

Contaminant transport mechanisms in karst terranes

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Abstract Identification of transport path-lines of typical contaminant constituents within the subsurface is difficult if not impossible in the karst setting. Both the nature of contaminant migration and the complexity of conduit and fracture flow typical of karst have made the characterization of past waste disposal sites using routine karst investigative techniques cost prohibitive and inefficient. Remediation of some sites is impossible. Investigative techniques for predicting the probable location of dissolved-phase leachates, light- and dense-non-aqueous phase liquid (LNAPL and DNAPL) contaminants are presented in this paper, with examples from existing waste disposal sites under environmental investigation. In the light of the lessons learned, coupled with the known geologic hazard associated with construction in karst, the siting of new waste disposal facilities cannot be justified.

Mechanismos de transporte de contaminantes en macizos autóctonos kársticos

Resumen En un ambiente kárstico, la identificación de trayectorias de transporte de constituyentes contaminantes típicos es difícil, si no imposible. Tanto la naturaleza de la migración de contaminantes como la compeljidad del flujo de conducto y fractura que es típico del karst han hecho que la caracterización de sitios de basureros antiguos, mediante técnicas de investigación de rutina en el karst sea ineficiente y prohibitive en lo que se refiere a los costos. La corrección de algunos sitios es imposible. En esta ponencia se presentan técnicas de investigación para predecir la ubicación probable de contaminantes lixiviados de fase disuelta y líquidos de fase no acuosa ligera y densa (LNAPL y DNAPL, siglas en inglés), con ejemplos de sitios de basureros existentes sometidos a investigaciones ambientales. En vista de las lecciones aprendidas, unidas a los riesgos geológicos conocidos que se asocian a las construcciones en karst, no se puede justificar el asentamiento de nuevas instalaciones de eliminación de desechos.

GOALS OF SITE CHARACTERIZATION FOR NEW WASTE DISPOSAL FACILITIES

The principal focus of site characterization for siting a waste disposal facility in a karst setting is to obtain data sufficient to provide geotechnical characteristics, identify specific karst features including preferential groundwater flow paths, and locate potential receptors which may include seeps, springs, and/or wells, in the

event of a release from the facility. The geotechnical hazards associated with siting any structure in karst has been exhaustively examined by others (Beck, 1995) so the focus of this paper is to discuss the implications of containment failure and contaminant release.

Given the potential complexities of groundwater flow in the karst setting, an understanding of typical containment transport mechanisms and how those mechanisms will be altered by the unique enhanced flow opportunities of karst is important. For example, the contouring of potentiometric elevations and the depiction of apparent plumes of groundwater contaminants is typically of little to no use because contouring assumes a continuity of flow such as found in porous media aquifers. Plume depiction is an inappropriate conceptualization of the intermingling of groundwater flow paths and conduit flow typical of karst.

The degree of karstification determines the mobility of water and contaminants through the subsurface, ranging from sensitive (diffuse flow similar to porous media aquifers) to hypersensitive karst aquifers (conduit and cavernous flow that occurs in the Mammoth Cave system in east central Kentucky). Lack of knowledge of how a karst aquifer system works can lead to irrelevant monitoring strategies and corrective measures if a release were to occur (ASTM, 1995). In developing a siting approach, it is imperative to interpret site data within the framework of a conceptual model of contaminant transport mechanisms within the karst setting, and to accept that some contaminants in some settings simply cannot be contained within an engineered waste disposal facility.

KARST WATER HYDROLOGY

To understand how contaminants are transported in a karst aquifer and to properly characterize the groundwater system in a karst terrane, a complete understanding of the processes that result in the formation of karst systems is critical for the establishment of a reliable conceptual model. In most aquifers, water is stored in the saturated zone; however, karst aquifers can store large volumes of water in a part of the unsaturated zone known as the epikarst. This zone is the upper 10–15 m of the carbonate bedrock, consisting of highly fractured and dissolved bedrock. The epikarst can behave as a locally saturated, sometimes perennial, storage zone that is similar to a perched aquifer, but is not perched on a lithologic discontinuity. Flow into this zone is more rapid than flow out of it, as limited pathways transmit water downward to the aquifer.

