

Vulnerability (Risk) Mapping of the Madison Aquifer near Rapid City, South Dakota

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ABSTRACT

Water supplies for Rapid City, South Dakota, and surrounding suburban and rural areas are extremely vulnerable to contamination. The impact of ground-water contamination could occur quickly and linger for many years. The City of Rapid City is located within the Rapid Creek watershed in the east-central Black Hills and relies heavily on the Mississippian Madison karst aquifer for drinking-water supplies, utilizing several wells and springs. The aquifer consists of limestone and dolomite and contains paleokarst and recent karst that probably formed along a well-developed fracture system. Previous work indicates stream-related aquifer recharge from the watersheds of Spring Creek (to the south), Boxelder Creek (to the north), and Rapid Creek as well as direct recharge by precipitation on the entire outcrop area west of Rapid City. Spring Creek and Boxelder Creek lose all their flow to karst sinkholes in the aquifer except during periods of high discharge (greater than approximately 28 ft³/sec for Spring Creek and 50 ft³/sec for Boxelder Creek). Ground water from these watersheds converges on wells and springs in the Rapid City area several miles away. Dye-tracer tests for this area indicate ground-water velocities on the order of 1,000 feet per day and residence times range from a few days to several years.

A database of 329 wells, geologic maps, fractures, faults, geologic structures, water-quality data, and dye-tracer test results were analyzed to develop a geologic model to better define local ground-water flow paths and characterize susceptibility zones. Structure contour and depth-to-aquifer maps have been completed for the Madison aquifer. Inherent aquifer susceptibility, combined with human influences, was used to develop a vulnerability (risk) map (1:24,000 scale) for the Madison aquifer for the Rapid City area.

Hydrogeologic Characteristics of Four Public Drinking-Water Supply Springs in the Ozark Plateaus of Northern Arkansas

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ABSTRACT

In October 2000, a study was undertaken by the U.S. Geological Survey in cooperation with the Arkansas Department of Health to determine the hydrogeologic characteristics, including the extent of the recharge areas, for four springs in northern Arkansas used for public drinking-water supply. Information pertaining to each spring can be used to enable development of effective management plans to protect these water resources and public health. Analyses of discharge, temperature, and water quality were completed to describe ground-water flow characteristics, source-water characteristics, and connectivity of the ground-water system with surface runoff. Water-level contour maps were constructed to determine ground-water flow directions, and ground-water tracer tests were conducted to determine the extent of the recharge areas and ground-water flow velocities.

Two of the springs (Hughes and Stark Springs) were characterized as being influenced by local recharge areas and two springs (Evening Shade and Roaring Springs) reflected regional aquifer recharge. The discharge and water-quality data for Hughes and Stark Springs show the ground-water systems are dominated by rapid recharge from surface runoff and mainly consist of conduit-type flow systems with little diffuse-type flow. The local recharge area for Hughes Spring was estimated as 15.8 square miles, and the local recharge area for Stark spring was estimated as 0.79 square mile. Recharge to Evening Shade and Roaring Springs originates from water entering geologic formations in the Ozark aquifer. As a result, a local recharge area was not delineated, as the area could include relatively remote locations where geologic formations composing the Ozark aquifer are exposed and have sufficient porosity and hydraulic conductivity to convey water that falls as precipitation to the subsurface.

INTRODUCTION

Hughes Spring, Stark Spring, Evening Shade Spring, and Roaring Spring supply the public drinking water to the communities of Marshall, Cushman, Evening Shade, and Cherokee Village, Arkansas (fig. 1). Anticipated nearby land-use changes may increase threats to the quality of the shallow ground water in part because of the karst terrain, and the extent and location of the recharge areas that contribute water to these four public drinking-water supply springs were unknown. Shallow ground-water systems dominated by fracture or conduit flow may be subject to rapid input of surface contaminants and rapid transport of these contaminants to wells and springs with little opportunity for natural attenuation processes to occur. Many communities

and towns in Arkansas have discontinued the use of springs that discharge shallow ground water because of surface-derived contamination.

In October 2000, the U.S. Geological Survey (USGS) began a cooperative study with the Arkansas Department of Health to characterize the hydrogeology and extent of the recharge area for the springs. The purpose of this report is to describe the hydrogeologic characteristics, including the extent of the recharge areas, of Hughes, Stark, Evening Shade, and Roaring Springs. A more detailed description of the results is discussed in Galloway (2004). This information will help water managers to develop plans to protect the recharge area from contamination related to land use and potential spills.

