A Conceptual Model for DNAPL Transport in Karst Ground Water Basins

by Caroline M. Loop[1] and William B. White[1]

Abstract

Dense nonaqueous phase liquids (DNAPLs) such as perchloroethylene, polychlorinated biphenyls, creosote mixtures, and many solvents and degreasers can be released into karst aquifers through sinkholes and sinking streams in quantities up to tanker car volumes. Although DNAPLs are easily injected into karst aquifers, discharge of the contaminants through springs may be significantly delayed depending on transport mechanism, storm water recharge, and storage sites within the karst aquifer. Storage sites include (1) the epikarst; (2) pools and depressions within underground streams; (3) incorporation of DNAPL within clastic sediments that are present in most conduits; (4) adsorption onto organic materials and onto manganese oxides, iron oxides, and other substrates; and (5) migration to depth within the fracture system. Effective transport of DNAPL contaminants during storm flow pulses requires the exceedance of thresholds best defined in terms of the conduit stream power. Movement of pooled DNAPL requires a boundary shear between the liquid and water flowing over it. DNAPL stored in clastic sediment bleeds out slowly or dissolves into surrounding pore water until storm pulses create a stream flow sufficient to flush the pore water, or possibly move the sediment pile itself. Under extreme flow conditions the entire sediment pile, including the DNAPL, can be entrained and ejected from the conduit system.

Introduction

Organic contaminants move through karst aquifers by complex pathways and can be stored within the aquifer, unobserved and unsuspected, for long periods of time. The concept of a developing three-dimensional plume extending from the contamination source, which can be described by the mathematics of diffusion and advection, is not valid for karst systems. This model must be replaced with the concept of flow along sequences of one-dimensional conduits interconnected in various ways with fracture and pore porosity. The karst aquifer system provides for both rapid and slow movement of injected contaminants and for long-term storage of contaminants so that unexpected releases may occur long after the initial injection (e.g., Crawford and Ulmer 1994). Long-term storage is demonstrated by case studies that failed to find nonaqueous phase contaminants even in the aftermath of large spills (e.g., Moore and Moore 1997).

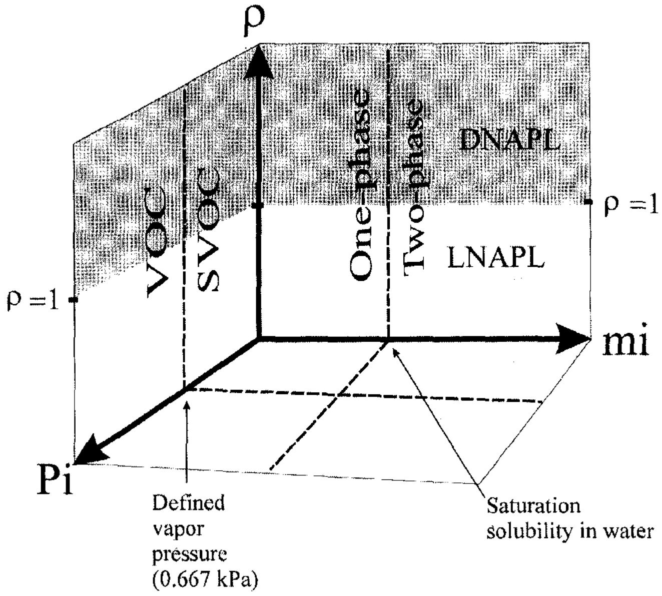

Figure 1. Sketch showing key parameters for describing organic contaminants. ρ = density (g/cm^3), m_i = solubility of contaminant i in water, P_i = vapor pressure of contaminant i.

The organic contaminants themselves are usually classified according to three important physical properties: density, solubility, and vapor pressure (Figure 1). The density of the contaminant compared to the density of water separates the liquids into dense nonaqueous phase liquids (DNAPLs) and light nonaqueous phase liquids (LNAPLs). The present paper is concerned with only the DNAPL class of compounds. The solubility of the organic component in water is of special interest for karst aquifers. Common organic contaminants exhibit a wide range of solubilities. Solubilities are usually sufficiently low that any large injection of contaminants will result in a two-phase liquid system. Solubilities for these hydrophobic compounds are typically less than 5000 mg/L for chlorinated solvents (Litherland and Anderson 1990) and less than 1.0 mg/L for polychlorinated biphenyls (PCBs) and related compounds (U.S. EPA 1987). The vapor pressure of the organic component varies widely depending on the specific compound of interest. An operational value of 0.667 kPa (5 torr) divides organic compounds into a volatile (VOC) class and a semivolatile (SVOC) class. Viscosity, which varies over a wide range, is also important

---

[1] Department of Geosciences, The Pennsylvania State University, University Park, PA 16802; loop@geosc.psu.edu and wbw2@psu.edu
Received February 2000, accepted August 2000.

in the interpretation of the flow mechanisms and storage of the contaminants, and should also be included in the list of variables.

Sources of DNAPL contaminants can be broadly divided into continuous and discontinuous types (Fetter 1994). Discontinuous sources are often discrete spills, such as when wrecked tanker trucks and derailed tanker cars release large quantities of contaminant over a short period of time. In this scenario, pools may initially form in the conduit system due to the large volume of the nonaqueous phase. Continuous sources may be leaks from pipelines, storage tanks, and related sources, which release small quantities of contaminant, possibly over long periods of time. There are also improperly operated waste disposal sites, salvage operations, and chemical dumps where the quantity and time scale of released contaminants are intermediate between continuous and discontinuous.

There has been progress in the modeling of DNAPL transport in fractures and solutionally modified fractures (Annable and Sudicky 1999). Kueper and McWhorter (1991) ran numerical simulations and found that the time needed for a DNAPL to cross a fractured aquitard is inversely proportional to the fracture aperture, the fracture dip from the horizontal, and the height of the pool above the aquitard. Parker et al. (1994) investigated the time required for a given volume of immiscible liquid to diffuse from fractures into the surrounding porous walls. In this case, the DNAPL is transferred to the dissolved and sorbed phases in the rock matrix. Later studies found that the dissolution time of the DNAPL is directly related to flow and transport properties of both the rock matrix and the fracture system, specifically the interconnection of the latter (VanderKwaak and Sudicky 1996). More recent studies have focused on the distribution of DNAPL between fractures and the matrix and elucidation of the influence of fracture constrictions and matrix entry pressures (Ross and Lu 1999; Slough et al. 1999).

Whereas an understanding of DNAPL transport in the porous and fractured subsurface is important for predicting its storage and transport in karst, equally as applicable are the mechanisms of DNAPL movement in rivers and streams. Karst conduit flow often resembles that of an above ground stream. Two major differences are: (1) some portions of the flowpath may be in pipefull condition; and (2) the composition of autochthonous material in the cave system is often significantly more constrained than the sediment one would find in a river (e.g., Mahler and Lynch 1999). There exist useful equations for predicting dissolution from macrophase pools, globs, and drops of DNAPL in a river or stream (Thibodeaux et al. 1980; Thibodeaux 1996).