Below the epikarst, preferential flow paths develop along major vertical joints, faults, and bedding plane partings. Under the influence of gravity, vadose water moves progressively downward to lower flow-routes where the water may feed into several conduits over a large area. As recharge reaches the phreatic zone, the conduits may or may not be integrated along their entire length, thus causing some opportunity for physical dispersion (Field, 1993).

Groundwater flow in a karst aquifer can be described as diffuse or conduit flow, with most flow in a karst aquifer a mixture of the two. Groundwater in large

passages allows for relatively high velocities under turbulent flow conditions. Passage orientation depends on the local stratigraphy and structure. Flow velocities are greatest in open-channel vadose passages as compared with tube-filled phreatic conduits. The concept of a continuous potentiometric surface becomes less appropriate as conduit flow becomes dominant. However, conduit dominated flow systems still contain a diffuse flow component feeding the conduits. The transport mechanisms of some typical contaminants will take on unique variations within these karst features; anticipating these variations is important to understanding contaminant transport in karst.

CONTAMINANT TRANSPORT CONSIDERATIONS

If a release occurred from a waste disposal facility, the transport characteristics of the released contaminants in the karst environment will determine whether that chemical is amenable to remediation. Dissolved-phase contaminants, typical of municipal landfill leachate, will generally flow as and with groundwater, with transport velocities and path-lines sometimes differing from groundwater due to factors including chemical concentration gradients, mechanical dispersion, and chemical diffusion. Apparent groundwater flow direction may differ from actual flow, as shown in Fig. 1. The aquifer matrix may also impact contaminant transport velocities by retention and retardation of the contaminant due to chemical reactions

