley form one of the classic karst areas of North America (White and White, 1983; Crawford, 1987, 1989, 1992). The relatively thick, impervious cap of siliciclastic rocks concentrates recharge at points where the cap is breached by erosion. Under the influence of concentrated recharge, driven by several hundred meters of relief, the thick, relatively pure limestones have developed highly efficient conduit systems capable of accommodating perennially flowing streams. Along the face of the escarpments and the valley walls, the recurring sequence of cavernous limestone alternating with shaley or cherty confining units produces a characteristic pattern of ground-water/surface-water interaction (fig. 9). Numerous springs emerge where confining units crop out, then re-enter the ground-water system through dissolution openings in the next limestone unit down the sequence (White and White, 1983; Crawford, 1989). The combination of concentrated recharge, high relief, low aquifer storage, and well-developed conduit systems make the karst aquifers of the Cumberland Plateau vulnerable to contamination wherever the caprock has been breached.

The floor of the Sequatchie Valley is cut by the Sequatchie Valley (thrust) Fault (Milici, 1968). West of the fault, the rock units that crop out and the general physiographic relations are broadly analogous to those of the Eastern Highland Rim. East of the fault, the floor of the Sequatchie Valley can be considered an extension of the Valley and Ridge karst region discussed in the next section.

Valley and Ridge and Western Toe of the Blue Ridge

The Valley and Ridge Physiographic Province (Fenneman and Johnson, 1946) is a linear belt of folded and faulted sedimentary rocks that extends about 2,000 km, trending northeast-southwest from the St. Lawrence Valley to the Coastal Plain in Alabama (Fenneman, 1938). The Valley and Ridge takes its name from the characteristic topographic sequence of alternating ridges and stream valleys whose structurally controlled orientations are roughly parallel to the axis of the entire province (Fenneman, 1938). In Tennessee, the Valley and Ridge occupies roughly

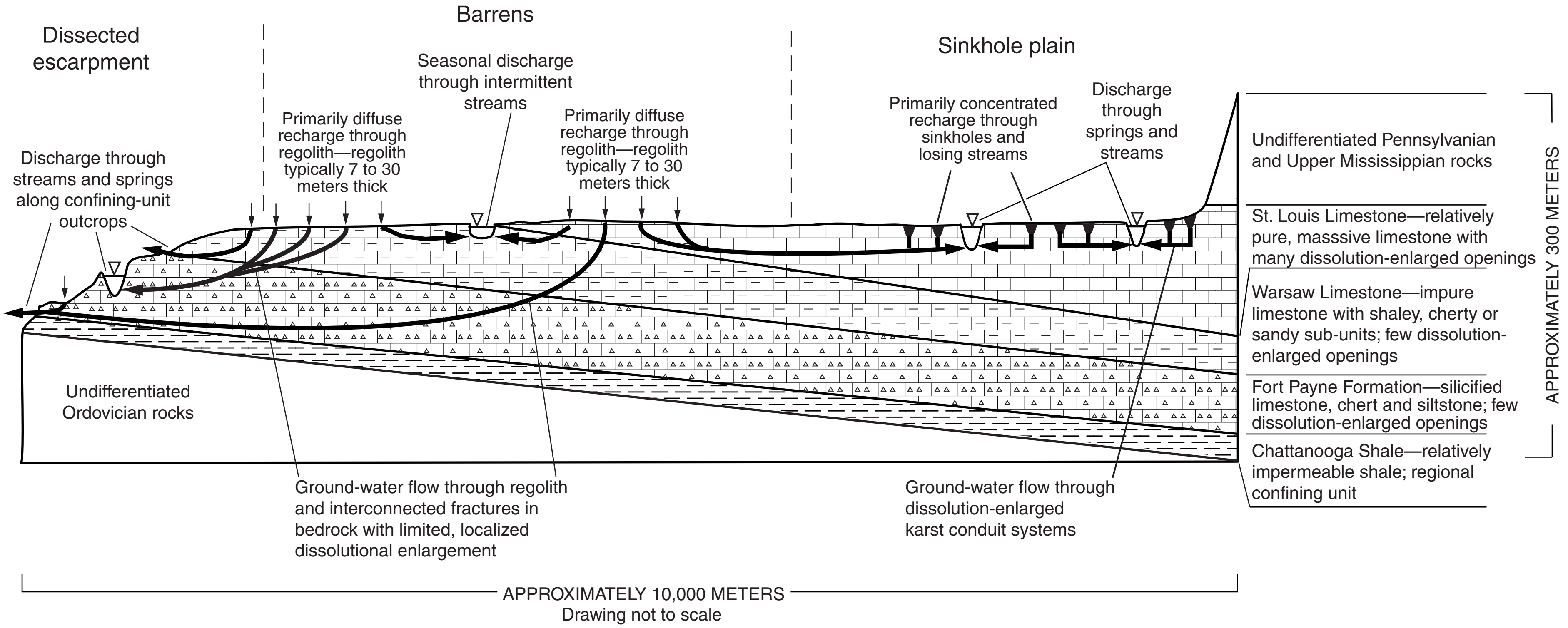


Figure 8. Generalized hydrogeologic section of the Eastern Highland Rim in Tennessee.

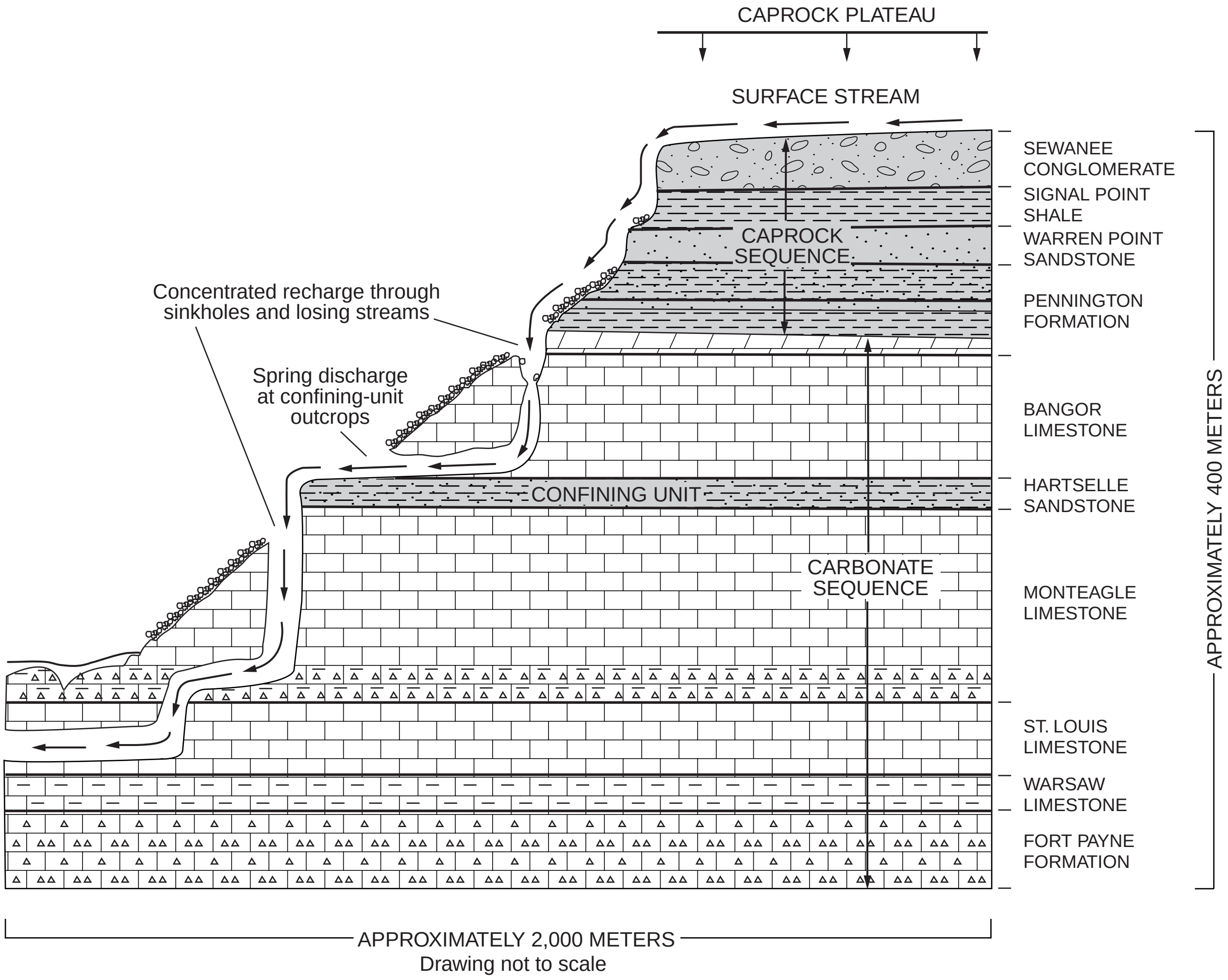


Figure 9. Generalized hydrogeologic section of the Cumberland Plateau escarpments in Tennessee. (Modified from Crawford, 1987.)

21,000 km^2, making it the second largest karst region in Tennessee, after the Highland Rim.

The major characteristic that distinguishes Valley and Ridge karst from karst in the Nashville Basin and Highland Rim or along the Cumberland Plateau is the strongly folded and faulted structure (fig. 10). Large-scale structures, such as major folds and thrust faults, control the spatial arrangement of the various rock units and determine (1) which units crop out at the surface, (2) where weathering and ground-water recharge occur, and (3) where secondary porosity can best develop in rocks of suitable lithology (Hollyday and Hileman, in press). Dissolution openings and active karst development may extend to depths of 180 m or deeper in the Valley and Ridge, compared to 30 m in the outer Central Basin, because karst aquifers and confining units are not horizontal (Hollyday and Hileman, in press; Sid Jones, Tennessee Department of Environment and Conservation, oral commun., 1997).

Throughout much of the Valley and Ridge, thick accumulations of regolith store and transmit large quantities of ground water (Bailey and Lee, 1991; Hollyday and Hileman, in press). In some areas, the dominant direction of ground-water movement in regolith tends to be normal to strike and toward the structurally controlled valley bottoms, with valley streams acting as discharge points (Bailey and Lee, 1991). Elsewhere, relict bedding structures may cause water to flow along strike in the regolith (Sid Jones, Tennessee Department of Environment and Conservation, oral commun., 1997). Potential for ground water to move relatively long distances parallel to strike (along the

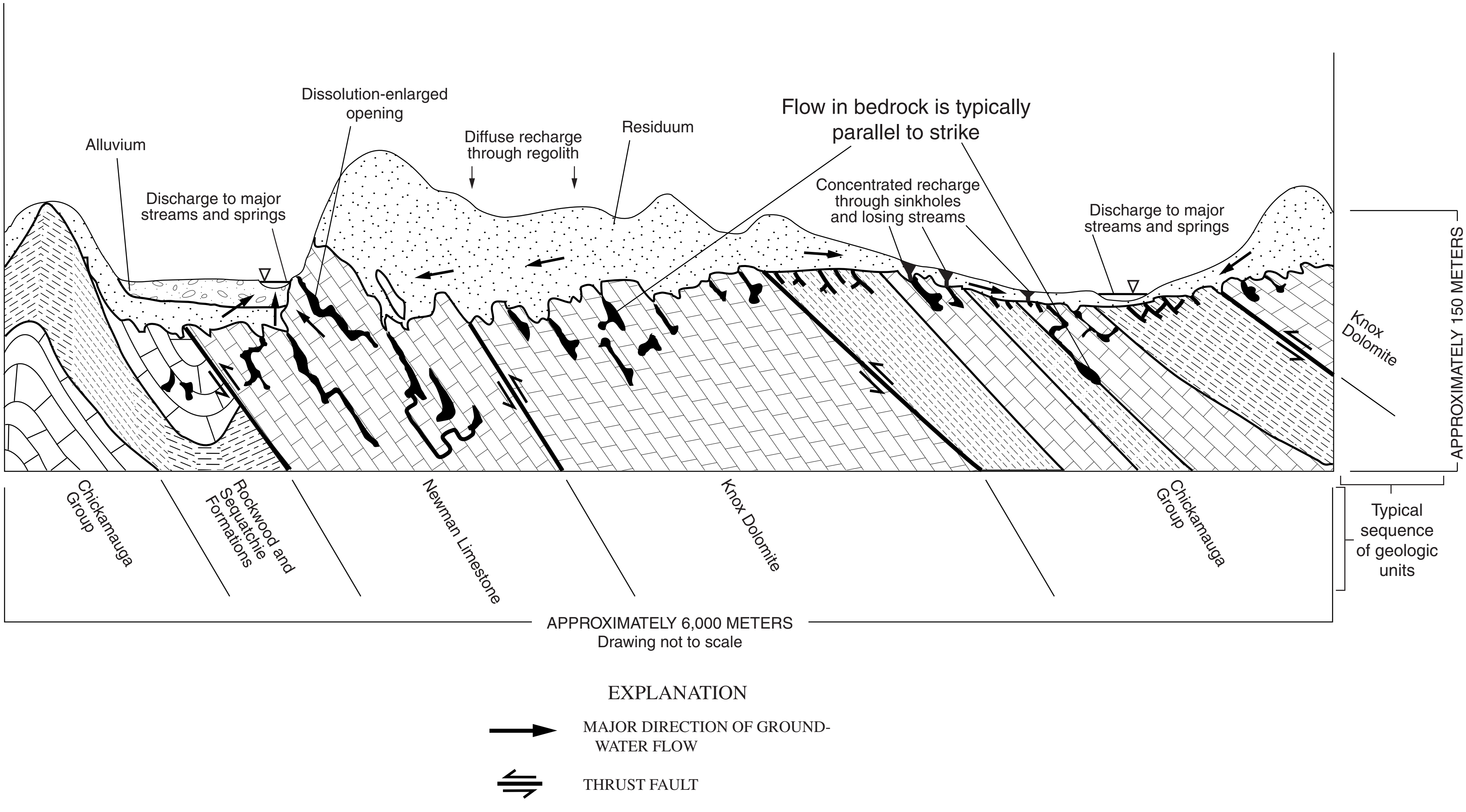


Figure 10. Generalized hydrogeologic section in the Valley and Ridge karst region.

valley axis) is greatest in carbonate units with well-developed conduit systems (Bailey and Lee, 1991).