In the chemical engineering literature, there are data on three phase horizontal flow in either air-water-sand or air-oil-water systems (Oudeman 1993; Acikgoz et al. 1992; Neogi et al. 1994; Stapelberg and Mewes 1994). Critical boundaries for bed movement and regimes have been drawn on plots of velocities of two of the phases; the boundaries shift when the velocity of the third phase is varied. Flow in microchannels (on the order of 1 mm) has been found to differ significantly from multiphase flow in larger channels (Triplett et al. 1999). An awareness of the mechanisms of the air-oil-water system is of greatest importance when a large volume of DNAPL is spilled into the karst system. Conversely, if there is a slow leak of minimal size into a karst system containing a large supply of fresh water, the dissolved phase may be the dominant phase of transport.

Some conceptual models have been proposed for contaminant transport in complete karstic aquifer systems along with documentation of specific examples. Gilbert (1990) presents a comparison of the ability to transmit contaminants in karst versus porous media based on the extent of filtration. Models of DNAPL accumulation sites in karst were described by Wolfe et al. (1997) in addition to numerous examples of DNAPL release into the karst of Tennessee. Case studies have been important for observing the behavior of DNAPLs in karst (Crawford and Ulmer 1994; Moore and Moore 1997; Jancin and Ebaugh 1999). For example, Talarovich and Krothe (1998) present data correlating PCB concentration with spring discharge. A storm with 6.6 cm of rainfall caused a twenty-fold increase in discharge, which was accompanied by a spike in dissolved PCB concentration. Although PCBs were placed in the two contributing sinkholes more than 30 years ago, and covered with a protective cap in 1987, there was still, in 1997, a detectable pulse of contaminant corresponding with the rising limb of the hydrograph, approximately 28 hours after the beginning of the storm. Due to the significant subsurface heterogeneity and relatively recent interest, it is probably fair to say that there is only the beginning of a comprehensive understanding of DNAPL storage and migration in karst aquifers.

It is the objective of this paper to set down the various sources, transport routes, and storage locations for DNAPLs in karst aquifers in the form of a complete conceptual model. The conceptual framework may be useful in identifying flowpaths and transport mechanisms where research is necessary.

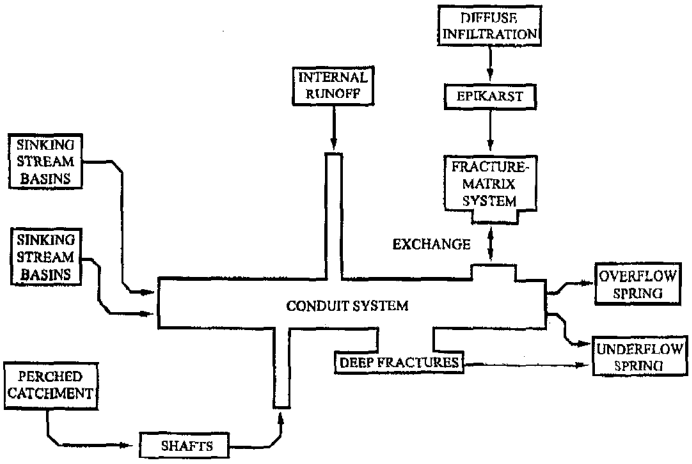

Figure 2. Conceptual model for carbonate aquifers. From White (1999a) with modifications suggested by J.A. Ray (personal communication 1999).

Karst Aquifers and Contaminant Input

Many variations have been drawn for the basic conceptual model of ground water flow in karst aquifers (White 1993, 1998, 1999a, 1999b). One possible conceptual model for a karst aquifer is sketched in Figure 2. A unique characteristic of karst aquifers is the interconnection and rapid interchange between ground water and surface water. Surface streams sink abruptly at swallets or are lost in their beds. The underground flow may reappear at karst windows or may discharge from springs and flow as surface streams before disappearing underground again. Spills, leaks, or outfalls that reach such surface streams are carried immediately into the conduit system of the karst aquifer. LNAPLs will float on the surface of an underground stream; DNAPLs can be dragged along the bottom or can be dispersed in fast-flowing water.

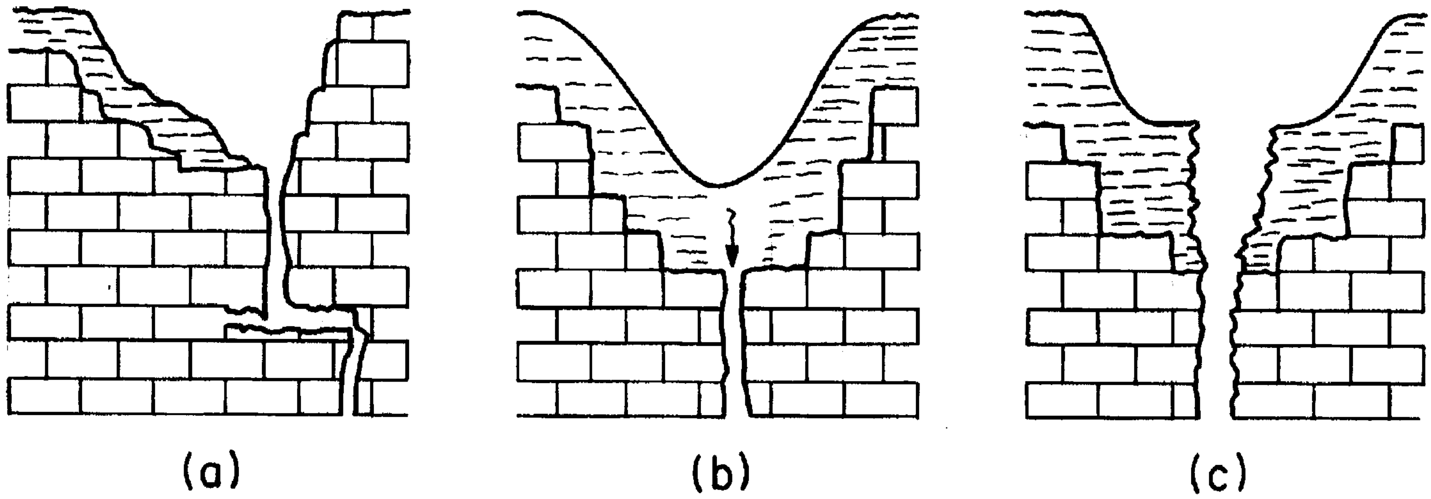

Figure 3. Three situations for contaminant injection through sinkholes: (a) direct injection though open drain; (b) slow infiltration through soil plug; (c) piping failure of soil plug with injection of contaminated soil into subsurface.

Sinkholes form localized catchments for storm runoff in karst regions. Some sinkholes have open drains so that any runoff captured by the sinkhole will be immediately carried into the subsurface (Figure 3a). Others are plugged with soil so that the sinkhole acts more like a detention basin and allows storm water to drain slowly into the subsurface (Figure 3b). These soil plugs themselves are transient and are subject to piping failures that carry the soil and any associated contaminant into the subsurface (Figure 3c). Sinkholes are critical interceptors for contaminant spills from tanker trucks and from railway tank cars since the downslope direction from a highway or railway in a karst area is likely to be into a sinkhole. Quantities of both water and sediment entering sinkholes dramatically increase with the spread of paved areas typical of urbanization. Sinkhole drains are usually connected directly to the conduit system, allowing contaminants to move rapidly into the aquifer.