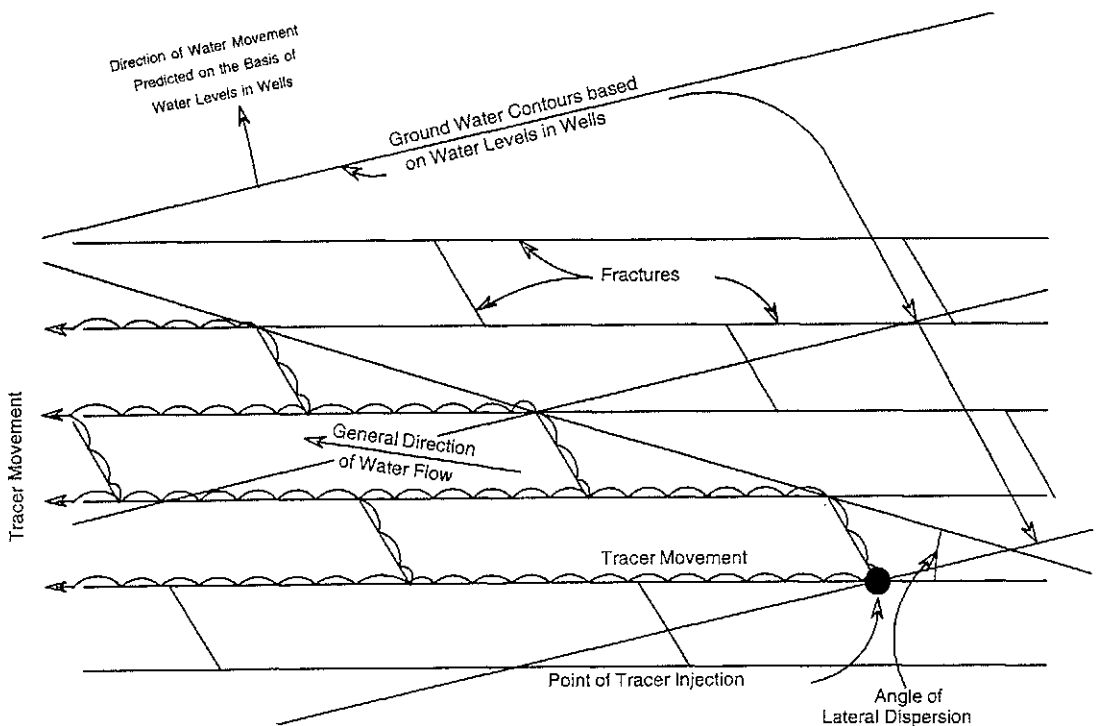


Fig. 1 Strike parallel-flow: groundwater transport (after Davis & DeWiest, 1966).

with the geologic material. But, in general, a finite mass of dissolved contaminants will eventually flush from the aquifer. Dissolved phased constituents of a finite volume transported in the fractures, channels and conduits established in the more mature karst setting will efficiently flush more rapidly due to the short residence-times characteristic of these karst systems.

A common misconception is that a karst aquifer will always rapidly flush out contaminants, thus cleansing itself. Chemicals released in karst terranes will infiltrate the soil zone, and these contaminants may sorb onto soil, or through limestone structures. Once the contaminants reach the epikarst (the upper 10 m of the limestone bedrock) sufficient storage may occur, and chemicals can be retained for many years, slowly releasing small amounts over time. Subsequent flooding will drive portions of these chemicals out of the rock matrix and into the main conduit for rapid transport, thus polluting the aquifer.

Natural attenuation of contaminants in a karst aquifer may be limited by a variety of geological, biological and chemical factors, including: (a) poor adsorption or ion exchange of contaminants coupled with little colonization of microorganisms; this is due to a significant lack of available surface area as compared to a granular aquifer; (b) a reduction in the ability to evaporate volatile organic compounds (VOCs) from the ground surface due to extremely rapid infiltration rates; (c) little infiltration of contaminants as a result of thin soils and solutionally enlarged fractures in the bedrock typical in karst terranes; (d) assistance in the transmission of contaminants by the turbulent flow regime typical of conduit flow; and (e) the reduction in adsorption/desorption processes and microbiological activities being affected as a result of the rapid flow-through rates in conduits (Ford & Williams, 1989).

Acceptance that the remediation of karst aquifers contaminated by organic chemical compounds may not be achievable within an economically acceptable time frame will eliminate the karst setting from serious consideration of siting of a facility designed to accept these chemicals. These sites have been the focus of intense debate as to the appropriateness of any remediation approach (Quinlan & Ray, 1991). Some contaminants, such as those resulting from the release of dense organic compounds, can be transported deep within the aquifer; if the organic contaminants remain in-phase and do not dissolve, the deep source area may result in a continuous generation of leached, dissolved-phase stream of contaminants that cannot be remediated.

The complete recovery of non-aqueous phase liquid (NAPL) organic contaminants from the subsurface is not feasible because plumes of groundwater contaminants emanating from NAPL sources are potentially infinite in dimension. NAPL chemicals are generally immiscible in water and, due to their hydrophobic characteristics, tend to be absorbed and retained indefinitely in the interstitial spaces of the aquifer matrix (Dasinger, 1994). Residual NAPLs act as continuous sources of groundwater contaminants and, if not removed from contact with water, will continue to generate a plume of dissolved chemical constituents. Failure of many remediation programs has been the result of underestimating the length of time required to flush contaminants out of the aquifer because the NAPL source continues to generate the plume, and continued pumping induces continuous plume generation. Thorough characterization and identification of groundwater contaminant source

areas resulting from NAPL transport is therefore imperative to defining the appropriate remediation strategy. Elimination of a karst site from consideration for future siting of a new waste disposal facility is more reasonable.

