



Contaminant transport in karst aquifers

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Abstract

Contaminants are easily injected into karst aquifers through sinking streams, sinkholes, or through open fractures and shafts in the carbonate rock. Transport of the contaminants through the aquifer is by a variety of mechanisms depending on the physical and chemical properties of the contaminant. Contaminants consist of (1) water soluble compounds, both organic and inorganic, (2) slightly soluble organic compounds, less dense than water (LNAPLs), (3) slightly soluble organic compounds, more dense than water (DNAPLs), (4) pathogens, (5) metals, and (6) trash. Water soluble compounds (e.g. nitrates, cyanides, carboxylic acids, phenols) move with the water. But rather than forming a plume spreading from the input point, the contaminated water forms linear stringers migrating down the conduit system toward the discharge point. LNAPLs (e.g. petroleum hydrocarbons) float on the water table and can migrate down the water table gradient to cave streams where they tend to pond behind obstructions. DNAPLs (e.g. chlorinated hydrocarbons), in contrast, sink to the bottom of the aquifer. In the conduit system, DNAPLs pond in low spots at the bottom of the conduit and infiltrate sediment piles. Transport of both LNAPL and DNAPL is dependent on storm flow which can force LNAPL through the system as plug flow and can move DNAPLs by mobilizing the sediment piles. Pathogens (viruses, bacteria, parasites) are transported through the karstic drainage system because of the absence of filtration and retain their activity for long distances. Metals (e.g. chromium, nickel, cadmium, mercury, and lead) tend to precipitate as hydroxides and carbonates in the neutral pH, carbonate rich water of the karst aquifer. Metal transport is mainly as particulates and as metal adsorbed onto small particulates such as clays and colloids. Metal transport is also episodic. Metals migrate down the flow path under flow conditions that take small particulates into suspension. Trash is carried into karst aquifers through sinkholes and sinking streams. It is, in effect, a form of clastic sediment, and can be carried deep into the conduit system where it can act as a source term for other contaminants leached from the trash.

Keywords: LNAPL, DNAPL, metal contaminants, transport, aquifers.

Introduction

It is a truism that karst aquifers are more vulnerable to contamination than other types of aquifers. Sinking streams, sinkhole drains, and open fractures in the bedrock provide little or no filtration of incoming water. Large aperture solution openings provide easy pathways for the movement of contaminants. Localization of ground water flow in open conduits means that contaminants can be transported long distances with little dilution. All of these statements have been repeated many times. What has been given less attention is the great variability in both volume and velocity of water

moving through conduit systems and the impact of this variability on contaminant transport. In those aquifers with well-developed conduits, peak flows may be 100 times the base flows. Velocities within the conduit system are much higher during storm flow than during base flow. A further variable is the characteristics of the contaminants themselves. All contaminants do not respond equally to the driving forces for transport through the karst aquifer.

The ability of the conduit system to store and release contaminants is dependent both on the nature of the contaminants and on the storm flow characteristics of the system. Although there is an extensive and rapidly growing literature on

contaminants in porous media and fracture aquifers, the analysis of contaminant transport in karstic aquifers is just beginning (e.g. Hoke and Wicks, 1997). Our objective in the present paper is to describe the various types of contaminants and summarize some of the ways in which they are stored and transported in karst aquifers. The examples are drawn from our own research and from some previous thesis work at the Pennsylvania State University.

Sources and types of contaminants

Investigations of contaminant transport often classify the source terms into "point sources" and "diffuse sources" depending on whether the contaminant source is highly localized such as a pipeline break or spread out such as the runoff of agricultural chemicals from croplands. This distinction is less useful in karst where most contaminants tend to be input through sinkholes and sinking streams and thus are intrinsically point sources.

A more useful distinction is between "spills" and "leaks". A spill is an abrupt input of (usually) a large volume of contaminant. For example, a gasoline tanker truck wrecks on the highway. The gasoline flows into a nearby sinkhole. A leak is a continuous input of (usually) a relatively small volume of contaminant. The best examples are leaky underground storage tanks which continuously drip their contents into the underlying aquifer. The volume of contaminant is small at any given time although the quantity of contaminant may become quite large over long periods of time.

Contaminants can be classified depending on their physical and chemical properties. For liquids, the pertinent properties are their solubility in water, their density, and their vapor pressure (Fig. 1). Some liquids such as low molecular weight alcohols, are miscible with water in all proportions. Others have sufficient solubility that they are taken completely into solution at the concentrations that occur in ground water systems. Still others have low solubilities so that they separate from water to form immiscible phases separated from the water. The density of immiscible liquids is a key parameter. If the immiscible phase is less dense than water, it will float on the water surface. If it is more dense, it will sink. The third variable is the vapor pressure which separates organic liquids into a "volatile organic compound (VOC)" class and a "semivolatile organic compound (SVOC)" class. The boundary vapor pressure is set at an arbitrary 5 Torr (0.667 kPa). Although the boundaries in solubility and vapor

pressure are set by arbitrary choices, it is important to remember that no compound is completely insoluble and no compound is completely non-volatile. This caveat is especially important in karst aquifers.