In addition to the injection points provided by sinking streams and sinkholes, there is a diffuse input through the regolith to the underlying fractured bedrock. However, the regolith/bedrock interfaces in karst often have a quite different character than these interfaces on other rock types and merit a separate name, the epikarst (White 1988).

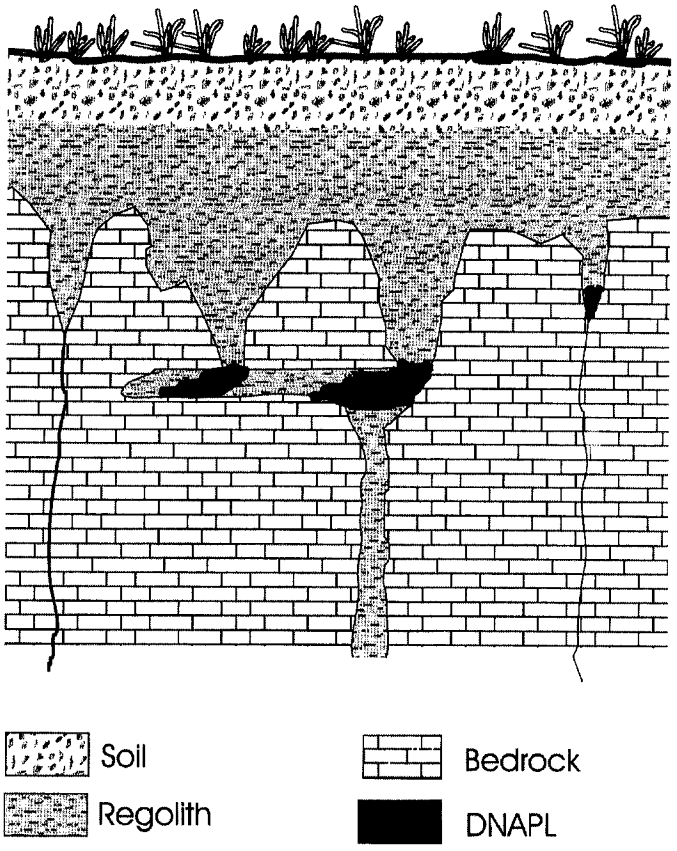

Figure 4. The epikarst showing possible trapping sites for DNAPL.

Contaminant Storage

Contaminant Storage in the Epikarst

Spills or leaks into karst soils behave similarly to spills or leaks onto soils in other terrains. Contaminants can pool on the surface, volitilize from the surface, and migrate downward through pores (or macropores) in the soil. Driven by gravity, the DNAPL will slowly make its way down until it encounters an impermeable layer, at which point it may spread horizontally, build up a pressure head until it continues to migrate, or both.

When DNAPL is held between grains, pressure head may increase from liquid accumulating above the trapped portion, which causes the DNAPL to migrate into deeper pores. The soil moisture content affects the amount of DNAPL present in the aqueous phase in the soil. If the soil is moist and grains are preferentially wetted by water, then when the DNAPL enters the pore space, it will be separated from the soil by a thin water layer. This will cause rate-limited diffusion across the water layer. If the soil particle is preferentially wetted by DNAPL in the presence of water or air, the contaminant will be in direct contact with the sediment.

Whether the DNAPL is separated from the sediment by a film of water or not, the contaminant may slowly enter the matrix of the soil grains, adhere to the surface of metal oxide coatings, or partition to organic matter in the soil. This depends in part on the rate of drainage through the soil, and the available contact area with particle surfaces. Therefore, soil particle size and size distribution both influence the rate and extent of sorption. Sorption is a long-term storage mechanism in the soil, as the contaminant becomes significantly less mobile when this process occurs. Although soils in karst areas are usually thin (Gilbert 1990), they can act as a significant storage site for NAPLs. As an example of the storage capacity of karst soils, Simmleit and Herrmann (1987) estimated that

87.5% to 99.7% of polyaromatic hydrocarbons (PAHs) and chlorinated pesticides released from snow cover in Upper Franconia, Germany, were stored in karst catchment soils. One might expect a lower percentage of DNAPL to remain in the soil after a large spill, due to the driving force of the pressure head. Regained mobility may result from either the entire soil grain moving, or DNAPL desorbing from the soil into the aqueous phase and being transported.

The soil/bedrock interface on carbonate rock is usually sharp. The weathered zone or C-horizon usually found on other rock types is present only on impure and cherty carbonate rock units. The top of bedrock is an irregular sculptured surface with deep crevices along joints and fractures separated by intermediate pinnacles. This zone of soil- and regolith-filled crevices is included in the epikarst (Figure 4).

Water, moving downward from overlying soil into the epikarst, must often move laterally for substantial distances before finding an open fracture or shaft that will permit vertical movement into the unsaturated zone of the bedrock. Infiltrating ground water may be held for days or weeks as a perched water body in the epikarst (Kogovsek 1981; Williams 1983). Likewise, contaminants may be stored by pooling at the bottoms of the crevices.

Once DNAPL has migrated to the epikarst, it may become stored in pools along the relatively impermeable, irregular, limestone surface. These pools can most accurately be described as microphase pools, as they are present in voids within the soil mass or in the pores between soil grains that are nearly saturated with DNAPL compound. This is in contrast to macrophase pools that may occur in the conduits and are a continuous layer of bulk liquid. DNAPL may remain perched in microphase pools in the epikarst for long periods of time, migrating slowly to downdip locations.

Open fractures or shafts below the epikarst may act as drains leading to the conduit system. A useful equation for the critical height needed for initial DNAPL entry to a water saturated fracture is

$$H_D = \frac{2\sigma \cos \theta}{\Delta \rho g e} \qquad (1)$$

where H_D is the height of the DNAPL pool (m), σ is the interfacial tension between DNAPL and water (N/m), θ is the wetting or contact angle formed by the DNAPL and a solid surface in the presence of the pore water, $\Delta \rho$ is the density difference between the DNAPL and water (kg/m^3), g is the gravitational acceleration (m/sec^2), and e is the fracture aperture (m) (Berg 1975; Villaume 1985; Kueper and McWhorter 1991).

Contaminant Storage in the Bedrock

Contaminants migrating below the level of the epikarst will, in general, be following fractures, some of which may be widened by solution. Possible storage locations in the aquifer can be tabulated as follows:

- Contaminants may be trapped in fractures, solution cavities, and dry cave passages in the vadose zone.
- Contaminants may migrate to the water table with further downward migration into fractures in the phreatic zone.
- Contaminants may make their way into the active conduit system where they can be stored as macrophase pools under flowing water in free-surface underground streams or in pipe-full conduits.
- Contaminants in conduits can be stored in the clastic sediment that occupies substantial fractions of most conduits.