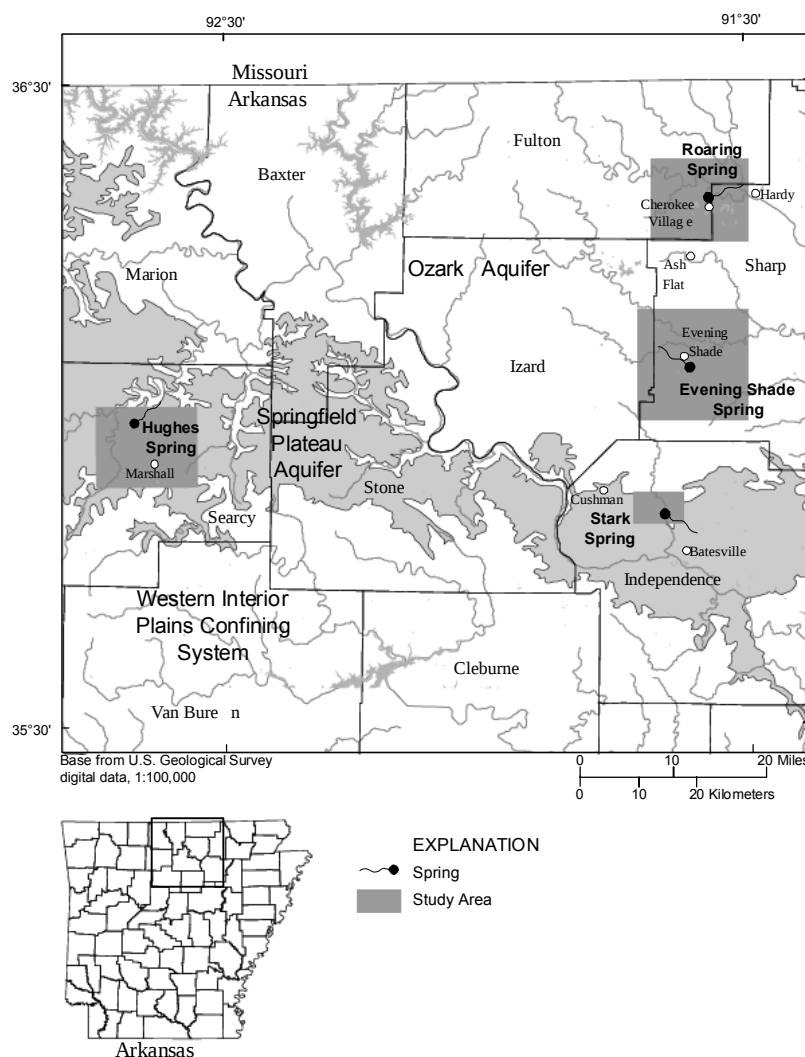


Figure 1. Location of springs and study areas.

METHODS OF INVESTIGATION

Several methods were used to determine the hydrogeologic characteristics of each study area. Geomorphic and topographic data from existing maps were gathered and assessed to determine surficial controls on infiltration, ground-water flow pathways, and boundaries to ground-water flow. A field inventory of karst features (caves, sinkholes, sinking streams, and enlarged vertical fractures and bedding planes), wells, and springs also was conducted in each study area to provide information on the connection of the ground-water system to the land surface and to develop water-level contour maps of the study areas. Several wells were used for

borehole geophysical surveys within the study areas to provide information about the lithology, distribution of permeability, and nature of vertical flow within the ground-water system. To determine flow characteristics and aid in the estimate of the recharge area, the four springs were instrumented to measure discharge, water temperature, and precipitation for October 2001 to October 2002. Water-quality samples were collected at each spring to determine the geochemistry of the contributing geologic units and the susceptibility of the spring to contamination. Samples were collected during base-flow and high-flow conditions and were analyzed for major ions, selected trace constituents, nutrients, fecal indicator bacteria, wastewater constituents, stable isotopes,

and radiogenic isotopes. Qualitative tracer tests were conducted from January to June 2002 to identify possible ground-water flowpaths and velocities and confirm the locations of inferred ground-water-basin boundaries. A more detailed discussion of the methods used in the study is presented in Galloway (2004).

LOCALLY RECHARGED SPRINGS

The study area for Hughes Spring includes the Western Interior Plains confining system and the Springfield Plateau and Ozark aquifers. Exposures of geologic units of the Springfield Plateau aquifer dominate the area, smaller parts of the Ozark aquifer are exposed in the northern part of the study area, and parts of the Western Interior Plains confining system are exposed in the southern part of the study area. Units generally dip south-southeast by 3 to 12 degrees and the only large structural feature is a fault, located in the southern part of the study area (Galloway, 2004). The Western Interior Plains confining system contains Pennsylvanian-age shale, sandstone, and limestone (Pitkin Limestone, Fayetteville Shale, and Batesville Sandstone) (fig. 2). The geologic units of the Springfield Plateau aquifer consist of Mississippian-age limestone (Boone Formation) and are typically separated from the underlying Ozark aquifer by the Ozark confining unit composed of Devonian-age shale in areas of northern Arkansas (fig. 2). Borehole geophysical surveys in several wells show the Ozark confining unit was thin or absent in the Hughes Spring study area; therefore, the unit is not shown in figure 2. The Ozark aquifer is exposed at low altitudes in stream valleys in the northern portion of the Hughes Spring study area. Geologic formations that compose the Ozark aquifer and are exposed in the study area include Devonian- and Silurian-age limestone (Cason Shale, Fernvale Limestone, and Platin Limestone), and Ordovician-age shale and limestones, dolomites, and sandstones (St. Peter Sandstone and Everton Formation). Water-level data indicate a hydrologic connection exists between the Springfield Plateau aquifer and the Ozark aquifer because of the discontinuous presence of the Ozark confining unit (fig. 2). Karstic features were found in the Hughes Spring study area, mainly in the Mississippian-age Boone Formation. These features

develop as ground water percolates through the limestone resulting in the enlargement of fractures through the dissolution of the carbonate rock forming solution channels (fig. 2). Karst features present in the study area include sinkholes, springs, sinking streams, and caves. No surface streams were observed to have flow throughout the year. Brush Creek was observed to have flow along its entire length in the study area only during periods of intense rainfall events. Hughes Spring discharges from fractures in units of the Ozark aquifer, although most of the water probably originates from the overlying Springfield Plateau aquifer as indicated by the geophysical data, ground-water tracer tests, and geochemical data discussed later in this report.

The Boone Formation is exposed throughout most of the Stark Spring study area at higher altitudes. Silurian- and Devonian-age units are present in the northern and western parts of the study area, but are absent near Stark Spring, resulting in an unconformable contact of the Boone Formation and the Ordovician-age shales and dolomites (fig. 2). Field observations in the area indicate that where the Boone Formation is exposed, surface runoff only occurs during periods of intense rainfall. Stark Spring is located near the contact of the Boone Formation and the underlying less permeable and less karstic Cason Shale.