With these and other aspects of contaminants in mind, it is possible to construct the following classification:

(1) *Water soluble compounds*. These are materials which would be taken completely into solution at all concentrations likely to be found. Water soluble inorganic compounds include ammonia and the nitrate ion, mostly derived from human and animal wastes and perhaps the most widespread of inorganic contaminants. Also water soluble are other inorganic ions such as chloride and sulfate as well as some highly toxic species such as cyanide ions derived from some industrial wastes. Some organic compounds are also water soluble such as alcohols, carboxylic acids, phenols and some agricultural chemicals.

(2) *Light, slightly soluble organic compounds*. Light, non-aqueous phase liquids (LNAPLs) are those that will float on water. Gasoline, diesel fuel, home heating oil and related petroleum hydrocarbons are the most common examples. Gasoline is a complex mixture of low molecular weight, relatively volatile, saturated hydrocarbons. It is the presence of percentage quantities of aromatic hydrocarbons, benzene, toluene, ethyl benzene, and xylene (BTEX) that give gasoline its toxicity.

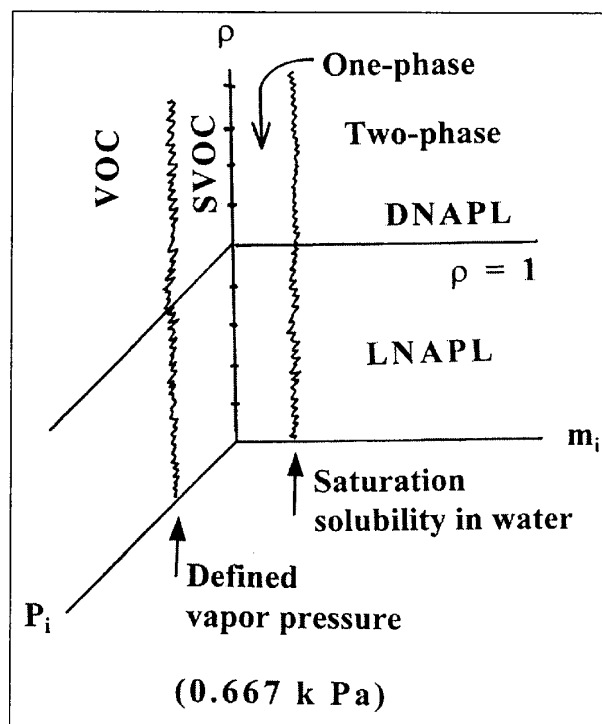


Fig. 1. Variables describing liquid and water-soluble contaminants.

(3) *Heavy, slightly soluble organic compounds.* Dense, non-aqueous phase liquids (DNAPLs) will sink in water. Mostly these are chlorinated (or brominated) compounds. They include such low molecular weight, relatively volatile compounds as methylene chloride, CH_2Cl_2 , trichloroethylene, C_2HCl_2 (TCE), and percioroethylene, C_2Cl_4 (PCE) which are widely used as solvents, de-greasers, and dry cleaning agents. These materials are transported in tank car quantities and are often stored in underground tanks. Other DNAPLs include a family of compounds called polychlorinated biphenyls (PCBs). These materials are non-volatile, oily liquids which were once extensively used in electrical transformers and have been widely injected into karst and other aquifers by salvage operations intended to recover copper from scrap transformers. For some reason, old limestone quarries have frequently been the site of such operations.

(4) *Metals.* The term "metal", of course, is ambiguous. About two-thirds of the elements on the periodic table are metals. Most of these do not impose environmental problems because they are rare in nature and are rarely used in commercial products. We deal here only with a limited set of metallic elements, which, however, cover much of the range of behavior of the remaining elements. Two metals, iron and manganese, make up most of the natural background. These metals occur widely in sedimentary rocks and their oxides and hydrated oxides are common in cave deposits. Nickel and chromium appear in waste from chrome-plating and other non-ferrous metals industry and are typical representatives of the iron-group or transition-group elements. Both are toxic and both have been implicated as carcinogens. Zinc ores occur in carbonate rocks. Zinc and the chemically similar but more toxic cadmium occur widely as "galvanized" coatings on utensils, building materials, and other objects likely to end up in trash dumps.

(5) *Pathogens.* Viruses, bacteria, protozoa, and larger organisms are easily transported into karst aquifers because of the absence of filtering from the soil. Most wide spread of these are the fecal coliform group of organisms and the fecal streptococci bacteria. The presence of these organisms is the most common indicator of pollution from sewage or animal waste. Of most concern among protozoa is "Giarida lamblia" which is released in a cyst form in animal feces and is present in many surface waters. Sinking streams carry the stable cysts to the subsurface.

(6) *Trash.* Rural residents and even entire communities have from long tradition used sinkholes as waste disposal sites. Farmers routinely use

sinkholes to dispose of dead animals and also empty containers of their agricultural chemicals. Unique among aquifers, sinking streams and sinkhole drains provide routes along which bulk trash can be carried for long distances inside the aquifer. The deposition of trash as "clastic sediment" provides a source term for leaching and release of contaminants for long periods of time.