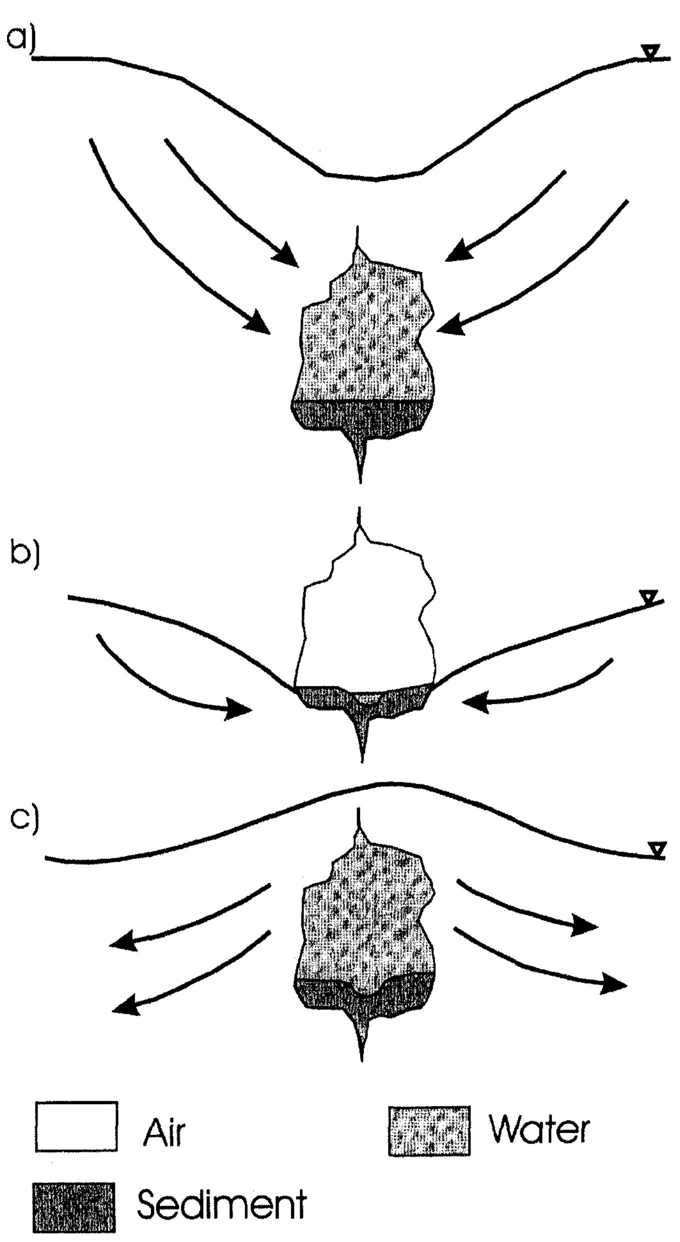

Figure 5. (a) Potentiometric surface sloping toward continuously flooded conduit. b) Potentiometric surface sloping toward open conduit during base flow conditions. (c) Flooded conduit with mounding of potentiometric surface during intense storm flow.

The vadose zone in carbonate aquifers is often riddled with large-scale secondary porosity. The voids range from solutionally widened fractures with apertures from millimeters to centimeters to open solution chimneys and shafts with apertures of meters to tens of meters. On the average, these are vertical pathways, but in detail they are offset along bedding plane partings and deflected by shale or chert horizons and other lithologic and structural barriers. Along the path are cavities and pockets of various sizes that can serve to intercept a vertically migrating contaminant. Vertical pathways often intercept abandoned conduits (caves) left behind in the vadose zone as base levels are lowered. Depending on details of the cavity geometry and the paths of active ground water infiltration, many of these traps in the vadose zone can hold a DNAPL indefinitely because once the material is deposited in the trap, there is no mechanism to reinject it into the active flowpath.

The water table generally stands higher near the borders of karst ground water basins and slopes to a ground water trough defined

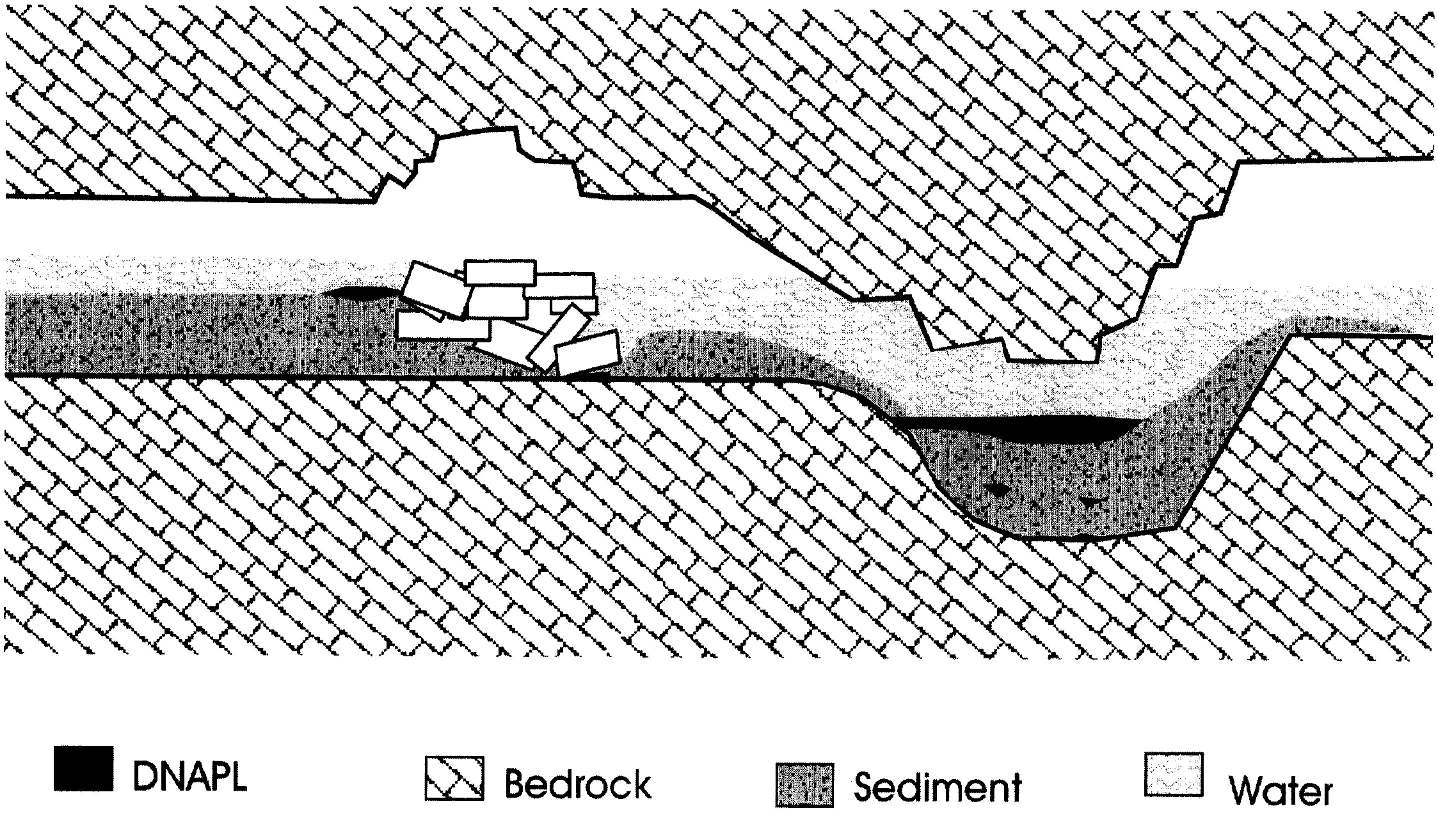

Figure 6. Segment of conduit showing undulating profile with contaminant trapping sites.

by the conduit system. Dense contaminants reaching the water table do not necessarily follow the ground water flow downgradient toward the conduit, but can instead continue to move vertically into any available porosity below local base level or can follow the dip of the beds in directions quite different from the hydraulic gradient (Jancin and Ebaugh 1999). Once in the deep portion of the aquifer, they can remain in storage for long periods of time because flow rates are low with most of the active circulation being in the conduit system above.