Hollyday and Hileman (in press) divided the Valley and Ridge Physiographic Province into hydrogeologic terranes based on lithology and well yields. They noted three major karst terranes: limestone, dolomite, and argillaceous carbonate rock. Limestone, such as the Jonesboro Limestone, and dolomite, such as the Knox Dolomite, develop significant conduit porosity in the Valley and Ridge. Limestone forms broad valley bottoms with varying thicknesses of alluvial cover. Dolomite also crops out in valley bottoms, but some dolomite, notably the Knox, also forms knobby ridges with chert-capped residual cover tens of meters thick (E.F. Hollyday, U.S. Geological Survey, oral commun., 1996). Argillaceous carbonate rock, such as the Moccasin or Lenoir Limestones of the Chickamauga Group, contains sufficient carbonate minerals to develop dissolution-enlarged openings. However, the high concentrations of insoluble materials in these units limit conduit development and tend to clog dissolution-enlarged openings with insoluble residue (Hollyday and Hileman, in press).

The “western toe of the Blue Ridge” (Hinkle and Sterrett, 1976, 1978; Hollyday and Hileman, in press) is a special localized setting like the coves and escarpments of the Cumberland Plateau. The western toe occurs along the boundary between the Valley and Ridge and Blue Ridge Physiographic Provinces with isolated outliers scattered within the Blue Ridge. Although these areas are highly localized, they provide important sources of ground water (Leonard, 1962; Hinkle and Sterrett, 1976, 1978; Meng and others, 1985, p. 431; Hollyday and others, 1997; Hollyday and Hileman, in press) and have ecological significance as habitat for rare plants and animals (Killebrew and Safford, 1874; Tryon, 1992; Wolfe, 1994). The main features of the western toe settings are (1) topographic juxtaposition of a dolomite or (less commonly) limestone valley bottom with quartzite slopes; and (2) a sequence, from top to bottom, of coarse clastic alluvium and colluvium, fine-grained residuum, and fractured, cavernous carbonate rock (fig. 11).

The heavily folded and faulted structure of the Valley and Ridge has significant implications for the fate and transport of pollutants. Steeply dipping, dissolution-enlarged joints and bedding planes are potential pathways for penetration of DNAPL deep into the ground-water system. The lithologic conditions under which such deep migration of DNAPL is most likely to occur are the same conditions that have the highest potential for long-distance movement of ground water, and dissolved contaminants, parallel to strike.

CONCEPTUAL MODELS OF CHLORINATED SOLVENTS IN KARST AQUIFERS

Chlorinated solvents generally enter the subsurface environment as DNAPL and migrate downward and laterally until local conditions favor their accumulation (Schwille, 1988; Cohen and Mercer, 1993; Pankow and Cherry, 1996). Such accumulation can occur in any of several phases: DNAPL, vapor, sorbed to solids, or dissolved in ground water. Wherever and in whatever phase chlorinated solvents accumulate in the subsurface, they function as secondary sources for dissolved contaminant plumes. In the dissolved phase, chlorinated solvents can enter drinking-water supplies and threaten human health.

Major controls of the movement and ultimate fate of chlorinated solvents in the subsurface are (1) the physical and chemical properties and mass of specific contaminants released, (2) the areal extent and rate of contaminant release, and (3) the nature of the hydrogeologic environment into which the contaminant migrates (Cohen and Mercer, 1993; Pankow and Cherry, 1996). For a chlorinated-solvent release in karst, specific factors that control the residence time of contaminant accumulations and the concentration and movement of dissolved-phase contamination include:

1. the mass of the bulk contaminant source and its location relative to the water table;
2. the sorption properties of the material through which the contaminant migrates and in which it accumulates;
3. the surface-area to volume ratio of DNAPL ganglia, blobs, pools, and residual accumulations;
4. the local ground-water flow regime in areas of chlorinated-solvent accumulation;
5. the degree of hydraulic connection between areas of chlorinated-solvent accumulation and karst conduit systems; and
6. the overall ground-water flow regime of the area surrounding the site and the location of the contaminant source relative to recharge and discharge boundaries.

In principle, knowledge of the above factors would greatly improve prospects for assessing (1) the rate of release of dissolved-phase contaminant to major ground-water flow systems, (2) the distance

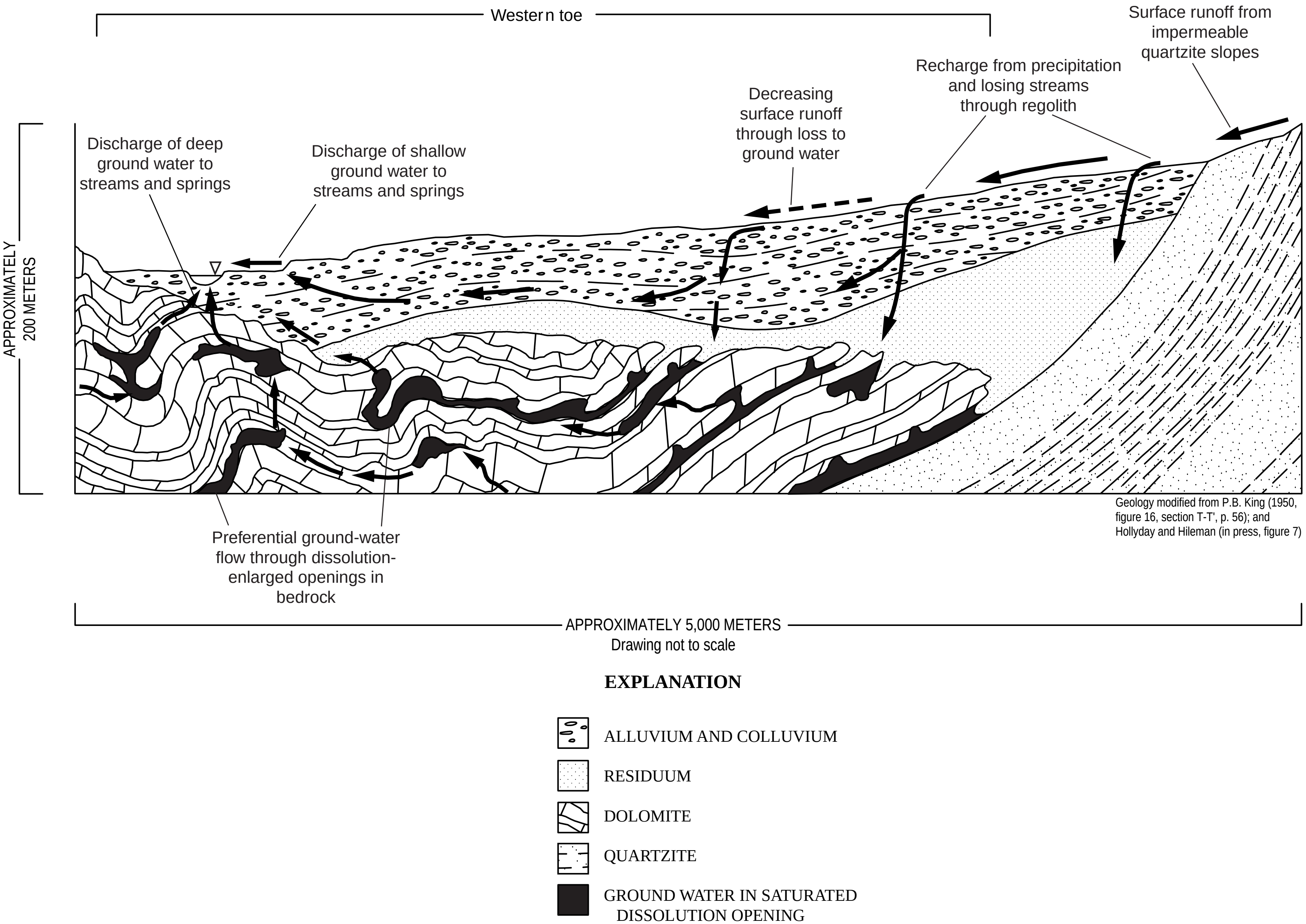


Figure 11. Generalized hydrogeologic section of the western toe of the Blue Ridge karst region.

and direction of dissolved-phase contaminant movement, (3) the degree of dilution at different points along the dissolved-phase contaminant flow path, and (4) whether contaminant concentrations in ground water are likely to increase or decrease through time. In practice, information on these controls is commonly sparse or absent. The identity and amounts of contaminant and details about how, when, and where the release occurred are poorly documented at many sites (Pankow and Cherry, 1996). Even presumably simple hydrogeologic settings can turn out to be difficult and expensive to characterize in detail (Cherry, 1996). Karst settings are almost never simple, and there are currently no widely disseminated and applied standards for characterizing DNAPL spills in karst (Barner and Uhlman, 1995).

A necessary first step toward improving site characterization for chlorinated-solvent spills in karst settings is the development of conceptual models of where the contaminants are likely to have accumulated and where and how they may be moving. A good conceptual model provides numerous working hypotheses that can be evaluated and refined as new information becomes available. The absence of an adequate conceptual model commonly leads to wasted effort and expense as data are collected which do little to illuminate the problem at hand. Standard techniques of site characterization developed for aqueous-phase contaminants or for porous granular media may provide irrelevant or erroneous results at DNAPL sites in karst settings (Quinlan and Ray, 1991; Cohen and Mercer, 1993; Barner and Uhlman, 1995).

This section presents five conceptual models of DNAPL accumulation in karst settings. The models emphasize DNAPL accumulation in different compartments of the subsurface environment. The emphasis on DNAPL emplacement reflects the preliminary nature of the five conceptual models and the complexity of chlorinated-solvent contamination and karst hydrogeology. An emphasis on the behavior of dissolved-phase contamination might be preferable in terms of contaminant delivery to drinking water (Sid Jones, Tennessee Department of Environment and Conservation, written commun., 1997). However, current understanding of the behavior of chlorinated solvents in karst is not sufficient to support generalizations about the movement and behavior of dissolved-phase chlorinated solvents without first considering the location of subsurface contaminant sources. The five conceptual models therefore assume that, subsequent to initial release, the distribution of DNAPL in the subsurface will largely determine the distribution and movement of other phases. The models were developed for the karst environments of Tennessee, but the concepts presented in this section are intended to be transferable to similar karst settings in adjacent states and applicable in other areas.

The five conceptual models of DNAPL accumulation in karst settings (fig. 12) are:

1. DNAPL trapping in regolith,
2. DNAPL pooling at the top of bedrock,
3. DNAPL pooling in bedrock diffuse-flow zones,
4. DNAPL pooling in karst conduits,
5. DNAPL pooling in isolation from active ground-water flow.

The conceptual models presented in this section are scale neutral. There is no minimum amount of DNAPL that could be stored in any of these environmental compartments, and the maximum amounts are a function of the size and nature of the release and the hydrogeologic character of specific sites. The models are mutually compatible in that more than one model may be applicable to a given site.

Trapping in the Regolith

Numerous local and regional studies throughout Middle and East Tennessee indicate the regolith is highly variable and heterogeneous. The regolith typically consists of clays and silts that may be mixed and interbedded with sands, gravels, and rock fragments. Depending on the local setting, the regolith may be composed of residuum, alluvium, or colluvium, singly or in combination (Bradley, 1984; Hanchar, 1988; Moore, 1988; Webster and Bradley, 1988; Bradfield, 1992; Haugh and others, 1992; Haugh, 1996; Rutledge and Mesko, 1996).

In the regolith, DNAPL can migrate through macropores, fractures, and intergranular pores. Flow through macropores and fractures is important in fine-grained layers where DNAPL may not be able to enter the intergranular pores (Helton, 1987; Cherry, 1989).

Several mechanisms work to trap DNAPL in the regolith. DNAPL can be retained by capillary forces as residual DNAPL under both unsaturated and saturated conditions. DNAPL can pool on top of layers that are lower in permeability relative to the overlying layer and provide a capillary barrier to further downward movement of DNAPL. Low-permeability layers can be

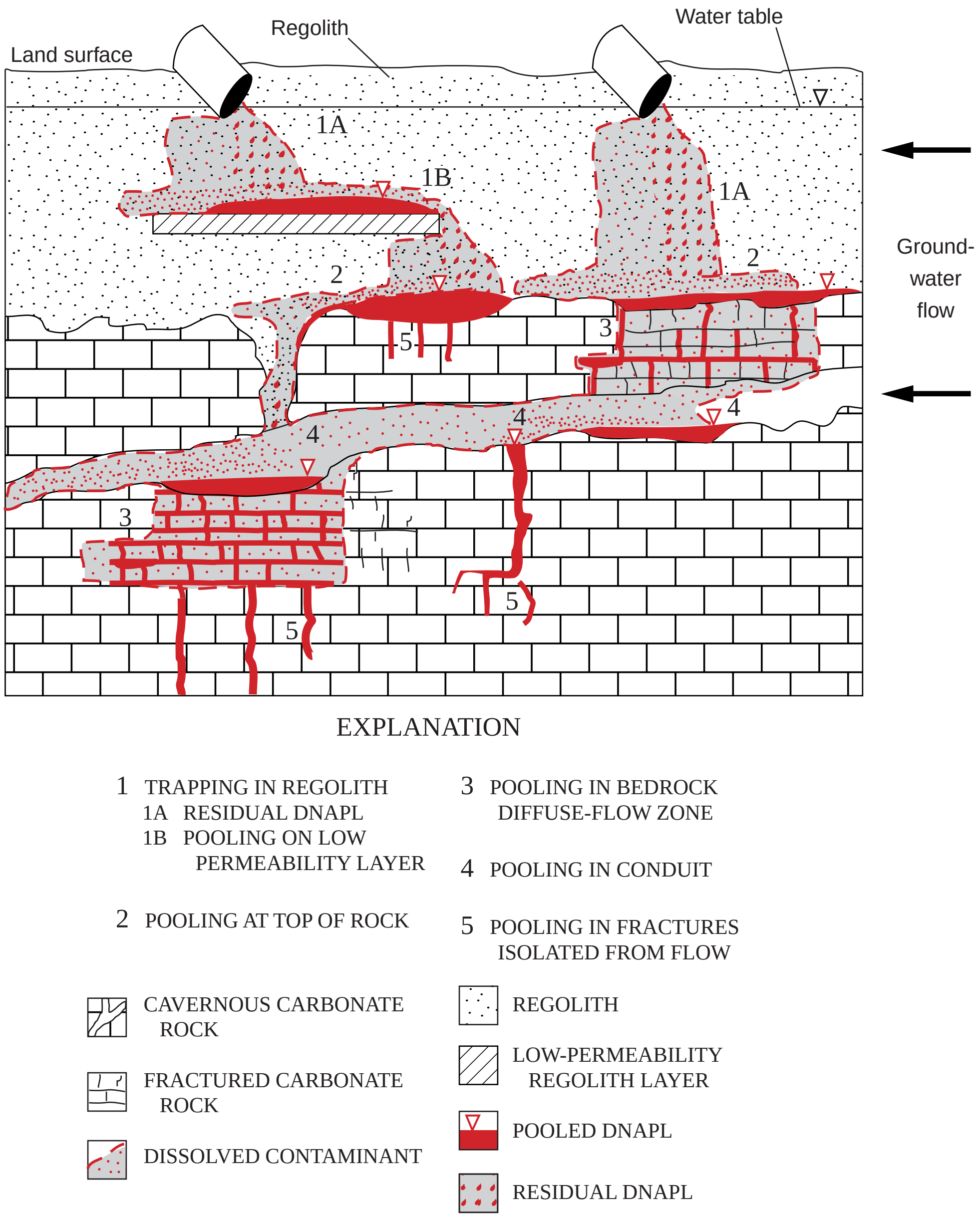


Figure 12. Distribution of potential DNAPL-accumulation sites in a hypothetical karst setting.

perennially saturated, perennially drained, or alternately saturated and drained. If low permeability layers contain fractures which pinch out with depth, DNAPL may pool in these fractures.