Transport and storage of contaminants

The defining characteristics of karst aquifers are the rapid throughput times, localization of flow within essentially one-dimensional flow paths within the conduit system, and the presence of deposits of clastic sediments in most of the conduits. Each of these characteristics plays a role but a different role depending on the specific contaminant and on the detailed hydrogeology of the karst aquifer.

Water soluble contaminants

Soluble contaminants move with the water. In karst aquifers the water from diffuse infiltration through the soil, from sinkhole drains, and from sinking streams ultimately makes its way into the conduit system. The concentration of soluble contaminant should be determined by the concentration at the source adjusted for dilution by other water sources merging in the main conduit. By this model, the concentration of nitrates or other water soluble contaminants should decrease during storm flow because of dilution by the storm water. Although storm water dilution has been observed, what is observed in many cases, is a pulse of contaminant during storm flow. The contaminant tends to ride the hydrograph, reaching a maximum concentration during peak flow (Fig. 2). The data in Fig. 2 are from central Pennsylvania (Underwood, 1994). Similar results have been observed in Kentucky (Currens, 2000).

Nitrate levels in conduit fed springs tend to be highly variable because of the effects of dilution by storms whereas nitrate levels in fracture-fed springs tend to be relatively constant although the actual nitrate levels vary greatly from one spring to another (Kastrinos and White, 1986). The agricultural chemical atrazine also exhibits a storm pulse (Fig. 3). Since both flow and contaminant increase during storm flow, the actual flux of contaminant discharged from the aquifer is the convolution of the hydrograph and contaminant chemograph integrated over the storm pulse.

$$\text{Flux} = \int Q(t)C(t)dt \quad (1)$$

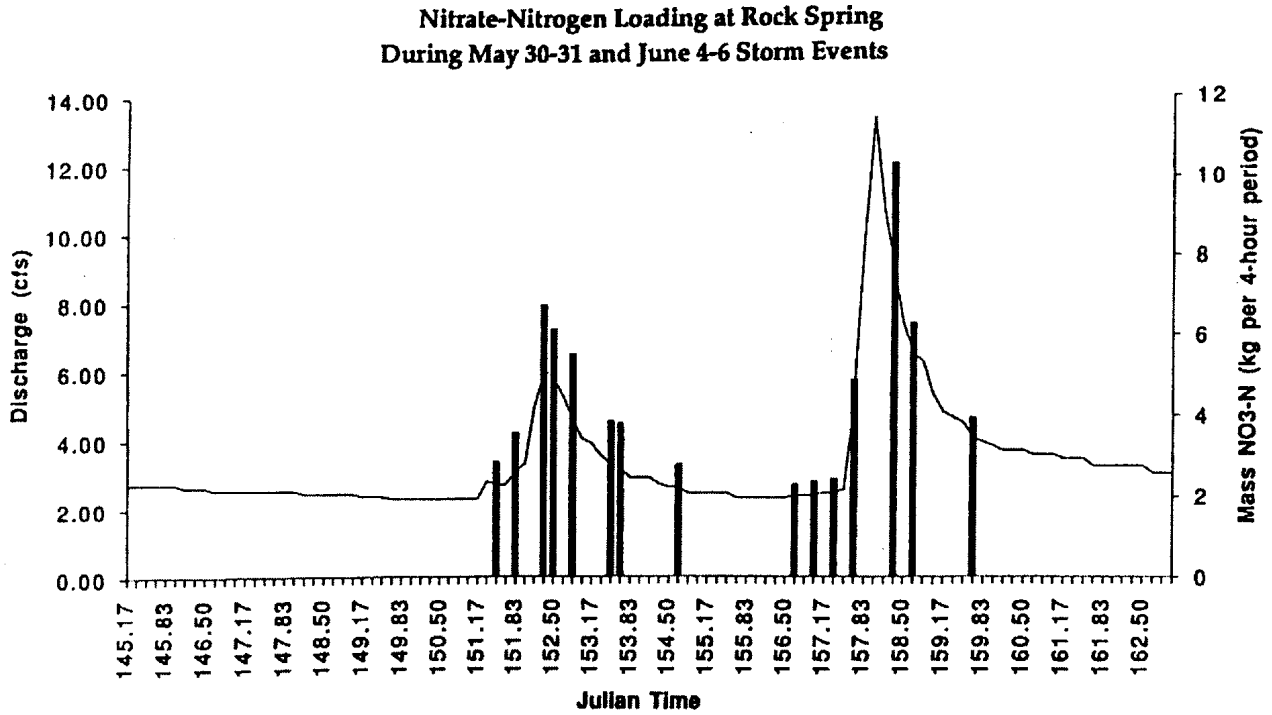


Fig. 2. Nitrate bursts during storm flow in Rock Spring Basin, Centre County, Pennsylvania. Data from Underwood (1994).