The discharge for Hughes Spring and Stark Spring varied seasonally and temporally (fig. 3). The mean annual discharges for Hughes Spring for water years 2001 and 2002 were 2.9 and 5.2 cubic feet per second (ft^3/s), respectively (Brossett and Evans, 2003). Mean daily discharge ranged from approximately 0.5 to 14 ft^3/s for water years 2001 and 2002. The mean annual discharge for Stark Spring for water years 2001 and 2002 was 0.5 and 1.5 ft^3/s , respectively (Brossett and Evans, 2003). Mean daily discharge ranged from approximately 0.1 to 23 ft^3/s for water year 2001 and from 0.1 to 49 ft^3/s for water year 2002. The ratios of annual peak flow to base flow for Hughes Spring (28) and Stark Spring (491) indicated fast-response springs (White, 1988).

Water temperature for Hughes Spring reflected seasonal variations throughout the monitoring

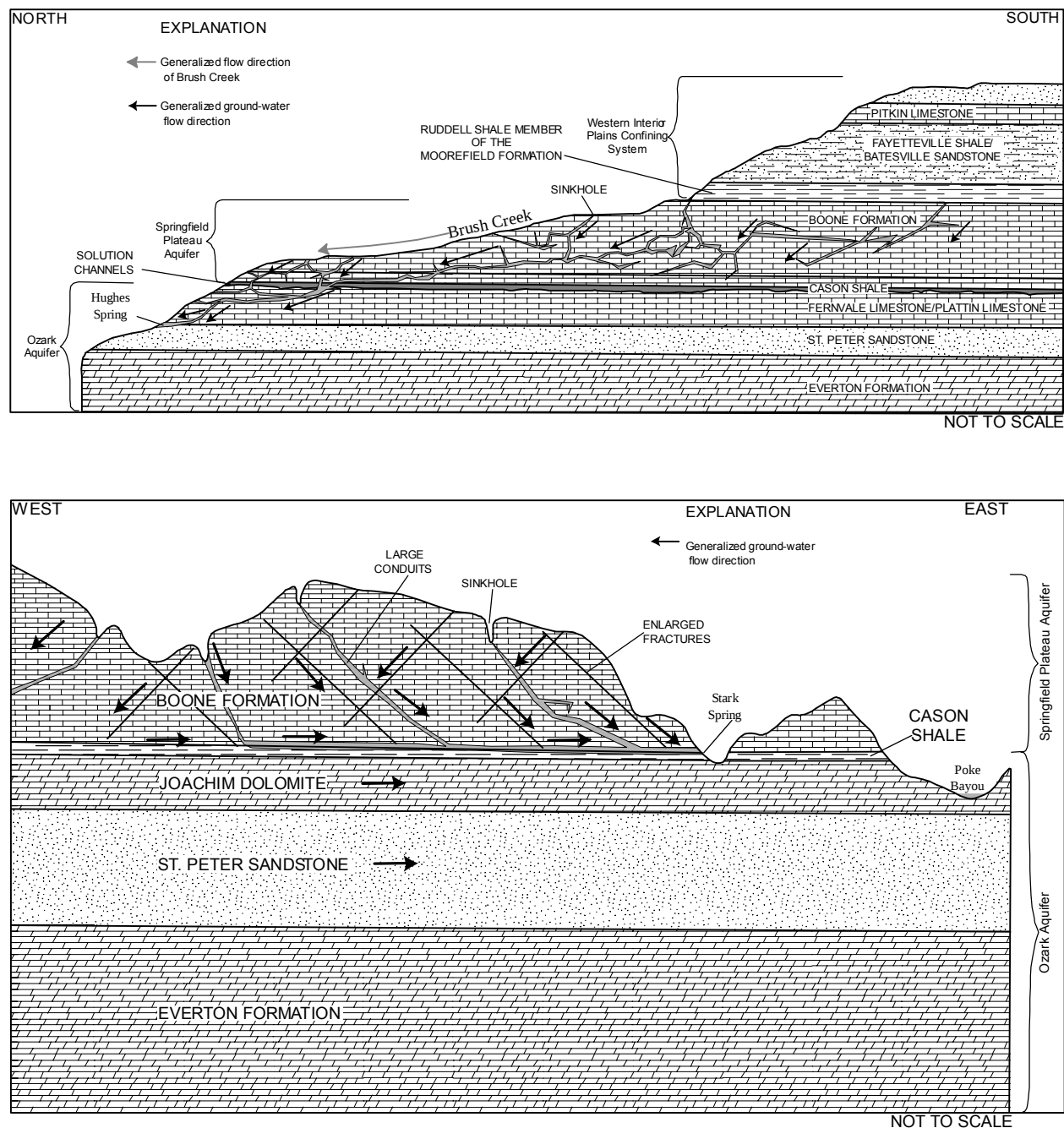


Figure 2. Conceptual model of ground-water flow to Hughes Spring and Stark Spring.

period and demonstrated considerable changes during summer high-flow events (fig. 3). The highest temperatures were recorded in the summer and fall with average temperatures of approximately 17 °C for both seasons. The winter and spring had lower average temperatures of approximately 12 °C and 13 °C, respectively. Large water temperature varia-

tions corresponded to high-flow events. Large water temperature fluctuations were not noticeable for Stark Spring, although slight variations did occur during high-flow events (fig. 3). Recorded water temperature ranged from 13.5 °C to 14.7 °C with a mean of 14.5 °C.