Low permeability layers must be free of erosional or depositional gaps and fractures for pooling of DNAPL to occur. In most cases, the low permeability layers will deflect the downward movement of DNAPL, but will not be of sufficient lateral extent and composition to serve as a significant barrier to downward migration of DNAPL. Where these layers are discontinuous laterally, they can cause horizontal spreading of DNAPL, which can continue moving downward once the edge of the restrictive layer is reached, resulting in a complex DNAPL distribution. Typically, many small pools in discontinuous lenses and fractures would be expected to form. Contrasts in permeability can be important because even small scale variations play a major role in determining the DNAPL distribution in the regolith.

Capillary forces in any porous medium that DNAPL can enter will trap a certain amount as residual

DNAPL. In the vadose zone, in the rare case of dry conditions in Tennessee regolith, DNAPL will be the wetting fluid and will be retained as films and wetting rings coating the media. The amount held as residual DNAPL will increase with decreasing intrinsic permeability, effective porosity, and moisture content (Cohen and Mercer, 1993). More commonly, the vadose zone will be partly saturated with water and DNAPL will be retained as nonwetting ganglia in the pore throats and bodies of the media. In the saturated zone, DNAPL will be retained as isolated ganglia in the large pore body spaces. Residual saturation will be less in the unsaturated zone because DNAPL drains more easily in the presence of air than in a water-saturated system.

Macropores and fractures may be important pathways for DNAPL movement in clay-rich regolith. As with porous media, residual DNAPL will be held in these fractures by capillary forces as disconnected blobs and ganglia. Values of residual saturation in fractured clays will be less than in porous media (Pankow and Cherry, 1996) and will increase with decreasing fracture aperture (Schwille, 1988). DNAPL pools will accumulate in fractures that pinch out sufficiently with depth to provide a capillary barrier.

Large DNAPL pools in the regolith are expected to be rare in carbonate settings. Many small pools in course-grained layers within fine-grained layers may be typical. The amount of product released along with the local thickness and composition of the regolith will determine how significant regolith trapping will be at a site. The regolith is typically thinnest in the inner Central Basin, Cumberland Plateau, and outer Central Basin and thickest in the Highland Rim and Valley and Ridge (table 4). Substantial pooling on a low permeability layer in the regolith has been documented in case study 26-505 (described later in this report), located in The Barrens area of the Eastern Highland Rim.

In the situation where DNAPL has pooled on top of a low permeability layer, the residence time and removal processes depend on where the pool is located. The two main processes that determine the residence time are volatilization and dissolution. The DNAPL may be located above the water table, below the water table, or within the zone where the water-table surface fluctuates. In the vadose zone, volatilization is the dominant process for removal of DNAPL. After volatilizing into the soil gas, the vapor will dissolve into infiltrating water to contribute to dissolved-phase contamination of ground water. Dissolution also will occur from the DNAPL pool into infiltrating water. In the saturated zone, dissolution into the ground water is the dominant process of DNAPL depletion. A DNAPL pool located in the zone where the water-table surface fluctuates would be depleted through both volatilization and dissolution. DNAPL pools trapped in the vadose zone have shorter residence times than pools trapped below the water table. However, residence times in the vadose zone may still be of sufficient duration to present a long-term source of dissolved-phase contamination. The same processes just described also apply to residual DNAPL in intergranular pores and fractures.

Residual DNAPL will have a shorter residence time than DNAPL in pools because the higher ratio of surface area to volume of residual DNAPL increases the rates of the processes that deplete the DNAPL. Results of laboratory and modeling experiments show that residence time on the order of months to years can be expected for residual DNAPL. Residence time for thin, horizontal pools can be expected to be on the order of decades to centuries. DNAPL pools in clay fractures can be depleted by matrix diffusion in time-frames on the order of weeks to a few years (Pankow and Cherry, 1996).

If the regolith is sufficiently thin and the contaminated area limited, excavation and removal of the DNAPL is effective. If pools are found on top of low permeability layers at shallow depths, DNAPL can be successfully excavated, significantly reducing the source mass. More typically, the DNAPL will be distributed in many small pools that will be difficult to find. Patterns of residual DNAPL will be similarly complex, making location and remediation difficult. Solvent that has diffused into low-permeability layers will be slow to diffuse back out.

Pooling at Top of Rock

DNAPL contamination at land surface and in the shallow soil zone can migrate down through the regolith to the top of the underlying bedrock. In this report, “top of rock” refers to the surface between the regolith and bedrock. In karst settings, this surface is commonly irregular, highly weathered, and variable in depth. The top of rock is part of a transitional zone (the subcutaneous zone or epikarst) that includes weathered rock fragments in the regolith and dissolution openings within the upper part of the bedrock. The transitional epikarst zone is commonly 3 to 10 m thick and extends above and below the top of rock (Quinlan, 1989).

For DNAPL to accumulate at the top of rock, the DNAPL must pass through the regolith and encounter a low-permeability pooling site at the bedrock surface. Even small volumes of DNAPL will in general have the potential to migrate down to the top of rock (Cohen and Mercer, 1993; Pankow and Cherry, 1996). At top of rock, DNAPL may accumulate in pools where differential weathering or structure has created irregularities in the bedrock surface.

For a given DNAPL release, the relative importance of pooling at top of rock will be influenced by the thickness and physical properties of the regolith, the bedrock lithology, and the geologic structure. Thin, permeable regolith will allow DNAPL to reach top of rock more easily than thick regolith with high residual saturation or numerous impermeable layers. Rocks with low secondary porosity or in which dissolution openings in epikarst pinch out with depth (Williams, 1983, 1985) will trap DNAPL more effectively than rocks with efficient hydraulic connections between their surface and underlying bedrock aquifers. DNAPL is more likely to be trapped by flat-lying or gently dipping rocks than by steeply dipping rocks, especially in cases where secondary porosity develops preferentially along bedding planes.

All of the carbonate formations of Tennessee have the potential to trap at least some DNAPL at their upper surfaces. In the Central Basin, the thin soils, gently dipping strata, and numerous outcrops of confining units, such as the Hermitage Formation, are conducive to top-of-rock pooling. Areas of the Highland Rim also have high potential to trap DNAPL at the bedrock surface, especially where point-recharge features are locally uncommon. DNAPL pooling at top of rock is less likely along the coves and escarpments of the Cumberland Plateau where high sinkhole density (Crawford and Veni, 1986) and close hydraulic integration between sinkholes and karst conduits (Crawford, 1987) provide efficient pathways for water and contaminants to move below the regolith-bedrock interface. Similarly, the steeply dipping strata and dissolution-enlarged bedding planes of carbonate units in the Valley and Ridge have high potential to transmit DNAPL beneath the top of rock.

The top of rock can be perennially saturated, perennially dry, or alternately wet and dry. For perennially saturated DNAPL pools, dissolution is the main mechanism of depletion. A DNAPL pool has a lower surface-area to volume ratio than has residual DNAPL. Only the pool surface and margins can come into contact with flowing water. Flow velocities through the regolith and the rate at which the DNAPL-water boundary layer is flushed are likely to be limiting factors for DNAPL dissolution. Residence time for DNAPL pools that are permanently below the water table are likely to be relatively long (years to decades). Top-of-rock pools that are exposed to air will be depleted mainly by volatilization. In most cases, the vapor is likely to remain in the subsurface as a persistent source of aqueous contamination. In areas such as the Eastern Highland Rim where the top-of-rock zone is an important aquifer (Haugh and others, 1992), DNAPL pooling at the bedrock surface could have a substantial effect on ground-water resources.

Location and removal of DNAPL at top of rock is complicated by increased depth to bedrock, topographic complexity of the bedrock surface, and distance between the initial release and the site of subsurface accumulation. The average depth to bedrock and, perhaps more important, the complexity of the top-of-rock geometry are two critical factors that can be evaluated in the early stages of a site investigation. Where epikarst is poorly developed, maps of top-of-rock topography, contaminant concentrations, and geologic structure may be useful tools for locating DNAPL. Epikarst development is commonly greatest in relatively pure limestones and dolomites, but impure carbonates such as the Warsaw Limestone and Fort Payne Formation of the Highland Rim can have well-developed epikarst (Burchett and Hollyday, 1974; Haugh and others, 1992). If DNAPL is found in a relatively simple depression in the bedrock surface beneath relatively shallow regolith, direct excavation of the contaminated regolith is an effective mitigation method.

In many cases, thick regolith, highly developed epikarst, or migration along capillary barriers will interfere with the location or removal of DNAPL. In such cases, evaluating contaminant concentrations in ground-water or soil samples and techniques such as soil-gas analysis may be effective methods for estimating DNAPL location. If DNAPL has not migrated far from the site where it was spilled, it may be possible to find part of the DNAPL mass using these techniques. If located, DNAPL may be at least partly removed by direct pumping, air-sparging, or other techniques, depending on local conditions.

Pooling in Bedrock Diffuse-Flow Zone

A diffuse-flow zone in bedrock occurs where many small fractures are present but where dissolution is minor, or where dissolution-enlarged fractures are filled with granular material. A typical environment for this situation is fractured shales and carbonates or conduits that have been filled with sediment washed in from land surface. Ground water moves through a diffuse network of small fractures or through granular material within conduits rather than through discrete conduits. Flow through the diffuse network may converge on larger conduits with more concentrated flow. In this situation, DNAPL present in a diffuse-flow zone could provide a source of aqueous-phase contamination to the more rapid flow in a large conduit.

DNAPL will migrate down through the network of fractures until the capillary resistance becomes too high for continued downward movement. DNAPL will then pool in the fractures. Within a network of small fractures, large vertical accumulations of DNAPL are possible.

Fractured shales in the Valley and Ridge form locally important aquifers (Hollyday and Hileman, in press). Zones of diffuse flow may also occur within the shales, sandstones, and carbonates of the Cumberland Plateau, Highland Rim, and Central Basin. Case study 82-516 (described later in this report) provides an example of a site where DNAPL has been documented to be pooled in a fracture network in the Sevier Formation in the Valley and Ridge. At this site, most ground-water flow occurs through the fracture network. Chieruzzi and others (1995) describe a site in southwestern Kentucky where DNAPL is being recovered by wells in the Ste. Genevieve and St. Louis Limestones from a diffuse-flow zone of pores and vugs in permeable beds or bedding planes. At this site, diffuse-flow blocks are believed to be bounded by a poorly connected system of conduits.

The residence time of DNAPL pooled in zones of diffuse flow is determined by dissolution and matrix diffusion. Dissolution into the actively flowing ground water is slow because of the small surface area available for DNAPL pooled in fractures. The rate of ground-water movement also limits the amount of DNAPL that can be depleted by dissolution. In cases where DNAPL is pooled in a network of fractures, a much larger surface area is available for matrix diffusion. Matrix diffusion can be an important process if the rock matrix has significant primary porosity. In Tennessee karst, significant primary porosity is likely only in a zone surrounding fractures and bedding planes where a significant width of dissolution has left a broad band of insoluble residue within an impure soluble rock. DNAPL depletion by matrix diffusion from all but the smallest (less than 0.1 mm) aperture fractures may take years or longer (Pankow and Cherry, 1996). After DNAPL has been depleted from fractures, solvent dissolved in the matrix pore water diffuses back into the fracture, serving as a persistent source of dissolved-phase contamination.

When found in fractures, some of the DNAPL may be removed by pumping, thereby reducing the source mass. However, the complex nature of DNAPL distribution in a fracture network makes the DNAPL mass difficult to find. Even when found, some of the DNAPL may be in dead-end fractures or fractures removed from active ground-water flow.

Pooling in Karst Conduits

Flow in dissolution-enlarged openings is one of the most characteristic and best studied features of ground water in karst terranes. Much effort has been devoted in recent decades to the establishment of general principles governing this complex and variable phenomenon (White, 1969, 1977, 1988; Ford and Williams, 1989; Quinlan and others, 1992). In general, the best understood aspects of karst-conduit flow concern flow in large conduits (caves) directly accessible to researchers (White and Deike, 1989). The hydraulics of the much more numerous small (millimeter to centimeter scale) conduits are known only in the most general terms (Ford and Williams, 1989, ch. 5-6), though there is no basis for assuming that flow in small conduits is less important than flow in explorable caves in terms of overall aquifer hydraulics or contaminant transport. For many karst aquifers, with few or no explorable caves, small conduits represent most or all of the conduit-flow system. Empirical methods, such as dye tracing and spring sampling, are the most powerful tools currently available for characterizing karst-conduit flow systems. These methods are directly applicable to contaminants in aqueous solution (Quinlan and Ewers, 1985; Quinlan and others, 1992; Field, 1993), but provide only a limited basis for assessing DNAPL movement and storage within conduits.

The characteristic size range of karst conduits, typically on the order of millimeters to tens of meters (Ford and Williams, 1989, ch. 7), is too large for capillary forces to significantly restrict DNAPL movement.

Thus, DNAPL will freely flow into most of the open conduits it encounters. Once it enters a conduit, DNAPL will flow along the conduit floor, collecting in cracks, pits, or other depressions. The movement, transformation, and persistence of a given DNAPL mass in a karst conduit depends on such case-specific factors as the size and shape of the conduit, the topography of the conduit floor, the degree of residual or sedimentary fill, and the position of the conduit relative to water-table fluctuations. All of these factors exhibit enormous variation in karst terranes (White, 1988; Ford and Williams, 1989).