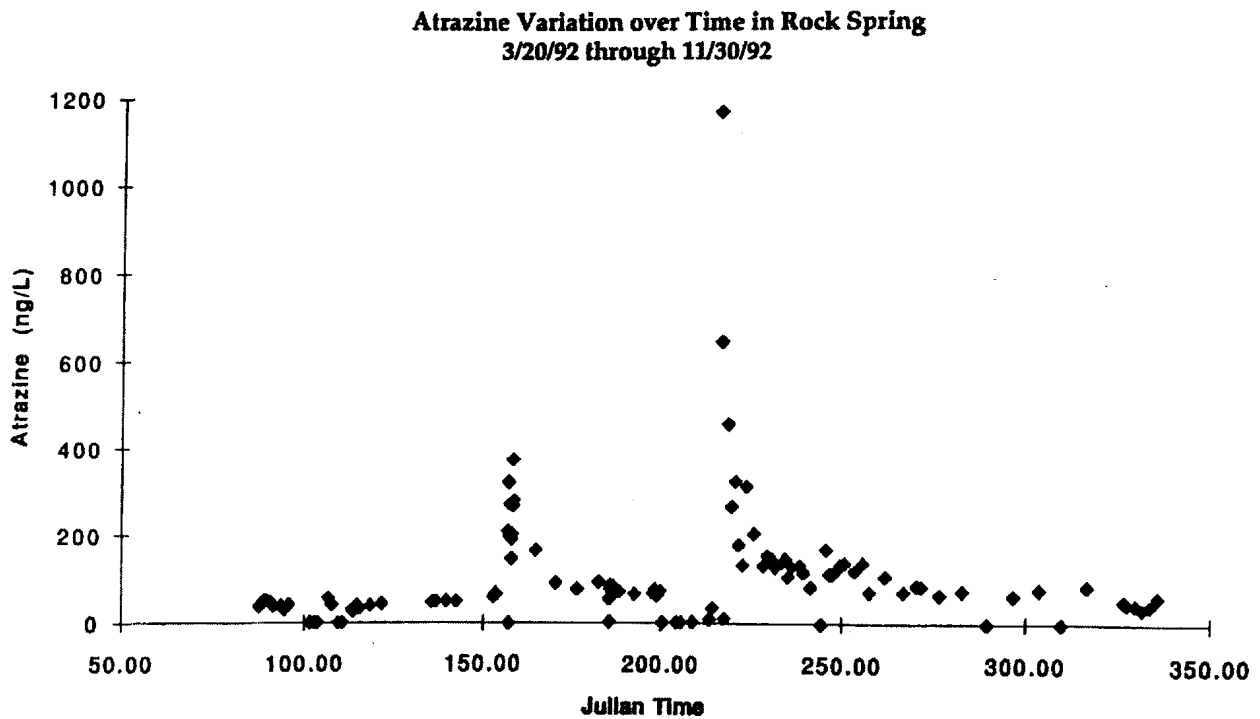


Fig. 3. Atrazine bursts during storm flow in Rock Spring Basin, Centre County, Pennsylvania. Data from Underwood (1994).

Although the source of the spike in the contaminant is not known for certain, it seems possible that the role of storm flow is to leach contaminants stored in the overlying soil or in the epikarst.

Light non-aqueous phase liquids

LNAPLs will float on ground water. This has led to some remarkable contamination problems such as a lake of gasoline nearly two meters deep floating on the water table near Mechanicsburg, Pennsylvania (Rhindress, 1971). LNAPLs will float on underground streams and be carried along with the flowing water. The LNAPL will pond when the water ponds behind obstructions and becomes temporarily entrapped. Conduits generally create a trough in the water table so the LNAPL contamination in the conduit tributaries and in the fracture system tends to migrate toward the master conduit. During flood flow, the trough fills and conduits with free surface streams shift into a regime of pipe flow. Pondered LNAPL is lifted with the rising water and pressed against the ceiling. Any pockets in the ceiling will form traps for the LNAPL (Ewers et al., 1991). If the ceiling is tight, the LNAPL is forced through the obstructions as piston flow. A burst of LNAPL then continues down the conduit. For this reason, spills of LNAPL do not necessarily appear at the karst springs immediately after the spill. Alternatively, if the ceiling is fractured, the piston flow drives the LNAPL upward where the vapors may rise into structures on the land surface. Fume problems in homes and other structures overlying conduit systems contaminated by LNAPLs may arise long after the initial spills (Stroud et al., 1986).

Many common light hydrocarbon compounds have substantial solubilities and vapor pressures (Table 1). For accumulations of LNAPL ponded behind obstructions in conduits, the continuous sweep of fresh water beneath the pool will eventually dissolve and remove the pool. Likewise, the pondered LNAPL will gradually evaporate because of the vapor pressure of the compounds. In the process, of course, the air-filled cave passages become contaminated with hydrocarbon fumes. The turnover in cave air due to barometric changes will eventually flush out the contaminants but while they are present they are a substantial hazard to cave explorers, especially those who explore by carbide lamp. One of the most serious incidents occurred in Howard's Cave, Georgia in 1966 where a gasoline explosion set off by carbide lamps claimed three lives (Black, 1966).

TABLE 1

Solubilities of some light aromatic hydrocarbons (selected from Ferrer, 1993).