The conduit system responds rapidly to storm recharge. Caves that contain free surface streams during base flow can be under pipefull conditions in a matter of hours or less. The potentiometric surface can rise many meters above the conduit and indeed change the ground water trough into a ground water mound. During base flow the hydraulic gradient is directed from the surrounding matrix and fracture system toward the conduit. Contaminants extracted from the matrix and fracture system can be carried into the conduit. During flood flow the gradients are reversed and water flows from the conduit out into the surrounding matrix and fracture system, perhaps carrying contaminants with it (Figure 5).

Conduit systems provide a set of storage sites that have no analog in nonkarstic aquifers. The main mass of water moves through the conduit as open channel flow or as pipe flow. The same conduit may have reaches in which water flows as a free-surface stream and other reaches where the conduit is completely flooded even during base flow conditions. Velocities in the conduits range from centimeters per second to meters per second but are almost always many orders of magnitude faster than ground water flow velocities in porous media aquifers or in the fracture and matrix portion of karstic aquifers. Conduit flow velocities are usually in the turbulent regime. The bed of the conduit is likely to be irregular over masses of clastic sediment, and in some places blocked by highly perme-

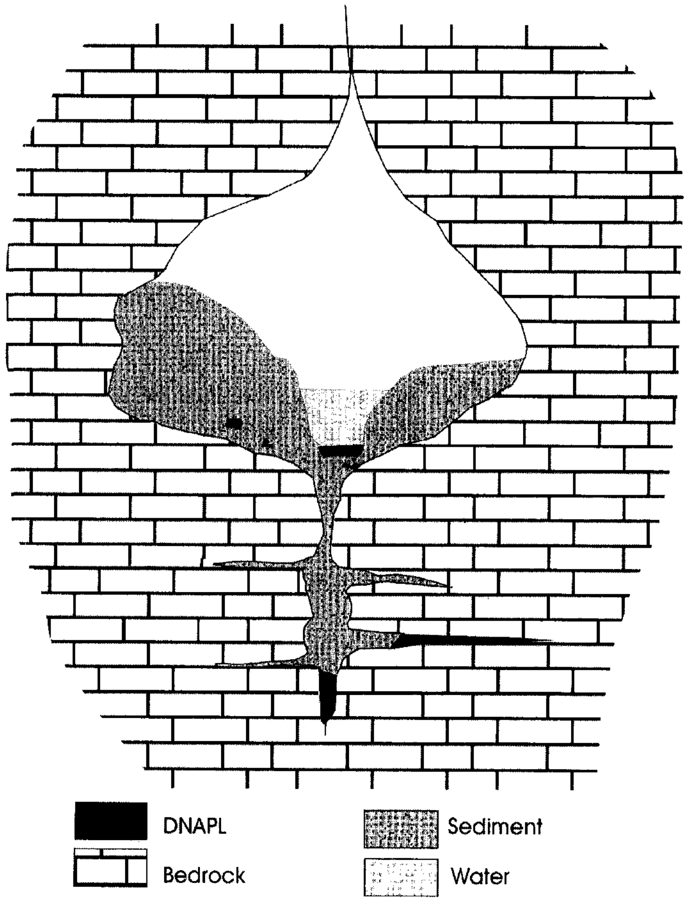

Figure 7. Conduit cross section showing sediment infilling and contaminant trapping.

able masses of breakdown that serve to retard the flow. The water-filled portion of the conduits may descend to sumps and then rise again to open channels. The down-loops in the conduit, as well as depressions in the bed, all serve as traps for pooling DNAPL (Figure 6).

Another distinguishing characteristic of conduit systems is the presence of clastic sediment, much of which has been transported into the aquifer by sinking streams and other upgradient sources. The sediment piles are composed for the most part of some clay along with quartz silt and sand, and coarser rock fragments in the gravel to boulder size range. These are frequently intermixed with limestone rock fragments (breakdown) derived locally from collapse of cave walls and ceilings. Transported rock fragments are composed of whatever material is available in the allogenic recharge basins, with sandstone perhaps being the most common. Sediment piles can range in thickness from zero to tens of meters but almost all conduits have some thickness of clastic material. The clastic sediments form, in effect, a medium of high primary permeability encapsulated by the relatively impermeable limestone or dolomite walls of the conduit. DNAPL can occupy the pore spaces and open voids within the sediment pile and also be sorbed onto the surfaces of the sediment grains (Figure 7).

Additional sorption sites are provided by iron and manganese oxides that coat stream beds and sediment particles. Organic material carried into some conduits and humic substances brought into the conduit system from overlying soils can also act as substrates for sorption.

Contaminant Transport and Dissipation

At least six processes can be visualized for the release or dissipation of DNAPLs that have become trapped in karst conduit systems:

- Volatilization
- Degradation
- Dissolution
- Transport on suspended sediment
- Bulk transport
- Transport with entrained bulk sediment.

Volatilization and degradation are essentially independent of flow regime and movement of water within the conduit system. The other four processes represent interactions between contaminant transport, ground water flow, and sediment transport. Transport and release of contaminants tend to be highly dependent on the hydraulics of ground water flow, as well as the quantity and timing of input. Two transport regimes can be distinguished: low to moderate flows that do not disturb sediment piles and intense storm flows that do. Dissolution and transport on suspended sediment are primary mechanisms for transport of DNAPLs through the system during low to moderate flow. In flood flow conditions, bulk transport and transport on entrained bulk sediment are controlling mechanisms for movement through the karst system.

The relative significance of each of the six transport processes described will also vary by the timing and quantity of DNAPL injected into a given karst system. Slow leaks or small spills are more likely to be volatilized, degraded, dissolved, or transported on sediment than fast leaks or large spills that would accumulate in the system as macrophase pools. With a small surface area to volume ratio, the DNAPL will either have a long lifetime in the system, be broken up into smaller particles, or be flushed out with fast moving water. Macrophase pools have less surface area available for volatilization, dissolution, or sorption, while hindering the ability of microorganisms to establish a nontoxic environment.