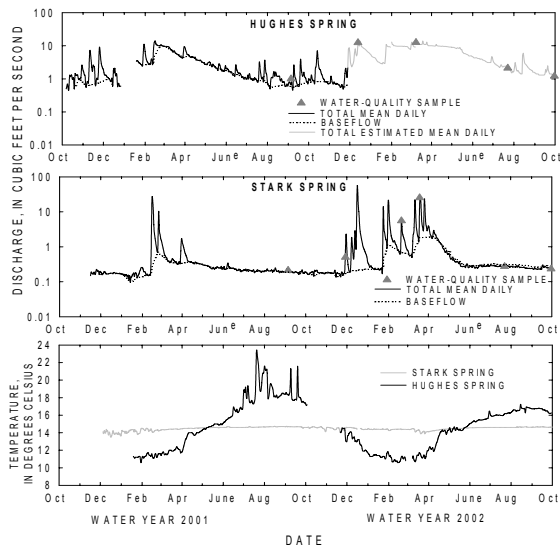


Figure 3. Daily discharge and water temperature recorded at Hughes Spring and Stark Spring.

The major ion analyses for samples collected between September 2001 to October 2002 for Hughes Spring and Stark Spring show a chemistry that is a calcium bicarbonate type (Hem, 1989) and are indicative of waters from the Springfield Plateau aquifer. The calcium to magnesium ratio ranged from 26 to 38 for Hughes Spring and from 9 to 10 for Stark Spring, indicating contribution from limestone mineralogy (White, 1988). Ratios of calcium to magnesium calculated for other samples collected from wells and springs representing the Springfield Plateau aquifer indicate ratios ranging from 3 to 70, with a median ratio value of 18, also indicating limestone mineralogy. Wells and springs representing units in the Ozark aquifer had values for calcium to magnesium ratios ranging from 1 to 3 with a median value of 1, indicating a dolomitic mineralogy.

The geochemistry of Hughes Spring and Stark Spring is characteristic of conduit-dominated ground-water flow systems. Samples collected during base-flow conditions had calcite saturation index (SI_{calcite}) (Adamski, 2000) values near or greater than 0.4 (supersaturated with respect to calcite) for Hughes Spring and ranged from -0.12 to 0.16 for Stark Spring. High-flow samples had SI_{calcite} values of 0.3 and -0.15 (supersaturated to undersaturated with respect to calcite) for Hughes Spring and ranged from -1.05 to 0.34 for Stark Spring. Total

dissolved solids (TDS) concentrations and hardness also changed with flow conditions. Both values decreased as discharge increased, reflecting the effects of reduced residence time of the water with the source rock at higher discharge, allowing for less dissolution at both springs.

Stable isotopes of carbon ($\delta^{13}\text{C}$) indicated different characteristics of the recharge water as it enters the ground-water system at Hughes Spring compared to Stark Spring. The $\delta^{13}\text{C}$ data for Hughes Spring indicate that although the ground-water system is dominated by conduit flow, a substantial component of the source water interacts with surface material, such as soils and regolith, before entering the ground-water system during high-flow events. An enrichment of organically derived carbon occurs in the Hughes Spring discharge during high-flow events from water infiltrating into soils in the recharge area before entering the aquifer system. A connection of Hughes Spring with Brush Creek, shown by ground-water tracer tests, would provide pathways for water enriched in organically derived carbon to reach the spring discharge. During base-flow conditions, water in the ground-water system that feeds the Hughes Spring discharge has a longer residence time in the system that allows it to approach equilibrium and maintain an even distribution of inorganically and organically derived carbon, caused by buffering (lowering the acidity) from carbonate dissolution. The $\delta^{13}\text{C}$ data show that the recharge water for Stark Spring has less interaction with the soil and regolith before entering the ground-water system than observed at Hughes Spring. Stark Spring displayed a decrease in the calculated percentage of organically derived carbon during high-flow conditions. These data indicate that runoff enters the ground-water system at a more rapid rate near Stark Spring than near Hughes Spring, and does not allow sufficient interaction with surface material in the recharge area for the transport of organically derived carbon into the ground-water system.

Based on the ground-water tracer test data and the spring discharge, it appears that the recharge area for Hughes Spring generally coincides with the surface drainage area, which is approximately 15.8 square miles (mi^2). Tracers injected outside the surface drainage area (sites 5-7) were not detected

within the surface-drainage area (fig. 4). Tracers injected at two sites inside the surface drainage area (sites 2 and 3) were detected at Hughes Spring and at springs along Brush Creek and in Brush Creek itself, indicating a connection between the surface flow in the stream and Hughes Spring. The tracer-test data and spring-discharge data show that Hughes Spring may act as a distributary from Brush Creek during high-flow events, discharging a portion of runoff waters resulting from precipitation that occurs in the surface-drainage area.

The recharge area computed from the recorded discharge indicated that the area approximated by the surface drainage was not large enough to produce the discharge observed at Stark Spring. The surface-drainage area is approximately 0.34 mi². An average computed recharge area of 0.79 mi² from five storms, assuming a 10 percent reduction in recharge volume from evapotranspiration, soil absorption, and vegetation interception, was used with ground-water tracer test data to delineate the recharge area for Stark Spring.

The configuration of the recharge area for Stark Spring was found to be considerably different than the surface drainage from tracer-test data and geologic characteristics of the area. The recharge area is controlled predominantly by the occurrence of the Boone Formation outcrop. No major structural features were observed from geologic mapping or field observations near the spring, and tracer-test results show that the recharge area extends outside the surface-drainage area to the west of the spring surface-drainage area (fig. 4).

Tracer tests demonstrated rapid ground-water flow velocities in both study areas, which are characteristic of conduit-type flow often found in karst

systems (White, 1988). Using distances measured along implied flowpaths from injection sites to recovery sites, estimated minimum velocities ranged from 0.04 to 1.30 miles per day for Hughes Spring and 0.06 miles per day for Stark Spring.