Compound	Solubility in water (mg/l)
Benzene	1780
Toluene	500
o-Xylene	170
Ethyl Benzene	150

Dense non-aqueous phase liquids

The pathways for heavy organic liquids migrating below the level of the epikarst will be fractures, shafts, and chimneys of various kinds. Possible storage sites in the aquifer include cavities and dry cave passages in the vadose zone, fractures in the phreatic zone, and the main conduit system where DNAPL can collect in pools beneath the water surface, and become incorporated into the clastic sediments that occupy the conduit. Because of the density difference, DNAPL compounds can occupy the pore spaces within the sediment pile where they can be sequestered for long periods of time.

The water table generally stands higher near the boundaries of karst ground water basins with hydraulic gradients that point toward the conduit system. DNAPLs reaching the water table do not necessarily follow the ground water down gradient toward the conduit but can continue to move vertically into any available storage spaces below local base level or can follow the dip of bedding planes in directions quite different from the hydraulic gradient.

The transport of DNAPL has both similarities and differences to the transport of LNAPLs. Processes in common include volatilization although this process is not as effective because in the case of DNAPL, the overlying water provides a protective blanket. Either type of contaminant can degrade in the carbonate water environment. The effectiveness of this process is strongly dependent on the specific DNAPL being considered. DNAPLs have a finite solubility (Table 2) and are also gradually stripped away by the continuing flow of fresh water in the conduit. DNAPL that forms distinct pools beneath flowing streams or in low places in water-filled conduits dissolves at rates given by the exposed area of the DNAPL pool and the specific dissolution kinetics of the particular compound. DNAPL pools can also be regarded as a sort of bedload and can be dragged downstream when flow velocities exceed a necessary threshold. Higher velocities may actually entrain the DNAPL pool so that it is flushed downstream in

TABLE 2

Vapor pressures and solubilities of some chlorinated hydrocarbons (Fetter, 1993).

Compound	Vapor Pressure (Torr, 20 °C)	Solubility in Water (mg/L)
Methylene Chloride	349	20,000
Carbon Tetrachloride	90	800
Vinyl Chloride	2660	1.1
Trichloroethylene (TCE)	60	1100
Tetrachloroethylene (PCE)	14	150

suspension. Unlike LNAPLs floating on the water surface and thus continuously in contact with the water, DNAPL that has sunk into the sediment pile on the floor of the conduit is protected. There will be a slow percolation of water through the sediment much like any other porous media flow but like other porous media flow, the flow velocities are very small, with only a slow turnover with the fast-moving water above. Thus, the stripping of DNAPL from the sediment pile will be much slower than the stripping of DNAPL constrained in distinct pools.

DNAPLs and other compounds are slowly degraded by chemical reaction with the water. The actual kinetics of this process have been measured by Knauss et al. (1999) for the specific example of trichloroethylene. The degradation reaction is:



The end products of the breakdown process are CO_2 and HCl . Because the reaction is with oxygenated water which is always in excess supply, the rate equation has the simple form:

$$\frac{dC}{dt} = -kC_0^n \quad (2)$$

By laboratory experiments, Knauss et al. (1999) found $n = 0.85$ and $k = 5.8 \times 10^{-7} \text{ sec}^{-1}$ at 100°C .

A process that applies to DNAPL but not as much to LNAPL is the movement of the sediment pile itself. Sediments in active conduits themselves form a continuous flux. New sediment is continuously injected into the conduit system and must be continuously flushed through and discharged at the spring. Otherwise, the conduit system would eventually clog completely. Unlike the flow of water, the flow of sediments is episodic. Flood flows must reach a certain threshold before the sediments can move as bedload and an even higher threshold before the sediment pile becomes completely entrained so that both sediment and any incorporated DNAPL are transported downstream.

A conceptual model for DNAPL transport in karst aquifers has been published by Wolfe et al. (1997).

The rather complicated process of storage and DNAPL transport in karst aquifers has been reviewed by Loop and White (2001). Their conceptual model for DNAPL transport is given in Fig. 4.

Metals

Metals in karst aquifers can be divided into three categories (a) alkaline earth metals derived from the carbonate rock — mainly calcium and magnesium with minor amounts of strontium and barium, (b) heavy metals occurring as part of the natural background — mainly aluminum, iron, and manganese with trace amounts of many other metals, and (c) contaminant metals introduced into the aquifer through human influences. The chemistry of the alkaline earth metals in karst ground waters is the subject of a huge literature on karst water geochemistry and is not of concern here. However, the concentrations and transport of other metals in karst systems has received much less attention.

In a recent study, Hodge et al. (1998) assessed trace metal concentrations in a carbonate spring as an indicator of the trace metal concentrations in the ancient marine environment. As expected, calcium and magnesium were present at much higher concentrations (10^{-3} – 10^{-4} mol/kg) than the potentially toxic metals arsenic, copper, chromium, and cobalt (10^{-7} – 10^{-9} mol/kg). Quinlan and Rowe (1977) found nickel and chromium in a Kentucky karst spring presumably derived from a metal plating plant in the upper reaches of the ground water basin.