Transport Independent of Flow Regime

Many active conduit systems are partially air-filled, at least during periods of low flow. There are also dry cave passages at higher elevations that connect with the active conduits. Further, most caves have good air circulation, partly convective flow and partly the pumping action of rising and falling barometric pressure. Depending on the vapor pressure of the DNAPL, contaminants captured in cave passages in the vadose zone could eventually be lost by volatilization. The DNAPL compound would first be transferred to the cave atmosphere and then transferred to the surface atmosphere through natural air exchange within the cave system. The rate at which this occurs is a function of wind velocity, degree of turbulence, the length of the cave, the pressure or temperature differential between the cave and outside air, and the rapidity with which these conditions change. Cave explorers usually find cave air to be fresh. There have been many studies of air flow within caves, but the rate of turnover of the entire air mass does not seem to have been calculated.

Abiotic degradation rates of chlorinated hydrocarbons in simulated aquatic environments have been found to vary by more than 10 orders of magnitude (Barbee 1994). Microbial transformation either directly or by cometabolism is equally variable. DNAPLs are highly hostile environments for microbes (Huling and Weaver 1991); in order for the contaminant to be degraded, it must be present in a less toxic phase. A study by Isalou et al. (1998) highlights some of the many questions of interest in characterizing the ability of organisms to degrade halogenated compounds. Among them:

- What is the optimum dissolved DNAPL and electron donor concentration needed for rapid degradation?
- What are the necessary members of a microbial community for degradation to a favorable product (e.g., ethylene vs. vinyl chloride)?
- What is the extent of variation between laboratory results and field expectations?
- What is the length of time a microbial community will retain the ability to dechlorinate in the absence of chlorinated compounds?

Microorganisms are known to exist in conduit systems, but organisms that would assist in DNAPL degradation have not been identified.

Continuous Transport at Low to Moderate Flow

Low to moderate flows mainly impact free DNAPL pooled in cave streams and water-filled conduits, but they may also affect DNAPL stored in sediment piles. Because of the rapid flow of water in the conduit system, pools of DNAPL and DNAPL sorbed on stream bed sediments are being continually flushed with fresh water. The rate at which pooled contaminant is carried away in solution will be determined by the flow rate of the water and by the kinetics of dissolution of the DNAPL, essentially a problem of mass transfer across the liquid-liquid interface and by the rate of replenishment.

A general equation for the rate of dissolution is

$$^{dc}/_{dt} = \frac{A}{V} k_T (C^* - C)^n \qquad (2)$$

where dc/dt is the rate of change of aqueous DNAPL concentration, A is the area of the DNAPL/water interface, V is the volume of water over the pool, k_T is the mass transfer coefficient, C* is the saturated concentration of DNAPL in the water, C is the actual concentration of DNAPL in the water, and n is the order of the dissolution reaction. This type of rate equation has been applied to the oxidation of TCE in a laboratory setting (Knauss et al. 1999). Solubility values for pure DNAPL compounds can be found in chemical handbooks, and the other variables are dependent on subsurface flow and contaminant placement. The mass-transfer coefficient equation will vary by flow regime. For laminar flow, a mass-transfer coefficient can be calculated using boundary layer theory from the relationships of the Reynolds, Schmidt, and Sherwood dimensionless numbers. The Sherwood number has the form of

$$Sh = \frac{k_T L}{D} \qquad (3)$$

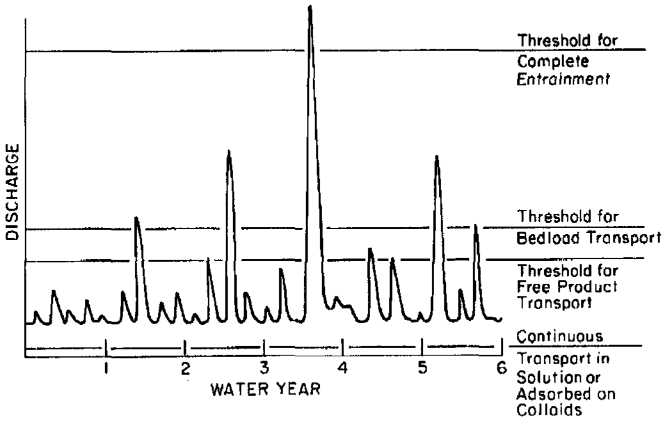

Figure 8. Schematic of hydrograph showing thresholds for different sediment transport processes.

