

# Preliminary Conceptual Models Of Chlorinated-Solvent Accumulation in Karst Aquifers

By William J. Wolfe and Connor J. Haugh

U.S. Geological Survey, 640 Grassmere Park, Suite 100, Nashville, TN 37211

## Abstract

Conceptual models are needed to assist regulators and site managers in characterizing chlorinated-solvent contamination in karst settings and 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 karst conduits; (4) pooling in bedrock diffuse-flow zones; 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 where the regolith is thick and relatively impermeable with few large cracks and fissures. 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 type of bedrock aquifer into an underlying aquifer of a different type or into openings that are isolated from significant ground-water flow.

## INTRODUCTION

Chlorinated solvents are widely used in many industrial operations. High density, low viscosity, and low interfacial tension relative to water make chlorinated solvents mobile contaminants that are difficult to find or remove when released into the ground-water system. Because karst conduits are commonly too large to develop significant capillary pressures, chlorinated solvents can migrate to considerable depth in karst aquifers as dense non-aqueous-phase liquids (DNAPL's). Within the context of this report, the term DNAPL is used to describe the immiscible or non-aqueous phase of chlorinated solvents and applies only to liquids with high density and low viscosity.

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). Major controls of the movement and ultimate fate of chlorinated DNAPL in the subsurface are: (a) the physical and chemical properties and mass of specific contaminants, (b) the areal extent and rate of contaminant release, and (c) the nature of the hydrogeologic environment into which the contaminant migrates (Mercer and Cohen, 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 related 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.

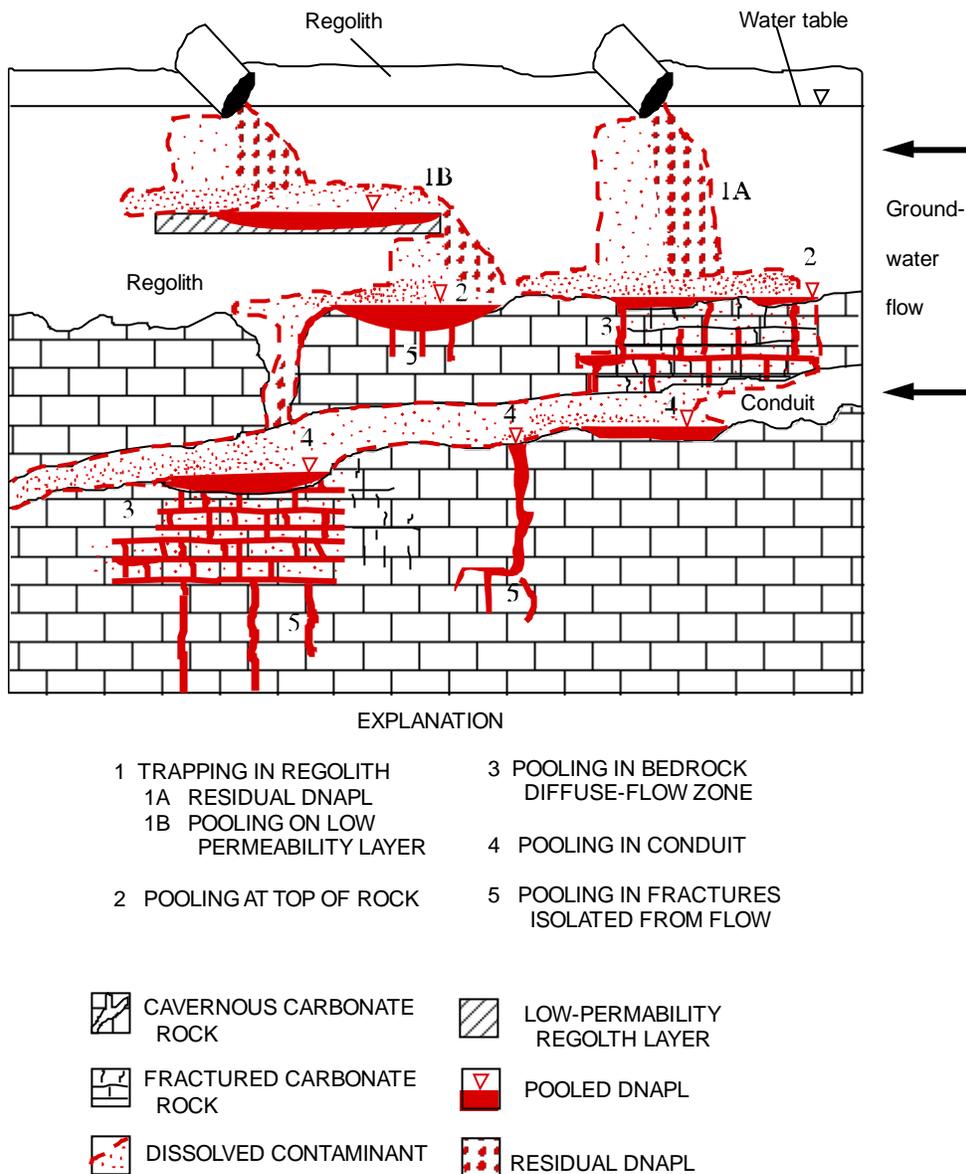
A necessary first step toward improving site characterization for chlorinated-solvent spills in karst settings is the development of conceptual models of where the contaminants are likely to accumulate and where and how they may be moving. A good conceptual model provides numerous working hypotheses 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 report presents five conceptual models of DNAPL accumulation in karst settings, developed by the U.S. Geological Survey in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund. The models emphasize DNAPL accumulation in different compartments of the subsurface environment. 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 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; and  
 5) DNAPL pooling in isolation from active ground-water flow (fig. 1).