ORGANIC CONTAMINANT CHARACTERISTICS AND TRANSPORT MECHANISMS

NAPLs include organic compounds such as chlorinated organic solvents (also known as volatile organic compounds, VOCs), cresols, creosote, some pesticides, and fuel hydrocarbons. NAPLs are immiscible with, and typically of dissimilar density to, water in their undiluted form. Although the less dense light NAPLs (such as gasoline) are prevalent contaminants, because they are lighter than, and therefore float on top of, the water table, they are more amenable to clean up. Where a water table exists in the soils above a karst aquifer, cones of depression centred on vertical cracks and other macropores hydraulically connected to solutionally enhanced conduits are found to be preferred transport routes of the separate phase as well as dissolved-phase components of LNAPL hydrocarbons (Cooley, 1991), as shown in Fig. 2. Areas A, B and C of this Figure show trapped pools of LNAPL, whereas residual separate-phase LNAPLs, are held in the interstitial soil spaces in area D. Some field investigators have found that LNAPL hydrocarbons can move in karst

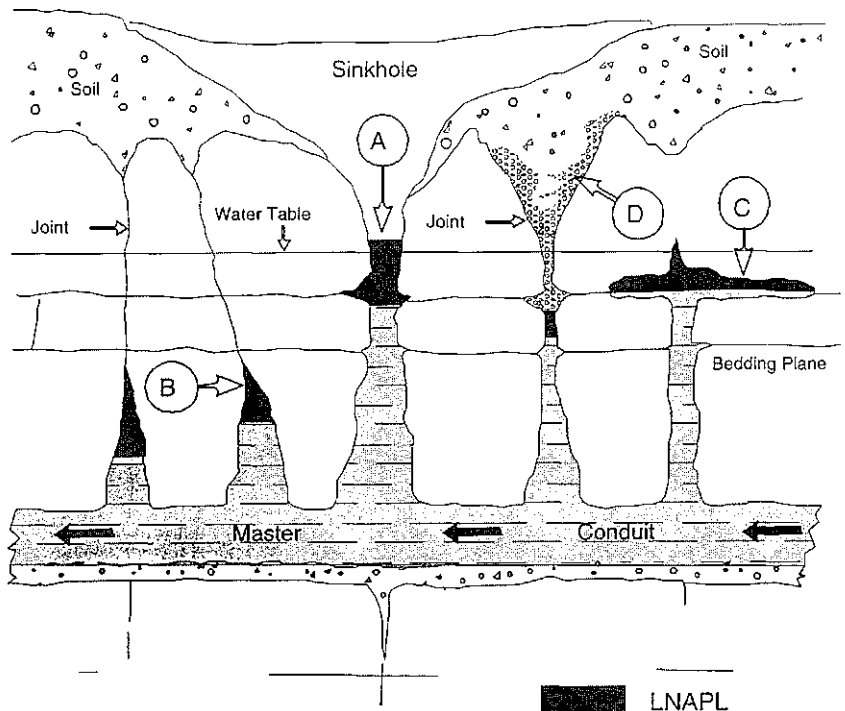


Fig. 2 Residual LNAPL contaminant source (revised from Ewers *et al.*, 1991).

conduits as gross concentrations of free product at speeds of the order of kilometres per hour (Ewers *et al.*, 1991). A typical LNAPL remediation involves removal of source areas (excavation, vapour extraction, *in situ* soil washing and sparging), coupled with groundwater gradient control to induce the flow of LNAPLs downgradient towards collection wells or trenches (Recker, 1991).

Dense NAPLs (DNAPLs) flow by gravity through the aquifer, as shown in Fig. 3. The transport of typical DNAPLs, the most prevalent of which are degreasing solvents such as tetrachloroethylene (PCE), trichloroethylene (TCE), and creosote, may be influenced by the slope of the bedrock surface, bedding planes, solution channels, fractures and cracks. The pool of contaminant constituents will settle by gravity at the lowest point it can drop under a gravity head and there it will remain as a deep contaminating source indefinitely within the aquifer, as depicted in Fig. 4. Unless a significant volume of separate phase contaminants exists to maintain a head to induce horizontal flow, DNAPLs are not expected to be transported horizontally (Barbee, 1994).