Karst conduits develop along preferential pathways between areas of ground-water recharge and discharge, and are enlarged by dissolution (White, 1988). Karst landforms, such as sinkholes, that concentrate recharge may be closely integrated with conduits and thus provide direct routes for contaminants to conduit flow systems (Quinlan and others, 1992; Field, 1993).

Once DNAPL enters a conduit, any irregularity or obstruction in the conduit floor or inflection in conduit orientation will provide a place for the DNAPL to pool. Studies of springs show that karst conduit systems retain significant volumes of easily displaced vadose storage (water) in pools (Joseph Meiman, U.S. National Park Service, oral commun., 1997). The same pools will also hold DNAPL and may have enough volume to contain large DNAPL spills. Low spots along the floor of a conduit where DNAPL can pool (sumps) may be without capillary cracks, leaving all the pooled DNAPL exposed to flow. Such conduits can develop along the tops of confining units, or through massive limestone. Other conduits have sumps coinciding with cracks in the conduit floor through which DNAPL could migrate downward and out of the conduit-flow system.

All karst settings in Tennessee contain conduit-flow systems capable of storing DNAPL. The best developed conduit systems are in the Central Basin, the sinkhole plains of the Highland Rim, the coves and escarpments of the Cumberland Plateau, and the limestone and dolomite outcrops of the Valley and Ridge.

DNAPL pools in karst conduits can be perennially submerged in water or periodically exposed to air. DNAPL pools exposed to air will be depleted through volatilization. The fate of the resulting vapor will depend on the air-flow characteristics of the conduit. In many cases, vapor-phase chlorinated solvents may be as persistent in karst conduits as in other parts of the ground-water system. On the other hand, cave systems with high air flows (Bruce Zerr, Oak Ridge National Laboratory, oral commun., 1996) may efficiently route chlorinated-solvent vapors to the surface.

Flow velocities in conduits are high relative to ground-water flow rates in other settings (White, 1988; Quinlan and others, 1992). Recurrent inputs of fresh water tend to flush aqueous-phase contaminants and maintain a high concentration gradient close to the DNAPL pool. Dissolution is more likely governed by the maximum rate of dissolution into pure water than by the replacement of saturated solution in contact with the DNAPL. Frequent flushing of the DNAPL-water boundary layer would encourage relatively rapid dissolution and a short residence time (from weeks to years). However, Field (1993) notes that karst conduits can rapidly deliver significant quantities of contaminant to a discharge point yet still retain enough contaminant in storage to result in long-term ground-water contamination.

The configuration of DNAPL pools in conduits determines the surface area exposed to flowing water, and, in turn, the residence time of the pool. Karst conduits can be long and narrow or nearly round in cross section; they can be nearly level or vertical; they can be open or filled with unconsolidated material (White, 1988; Ford and Williams, 1989). All of these factors will affect residence time and movement of DNAPL in karst conduits. In narrow passages with appreciable dip, DNAPL will drain down-dip to fill the lowest depressions. Narrow, deep pools of DNAPL exposed to flow only along their upper edge will dissolve more slowly than wide, shallow pools.

The amount and pore-size distribution of unconsolidated fill in a conduit influence the ability of DNAPL to enter the conduit and the distribution and eventual fate of any DNAPL that does enter. Unconsolidated fill may largely exclude DNAPL from some parts of a conduit system. Conversely, infiltration of DNAPL into coarse-grained cave sediment or residuum, burial of a DNAPL pool by sediment, or the formation of DNAPL sludges in combination with organic matter will reduce the pool's exposure to flowing water (Palmer, 1984, 1986), potentially increasing residence time to decades or longer.

Pooling of DNAPL in active karst conduits can result in delivery of dissolved contaminants to springs and to any wells that intercept the conduits downgradient of the pools. Because of the high flow velocities and convergent flow patterns of karst conduits, such contamination may be concentrated in relatively few wells or springs. Where DNAPL residence time is short because a wide, shallow DNAPL pool is exposed to large rapid flow, the mass flux of aqueous-contaminant will be correspondingly high. Dilution by uncontaminated water from converging conduits may partly attenuate concentrations in such cases, but concentration may still exceed drinking-water standards.

Ground-water levels in karst conduit systems can fluctuate several meters to tens of meters during periods as short as a few hours or days (Milanovic, 1981, p. 128-132; Quinlan and Ewers, 1985; Wolfe, 1996a, b). Many karst conduit systems have several levels of conduits and discharge points whose relative importance varies with fluctuations in ground-water levels (Palmer, 1986; White, 1988). At high water levels, discharge is commonly routed to overflow springs that remain dry at lower ground-water levels. Ground-water mixing may deliver dissolved contaminant to these overflow springs. Such mixing will probably reduce contaminant concentrations, but not necessarily below acceptable levels. Only dye traces and sampling under a variety of hydrologic conditions, based on careful inventory of springs, seeps, and other karst features, will reveal the presence of multilevel discharge points.

The complexity and high localization of karst conduit systems make the prospects of finding a DNAPL pool in conduit storage unlikely. One approach to remediation may be to identify discharge points and potentially affected parties using dye traces and water sampling and to provide alternative water supply until concentrations fall below drinking water standards. Depending on the details of the contaminant release and the conduit system, such reduction may take years or decades. Any conduit system that has transported or stored DNAPL in the past may still contain DNAPL pools. High-discharge events may exhume such isolated pools and deliver additional contaminants to discharge points.

Most karst conduits ultimately discharge at springs. Contaminated springs may be distant from the source of contamination or in nonintuitive locations. Comprehensive karst inventories, dye-tracing studies, and long-term spring sampling under different hydrologic conditions offer the best chance of determining the destination of dissolved contaminants (Quinlan and Ewers, 1985; Quinlan, 1989). Temporal patterns of contaminant-mass flux at springs may provide information about DNAPL distribution relative to the water table (Sid Jones, Tennessee Department of Environment and Conservation, written commun., 1997).

Pooling in Fractures Isolated from Major Zones of Ground-Water Flow

The high densities and low viscosities of chlorinated solvents cause these compounds to migrate downward until they encounter openings too small to enter. Under certain conditions, this downward migration can take DNAPL to fractures that are relatively isolated from major ground-water flow zones. In contrast to the previous cases discussed in this section, pools of DNAPL in isolated fractures have minimal interaction with flowing water. Reduced exposure to flowing water has major implications for DNAPL residence time, mitigation, and delivery to drinking-water supplies.

Every karst aquifer has a lower boundary below which flow is greatly reduced. In general, smooth, abrupt lower boundaries are probably much less common than are rough, gradational boundaries. Karst develops through the interaction of atmospheric water with soluble rock (White, 1988). In many cases, dissolution and the resulting secondary porosity are concentrated in the upper parts of a carbonate rock unit and decrease with depth (Ford and Williams, 1989, p. 158-162). The base of karstification is typically a zone in which the karst-conduit system propagates downward through the progressive enlargement and integration of discrete voids which initially have only poor interconnection. This zone may be at considerable depth below the zone of major flow within the aquifer (Ford and Williams, 1989, p. 177-178). The network of conduits and fractures above the base of karstification provides potential flow paths for DNAPL through the major flow zone to the smaller, more isolated voids below.

Regionally, epikarst systems may be thought of as karst aquifers which have been partly exhumed through weathering and erosion. Near their lower limits, epikarst systems exhibit a decrease in the frequency and size of dissolution openings analogous to the pattern described above (Williams, 1983). Dissolution openings in epikarst can store significant quantities of ground water, in part because relatively few such openings are directly connected to underlying aquifers (Williams, 1983, 1985). Blind epikarst openings that decrease in width toward their lower limits may store DNAPL in isolation from ground-water flow, provided the openings are not filled with regolith that is impermeable to DNAPL.

Similar to karst aquifers, noncarbonate fractured-rock aquifers commonly have secondary porosity and associated ground-water flow that decrease with depth (Davis and Turk, 1964; Davis, 1988). In the case of fractured, noncarbonate rocks, forces such as tectonic stress initiate fracturing, but progressive unloading through erosion and uplift is a major mechanism through which these incipient fractures are sufficiently enlarged to convey significant ground-water flow (Trainer, 1988). DNAPL entering the more permeable, highly fractured part of a fractured-rock aquifer has potential to migrate downward to the smaller, less numerous fractures at the base of the aquifer where it will be isolated from flow.

Migration of DNAPL to fractures isolated from ground-water flow is most likely where ground-water flow is concentrated in the upper part of the aquifer and secondary porosity extends to considerable depth below the major flow zone. These conditions are met in the several karst aquifers of the Central Basin, the carbonates and fractured shales of the Valley and Ridge, the cavernous dolomites of the western toe of the Blue Ridge, the fractured sandstones of the Cumberland Plateau (Brahana, Macy, and others, 1986), and the fractured crystalline rocks of the Blue Ridge (Brahana, Mulderink, and others, 1986). In the Highland Rim, potential for pooling in isolation from ground-water flow depends largely on the local thickness of the Mississippian carbonate sequence, which decreases where the Chattanooga Shale confining unit is near the surface. The high hydraulic gradients and well-developed conduit systems of the Cumberland Plateau escarpments make isolation of DNAPL pools from ground-water flow less likely than in other karst settings.

A DNAPL pool isolated from ground-water flow will have a long residence time (on the order of decades or longer). The major mechanism for removal will be diffusion into adjacent fractures and primary pores. The low rate of local flow will limit flushing of the aqueous phase, resulting in a relatively low concentration gradient near the DNAPL mass and a correspondingly low rate of diffusion and dissolution. Migration of aqueous phase to zones of higher ground-water flow will occur through diffusion. Depending on the flow system, the rate of diffusion may be small relative to the flow, resulting in greater or lesser attenuation by dilution. Whatever the attenuation achieved by dilution, aqueous-phase contamination of ground water from DNAPL pools isolated from ground-water flow is likely to persist for many decades.

Isolation from major ground-water flow does not preclude severe local impacts on ground-water resources. In areas where ground water is scarce, such as in parts of the Cumberland Plateau and Blue Ridge, water-supply wells are commonly drilled into low-yielding units that would be considered confining units elsewhere. Pooled DNAPL in such settings might contaminate existing wells, further depleting an already scarce resource. DNAPL masses that sink below zones of ground-water flow are unlikely to be located. If found, mitigation will be limited by the same factors that operate in the case of DNAPL in bedrock diffuse-flow zones discussed previously.

CASE STUDIES IN SELECTED KARST REGIONS

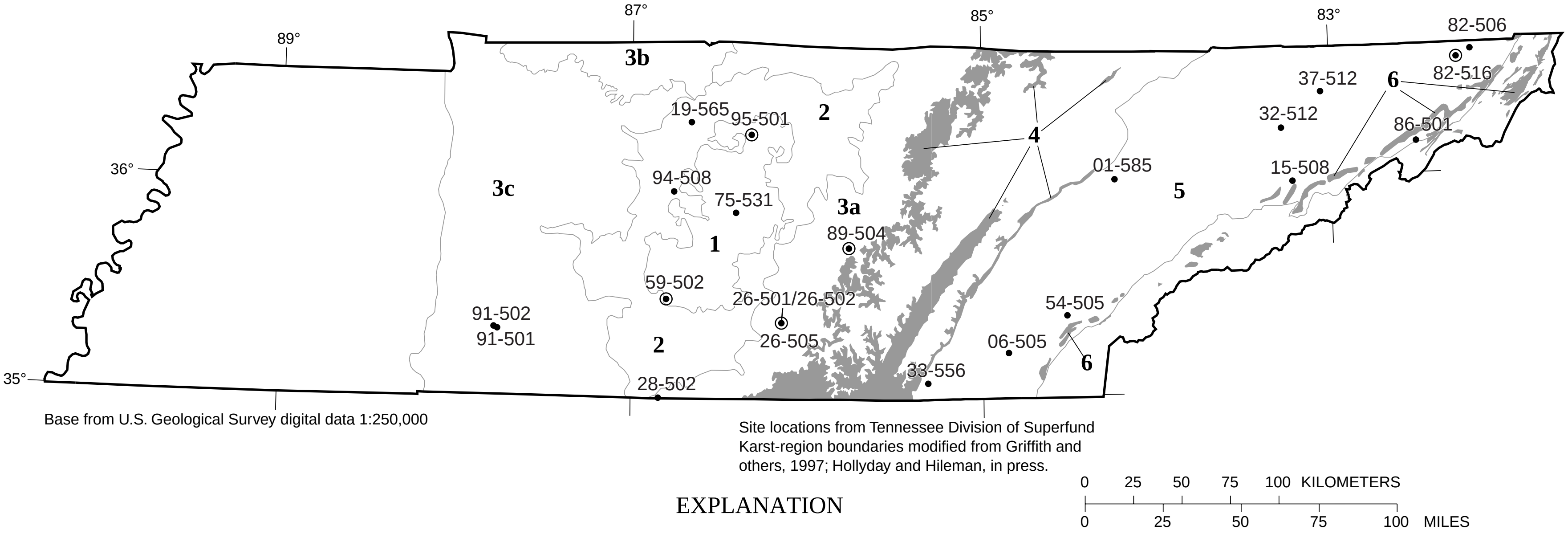
Selection Criteria for Case Studies

Twenty-two case studies were selected from the Tennessee Division of Superfund files to evaluate chlorinated-solvent contamination in the karst regions of Middle and East Tennessee (fig. 13, and table 5). The Division of Superfund files are available for review at the Division of Superfund central office in Nashville, Tennessee, and in the Division’s regional field offices. For a thorough review, both sources should be consulted. Additional information for a few sites was gathered from other State agencies. State Superfund sites are organized by county and individual site number.

These sites are at different stages of the investigation-remediation process, and the amount of data varies from site to site. Available site data was evaluated to select the case studies. The information included in this report is based on available data at the time the case study evaluation was completed (March 1997).

Criteria used to select the case studies for this report consisted of the following: (1) the site is located in a karst region of Tennessee, (2) the volume and type of release of chlorinated solvents is known, (3) the vertical and horizontal extent of the dissolved chlorinated solvents is defined, (4) dye-tracer tests were completed for the site, and (5) chlorinated DNAPL is documented at the site. During the selection process, even the most extensively documented case studies did not meet all of these criteria. A discussion of the selection criteria is presented below. Detailed discussions of five case studies follow the discussion of the criteria.