REGIONALLY RECHARGED SPRINGS

The Evening Shade Spring and Roaring Spring study areas lie on the outcrop of the Ozark aquifer (fig. 1) and include Ordovician-age limestone, dolomite, and sandstone formations. The units generally have a slight dip to the south-southeast with an angle of less than 1 degree estimated from geophysical logs. No major structural features were evident in the study areas from field observations and geophysical logs. Few vertical fractures were observed in acoustic televiewer geophysical logs, but horizontal bedding planes were observed and likely provide the preferred pathways for dissolution (Galloway, 2004). Evening Shade Spring discharges through two main discharge points in the Everton Formation outcrop (fig. 5). One has been enclosed by a springhouse for utilization as a public-water supply and the other resurgent point is in the stream channel of Mill Creek near the springhouse. Roaring Spring discharges near the contact between the Cotter Dolomite and the Jefferson City Dolomite (fig. 5). The location of Evening Shade Spring and Roaring Spring may be caused by a set of enlarged vertical fractures or conduits not readily visible at the surface that may concentrate and convey flow to the surface from fractures and conduits in multiple formations composing the Ozark aquifer (fig. 5). Water-level contours, constructed from static water levels measured in wells and springs in both study areas, followed a similar pattern to the regional flow of the Ozark aquifer constructed by Pugh (1998) and Schrader (2001).

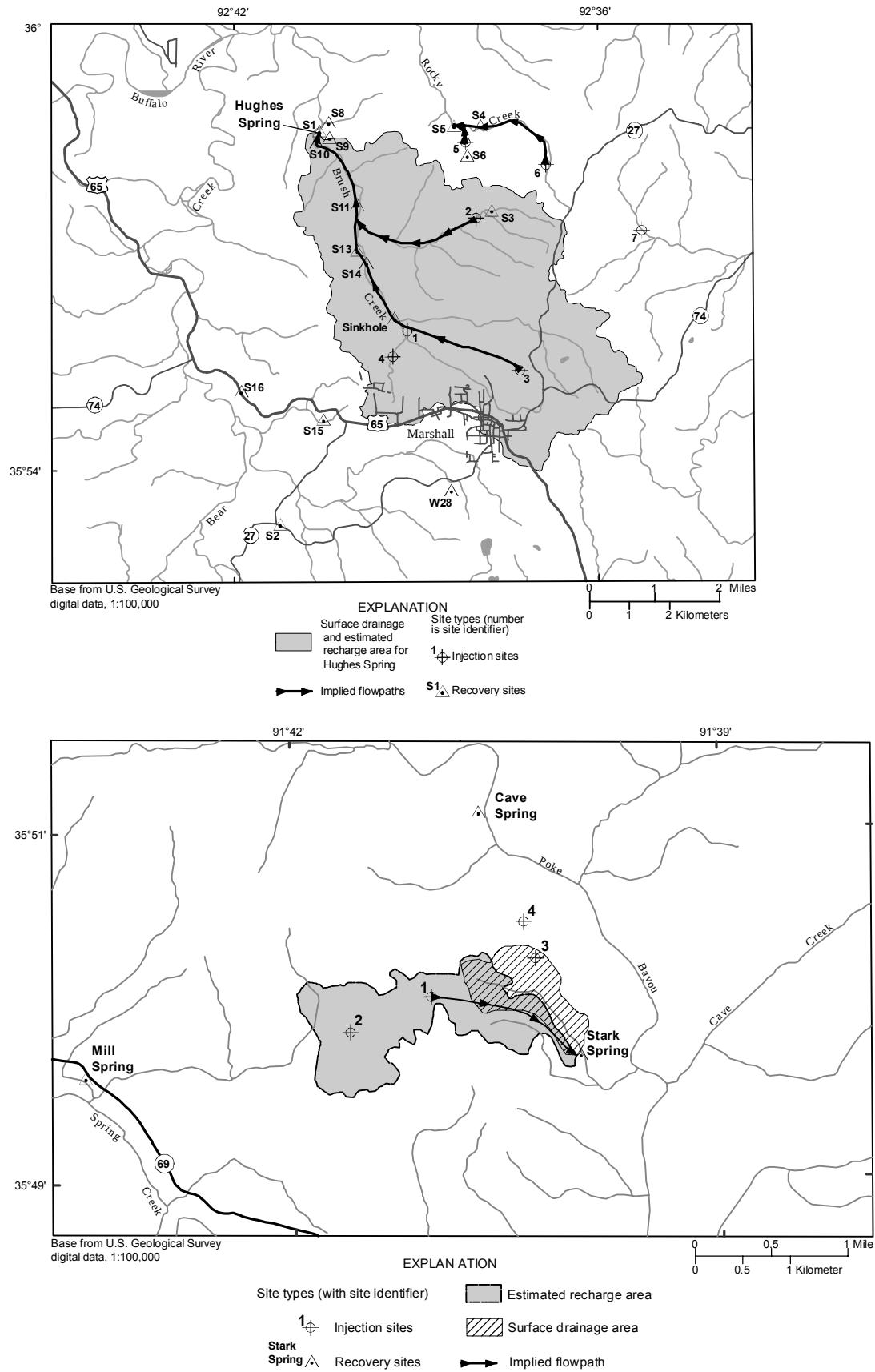


Figure 4. Locations of tracer injection and recovery sites with implied flowpaths of tracers and delineated recharge areas for Hughes and Stark Springs.