To get a sense of the range of metals that might be expected, a composite sample was prepared from springs draining the Fort Campbell Army Base in western Tennessee/Kentucky. Water from the large regional Millstone Spring was mixed with sediment from the smaller Blue Spring. The clastic material was allowed to settle and the slightly turbid water was analyzed by inductively coupled plasma-mass spectrometer. (Table 3). These data are indicative of the range of metallic elements that might be carried by karst ground waters.

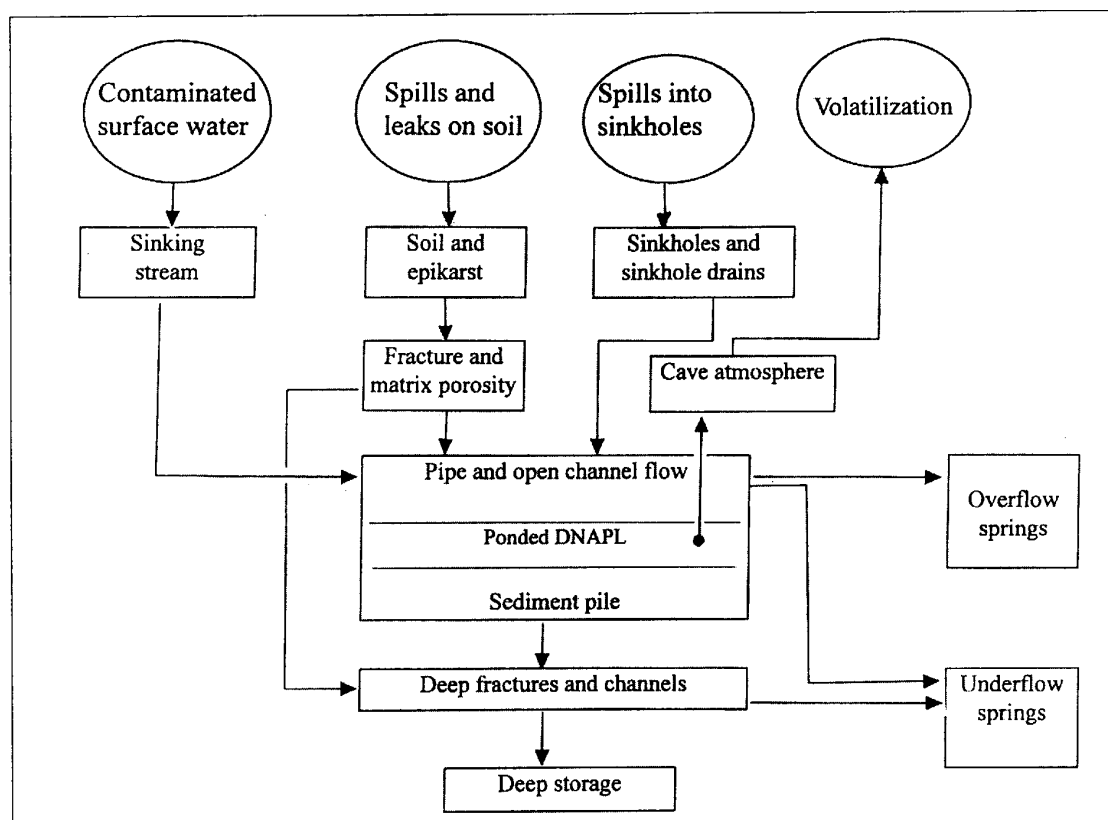


Fig. 4. Conceptual model for DNAPL storage and transport in karst aquifers. From Loop and White (2001).

TABLE 3
ICP-MS analyses of carbonate spring waters.

Element	Concentration (mg/L)
Al	16,300
As	17
Ba	157
Ca	51,000
Cd	0.93
Cr	26
Cu	13
Fe	11,000
K	4280
Mg	5800
Mn	1350
Na	5370
Ni	20
Pb	24
Zn	81

The aqueous chemistry of individual metal-water systems is, in general, well understood (Bags and Mesmer, 1976; Stumm and Morgan, 1996) and thermodynamic calculations can be made to determine the limiting solubilities. Fig. 5 illustrates the case of the Ni-O-H system where nickel hydroxy complexes control the solubility. In karstic systems,

the high carbon dioxide activities cause carbonates to be the limiting insoluble phase. Calculations for such systems as the Zn-O-H, Cd-O-H and Pb-O-H systems show that in all cases, precipitation of hydroxide or carbonate phases will limit the concentration of metal ions in karstic waters to low values. However, in all cases, at the pH and P_{CO_2} values of karst water, the equilibrium metal solubility would be well above drinking water standards.

The controlling factor in metal transport appears to be adsorption onto various substrates rather than equilibrium solubility. Metals can adsorb onto clays and other clastic particulates, onto organic material in the water, and onto iron or manganese oxides which often form coatings on cave streams.

Manganese oxides, precipitated onto stream sediments by the oxidation of the natural manganese background (White, 1997) act as extremely effective scavengers for heavy metals. Chemical analyses of manganese oxides from a selection of karst conduits revealed percentage quantities of such metals as copper, zinc, nickel and - in one case - cobalt (Table 4). These data also illustrate a "mutual exclusion" The hydrated iron oxide deposits contain negligible concentrations of other metals including manganese while the manganese oxide coatings are highly enriched in other transition metals but contain only relatively small amounts of iron.