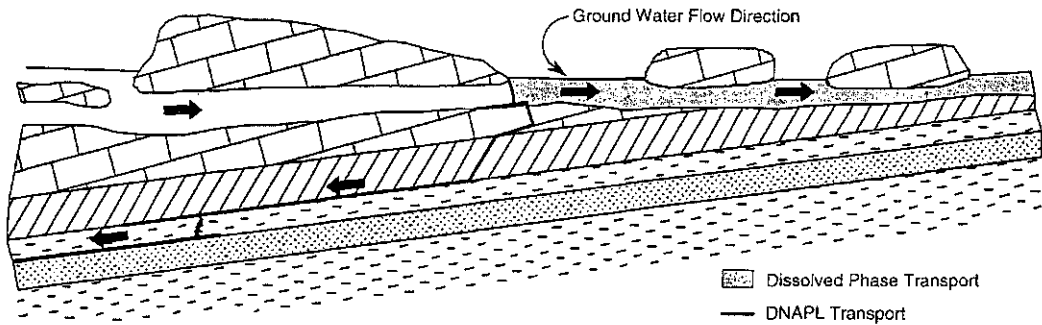
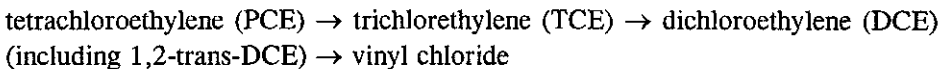


Fig. 3 Schematic cross section showing gravity controlled transport (revised from Ewers *et al.*, 1991).

Degradation of these organic compounds is caused by the ageing and transformation of the chemicals by exposure to various subsurface influences. A commonly described (Vogel *et al.*, 1987) degradation pathway for the organic solvents is:



Several degradation products and pathways have been identified (Smith & Dragun, 1984; Whelan *et al.*, 1994; Olsen & Davis, 1990) which indicate that the most commonly found products of microbial degradation come from reductive dehalogenation, while nonmicrobial degradations tend to involve hydrolysis and/or oxidations. The average half-life of abiotic transformations ranges from 2 months to greater than 10×10 years; biodegradation half-lives may vary considerably, but have been found to range from about 2 weeks to 8 months or more (Barbee, 1994). The distribution of VOCs in a groundwater plume will reflect degradation of a historic release that is ageing as it is travelling downgradient through the saturated system. With time, the concentration of degradation product will increase, while the

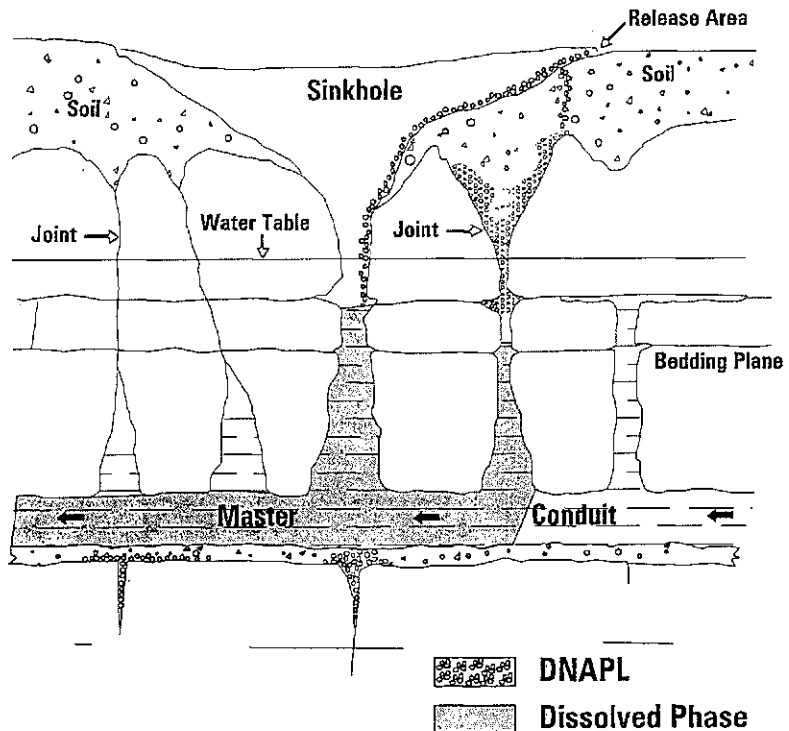


Fig. 4 Residual DNAPL contaminant source (revised from Ewers *et al.*, 1991).