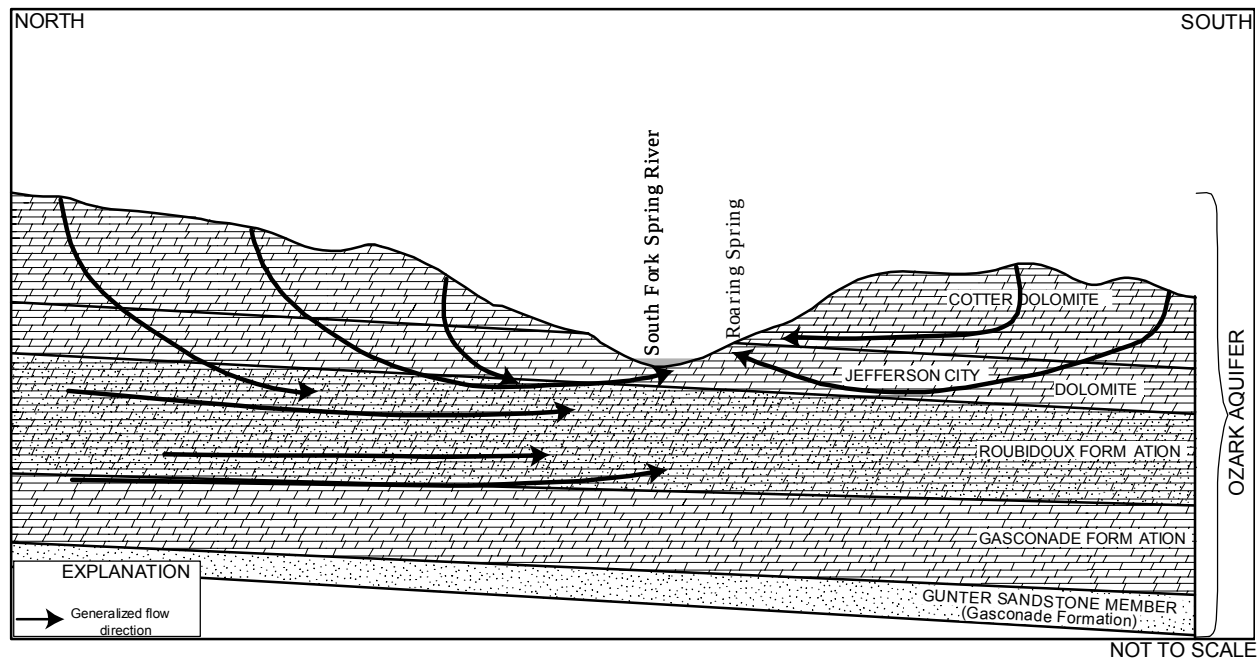
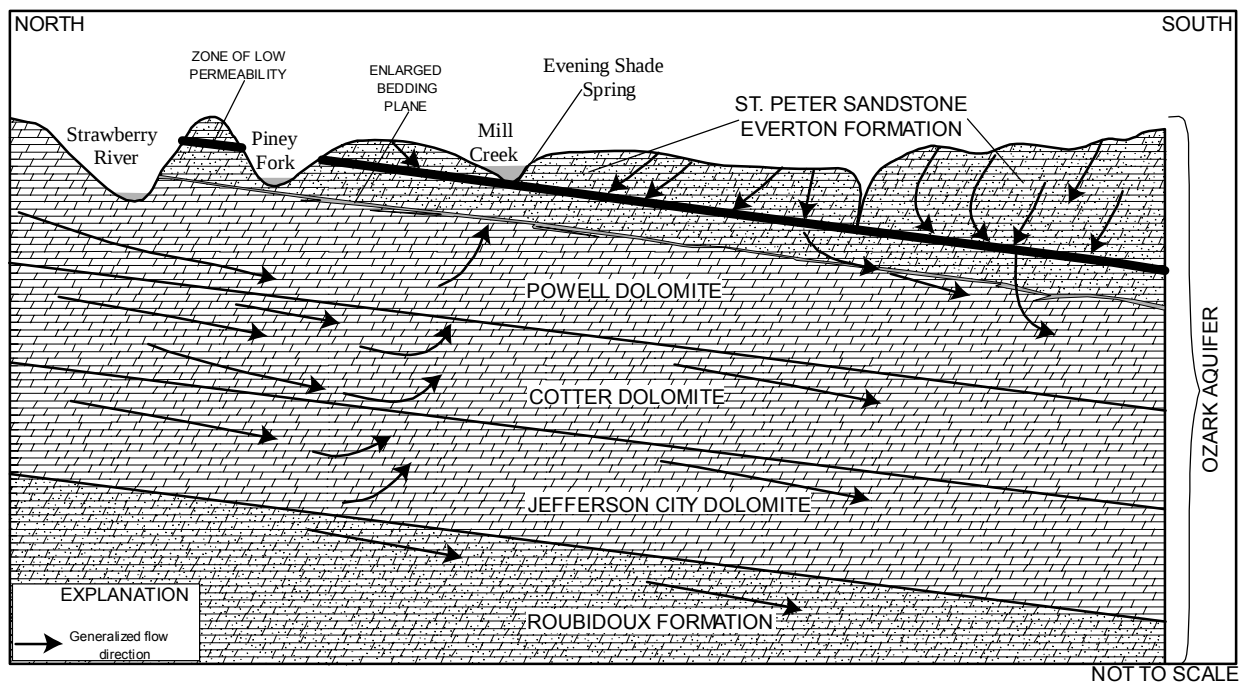


Figure 5. Conceptual model of ground-water flow to Evening Shade and Roaring Springs.