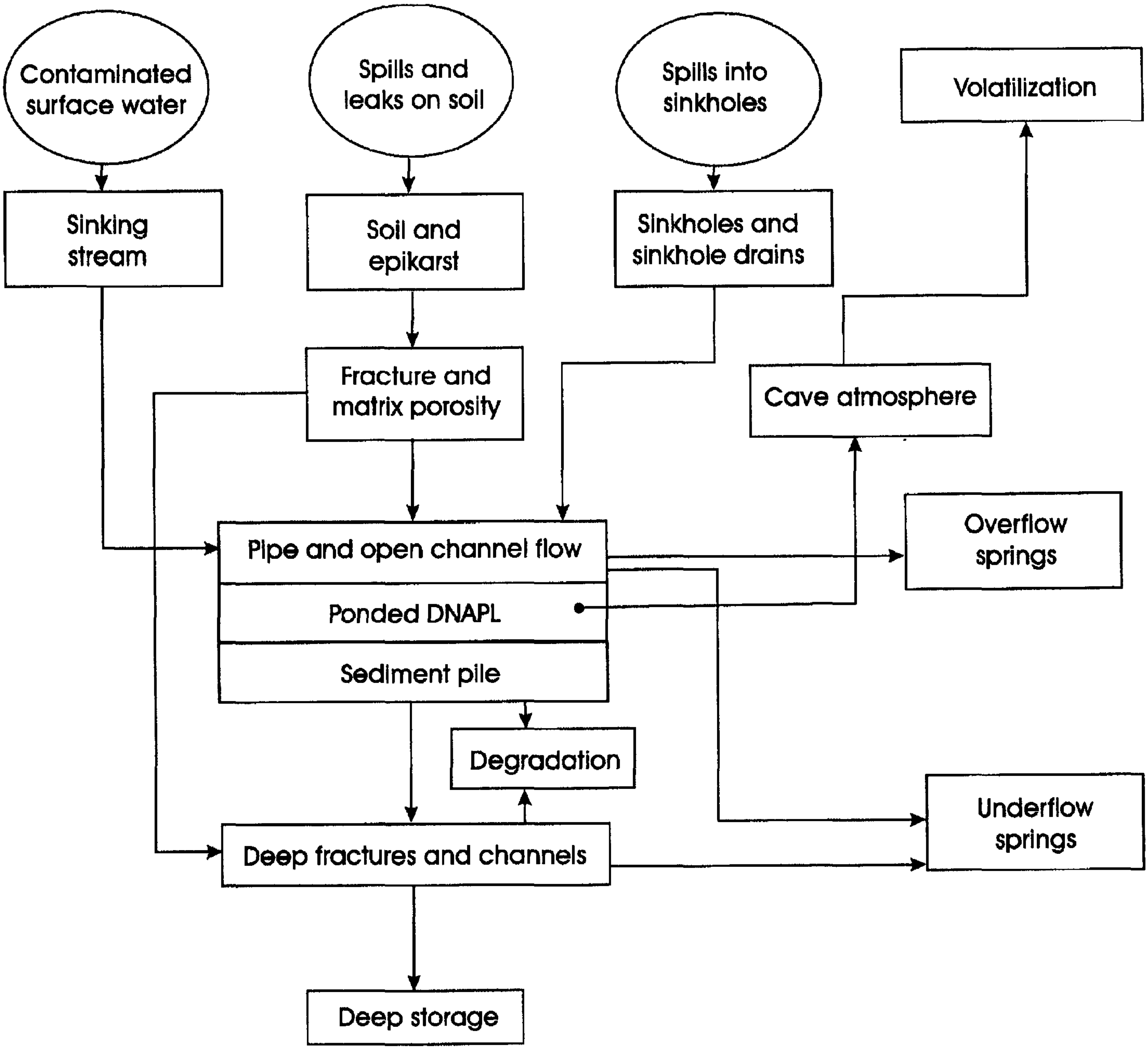

Figure 9. Conceptual model for DNAPL storage and transport in a karst aquifer.

where L is the surface length of the pool and D is the laminar diffusion coefficient. Equations for turbulent flow are based on data correlation; the theory is not yet well developed (Thibodeaux 1996).

Colloidal sized particulates remain indefinitely in suspension, and clay-sized particulates are easily entrained, even under base flow conditions. There is increasing evidence that both act as vehicles for the transport of contaminants sorbed onto their surfaces (Simmleit and Herrmann 1987; Mahler 1997). Recent studies in natural systems have shown colloidal material to have a diverse composition of clays, iron oxides, silica, organic matter, and bacteria (Atteia et al. 1998). Particulates in the colloid and clay size range can migrate through the fracture system of the aquifer and play an important role in the transport of contaminants in a continuous flux through the conduit.

Episodic Transport Under Flood Flows

Pooled DNAPL will remain stationary under low flow condition except for the gradual loss by dissolution. As flow velocity increases, particularly in rough stream beds, the DNAPL will first be dragged along the channel by the interfacial tension between flowing water and the liquid contaminant, and as velocity increases even further, the DNAPL can become entrained and transported in suspension. Once flood flow conditions entrain DNAPL, they may increase in power to form an emulsion with the contaminant, and also move the entire sediment pile, thus significantly altering the multiphase distribution of DNAPL. The more variable the karst aquifer response to a storm, the more DNAPL and related phase concentrations will fluctuate for a given release. Flood flow can send previously immobilized DNAPL to outflow points in toxic pulses.

To describe flow conditions in terms of a mobilizing force, we propose the stream power terminology, borrowed from the sedimentology literature. Specific stream power (ω), the work done by the flow on a unit area of the channel bed, is expressed as

$$\omega = (\rho\ g\ S\ Q)/w \qquad (4)$$

where ρ is the density of water (kg/m3), g is the gravitational constant (m/s^2), S can be approximated by the channel slope, Q is discharge (m^3/s), and w is the channel width (m). Talling and Sowter (1998) state that in empirical studies of loose-bed channels, a strong positive correlation is clearly shown between stream power, bed shear stress, and bedload transport rate. This equation can be similarly applied to karst conduits under nonpipe flow conditions. As specific stream power increases, one would expect an increase in both DNAPL and sediment transport rates.

Large-scale movement of sediment in karst has been observed. For example, a storm event in Austin, Texas, transported up to one metric ton of material through the Barton Springs Aquifer, with the sediment discharged within 24 hours of the rain event (Mahler 1997). Increased sediment content will continue to change the density and viscosity of the liquid mass, while at the same time releasing residual and pooled DNAPL from sediment pores. In this manner, the entire conduit contents may be churned and redistributed, leading to a downstream pulse of contaminant in the vapor, aqueous, nonaqueous, and solid phases. The extent to which the DNAPL will be present in these phases for a given conduit system and flow condition will depend on the properties of the compound, such as vapor pressure, solubility, density, and viscosity.

The main mechanisms for transporting contaminants through karst aquifers are determined by a series of thresholds (Figure 8). Depending on the type of sediment in the conduit and the DNAPL in question, the threshold for movement of either may be before or after the other. For example, one might expect a fine-grained sand to be transported as bedload before the entrainment of a viscous, highly weathered creosote. Conversely, a solvent with a density just slightly higher than $1 g/cm^3$ might be transported before clay material. Closer attention to sampling during storm events at DNAPL-contaminated sites will clarify the relative order of these two occurrences in a given situation.

Conclusions

Figure 9 presents a conceptual model for DNAPL transport through karst aquifers. The diagram attempts to encapsulate all of the processes previously described. Contaminant transport is superimposed on the more or less standard conceptual model for ground water behavior in carbonate aquifers. The distinguishing characteristics of karst aquifers are the system of conduits of various apertures and connectivities, and the clastic sediments that partially fill the conduits. Both water and DNAPL flow through the karst system may be highly variable. The open plumbing systems make the distinction between spills and leaks much more significant than in most other aquifers because the balance between the storage and transport mechanisms will depend on the volume of contaminant being injected. Bulk storage and movement of free contaminant will be significant only in the case of spills.

To carry the analysis beyond the conceptual will require devising quantitative expressions for each of the identified transport mechanisms. Some of these, for example the stripping of pooled DNAPL by fast-flowing fresh water, should be amenable to calculation. Others, such as the episodic movement of bulk sediment with entrained DNAPL, probably require further research.

Acknowledgments

We thank chemical engineers R. L. Kabel of the Pennsylvania State University and R. H. Heck of Mobil Oil Corp. for helpful discussion.

References

Acikgoz, M., F. Franca, and R.T. Lahey Jr. 1992. An experimental study of three-phase flow regimes. *International Journal of Multiphase Flow* 18, no. 3: 327-336.

Annable, W.K., and E.A. Sudicky. 1999. On predicting contaminant transport in carbonate terrains: Behavior and prediction. In *Karst Modeling,* ed. A.N. Palmer, M.V. Palmer, and I.D. Sasowsky, 133-145. Charles Town, West Virginia: Karst Waters Institute. Special Publication 5.

Atteia, O., D. Perret, T. Adatte, R. Kozel, and P. Rossi. 1998. Characterization of natural colloids from a river and spring in a karstic basin. *Environmental Geology* 34, no. 4: 257-269.

Barbee, G.C. 1994. Fate of chlorinated aliphatic hydrocarbons in the vadose zone and ground water. *Ground Water Monitoring and Remediation* 14, no. 1: 129-140.

Berg, R.R. 1975. Capillary pressures in stratigraphic traps. *AAPG Bulletin* 59, no. 6: 939-956.

Crawford, N.C., and C.S. Ulmer. 1994. Hydrogeologic investigations of contaminant movement in karst aquifers in the vicinity of a train derailment near Lewisburg, Tennessee. *Environmental Geology* 23, no. 1: 41-52.

Fetter, C.W. 1994. *Applied Hydrogeology,* 3rd ed. Englewood Cliffs, New Jersey: Prentice Hall.