Case studies were selected in five karst regions: the inner Central Basin (3 sites), the outer Central



Base from U.S. Geological Survey digital data 1:250,000

Site locations from Tennessee Division of Superfund
Karst-region boundaries modified from Griffith and others, 1997; Hollyday and Hileman, in press.

EXPLANATION

1 INNER CENTRAL BASIN
2 OUTER CENTRAL BASIN
3 HIGHLAND RIM
3a EASTERN HIGHLAND RIM
3b PENNYROYAL PLATEAU
3c WESTERN HIGHLAND RIM
4 COVES AND ESCARPMENTS OF THE CUMBERLAND PLATEAU
5 VALLEY AND RIDGE
6 WESTERN TOE

● 33-556 CASE STUDY SITE AND NUMBER
◉ 26-505 CASE STUDY DISCUSSED IN REPORT AND NUMBER

Figure 13. Location of selected Tennessee State Superfund sites with known chlorinated-solvent contamination within karst regions of Tennessee.

Table 5. Selected case studies from Tennessee Department of Environment and Conservation site files

[Data source: Tennessee Department of Environment and Conservation Superfund site files (unpublished); TCE, trichloroethylene; PCE, tetrachloroethylene; DCE, dichloroethylene; TCFM, Trichlorofluoromethane, TCA, trichloroethane; mg/kg, milligrams per kilogram; mg/L, milligrams per liter; DNAPL, dense nonaqueous phase liquid; U.S. EPA, U.S. Environmental Protection Agency]

Description	Inner Central Basin			Outer Central Basin	
Site Characteristics					
Site number	59-502	75-531	95-501	19-565	94-508
County	Marshall	Rutherford	Wilson	Davidson	Williamson
Activity	Manufacturing	Waste recycling, reclaiming.	Manufacturing	Manufacturing	Waste disposal.
Years of operation	17	2	25	36	1
Primary chlorinated solvent(s)	TCE	TCE/PCE	TCE	TCE/1,2-DCE	TCE/PCE
Estimated release volume (liters)	13,000	7,286	Unknown	570 to 800	Unknown
Dye-trace data available (Yes/No)	Yes	No	No	No	No
Site Hydrogeology					
Regolith thickness (meters)	4 to 9	Less than 1	0.45 to 2.8	Up to 18	1 to 5
Bedrock: Limestone (L), Dolomite (D), Shale (S)	L/S	L/S	L/S	L	L/S
Average depth to water (meters)	6 to 15	12 to 24	2	Varies	4.3 to 11
Fracture flow (Yes/No)	Yes	Yes	Yes	Yes	Yes
Karst features	Springs, sinking streams, caves.	Sinkholes	Sinkholes, springs.	Springs	Springs
Contaminant Characteristics					
Highest soil concentration (mg/kg)	TCE 1,160	PCE 0.52	TCE 2.1	TCE 0.022	PCE 0.024
Highest dissolved concentration (mg/L)	TCE 950,000	No wells	TCE 290	TCE 10	TCE 0.85
Measured dissolved horizontal extent (meters)	370 x 200	Unknown	200 x 430	183 x 243	300 x 110
Measured dissolved vertical extent (meters)	68	Unknown	20	12 to 15	5 to 13
Potential for DNAPL occurrence (U.S. EPA, 1992b).	Confirmed	Moderate	High	Moderate	Moderate
DNAPL observed (Yes/No)	Yes	No	No	No	No

Table 5. Selected case studies from Tennessee Department of Environment and Conservation site files—Continued

Description	Highland Rim			
Site Characteristics				
Site number	26-501	26-502	26-505	28-502
County	Coffee	Franklin	Coffee	Giles
Activity	Waste disposal.	Waste disposal.	Waste disposal.	Manufacturing
Years of operation	29	27	22	23
Primary chlorinated solvent(s)	PCE/TCE	TCFM/PCE/TCE	PCE/ 1,1,1-TCA	1,1,1-TCA/PCE
Estimated release volume (liters)	Unknown	Unknown	Unknown	Unknown
Dye-trace data available (Yes/No)	No	No	No	Yes
Site Hydrogeology				
Regolith thickness (meters)	22 to 29	18 to 25	20 to 26	20
Bedrock: Limestone (L), Dolomite (D), Shale (S)	L	L	L	L
Average depth to water (meters)	1.5 to 6	6 to 15	5 to 8	5 to 8
Fracture flow (Yes/No)	Yes	Yes	Yes	Yes
Karst features	None	Springs	None	Springs
Contaminant Characteristics				
Highest soil concentration (mg/kg)	PCE 95.6, TCE 39	PCE 7.3, TCE 1.0	PCE 3,000	1,1,1-TCA 250
Highest dissolved concentration (mg/L)	PCE 120, TCE 89	TCFM 170, TCE 26	PCE 140; 1,1,1-TCA 290	PCE 16
Measured dissolved horizontal extent (meters)	2,600 x 760	2,000 x 400	420 x 270	36 x 46
Measured dissolved vertical extent (meters)	30	26	11	2 to 5
Potential for DNAPL occurrence (U.S. EPA, 1992b)	High/moderate	High/moderate	Confirmed	High
DNAPL observed (Yes/No)	No	No	Yes	No

Table 5. Selected case studies from Tennessee Department of Environment and Conservation site files—Continued

Description	Highland Rim		
Site Characteristics			
Site number	89-504	91-501	91-502
County	Warren	Wayne	Wayne
Activity	Manufacturing	Manufacturing	Waste disposal
Years of operation	37	15	2
Primary chlorinated solvent(s)	TCE/1,2-DCE/PCE	TCE	TCE/PCE
Estimated release volume (liters)	Unknown	Unknown	40,000
Dye-trace data available (Yes/No)	Yes	No	No
Site Hydrogeology			
Regolith thickness (meters)	5 to 9	1 to 3	50
Bedrock: Limestone (L), Dolomite (D), Shale (S)	L	L	L
Average depth to water (meters)	2 to 4	Varies to 12	13 to 60
Fracture flow (Yes/No)	Yes	Yes	Yes
Karst features	Sinkholes, caves, springs, sinking streams.	Spring	Springs
Contaminant Characteristics			
Highest soil concentration (mg/kg)	TCE 0.048	TCE 0.019	TCE 0.215
Highest dissolved concentration (mg/L)	1,2-DCE 8.82	TCE 250	PCE 40
Measured dissolved horizontal extent (meters)	122 x 30	Greater than 320 x 251	Unknown
Measured dissolved vertical extent (meters)	16 to 22	30	53
Potential for DNAPL occurrence (U.S. EPA, 1992b)	Confirmed	High	High
DNAPL observed (Yes/No)	Yes	No	No

Table 5. Selected case studies from Tennessee Department of Environment and Conservation site files—Continued

Description	Valley and Ridge				
Site Characteristics					
Site Number	01-585	06-505	15-508	32-512	33-556
County	Anderson	Bradley	Cocke	Hamblen	Hamilton
Activity	Manufacturing	Manufacturing	Manufacturing	Manufacturing	Manufacturing
Years of operation	1	35	27	23	32
Primary chlorinated solvent(s)	TCE	TCE/PCE	TCE/1,1,1-TCA	TCE	PCE
Estimated release volume (liters)	Unknown	Unknown	Unknown	Unknown	Unknown
Dye-trace data available (Yes/No)	No	Nearby site	No	No	No
Site Hydrogeology					
Regolith thickness (meters)	5 to 11	4 to 12	1 to 5	5 to 17	8.5 to 15
Bedrock: Limestone (L), Dolomite (D), Shale (S)	S	L/S	S/D	S/D	S/L
Average depth to water (meters)	6 to 7	6 to 7	3 to 8	21 to 40	4.5 to 6
Fracture flow (Yes/No)	Yes	Yes	Yes	Yes	Yes
Karst features	Spring	Springs	Springs	Spring, sinks	None
Contaminant Characteristics					
Highest soil concentration (mg/kg)	TCE 12	PCE 890	TCE 0.035	TCE 25	Not detected
Highest dissolved concentration (mg/L)	TCE 26	PCE 25	TCE 5.76	TCE 0.19	PCE 84
Measured dissolved horizontal extent (meters)	53 x 29	430 x 120	300 x 220	95 x 73	300 x 200
Measured dissolved vertical extent (meters)	125	36	14 to 17	47 to 50	19.5
Potential for DNAPL occurrence (U.S. EPA, 1992b)	High	High/moderate	Moderate	Moderate	High/moderate
DNAPL observed (Yes/No)	No	No	No	No	No

Table 5. Selected case studies from Tennessee Department of Environment and Conservation site files—Continued

Case study characteristics	Valley and Ridge				Western toe of the Blue Ridge
Site Characteristics					
Site number	37-512	54-505	82-506	82-516	86-501
County	Hawkins	McMinn	Sullivan	Sullivan	Unicoi
Activity	Drum storage/ degreasing.	Waste disposal.	Storage/ drums.	Waste disposal.	Waste disposal.
Years of operation	5	12	4	7	7
Primary chlorinated solvent(s)	1,1,1-TCA	1,1,1-TCA/TCE	1,1,1-TCA	TCE	TCE
Estimated release volume (liters)	Unknown	Up to 420,000	Unknown	79,000 to 200,000	More than 800,000
Dye-trace data available (Yes/No)	No	No	No	No	No
Site Hydrogeology					
Regolith thickness (meters)	0.5 to 5	11 to 20	3	Less than 1.5	15 to 30
Bedrock: Limestone (L), Dolomite (D), Shale (S)	D/L/S	D	S	L/S	D
Average depth to water (meters)	1 to 9	Perched	0.3 to 2	Varies	10 to 40
Fracture flow (Yes/No)	Yes	Yes	Yes	Yes	Yes
Karst features	Springs	Sinks, springs	None	Springs, seeps	Springs
Contaminant Characteristics					
Highest soil concentration (mg/kg)	1,1,1-TCA 1.1	TCE 4.1	1,1,1-TCA 4.58	TCE 5.34	Not detected
Highest dissolved concentration (mg/L)	1,1,1-TCA 4.4	1,1,1-TCA 0.091	1,1,1-TCA 51.8	TCE 960	TCE 0.29, DCE 0.31
Measured dissolved horizontal extent (meters)	37 x 46	490 x 240	90 x 30	550 x 335	150
Measured dissolved vertical extent (meters)	13	26	3	108	54
Potential for DNAPL occurrence (U.S. EPA, 1992b).	High/moderate	High/moderate	High/moderate	Confirmed	High/moderate
DNAPL observed (Yes/No)	No	No	No	Yes	No

Basin (2 sites), the Highland Rim (7 sites), the Valley and Ridge (9 sites), and the western toe of the Blue Ridge (1 site). Most of the case studies reported springs, sinkholes, or seeps present at or near a site; however, four case studies did not have any documented evidence of karst features. No case studies were selected in the Pennyroyal Plateau part of the Highland Rim or in the coves and escarpments of the Cumberland Plateau due to the lack of sites with documented contamination from chlorinated solvents.

The volume of chlorinated solvents and types of release were documented at some sites. At other sites this information was estimated from the number of drums of solvent used or removed. Fifteen of the selected case studies did not have sufficient information to estimate the amount of released solvent.

The reported vertical and horizontal extent of the dissolved chlorinated solvents was determined from the chemical analyses of ground-water samples collected from monitoring wells and springs on or near the sites. When available, additional information of contaminant extent was provided by analyses of soil, surface-water, and domestic-well water samples. In some case studies, dissolved contaminants were present in creeks or streams. Documentation of the vertical extent of dissolved chlorinated solvents for each case study was limited by the depths and screened intervals of monitoring wells completed at a site. In karst, the effectiveness of monitoring wells depends on intercepting the localized ground-water flow paths along which contaminants may migrate. Dye-trace study results were available for 4 of the 22 selected case studies at the time of this study.

Documented evidence of chlorinated DNAPL was absent in most of the case studies chosen for this report. Only 4 of the 22 case studies reported visual evidence of DNAPL, usually described as a separate-phase liquid, denser than water, having a dark brownish/blackish color. Chlorinated solvents such as TCE and PCE are colorless or clear when pure or unused (Lucius and others, 1992).

The lack of evidence of DNAPL does not necessarily indicate its absence at a site but may reflect the complexity of the site and of the DNAPL distribution. The U.S. Environmental Protection Agency (U.S. EPA) published a guidance document (U.S. EPA, 1992b) that suggests a method to estimate the potential for DNAPL occurrence at a site.

The method, as described by the U.S. EPA (1992b), emphasizes the historical use of DNAPL and site characterization data. Relevant historical data include the industry type, processes, and waste-disposal practices for DNAPL and DNAPL-related chemicals. Important site characterization data include the observation of DNAPL and chemical analyses of ground water or soil samples collected at a site. Two important and often used chemical analytical conditions that suggest the presence of DNAPL include: (1) concentrations of DNAPL-related chemicals that are greater than 1 percent of the solubility limit (see table 2) in the ground water, and (2) concentrations of DNAPL-related chemicals that are greater than 10,000 milligrams per kilogram in the soil. Using this information, the potential for the occurrence of DNAPL is divided into three main categories: I—confirmed or high potential, II—moderate potential, and III—low potential. Based on the available data, combinations of these categories are possible.

Because four of the case studies already had documented evidence of DNAPL occurrence, the U.S. EPA method was applied to the remaining 18 sites to estimate potential DNAPL occurrence. These sites rated “high” or “moderate” potential for the occurrence of DNAPL. A limiting factor in the U.S. EPA method is that the approach to site characterization outlined is designed for granular porous media and may not be applicable in karst or fractured rock settings. Field (1988a), Quinlan and others (1992), and Quinlan (1994) address the problems associated with applying characterization techniques designed for porous media to karst settings.

Case Study Discussions

The 22 case studies selected for review in this report are grouped by karst regions of Tennessee (table 5 and Appendix). Each case study is designated with a Tennessee county number from 01 (Anderson County) to 95 (Wilson County) and a unique site number. Site background, hydrogeology, and contaminant characteristics allow a comparison of each case study (table 5). Five case studies were selected for discussion in detail to illustrate the relevance of their specific site characteristics to the previously described conceptual models. Case study summary sheets for each of the 22 sites are presented in the Appendix.