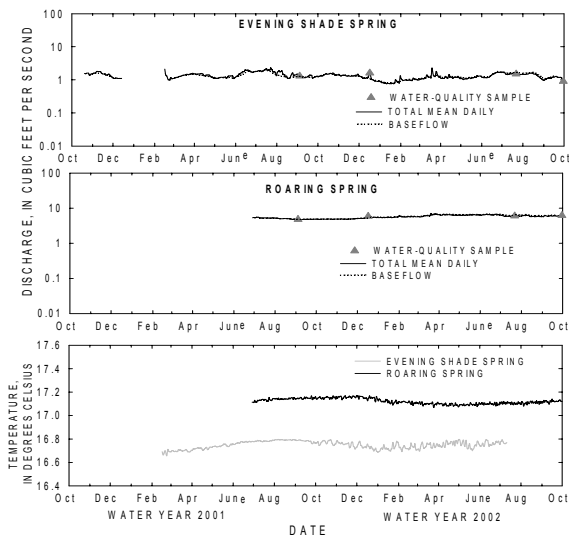


Figure 6. Daily discharge and water temperature recorded at Evening Shade Spring and Roaring Spring.

The discharge for Evening Shade Spring and Roaring Spring remained fairly constant with time. The mean daily discharge for Evening Shade Spring, computed from the springhouse discharge point, ranged from 0.88 to 2.29 ft³/s for water year 2001 and from 0.76 to 2.25 ft³/s for water year 2002 (fig. 6). The mean annual discharge for water years 2001 and 2002 was 1.44 and 1.24 ft³/s, respectively (Brossett and Evans, 2003). The spring discharge periodically measured in the channel of Mill Creek ranged from 3.6 to 9.0 ft³/s during water years 2001 and 2002 (fig. 6). The mean daily discharge for Roaring Spring ranged from 4.8 to 7.2 ft³/s, and the mean discharge was 5.7 ft³/s for July 2001 to October 2002 (Brossett and Evans, 2003). The ratio of base flow to peak flow for Evening Shade Spring ranged from 2.6 to 3.0 and the ratio for Roaring Spring was 1.5, indicating slow-response springs (White, 1988). The discharge for both springs contrasts with the fast response, storm input type of discharge that was observed at Hughes and Stark Springs.

The recorded water temperature for Evening Shade Spring ranged from 16.7 to 16.8 °C from February 2001 to July 2002, and the water temperature for Roaring Spring ranged from 17.1 to 17.2 °C (fig. 6). The relatively stable discharge and temper-

ature suggest that the Evening Shade Spring and Roaring Spring discharge is representative of a regional ground-water system.

The major ion analyses from Evening Shade Spring and Roaring Spring demonstrated a calcium bicarbonate type water typical of the Ozark aquifer. All samples collected from Evening Shade Spring and Roaring Spring had calcium to magnesium ratio values of 1.3 and 1.1, respectively, indicating contribution from a dolomitic mineralogy (White, 1988) that also is representative of formations of the Ozark aquifer. SI_{calcite} values from samples collected at Evening Shade Spring and Roaring Spring showed the waters are supersaturated with calcite. Values for SI_{calcite} appeared to have an inverse relation with the quantity of discharge at the time the sample was collected. At higher discharges, the SI_{calcite} decreased and at lower discharges the value increased. Although it has been shown that there is not a large variation in spring discharge during precipitation events, flow velocities in the ground-water system during periods of high precipitation (late winter, early spring) may increase enough to decrease the contact time of the water with the rock because of a steepening of the ground-water gradient. The $\delta^{13}\text{C}$ data show the water discharging from Evening Shade Spring and Roaring Spring reflected near-equilibrium conditions between the ground water and the aquifer material.

The discharge, geochemical, and hydrogeologic data indicate that the discharges for Evening Shade Spring and Roaring Spring are representative of a regional ground-water flow system (Ozark aquifer) and do not allow for a distinct boundary to be delineated for the recharge area contributing to the spring. Ground-water tracer tests conducted in the study area to identify a connection between Evening Shade Spring and local ground-water flow systems resulted in the negative recovery of the three tracers injected into two wells and a sinkhole. Although the tracer tests did not establish that a local recharge area does not exist conclusively, they lend support that the Evening Shade Spring is mainly recharged from the Ozark aquifer. Tracer tests were not attempted in the Roaring Spring study area. The recharge areas for the two springs could include relatively remote locations where hydrogeologic units

composing the Ozark aquifer are exposed and have sufficient porosity and hydraulic conductivity to convey water that falls as precipitation to the subsurface.

CONCLUSIONS

Recharge to Hughes Spring and Stark Spring occurs mainly from the Boone Formation that composes the Springfield Plateau aquifer. Ground-water tracer tests indicate that the recharge area for Hughes Spring generally coincides with the surface drainage area (15.8 mi²) and that Hughes Spring is directly connected to the surface flow in Brush Creek. Analyses of discharge data show that Stark Spring has a fast response to surface runoff and the estimated recharge area (0.79 mi²) is larger than the surface-drainage area (0.34 mi²). Ground-water tracer tests and the outcrop of the Boone Formation indicate that most of the recharge area extends outside the surface-drainage area.

The geochemistry of Hughes Spring and Stark Spring demonstrated variations with flow conditions and the influence of surface-runoff in the recharge area. Calcite saturation indices, total dissolved solids concentrations, and hardness demonstrate noticeable differences with flow conditions reflecting the reduced residence time and interaction of water with the source rock at high-flow conditions for Hughes Spring. Large water temperature variations also corresponded to high-flow events at Hughes Spring although variations were not as noticeable for Stark Spring during high-flow events.

Evening Shade and Roaring Springs originate from geologic formations composing the Ozark aquifer. Little variation in discharge and temperature was evident during high-flow events and throughout the monitoring period indicating that spring discharge is dominated by regional ground-water flow with small portions of local recharge. As a result, local recharge areas were not delineated, and the area could include relatively remote locations where geologic formations composing the Ozark aquifer are exposed and have sufficient porosity and hydraulic conductivity to convey water that falls as precipitation to the subsurface.