**Figure 1.** Distribution of potential DNAPL-accumulation sites in a hypothetical karst setting. (Modified from Wolfe and others, 1997.)

The conceptual models presented in this report are preliminary in nature. They are intended to be starting points for analysis of chlorinated-solvent contamination in karst settings and do not reduce the critical importance of careful characterization of the environmental settings and contaminant distributions at specific sites. These preliminary conceptual models 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

In the regolith, DNAPL will 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 will 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 over-lying layer and which provide a capillary barrier to further downward movement of DNAPL. Low permeability layers can be perennially saturated, perennially drained, or alternately saturated and drained.

Low permeability layers must be free of erosional or depositional gaps and free of fractures for pooling of DNAPL to occur. In many 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 then continued downward movement 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 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, under dry conditions, DNAPL will be the wetting fluid and will be retained as films and wetting rings coating the media. More commonly, the vadose zone will be partly saturated with water and DNAPL will be retained as non-wetting 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.

## POOLING NEAR TOP OF ROCK

DNAPL contamination 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 3-10 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 (Mercer and Cohen, 1993; Pankow and Cherry, 1996). At top of rock, DNAPL will 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. Flat-lying or gently dipping rocks are more likely to trap DNAPL

than steeply dipping rocks, especially in cases where secondary porosity develops preferentially along bedding planes.

## **POOLING IN BEDROCK DIFFUSE-FLOW ZONE**

A diffuse-flow zone in bedrock occurs where many small fractures are present, but 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 filled with sediment washed in from land surface. Ground water moves through a diffuse network of small fractures or intergranular pores rather than through discrete conduits. Flow through the diffuse network may converge on larger conduits with more active flow. In this situation, DNAPL present in a diffuse-flow zone could provide a source of aqueous-phase contamination to the more active flow in the conduit.

DNAPL will migrate down through the network of diffuse 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. The residence time of DNAPL pooled in zones of diffuse flow will be determined by dissolution and matrix diffusion. Dissolution into the actively flowing ground-water will be slow because of the small surface area available for DNAPL pooled in fractures. The rate of ground-water movement also will limit the amount of DNAPL that will 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 the dense, Paleozoic carbonates of Tennessee and similar settings, 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 (< 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 will diffuse back into the fracture, serving as a persistent source of dissolved-phase contamination.

## **POOLING IN KARST 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 (Wolfe and others, 1997). Thus, DNAPL will freely flow into most 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 networks (Quinlan and others, 1992; Field, 1993, Crawford and Ulmer, 1994).

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 the overlying flow. Such conduits can develop along the tops of aquicludes, 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.

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.

## **POOLING IN FRACTURES ISOLATED FROM MAJOR ZONES OF GROUND-WATER FLOW**

The high specific gravities and low viscosities of chlorinated solvents cause these compounds to migrate downwards 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 rough, gradational ones. 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 William, 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 flowpaths for DNAPL through the major flow zone to the smaller, more isolated voids below.

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 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 or large 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.

## **CONCLUSION**

Two of the most problematic topics in contaminant hydrogeology are chlorinated solvents and karst. Chlorinated solvents have physical and chemical properties that make this class of compounds particularly likely to cause groundwater 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.

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 conceptual models developed emphasize DNAPL accumulation in five compartments of the subsurface environment: (1) the regolith, (2) the top of bedrock, (3) karst conduits, (4) bedrock diffuse-flow zones, and (5) in openings isolated from active ground-water flow. These conceptual models are intended to be starting points for site-specific studies of chlorinated-solvent contamination in karst settings.

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