concentrations of the total VOCs will remain relatively constant. In a complex karst groundwater setting, evaluating the contaminant distribution based on relative concentrations of degradation products may support the interpretation that a DNAPL exists if apparent contaminant flow is divergent to groundwater flow (Shields & Uhlman, 1991).

In addition, although low-permeability stratigraphic units do retard the vertical migration of conservative contaminants, a number of laboratory and *in situ* field studies have demonstrated that DNAPL liquids do rapidly penetrate low-permeability clays and have dramatic breakthrough transport times (Brown & Thomas, 1987). In a karst setting, low-permeability clay residuals have masked localized zones of high permeability; the horizontal and vertical continuity of these clays cannot be assured (Aley, 1987). Clay minerals in contact with concentrated organic liquids undergo structural changes resulting in the shrinkage and cracking of the clay and a concomitant increase in its hydraulic conductivity to organic liquids. Assumptions as to the likelihood that DNAPL transport of contaminants will be restricted or retarded by the presence of low-permeability clays cannot be made.

Unless actual separate-phase VOCs are observed in groundwater samples, varying concentrations of dissolved constituents or distribution of degradation products cannot always pinpoint whether the contaminant source is a deep DNAPL, or a plume of dissolved constituents originating from a shallow (and therefore amenable to excavation or containment) soil location. Some investigators attempt to

suspect DNAPL contamination when aqueous concentrations approach the respective solubility of the chemical; however, bench-scale sand tank tests using trichloroethane (TCA) and TCE pools resulted in aqueous concentrations much lower than the respective solubilities (Whelan *et al.*, 1994). The investigator cannot rely exclusively on either contaminant concentration data or degradation product distribution to determine the probability of a deep DNAPL source.

SUMMARY OF STRATEGIES AND RECOMMENDATIONS

The transport characteristics of the expected contaminants that may be released from a waste disposal facility are key to the successful siting of these facilities in a karst setting. In addition, amenability of this contaminant to removal/remediation from groundwater is important in the siting process because some contaminant source areas simply cannot be removed and therefore the aquifer cannot be remediated. The following approach can assist the scientist in developing the appropriate strategy in addressing when, and if, a waste facility should be permitted in karst.

- Physical and chemical features of the aquifer matrix will impact the transport of all anticipated waste facility contaminants. Site characterization activities must address not only the fractures and solution channels that will influence the flow of water, but also the physical chemistry such as density that will influence the flow of contaminants.
- In some settings, identification and characterization of vertical inlets to deeper karst drainage features may assist in locating future potential NAPL transport pathways. Mapping of bedrock structural features such as horizontal bedding planes or transition in rock matrix may assist in locating where a DNAPL release may pool.
- Amenability of contaminant removal/remediation from groundwater is important, and knowledge of transport mechanisms can aid hydrogeologists in generating appropriate strategies for remediation issues, and developing mitigation plans in the event of a contaminant release from closed or older waste treatment facilities.

It should be stressed that any mature karst terrane eliminates a site from consideration for the location of waste treatment or disposal facilities. It is apparent from previous research that karst terranes promote rapid dispersal of contaminant spills of any kind, exponentially effecting overall water quality. It has also been shown that karst aquifers are particularly sensitive to long-term pollution episodes, hindering mitigation and impacting the viability of extensive areas of groundwater resources. Therefore, a prior assumption that research and monitoring of past spills will provide a long-term solution for future spills occurring from facilities that are located in such environments, is irresponsible, and the location of waste treatment facilities in such environments is not recommended.

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