Case Study 26-505, Coffee County, Highland Rim

Case study 26-505 provides an example of DNAPL accumulation on a low permeability layer in the regolith. This site was used as a leach pit for the disposal of waste solvents and acids from 1950 to 1972. An unknown quantity of chlorinated solvents were disposed at the site. PCE and 1,1,1-TCA are the main contaminants at the site. PCE has been measured in the ground water at 140 milligrams per liter (mg/L), approximately 70 percent of its water-solubility limit. 1,1,1-TCA has been measured in the ground water at 290 mg/L, approximately 22 percent of its solubility limit. A 3-m column of DNAPL has been documented in a shallow recovery well onsite.

This site is located in the Highland Rim. The site stratigraphy consists of regolith of up to 26 m in thickness over fractured, cherty limestone bedrock of the Fort Payne Formation. The regolith is composed of clay with silt, sand, and varying amounts of chert grading in size from clay-size particles to large gravels. The size and quantity of chert tend to increase with depth. Isolated sandy clay and sand layers also are reported to be present.

Both the DNAPL and dissolved-phase contamination at this site appear to be limited to shallow depths and have not been documented at depths below about 11 m. DNAPL reportedly appears to have pooled on top of a clay layer (capillary barrier) underlying a sand layer. This DNAPL pool will most likely provide a continuing source for dissolved-phase contaminant for a long time. DNAPL recovery operations are currently underway at this site. Of note, at two other nearby sites in the same geologic setting (26-501 and 26-502), contamination has been documented to move downward through the regolith into water-bearing zones at the top of rock and in fractures in the rock. Therefore, the significant DNAPL pooling observed in the regolith at this site has not been documented at the other similarly situated sites nearby. These data highlight the extreme variability of karst settings and the need for careful and thorough investigation of each individual contaminated site.

Case Study 59-502, Marshall County, Inner Central Basin

Case study 59-502 illustrates DNAPL accumulation at the top of rock and its persistence within this zone for an extended period. This site is a manufacturing plant that was established in 1937. In 1980, an underground pipe connecting a storage tank to an onsite degreaser burst inside a utility trench. An estimated 13,000 liters of TCE was lost and drained into the underground sewer pipes. Clean-up and containment activities at the site have consisted of: two shallow recovery trenches, two deep pump-and-treat recovery well systems, a weir in a nearby surface stream, and treatment of contaminated soils not covered by the site building.

This site is located in the inner Central Basin and is underlain by the Lebanon, Ridley, and Pierce Limestones (Crawford, 1992; Crawford and Ulmer, 1994). The Ridley Limestone is a karst aquifer at least 30 m thick at the site and is confined above and below by the relatively impure Lebanon and Pierce Limestones, respectively. The confining units vary from 5 to 20 m thick. Fractures and dissolutionally enlarged openings that occur along the bedding planes of the Ridley Limestone facilitate horizontal and vertical ground-water flow. Crawford (1992) suggested that caves and cave streams can develop at the contacts between the aquifer and confining units.

TCE and its breakdown products (DCE and vinyl chloride) were detected in soils, ground water, and a surface stream. Water samples from 53 monitoring wells indicate that aquifer contamination has spread at least 150 m across the site. Vertically, TCE and its breakdown products were detected in ground-water monitoring wells with total depths as great as 68 m below land surface. The highest concentration of TCE (950,000 mg/L) was detected in 1987, when a 61-cm column of DNAPL was measured in a shallow well completed above the bedrock. Nine years later in 1996, TCE (150 mg/L) was still detectable in a top-of-rock well. Chlorinated solvents detected in deep wells completed below the top of rock indicate that the Lebanon Limestone confining unit did not prevent downward vertical migration of the contaminants.

Case Study 82-516, Sullivan County, Valley and Ridge

Case study 82-516 provides an example of DNAPL distributed throughout a network of fractures. This site reportedly was used from 1967 to 1974 for the disposal of drummed and bulk liquids. An estimated 79,000 liters of liquid wastes were discharged to an open pit where they were burned. Clean-up activities in 1984 and 1989 removed nearly 600 buried or partially buried drums from the site. The primary contaminant at the site is TCE. Sampling has detected maximum concentrations of TCE in the ground water at 960 mg/L and in the soil at 5.34 milligrams per kilogram. The dissolved concentration measured is nearly 90 percent of the water-solubility limit for TCE, indicating the probable presence of DNAPL. DNAPL has been detected and recovered from six onsite wells.

This site is located in the Valley and Ridge karst region. Site stratigraphy consists of less than 1.5 m of shaley silt loam overlying the shale of the Sevier Formation. The top 21 m of bedrock shows low fracture density and poorly developed ground-water flow. The next 60 m contains highly developed fracture networks with well-developed ground-water flow. At depths greater than 90 m, the shale is dense and hard allowing for little ground-water flow.

The six wells where DNAPL has been detected are all located near the center of the site. They delineate an area of approximately 230 by 90 m where DNAPL has been found in fractures. DNAPL has been detected in every well completed in this area. The maximum depth where DNAPL has been detected is 72 m, near the bottom of the highly developed fracture zone. Surrounding this DNAPL area is a larger area of dissolved contamination measuring approximately 550 by 335 m and extending to a depth of 108 m. The DNAPL distributed in the fractures most likely will provide a persistent source for dissolved-phase contamination.

At this site, the upper 21 m is considered poorly fractured and not conducive to ground-water flow, but this zone did not inhibit penetration of DNAPL to the deeper, more fractured ground-water flow zone. The DNAPL migrated downward with little lateral spreading, contaminating the underlying, more productive ground-water zone.

Case Study 89-504, Warren County, Eastern Highland Rim

Case study 89-504 illustrates DNAPL accumulation in a perennially saturated zone at top of bedrock. This site is a manufacturing plant where TCE and PCE have been stored and used since 1960. Releases of solvents to the environment are known to have occurred. The actual quantities released are unknown.

The site is located in the Eastern Highland Rim and is underlain by approximately 8 to 9 m of St. Louis Limestone residuum, consisting of clay, silt, sand, and chert gravel. This regolith overlies less than 2 m of a calcareous siltstone confining unit that separates the regolith from the middle Warsaw Limestone. The middle Warsaw Limestone is an aquifer characterized by dissolutionally enlarged fractures and joints. According to the case study file reports, perched water in the regolith can breach the confining unit where it is thin and enter cave streams formed in the middle Warsaw Limestone. Wells completed in the bedrock aquifer have been dry on different occasions, indicating seasonal saturated and unsaturated conditions.

Twenty-five wells were installed to determine the extent of contamination at the site. Concentrations of TCE and some of its breakdown products were detected in the ground water to 22 m. The highest dissolved TCE concentrations (0.7 to 5 mg/L) were detected in a spring discharging from the base of the regolith approximately 200 m from the source area. The highest dissolved chlorinated solvent, 1,2-DCE (8.82 mg/L) was detected in a shallow well completed above the bedrock. In 1996, a 20-cm-thick black/dark brown column of DNAPL was detected in a bailer removed from this well. No DNAPL has been detected in wells completed in the limestone aquifer.

Case Study 95-501, Wilson County, Inner Central Basin

Case study 95-501 demonstrates the occurrence of elevated chlorinated-solvent concentrations in the saturated zone of the regolith, without confirmed presence of DNAPL. This site is a manufacturing facility that was in operation from 1961 to 1986. In 1989, a site investigation determined that an unknown amount of TCE had leaked from an onsite vapor degreaser. Additionally, usage and storage practices contributed to extensive spillage at the facility. Remedial activities at this site have included soil removal and a recovery well system to prevent further contaminant migration.

The site is located in the inner Central Basin. Stratigraphy consists of approximately 3 m of silty clayey regolith overlying thick beds of fossiliferous Ordovician limestone interspersed with shale. According to the file reports, horizontal bedding planes in the top 20 m of the bedrock exhibit dissolutionally enlarged openings and interconnected fractures and joints. Ground-water elevations in the regolith and upper 20 m of the bedrock are similar, indicating hydraulic connection between the two units. Pumping-test data indicate a hydraulic connection with a creek approximately 30 m away. Below 20 m, the bedrock is characterized by low fracture density and thin shale partings. Several deep borings completed within this zone were dry.

Six open-hole bedrock wells and 35 screened wells were installed to characterize the contamination at the site. Dissolved chlorinated solvents, including TCE and its breakdown products (vinyl chloride and cis-1,2-DCE), were detected in the regolith (horizontal extent about 60 by 430 m), and in the upper 10 to 20 m of the bedrock (horizontal extent about 200 by 360 m). The highest dissolved TCE concentration (290 mg/L) was detected in a shallow (less than 1 m deep) well at 26 percent of the solubility limit. However, the presence of DNAPL is not mentioned in the file reports. TCE concentrations in water samples collected from the upper 10 to 20 m of the bedrock were less than 2 mg/L. Neither DNAPL nor chlorinated-solvent concentrations above 0.005 mg/L were detected in water samples collected from bedrock wells below 20 m. The interconnected fractures in the upper bedrock have likely facilitated the lateral movement of the dissolved contaminants at the site. TCE was detected in a water sample collected from the nearby creek at a concentration of 1.2 mg/L.

SUMMARY AND CONCLUSIONS

Two of the most problematic topics in contaminant hydrogeology are chlorinated solvents and karst. Chlorinated solvents have physical, chemical, and biological properties that make this class of compounds particularly likely to cause ground-water contamination. The high densities and low viscosities of chlorinated solvents allow them to move readily downward as a DNAPL through the subsurface due to gravity. The same properties that make chlorinated solvents potent ground-water contaminants make them difficult to locate or remove once they enter the ground-water system. Nowhere is this more true than in karst settings.

Many publications deal with chlorinated-solvent contamination and contamination of karst aquifers, but relatively few published studies address chlorinated-solvent contamination in karst. Previous studies relevant to this report include (1) studies of chlorinated-solvent properties, (2) studies of karst properties and karst hydrogeology, and (3) studies of aqueous-phase contamination of karst.

The physical and chemical properties of chlorinated solvents govern their behavior in the environment. The exact pathway of downward migration is influenced by such factors as interfacial tension, capillary pressure, hydraulic gradients, structural controls, and the type and nature of openings in an aquifer. Effects of capillary pressure explain much of the distribution and movement of subsurface DNAPL. Dissolution-enlarged fractures in carbonate aquifers have apertures of a scale sufficiently large that entry pressures will be easily overcome by even a thin pool of DNAPL. In large fractures (greater than 1 cm), capillary forces will be insignificant and DNAPL will drain freely under the influence of gravity.

Carbonate rocks underlie most of Middle Tennessee and large areas of East Tennessee. Karst aquifers contain a variety of flow regimes, ranging from rapid turbulent flow in freely draining conduits to slow laminar flow through bedrock-fracture networks, cave sediments, or residuum. The carbonate areas of Tennessee can be divided into regions based on geologic structure, stratigraphy, relief, unconsolidated cover, and karst landforms. Six karst regions are considered in this report: (1) the inner Central Basin, (2) the outer Central Basin, (3) the Highland Rim, (4) the coves and escarpments of the Cumberland Plateau, (5) the Valley and Ridge, and (6) the western toe of the Blue Ridge. Thickness of karst regolith across the State ranges from less than 1 m in the inner Central Basin to greater than 38 m in the Valley and Ridge. Topographic relief varies from nearly flat in the inner Central Basin to steeply sloping along the escarpments of the Cumberland Plateau.

The extensiveness of karst aquifers and their distinctive hydraulic properties makes these aquifers vulnerable to contamination by chlorinated solvents. DNAPL-accumulation areas within an aquifer are important because they are source zones for dissolved-phase contamination. The five conceptual models described in this report emphasize DNAPL accumulation in different compartments of the subsurface environment. The models were developed with the karst environments of Tennessee in mind, but are intended to be transferable to karst settings in adjacent states and broadly applicable elsewhere.

The five models of DNAPL accumulation in karst settings are

1. trapping in regolith,
2. pooling at the top of bedrock,
3. pooling in bedrock diffuse-flow zones,
4. pooling in karst conduits, and
5. pooling in isolation from active ground-water flow.

The conceptual models presented in this report are preliminary. They are intended to be starting points for analysis of chlorinated-solvent contamination in karst settings and site-specific studies. Nothing in this report in any way reduces the critical importance of careful characterization of the environmental settings and contaminant distributions at specific sites. Every contaminated site is unique and requires an individual characterization to successfully understand the site and to plan for mitigation. Under the best of circumstances, chlorinated solvents are difficult to find and recover once they have entered the subsurface. The complexity and variability of karst aquifers greatly compound this difficulty.

Twenty-two case studies were selected from the Tennessee Division of Superfund files to evaluate chlorinated-solvent contamination in the karst regions of Tennessee. Only 4 of the 22 case studies document visual evidence of DNAPL although the presence of DNAPL can be inferred from historical and field data for many of the sites. Five case studies are presented in detail to illustrate the relevance of their specific site characteristics to the conceptual models. DNAPL pools are documented at the top of rock 6 m below land surface at one site; in regolith, less than 11 m below land surface at another site; and in fractured rock, 72 m below land surface at a third site.

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APPENDIX

Case Study Summary Sheets

Information in this appendix was gathered from the TDEC Division of Superfund files. The “period of operation” is the time during which a site handled or disposed of chlorinated solvents. All quantitative data retrieved from the TDEC files were converted into metric units. Hydrologic property abbreviations include: k–hydraulic conductivity, k_v–vertical hydraulic conductivity, and T–transmissivity. A dashed symbol “--” indicates the value was either unknown, unavailable, or not found in the case study files. Depth to water is reported as meters below land surface. Soil and ground-water concentrations are reported for the “primary chlorinated solvent of concern” unless otherwise noted. The suspected presence of DNAPL is based on the highest measured ground-water and soil concentrations as described in the U.S. Environmental Protection Agency document (U.S. EPA, 1992b). Horizontal and vertical extents of contamination are reported for the local aquifers. Additional notes may be presented at the bottom of a case study summary sheet for data clarification.