TABLE 4

Chemical analyses of iron and manganese oxides from Rohrer's Cave, Pennsylvania.
Data extracted from Whith et al. (1985).

Specimen	Fe (wt %)	Mn (wt %)	Co (wt %)	Ni (wt %)	Cu (wt %)	Zn (wt %)
Iron Oxide stalactite	43	0.01	<0.01	<0.01	0.01	0.01
Iron Oxide stalagmite	50	<0.01	<0.01	<0.01	0.01	0.01
Manganese Oxide	3.5	12.4	1.60	1.57	0.45	1.52

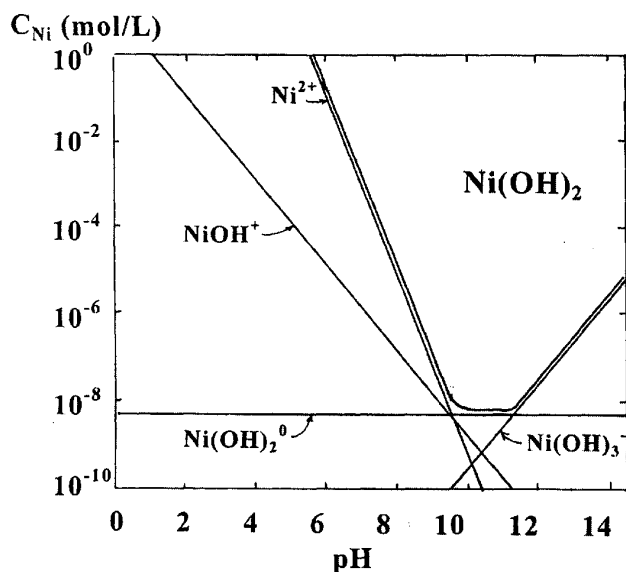


Fig. 5. Calculated speciation diagram for the system Ni-O-H. $\text{Ni}(\text{OH})_2$ is crystalline nickel hydroxide.

McCarthy and Shevenell (1998) confirmed the link between metals and solids for ground water in the karst aquifer that underlies the Oak Ridge Reservation, Tennessee. They determined colloidal compositions via: (a) the chemical difference in total and filtered water samples, (b) direct soil measurements using X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy, and (c) speciation modeling. In most wells, they found that aluminum, iron, manganese, and nickel were present primarily in the solid phase

Storm-associated changes in aquifer hydrology are known to impact ground water and karst spring chemistry. Recent research by Atteia and Kozel (1997) found that the abundance, size, and type of colloids discharged at a spring changed during storm events. The greatest abundance of large colloids was discharged coincident with the rising limb of the spring hydrograph. This has been interpreted as the re-suspension of colloids in the conduits due to increased ground water velocities. Colloids identified

during the study included clays, granular minerals, and bacteria.

Although the study of metal transport in karst aquifers is far from complete, it is apparent that metals are stored in the aquifer primarily by adsorption onto various substrates. They move through the aquifer to the discharging spring when the particulates on which they are adsorbed are swept out of the aquifer by storm pulses.

Pathogens

Although it has long been recognized that cave streams should not be used for drinking water, in reality, many cave streams and the springs to which they discharge are used as domestic and sometimes public water supplies. Because there is little filtering of recharge water from sinking streams or from storm runoff into sinkholes, it is quite obvious that microorganisms, including pathogenic ones, can be easily carried into the underground system. Typical sizes for microorganisms range from the submicrometer to hundreds of micrometers, in the range of fine-grained sediment. Organisms can be transported in suspension in the water and as attachments to particles of sediment or organic material.

Questions of the survival rate of microorganisms in karst aquifers is another matter. Recent investigations of cave microbiology (see e.g. Sasowsky and Palmer, 1994) have revealed a rich diversity of organisms that seem to thrive very well deep within karst systems. On the other hand, those organisms that pose the greatest threats to humans might be expected to exhibit a high die-off rate. Hard data are sparse. An investigation of total bacteria and coliform bacteria in the Butler Cave - Sinking Creek System of Virginia (Chess, 1987) showed no evidence of die-off anywhere in the system. Roughly the same populations of organisms were found in streams deep within the system and at the discharging spring as occurred in the sinking surface streams (Fig. 6).