Gilbert, J. 1990. Behavior of aquifers concerning contaminants: Differential permeability and importance of the different purification processes. *Water Science and Technology* 22, 101-108.

Huling, S.G., and J.W. Weaver. 1991. Dense nonaqueous phase liquids. Ground Water Issue, U.S. EPA report EPA/540/4-91-001.

Isalou, M., B.E. Sleep, and S.N. Liss. 1998. Biodegradation of a high concentration of tetrachloroethene in a continuous flow system. *Environmental Science and Technology* 32, no. 22: 3579-3585.

Jancin, M., and W. Ebaugh. 1999. Shallow lateral DNAPL migration within slightly dipping limestone, southwestern Kentucky. In *Hydrogeology and Engineering Geology of Sinkholes and Karst-1999,* ed. B.F. Beck, A.J. Petit, and J.G. Herring, 315-321. Rotterdam: A.A. Balkema.

Knauss, K.G., M.J. Dibley, R.N. Leif, D.A. Mew, and R.D Aines. 1999. Aqueous oxidation of trichloroethene (TCE): A kinetic analysis. *Applied Geochemistry* 14, no. 4: 531-541.

Kogovsek, J. 1981. Vertical percolation in Planina Cave in the period 1980/1981. *Acta Carsologica* 10, 111-125.

Kueper, B.H., and D.B. McWhorter. 1991. The behavior of dense, nonaqueous phase liquids in fractured clay and rock. *Ground Water* 29, no. 5: 716-728.

Litherland, S.T., and D.W. Anderson. 1990. The trouble with DNAPLs. In *Superfund '90 Proceedings of the National Conference* 11, 565-574. Hazardous Materials Control Research Institute, Silver Spring, Maryland.

Mahler, B.J., and F.L. Lynch. 1999. Muddy waters: Temporal variation in sediment discharging from a karst spring. *Journal of Hydrology* 214, no. 1-4: 165-178.

Mahler, B.J. 1997. Mobile sediments in a karst aquifer. Ph.D. diss., Department of Geological Sciences, University of Texas at Austin.

Moore, M.B., and L.L. Moore. 1997. The Edwards Aquifer, a case study of DNAPL in a karst aquifer which expands the DNAPL paradigm. *Abstracts with Programs, Geological Society of America Annual Meeting* 29, no. 6: 183. Salt Lake City, Utah.

Neogi, S., A. Lee, and W.P. Jepson. 1994. A model for multiphase (gas-water-oil) stratified flow in horizontal pipelines. *SPE Asia Pacific Oil and Gas Conference*, 553-562. Melbourne, Australia.

Oudeman, P. 1993. Sand transport and deposition in horizontal multiphase trunklines of subsea satellite developments. *SPE Production and Facilities* 8, no. 4: 237-241.

Parker, B.L., R.W. Gillham, and J.A. Cherry. 1994. Diffusive disappearance of immiscible-phase organic liquids in fractured geologic media. *Ground Water* 32, no. 5: 805-820.

Ray, J.A. 1999. Personal communication, March 8.

Ross, B., and N. Lu. 1999. Dynamics of DNAPL penetration into fractured porous media. *Ground Water* 37, no. 1: 140-147.

Simmleit, N., and R. Herrmann. 1987. The behavior of hydrophobic, organic micropollutants in different karst waters systems. 1. Transport of micropollutants and contaminant balances during the melting of snow. 2. Filtration capacity of karst systems and pollutant sinks. *Water, Air and Soil Pollution* 34, no. 1: 97-109.

Slough, K.J., E.A. Sudicky, and P.A. Forsyth. 1999. Importance of rock matrix entry pressure on DNAPL migration in fractured geologic materials. *Ground Water* 37, no. 2: 237-244.

Stapelberg, H.H., and D. Mewes. 1994. The pressure loss and slug frequency of liquid-liquid-gas slug flow in horizontal pipes. *International Journal of Multiphase Flow* 20, no. 2: 285-303.

Talarovich, S.G., and N.C. Krothe. 1998. Three-component storm hydrograph separation of a karst spring contaminated by polychlorinated biphenyls in central Indiana. *Environmental Geosciences* 5, no. 4: 162-176.

Talling, P.J., and M.J. Sowter. 1998. Erosion, deposition, and basin-wide variations in stream power and bed shear stress. *Basin Research* 10, no. 1: 87-107.

Thibodeaux, L.J., L.K. Chang, and D.J. Lewis. 1980. Dissolution rates of organic contaminants located at the sediment interface of rivers, streams, and tidal zones. In *Contaminants and Sediments,* volume 1: *Fate, Transport, Case Studies, Modeling, Toxicity*, ed. R.A. Baker, 349-371. Ann Arbor, Michigan: Ann Arbor Press.

Thibodeaux, L.J. 1996. *Environmental Chemodynamics,* 2nd ed. New York: John Wiley and Sons.

Triplett, K.A., S.M. Ghiaasiaan, S.I. Abdel-Khalik, and D.L. Sadowski. 1999. Gas-liquid two-phase flow in microchannels, Part I: Two-phase flow patterns. *International Journal of Multiphase Flow* 25, no. 3: 377-394.

U.S. EPA. 1987. Superfund public health evaluation manual. Report no. EPA/540/1-86-060.

Vanderkwaak, J.E., and E.A. Sudicky. 1996. Dissolution of non-aqueous phase liquids and aqueous phase contaminant transport in discretely fractured porous media. *Journal of Contaminant Hydrology* 23, no. 1-2: 45-68.

Villaume, J.F. 1985. Investigations at sites contaminated with dense non-aqueous phase liquids (NAPLs). *Ground Water Monitoring Review* 5, no. 2: 60-74.

White, W.B. 1988. *Geomorphology and Hydrology of Karst Terraines.* New York: Oxford University Press.

White, W.B. 1993. Analysis of karst aquifers. In *Regional Ground-Water Quality,* ed. W.M. Alley, 471-489. New York: Van Nostrand-Reinhold.

White, W.B. 1998. Groundwater flow in karst aquifers. In *The Handbook of Groundwater Engineering,* ed. J.W. Delleur, 1-36. Boca Raton, Florida: CRC Press.

White, W.B. 1999a. Conceptual models for karstic aquifers. In *Karst Modeling,* ed. A.N. Palmer, M.V. Palmer, and I.D. Sasowsky, 11-16. Charles Town, West Virginia: Karst Waters Institute. Special Publication 5.

White, W.B. 1999b. Karst hydrology: Recent developments and open questions. In *Hydrogeology and Engineering Geology of Sinkholes and Karst-1999,* ed. B.F. Beck, A.J. Petit, and J.G. Herring, 3-21. Rotterdam: A.A. Balkema.

Williams, P.W. 1983. The role of the subcutaneous zone in karst hydrology. *Journal of Hydrology* 61, no. 1-3: 45-67.

Wolfe, W.J., C.J. Haugh, A. Webbers, and T.H. Diehl. 1997. Preliminary conceptual models of the occurrence, fate, and transport of chlorinated solvents in karst regions of Tennessee. U.S. Geological Survey Water-Resources Investigations Report 97-4097.