CASE STUDY SUMMARY

Site number: 01-585
Karst region: Valley & Ridge
County: Anderson

Primary chlorinated solvent of concern: TCE
Period of operation: 2 to 3 months in 1970
Industrial activity: Manufacturing plant

Estimated volume and type of release: Unknown volume; 6-m deep dry well was installed for disposal of TCE, TCA, methanol, and freon

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Clay with chert	Alluvium	5 to 6	Unsaturated
Shales with thin beds of limestone	Conasauga Group	5 to 11	Fractures, joints, and dissolution-enlarged openings
Interbedded siltstone, sandstone and shale	Rome Formation	100 to 115	Fractures and joints

Average depth to water: 6 to 7 m
Karst features in site vicinity: Spring

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 26 mg/L
- **in soils:** TCE 12 mg/kg in dry well

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: Estimated 53 m x 29 m
Known vertical extent of dissolved contamination: 125 m in nearby process well
Concentration at natural discharge point: None given

Dye-trace study results: No dye traces

Notes: Dry well was used for disposal for a few months during 1970, beginning in approximately April

CASE STUDY SUMMARY

Site number: 06-505

Karst region: Valley & Ridge
County: Bradley

Primary chlorinated solvent of concern: TCE; PCE
Period of operation: 1962 to present
Industrial activity: Manufacturing plant

Estimated volume and type of release: Unknown volume. Approximately 7,880 kilograms of solvents used annually. Ruptured drums known to have leaked into sewer system during loading activities

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Clayey silt to silty clay with weathered shale and limestone	Alluvium, residuum, and colluvium	4 to 12	Granular porous material	--
Shale and limestone	Conasauga Group	6 to 41	Fractures, joints, and dissolution-enlarged openings	k_v = 6.5 x 10^{-4}cm/s

Average depth to water: 6 to 7 m
Karst features in site vicinity: Some wells were dry during investigation. Springs issue from faults

DNAPL observed: No

Highest concentration measured
- **in ground water:** PCE 25 mg/L; TCE 4 mg/L
- **in soils:** PCE 890 mg/kg; TCE 14 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: About 430 m x 120 m
Known vertical extent of dissolved contamination: 36 m
Concentration at natural discharge point: PCE 0.079 mg/L; TCE 0.008 mg/L in wetlands area next to Mouse Creek

Dye-trace study results: One was completed for nearby Cleveland Utilities District

Notes: Soil remediation area is 7 m x 7 m x 4 m deep

CASE STUDY SUMMARY

Site number: 15-508 **Karst region:** Valley & Ridge
County: Cocke

Primary chlorinated solvent of concern: TCE; 1,1,1-TCA
Period of operation: 1956-83
Industrial activity: Manufacturing plant

Estimated volume and type of release: Exact amount unknown. Reported volume of 4,500 liters 1,1,1-TCA. “Small” spills and leaks reported from drums and usage of TCE containers

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: II: Moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydrologic properties
Gravel, silty clay, sandy clay	Regolith	1 to 5	Unsaturated	--
Shale	Sevier Shale	4 to 5	Fractures and joints	k = less than 1×10^{-3} cm/s
Dolomite with interbedded limestone	Knox Group	16 to 30	Dissolution-enlarged openings	--

Average depth to water: 3 to 5 m in the shale and 6 to 8 m in dolomite
Karst features in site vicinity: Springs nearby

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 5.76 mg/L
- **in soils:** TCE 0.035 mg/kg at 2 m deep

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 300 m x 220 m
Known vertical extent of dissolved contamination: 14 to 17 m
Concentration at natural discharge point: 0.016 mg/L TCE in spring

Dye-trace study results: None

Notes:

CASE STUDY SUMMARY

Site number: 19-565

Karst region: Outer Central Basin
County: Davidson

Primary chlorinated solvent of concern: TCE; 1,2-DCE
Period of operation: pre-1961 to present
Industrial activity: Manufacturing plant

Estimated volume and type of release: Listed in file documents as "several hundred gallons." Estimated spill volume of 570 to 800 liters of TCE in 1976

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: II: Moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic Properties
Sand and clay	Fill	2 to 3	Unsaturated	--
Sandy, silty and gravel	Alluvium	Up to 15	Granular porous material; perched	k= 2.3 x 10^{-5}cm/s
Fossiliferous limestone with shale	Catheys and Leipers Formations	50 to 60	Dissolution-enlarged openings	

Average depth to water: 2 to 4 m in alluvium and 8 to 13 m in limestone
Karst features in site vicinity: Springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 10 mg/L; 1,2-DCE 2.1 mg/L
- **in soils:** TCE 0.022 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 183 m long x 243 m wide in 1993
Known vertical extent of dissolved contamination: 12 to 15 m
Concentration at natural discharge point: TCE 1.6 mg/L at seep location on unnamed creek

Dye-trace study results: None

Notes: Loss of sulfuric acid from manufacturing process created a dissolution opening beneath the site

CASE STUDY SUMMARY

Site number: 26-501 **Karst region:** Highland Rim
County: Coffee

Primary chlorinated solvent of concern: PCE; TCE
Period of operation: 1953-82
Industrial activity: Waste disposal

Estimated volume and type of release: Landfill and leaching pit, volume disposed unknown

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Clay with silt and sand	Shallow aquifer, regolith	9-14	Granular porous material	k=3.3x10^{-4} cm/s
Clayey gravel to gravelly clay	Intermediate aquifer, regolith	7-17	Granular porous material	k= average 9.3x10^{-3} cm/s, range 3.7x10^{-2} cm/s to 7.2x10^{-4} cm/s
Dense cherty limestone	Deep aquifer, Fort Payne Formation	3-9	Dissolution-enlarged openings	--
Dark, grayish black carbonaceous shale	Confining unit, Chattanooga Shale	6 - 8	Confining unit	--

Average depth to water: 1.5 to 6 m
Karst features in site vicinity: None

DNAPL observed: No

Highest concentration measured
- **in ground water:** PCE 120 mg/L; TCE 89 mg/L
- **in soils:** PCE 95.6 mg/kg; TCE 39 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 2,600 x 760 m
Known vertical extent of dissolved contamination: 30 m
Concentration at natural discharge point: None reported

Dye-trace study results: None

Notes: Most files for this site are at TDEC Division of Solid Waste Management

CASE STUDY SUMMARY

Site number: 26-502 **Karst region:** Highland Rim
County: Franklin

Primary chlorinated solvent of concern: TCFM; PCE; TCE
Period of operation: 1953-80
Industrial activity: Waste disposal

Estimated volume and type of release: Quantity unknown

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Clay with silt and sand	Shallow aquifer, regolith	12 - 20	Granular porous material
Clayey gravel to gravelly clay	Intermediate aquifer, regolith	3 - 9	Granular porous material
Dense cherty limestone	Deep aquifer, Fort Payne Formation	7 -11	Dissolution-enlarged openings
Dark, grayish black carbonaceous shale	Confining unit, Chattanooga Shale	6 - 8	Confining unit

Average depth to water: 6 to 15 meters
Karst features in site vicinity: Springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCFM 170 mg/L; PCE 12 mg/L; TCE 26 mg/L
- **in soils:** PCE 7.3 mg/kg; TCE 1.0 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 2,000 x 400 m
Known vertical extent of dissolved contamination: 26 m
Concentration at natural discharge point: None reported

Dye-trace study results: None

Notes: Most files for this site are at TDEC Division of Solid Waste Management.

CASE STUDY SUMMARY

Site number: 26-505 **Karst region:** Highland Rim
County: Coffee

Primary chlorinated solvent of concern: PCE; 1,1,1-TCA
Period of operation: 1950-72
Industrial activity: Disposal of waste solvents and acids

Estimated volume and type of release: Quantity unknown

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: Confirmed presence

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Clay with silt and sand	Shallow aquifer	3 - 9	Granular porous material	k=3.3x10^{-4} cm/s
Sandy clay	Confining layer	1 - 8	Granular porous material	--
Clayey gravel to gravelly clay	Intermediate aquifer	5- 15	Granular porous material	k=5.7x10^{-3} cm/s
Dense cherty limestone	Deep aquifer, Fort Payne Formation	3 - 6	Dissolution-enlarged openings	--
Dark, grayish black carbonaceous shale	Confining unit, Chattanooga Shale	6 - 8	Confining unit	--

Average depth to water: 5 - 8 m
Karst features in site vicinity: None

DNAPL observed: Yes

Highest concentration measured
- **in ground water:** 1,1,1-TCA 290 mg/L; PCE 140 mg/L
- **in soils:** PCE 3,000 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 420 x 270 m
Known vertical extent of dissolved contamination: 11 m
Concentration at natural discharge point: PCE 0.004 to 1.1 mg/L in ditch H; 1,1,1-TCA 1.0 to 0.37 mg/L in ditch H. Ditch H is approximately 75 m southeast of site

Dye-trace study results: None

Notes: Most files for this site are at TDEC Division of Solid Waste Management. DNAPL is currently being recovered from an extraction well at this site

CASE STUDY SUMMARY

Site number: 28-502 **Karst region:** Highland Rim
County: Giles

Primary chlorinated solvent of concern: 1,1,1-TCA; PCE
Period of operation: 1974 to present
Industrial activity: Manufacturing plant. Uses 2 degreasers

Estimated volume and type of release: Unknown. Generates 3 to 5 drums per year of spent degreaser which is shipped offsite within 90 days. An area about 8,800 square meters onsite is contaminated. In 1989, the plant generated 5,053 liters (28 drums) of PCE

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Yellow brown clay with gravel size chert	Fort Payne Formation (weathered)	20	Granular porous material
Cherty limestone and dolomite with shale base	Fort Payne Formation (partially weathered)	10	Dissolution-enlarged openings
Phosphatic shale	Maury Formation	1	Fractures and joints
Shale	Chattanooga Shale	0 to 4	Confining unit
Fossiliferous limestones and calcareous shale	Undifferentiated Ordovician limestones	Less than 300	Fractures, joints, and dissolution-enlarged openings

Average depth to water: 5 to 8 m
Karst features in site vicinity: Springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** PCE 16 mg/L
- **in soils:** 1,1,1-TCA 250 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 36 m x 46 m
Known vertical extent of dissolved contamination: 2 to 5 m
Concentration at natural discharge point: None given

Dye-trace study results: Yes

Notes:

CASE STUDY SUMMARY

Site number: 32-512 **Karst region:** Valley & Ridge

County: Hamblen

Primary chlorinated solvent of concern: TCE
Period of operation: 1967-90
Industrial activity: Manufacturing plant

Estimated volume and type of release: Unknown. Liquid wastes were poured directly onto ground near raw materials storage shed and the main plant. Approximately 1400 cubic meters of soil have been remediated

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: II: Moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Red clay with rock fragments	Regolith	5 to 17	Unsaturated
Silicious, grey, fine-grained dolomite	Longview Dolomite of the Knox Group	90	Dissolution-enlarged openings

21 m to 40 m

Average depth to water: Havely Spring, several sinkholes near site
Karst features in site vicinity: Free product was found in soils but not checked for TCE

DNAPL observed: TCE 0.19 mg/L at 38 to 41 m

Highest concentration measured
- **in ground water:** TCE 25 mg/kg in 3- to 3.6-m interval
- **in soils:** No

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: About 95 x

Known horizontal extent of dissolved contamination: 73 m
Known vertical extent of dissolved contamination: 47 to 50 m
Concentration at natural discharge point: No data for spring or nearby creek

Dye-trace study results: None completed

Notes: Storm drain at site may have been used to dispose of liquid hazardous waste

CASE STUDY SUMMARY

Site number: 33-556
Karst region: Valley and Ridge
County: Hamilton

Primary chlorinated solvent of concern: PCE
Period of operation: 1951-83
Industrial activity: Manufacturing plant

Estimated volume and type of release: Waste water containing solvents was discharged to surface lagoon, total volume unknown

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Regolith - mottled silty clay and clayey silt	Shallow zone	8.5 - 15	Granulated porous material	$k = 1.9 \times 10^{-4}$ cm/s $T = 1.95$ m^2/day
Alternating calcareous shale and argillaceous limestone	Bedrock zone, Leipers Formation and Sequatchie Formation	Undetermined as wells only penetrated upper 10 meters of rock	Fractures, joints, and dissolution-enlarged openings	--

Average depth to water: 4.5 to 6 m
Karst features in site vicinity: None noted

DNAPL observed: No

Highest concentration measured
- **in ground water:** PCE 84 mg/L; TCE 6.8 mg/L
- **in soils:** Not detected

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 300 x 200 m
Known vertical extent of dissolved contamination: 21 mg/L at 19.5 m
Concentration at natural discharge point: Tennessee River is major discharge point, approximately 450 m downgradient. Contaminant plume does not currently extend to Tennessee River

Dye-trace study results: None

Notes:

CASE STUDY SUMMARY

Site number: 37-512

Karst region: Valley and Ridge
County: Hawkins

Primary chlorinated solvent of concern: 1,1,1-TCA
Period of operation: 1979-84
Industrial activity: Drum storage and degreasing to clean parts

Estimated volume and type of release: Small spills and leaks

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Reddish brown clayey silt with shale and chert fragments	Regolith water-bearing unit	0.5 - 5	Granular porous material; perched in some areas	k = 1.1x10^{-6}cm/s
Weathered rock		0 - 6		k = 2.3x10^{-4} cm/s
Dolomite and limestone interbedded with shale	Bedrock water-bearing unit	--	Dissolution-enlarged openings	--

Note: Only low concentration (<0.005 mg/L) have been found in the bedrock

Average depth to water: 1 to 9 m
Karst features in site vicinity: Springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** 1,1,1-TCA 4.4 mg/L
- **in soils:** 1,1,1-TCA 1.1 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 37 x 46 m
Known vertical extent of dissolved contamination: 13 m
Concentration at natural discharge point: None reported

Dye-trace study results: None

Notes:

CASE STUDY SUMMARY

Site number: 54-505 **Karst region:** Valley and Ridge
County: McMinn

Primary chlorinated solvent of concern: 1,1,1-TCA; TCE
Period of operation: 1965-77
Industrial activity: Waste disposal of finishing oils; from 1965-72 burned in open pit, from 1972-77 disposal in pit continued, but burning stopped
Estimated volume and type of release: Estimates range from 4,000 to 420,000 liters discharged to open pit

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Regolith - clay with chert and sand particles	Unsaturated zone with some perched water	11 -20	Granular porous material; perched at top of rock
Dolomite	Aquifer. Longview and Chepultepec Dolomite of the Knox Group	--	Dissolution-enlarged openings

Note: The bedrock aquifer was not investigated at this site. No wells completed more than 6 m into bedrock

Average depth to water: Wells sampled perched water at the top of rock
Karst features in site vicinity: Sinkholes, springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** 1,1,1-TCA 0.091mg/L
- **in soils:** TCE 4.1 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 490 x 240 m
Known vertical extent of dissolved contamination: 26 m
Concentration at natural discharge point: 1,1,1-TCA 0.027 mg/L and 1,1-DCA 0.03 mg/L in Blair Spring, which is located approximately 365 meters southwest of the site

Dye-trace study results: None

Notes:

CASE STUDY SUMMARY

Site number: 59-502 **Karst region:** Inner Central Basin
County: Marshall

Primary chlorinated solvent of concern: TCE
Period of operation: 1973-90
Industrial activity: Manufacturing plant with degreaser

Estimated volume and type of release: Approximately 13,000 liters of TCE leaked from supply line into sewer

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High/Confirmed

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Clay and silt	Regolith	4 to 9	Granular porous material; perched
Thin limestone with shale partings	Lebanon Limestone	12 to 20	Leaky confining unit
Thick limestone	Ridley Limestone	24 to 30	Dissolution-enlarged openings
Argilllaceous limestone	Lower Ridley confinement*	10	Leaky confining layer
Thin limestone with shale partings	Pierce Limestone	4.5	Leaky confining unit

Average depth to water: About 6 to 15 m
Karst features in site vicinity: Springs, sinkholes, sinking streams, caves

DNAPL observed: Yes

Highest concentration measured
- **in ground water:** TCE 950,000 mg/L (about 0.6 m of DNAPL)
- **in soils:** TCE 1,160 mg/kg at 3.5 m

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 370 m x 200 m in bedrock
Known vertical extent of dissolved contamination: About 70 m
Concentration at natural discharge point: TCE 0.0072 mg/L in Snell Branch Creek

Dye-trace study results: Yes

Notes: * This unit may or may not correspond with the Pierce Limestone

CASE STUDY SUMMARY

Site number: 75-531 **Karst region:** Inner Central Basin
County: Rutherford

Primary chlorinated solvent of concern: TCE; PCE
Period of operation: 1977-79
Industrial activity: Waste recycler and reclaimer

Estimated volume and type of release: Reported receipt of 7,286 liters of chemical wastes

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: II: Moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Silts, clay, sand	Regolith	Less than 1	Unsaturated
Limestone with interbedded clay and some shale	Lebanon Limestone	16 to 36	Dissolution-enlarged openings
Limestone and shale	Ridley Limestone	Up to 33	Dissolution-enlarged openings

Average depth to water: Nearby domestic wells obtain water from 12 to 24 m deep
Karst features in site vicinity: Sinkholes located on and offsite

DNAPL observed: No

Highest concentration measured
- **in ground water:** Unknown. See notes
- **in soils:** PCE 0.52 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: Unknown
Known vertical extent of dissolved contamination: Unknown
Concentration at natural discharge point: PCE 0.036 mg/kg in sediment sample of tributary stream

Dye-trace study results: None

Notes: No ground-water samples have been collected
Vertical contamination detected in soil to at least 15 centimeters

CASE STUDY SUMMARY

Site number: 82-506

Karst region: Valley and Ridge (Alluvial plain)
County: Sullivan

Primary chlorinated solvent of concern: 1,1,1-TCA
Period of operation: 1975-79
Industrial activity: Storage and handling of drums containing waste chemicals

Estimated volume and type of release: Small spills and leaks, total quantity unknown

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Regolith - consisting of fill, alluvium and residuum	Alluvial water-table aquifer	0.5 - 1 meter fill 2 meters alluvium 0.5 meter residuum	Granular porous material	k = 1.5×10^{-7} cm/s
Shale	Aquifer, Sevier Shale	--	Fractures, joints, and dissolution-enlarged openings	--

Note: The bedrock aquifer was not investigated at this site. No wells have been completed in the bedrock aquifer

Average depth to water: 0.3 to 2 m
Karst features in site vicinity: None

DNAPL observed: No

Highest concentration measured
- **in ground water:** 1,1,1-TCA 51.84 mg/L
- **in soils:** 1,1,1-TCA 4.583 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 90 m x 30 m
Known vertical extent of dissolved contamination: 3 meters, bedrock not investigated
Concentration at natural discharge point: 1,1,1-TCA 0.01 mg/L in Cedar Creek, which is approximately 30 m west of the site

Dye-trace study results: None

Notes:

CASE STUDY SUMMARY

Site number: 82-516 **Karst region:** Valley and Ridge
County: Sullivan

Primary chlorinated solvent of concern: TCE
Period of operation: 1967-74
Industrial activity: Waste disposal

Estimated volume and type of release: About 79,000 liters of drummed and bulk liquids discharged to open pit where they were burned; 272 drums removed in surface cleanup in 1984; 289 drums removed in subsurface cleanup in 1989

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: Confirmed presence

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Depth to water	Comments	Hydraulic properties
Soil, shaley silt loam to silt loam.	Unsaturated zone	less than 1.5	--	Unsaturated	--
Weathered and fractured shale		6			
Siltstone and shale, calcareous, low fracture density	Shallow, Sevier Formation	21	12 to 35 meters	Low fracture density, poorly developed flow system	$k = 2.8 \times 10^{-4}$ cm/s $T = 0.09$ m^2/d
Siltstone and shale, calcareous, high fracture density	Deep, Sevier Formation	60	60 to 100 meters	Highly developed fracture network, high transmissivity	$k = 4.5 \times 10^{-4}$ cm/s $T = 21$ m^2/d
Dense hard shale	--	--	--	Dense hard rock; low transmissivity	$T < 0.01$m^2/d

Average depth to water: See table above
Karst features in site vicinity: Numerous springs and seeps

DNAPL observed: Yes, recovered from 6 wells onsite

Highest concentration measured
- **in ground water:** TCE 960 mg/L
- **in soils:** TCE 5.34 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: 550 x 335 m; DNAPL 230 x 90 m
Known vertical extent of dissolved contamination: 108 m; DNAPL at 72 m
Concentration at natural discharge point: TCE 0.025 mg/L in Black Creek, which is the main natural discharge point and is approximately 425 m downgradient from the site

Dye-trace study results: None

Notes:

CASE STUDY SUMMARY

Site number: 86-501 **Karst region:** Western Toe of the Blue Ridge
County: Unicoi

Primary chlorinated solvent of concern: TCE
Period of operation: 1972-79
Industrial activity: Waste disposal, landfill

Estimated volume and type of release: TDSF documented 14,517 drum equivalent of hazardous substance; operators reported 800,000 liters on CERCLA notification form; actual amount is unknown, but suspected to be greater than above estimates. Landfill covers 22 hectares

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I-II: High/moderate potential.

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Regolith - clay-rich with silt, sand, and boulder	Confining layer	15 - 30	Granular porous material; low conductivity
Highly fractured dolomite	Aquifer, Shady Dolomite	75 - 120	Highly fractured in some areas; flow through dissolution-enlarged opening in others
Siltstone, sandstone, and quartzite	Confining layer, Erwin Formation	--	Confining layer

A complex system of imbricate thrust faults underlie the landfill

Average depth to water: 10 to 40 m
Karst features in site vicinity: Springs, evidence of epikarst development

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 0.29 mg/L; DCE 0.31 mg/L
- **in soils:** Not detected

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 150 m from landfill boundary
Known vertical extent of dissolved contamination: 54 m
Concentration at natural discharge point: TCE 0.007 mg/L at Henley Spring, which is a small spring located approximately 120 m from the landfill boundary

Dye-trace study results: None

Notes: Many (more than 2,400) exploration boreholes for mining have been drilled in the area, some near the landfill

CASE STUDY SUMMARY

Site number: 89-504

Karst region: Highland Rim
County: Warren

Primary chlorinated solvent of concern: TCE; 1,2-DCE; PCE
Period of operation: 1960 to present
Industrial activity: Manufacturing plant

Estimated volume and type of release: Unknown. Suspected intermittent leaks
Potential dumping of drums

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High/Confirmed

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydraulic properties
Regolith of silt, clay and chert	Weathered St. Louis Limestone	5 to 9	Granular porous material; perched in some areas	K=3 x 10-4 to 8.1 x 10-4 cm/s
Calcareous siltstones or sandstone	Upper Warsaw Limestone	2	Fractures and joints; leaky confining unit	--
Limestone	Middle Warsaw Limestone	9 to 12	Cave streams; dissolution enlarged openings	--
Siliceous, calcareous cherty siltstone	Lower Warsaw Limestone	9 to 12	Fractures and joints; leaky confining unit	--

Average depth to water: 2 to 4 meters
Karst features in site vicinity: Sinkholes, sinking streams, caves, springs

DNAPL observed: Yes.

Highest concentration measured
- **in ground water:** 1,2-DCE 8.82 mg/L; TCE 1.11mg/L
- **in soils:** TCE 0.048 mg/kg about 7 m

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 122 m x 30 m in bedrock
Known vertical extent of dissolved contamination: 16- to 22-m screen interval
Concentration at natural discharge point: TCE 5.45 mg/L at spring north of site (1997 sample)

Dye-trace study results: Yes

Notes: Ground water from weathered St. Louis Limestone is discharging at a spring due north of the site. Approximately 20 centimeters of DNAPL detected in top of rock well. DNAPL was not present in well 5 days after initial detection

CASE STUDY SUMMARY

Site number: 91-501 **Karst region:** Highland Rim
County: Wayne

Primary chlorinated solvent of concern: TCE
Period of operation: 1969-84
Industrial activity: Manufacturing plant

Estimated volume and type of release: Historically, 221 55-gallon drums were stored during 1974; 1,690,000 kg of contaminated soil has been removed from the site

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Silt, sand, clay and gravel	Alluvium	About 2.4	Unsaturated
Clayey silts	Residuum	1 to 2.4	Granular porous material
Dolomitic limestone and siltstone	Fort Payne Formation	At least 30	Fractures, joints, and dissolution-enlarged openings
Sandstone with siltstone	Hardin Sandstone	At least 36	Fractures and joints

Average depth to water: 1 to 4.6 m and 4.3 to 12 m
Karst features in site vicinity: Spring located 360 m to west of site

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 250 mg/L
- **in soils:** TCE 0.019 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: See notes
Known vertical extent of dissolved contamination: 30 m
Concentration at natural discharge point: TCE 0.0025 mg/L in Green River

Dye-trace study results: None

Notes: Contaminant extent in shallow zone is approximately 320 x 251 m and in the bedrock it is approximately 297 x 160 m

CASE STUDY SUMMARY

Site number: 91-502

Karst region: Highland Rim
County: Wayne

Primary chlorinated solvent of concern: TCE; PCE
Period of operation: 1970-72
Industrial activity: Waste disposal

Estimated volume and type of release: About 40,000 liters (400 liters per week) were dumped at site. A settling pond of about 84 cubic meters contained TCE and PCB contaminants

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Gravel and chert	Tuscaloosa Formation	less than 0.5	Unsaturated
Sands, silts, gravel and-chert	Residuum of Fort Payne Formation	50	Granular porous material
Chert and limestone	Fort Payne Formation (partially weathered)	10	Dissolution-enlarged openings
Shale	Chattanooga Shale	15 to 16 (when present)	Leaky confining unit
Semi-confined shaley limestone	Wayne Formation and Brassfield Limestone	Unknown	Dissolution-enlarged openings

Average depth to water: 13 to 60 meters
Karst features in site vicinity: Springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 0.064 mg/L; PCE 40 mg/L
- **in soils:** TCE 0.215 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: Unknown
Known vertical extent of dissolved contamination: About 53 m
Concentration at natural discharge point: TCE 0.0007 mg/L in Beech Creek

Dye-trace study results: None

Notes: Dump dimensions given in file report as 60 m long x 91 m wide x 23 m deep. Screen intervals of monitoring wells ranged from 1 to 53 m long

CASE STUDY SUMMARY

Site number: 94-508 **Karst region:** Outer Central Basin
County: Williamson

Primary chlorinated solvent of concern: TCE; PCE
Period of operation: 1972-73
Industrial activity: Waste disposal

Estimated volume and type of release: Unknown. Approximately 800 55-gallon drums or about 170,000 liters were buried at site. In summer and fall of 1978, 50-80 barrels of unknown contents were buried in pits

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: II: Moderate potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments
Clay and silt, weathered rock	Colluvium	1 to 4.6	Unsaturated
Limestone with fossils	Bigby and Cannon Limestones	0 to 4	Dissolution-enlarged openings
Limestone with shale partings	Hermitage Formation	8 to 31	Fractures and joints; dissolution-enlarged openings near top; leaky confining unit
Limestone with fossils	Carters Limestone	20 to 24	Dissolution-enlarged openings
Fossiliferous limestone with shale	Lebanon Limestone	6 at site	Dissolution-enlarged openings; leaky confining unit

Average depth to water: 4.3 to 11 meters
Karst features in site vicinity: Springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE: 0.85 mg/L; PCE 0.21 mg/L
- **in soils:** PCE 0.024 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: No

Known horizontal extent of dissolved contamination: 300 m x 110 m
Known vertical extent of dissolved contamination: 4.9 to 13 m
Concentration at natural discharge point: trans-1,2-DCE 0.041 mg/L was detected in Hackett Spring

Dye-trace study results: No data available in case study file

Notes:

CASE STUDY SUMMARY

Site number: 95-501 **Karst region:** Inner Central Basin
County: Wilson

Primary chlorinated solvent of concern: TCE
Period of operation: 1961-86
Industrial activity: Manufacturing plant

Estimated volume and type of release: Unknown. Release of contaminants reported as leaks from vapor degreaser or improper storage of containers. About 1,200 cubic meters of soil were treated by December 1995

Potential of DNAPL occurrence [from U.S. EPA fact sheet (1992b)]: I: High potential

Site Hydrogeology

Generalized lithology	Hydrogeologic zone	Thickness, in meters	Comments	Hydrologic properties
Silty clay	Regolith	0.45 to 2.8	Granular porous material	k = 1 x 10^{-8} cm/s to 6 x 10^{-4} cm/s
Fossiliferous limestone with thin shale partings	Lebanon Limestone	16 to 30	Dissolution-enlarged openings; leaky confining unit	
Limestone with some chert and magnesium	upper Ridley Limestone	20 to 30	Dissolution-enlarged openings	--

Average depth to water: Approximately 2 m below top of rock
Karst features in site vicinity: Interconnected bedrock fractures, sinkholes, springs

DNAPL observed: No

Highest concentration measured
- **in ground water:** TCE 290 mg/L
- **in soils:** TCE 2.1 mg/kg

DNAPL suspected based on field sampling data [from U.S. EPA fact sheet (1992b)]: Yes

Known horizontal extent of dissolved contamination: See notes
Known vertical extent of dissolved contamination: About 20 m
Concentration at natural discharge point: TCE 2.3 mg/L in nearby ditch

Dye-trace study results: None

Notes: Contaminant extent in residuum is about 60 m x 430 m and about 200 m x 360 m in upper 20 m of bedrock