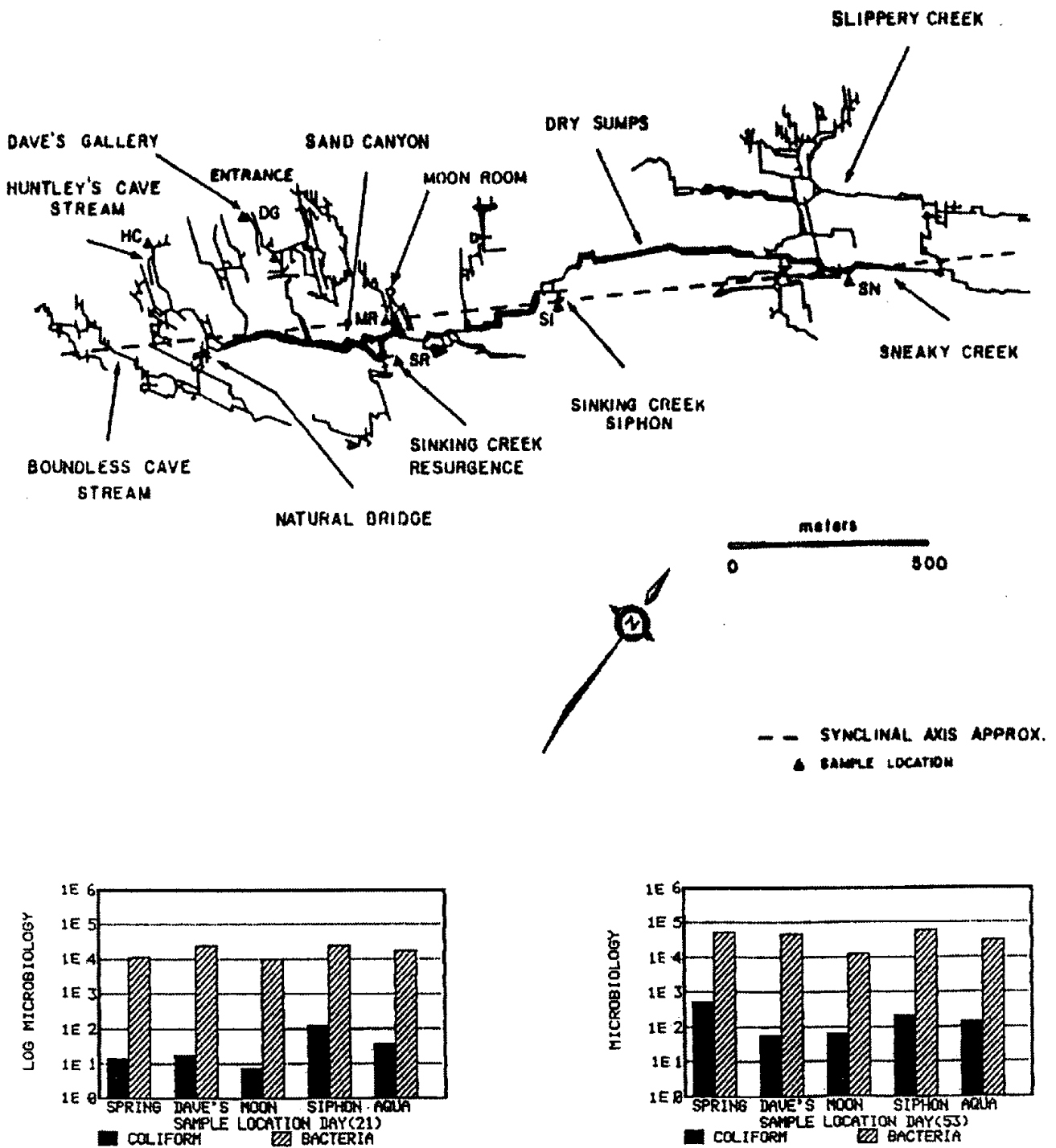


Fig. 6 Bacterial levels at various locations (shown on map) in the Butler Cave-Sinking Creek System, Bath County, Virginia, for day 21 (left plot) and day 56 (right plot) measured from August 1, the beginning of the water year. Data from Chess (1987).

Trash

In many karst areas, sinking streams have cut small blind valleys into the land surface. These depressions, along with the ubiquitous sinkholes, have been used as trash receptors as long as there have been human populations. Sinkhole dumps are as much characteristic karst land features as the

sinkholes themselves. Two aspects of sinkhole dumps relate to the general problem of ground water contamination in karst aquifers. Sinkholes act as funnels, collecting storm water runoff and channeling it into the sinkhole drain. The trash pile in a sinkhole behaves as an unlined landfill. Storm water leaches through the trash and what enters the

karst drainage system below is essentially landfill leachate. Secondly, inwash during intense storms and soil piping failures of the sinkhole sediment combine to transport solid trash into the underlying conduit system. The trash becomes a form of clastic sediment and is moved down the flow field during intense storm flow in the same manner as any other clastic sediment. Trash carried deep within the conduit system becomes a source term for continuing contamination of the ground water and is located where clean-up is essentially impossible.

Trash injections into karst systems have not been systematically examined. Categories include domestic waste - a mix of materials not different from those usually deposited in engineered landfills, dead, often diseased farm animals, and - in more recent time - chemical waste. The latter takes the form of improperly cleaned containers for paint and agricultural chemicals which may be dumped in sinkholes as an alternative to proper recycling.

Conclusions

Contaminants to karst aquifers have been broadly classified into water-soluble organic and inorganic contaminants, slightly soluble organic contaminants, metals, pathogens, and trash. For each of these categories, there are multiple, complex, and interacting mechanisms for the transport, storage, and eventual release of the materials. Some of these are becoming understood. Others await detailed investigation.

The subject of contaminant transport in karst aquifers is perhaps the most important of the current generation of karst research subjects.

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