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Adaptation of the Residence Time Distribution (RTD)-Biodegradation Model to Quantify Peroxide-Enhanced Fuel Biodegradation in a Single Karst Well

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ABSTRACT

This field study was conducted to determine if a numerical model incorporating residence time distribution (RTD) coupled to a first-order rate of biodegradation (k') could be used to quantify toluene and benzene removal in a single karst-well injection system. This study involved injecting sodium chloride (NaCl) as a conservative tracer, as well as hydrogen peroxide (H_2O_2), to enhance aerobic biodegradation of toluene and benzene. A 100-gallon volume of fuel-contaminated karst aquifer water was pumped into a container. NaCl (1.25 kilograms) and 33 percent H_2O_2 (4 liters) were mixed into the water and injected back into the bedrock aquifer. The NaCl, dissolved oxygen, benzene and toluene concentrations were monitored for several weeks. Results show that benzene and toluene concentrations declined approximately 10 times faster than the NaCl concentrations, indicating enhanced biodegradation. The RTD was calculated by using the declining NaCl-concentration curve through time. The biodegradation rate was derived from the benzene and toluene data. The RTD-biodegradation formula (described in this paper) was used to predict and quantify the enhanced biodegradation of benzene and toluene in the karst aquifer. The RTD-biodegradation formula predicted benzene and toluene concentrations in the well through time to within 1 microgram per liter ($\mu g/L$) of the actual concentration. This close agreement between the RTD-biodegradation model prediction and the measured concentration confirms that this method can be used to quantify enhanced biodegradation in a single karst injection well.

INTRODUCTION

Karst aquifers have been recognized as one of the most challenging geologic media in terms of ground-water modeling (Wolfe and others, 1997; White, 2002). Ground-water flow in karst aquifers is complex because of variability in conduit size, shape, and direction (Field, 1993). Numerical models based on Darcy's Law often are unable to accurately characterize contaminant flow through the heterogeneous fractures and dissolution features. To successfully model ground-water flow in karst, a numerical model must provide an accurate mathematical representation of the physical karst aquifer system. The non-ideal, complex flow in karst aquifers presents greater challenges for modeling biodegradation processes with partial differential

equations for flow and transport. Chemical engineers commonly use a residence-time distribution (RTD) formula to describe non-ideal flow through a reactor. This study adapted and used RTD to describe migration of a conservative tracer through a section of a karst aquifer in south-central Kentucky. The RTD formula was modified to incorporate a biodegradation rate for predicting the removal of benzene and toluene. The objective of this study was to develop and adapt the RTD-biodegradation formula for predicting and quantifying biodegradation in a single well injected with hydrogen peroxide. This numerical approach was tested in a field study where hydrogen peroxide (H_2O_2) was injected into a bedrock well to enhance aerobic biodegradation of jet fuel in the karst aquifer.

DERIVATION OF THE RTD-BIODEGRADATION FORMULA

Obtaining RTD for a Karst, Single-Well, Injection System

The degree of mixing within a non-ideal flow karst system can be characterized by the residence time distribution function, $E(t)$. Experimentally, the RTD function can be calculated using a quantitative tracer study. At an initial time of zero, $t = 0$, a known mass of conservative tracer (M_0) dissolved in a known volume is injected into the karst system. The concentration of the conservative tracer, C , is then measured in the well as a function of time (t).

When the change in time, Δt , is so small, the $C(t)$ is essentially constant. Therefore, the amount of the tracer (ΔM) flowing between t and $t + \Delta t$ can be expressed as:

$$\Delta M = C(t)u\Delta t \quad (1)$$

where the term $C(t)$ represents the concentration of the tracer at some time (t) and the term u represents the flow rate of the system, which is constant.

The fraction of the tracer in the non-ideal flow system between t and $t + \Delta t$ can be mathematically described by as:

$$\frac{dM}{M_0} = \frac{uC(t)}{M_0}\Delta t \quad (2)$$

Based on this mass balance for the continuous-input tracer study, the RTD function, $E(t)$ can be described as:

$$E(t) = \frac{d}{dt} \left[\frac{C(t)}{C_0} \right] \quad (3)$$

The ratio of $\frac{C(t)}{C_0}$ is the water discharging from the system that has spent less than the mean theoretical time in the flow. The first two moments of $E(t)$ can be defined as the mean residence time and variance of the distribution. The mean residence time (t_m) for the non-ideal flow system can be calculated using the equation:

$$t_m = \sum \left[t^* \frac{d}{dt} \left\{ \frac{C(t)}{C_{(0)}} \right\} \Delta t \right] \quad (4)$$

The variance (σ^2) is defined as:

$$\sigma^2 = \sum \left[t^{*2} \frac{d}{dt} \left\{ \frac{C(t)}{C_{(0)}} \right\} \Delta t - (t_m^2) \right] \quad (5)$$

The $E(t)$, t_m , and σ^2 for a single-well injection system can be obtained by numerical differentiation of the conservative tracer data.

Obtaining Peclet Number for a Non-Ideal Flow System

In describing a non-ideal flow system, the convective and dispersive nature of the flow is often considered. The Peclet number (P_e) characterizes the degree of flow diffusivity compared to the advective transport. This dimensionless parameter quantitatively characterizes the transport diffusion and is inversely related to the dispersion value, d , for a non-ideal flow system.

$$P_e = (1/d) \quad (6)$$

It can be shown that the moments from the $E(t)$, mean residence time and variance obtained from equations 7 and 8 below are related to the Peclet number (P_e) as follows:

$$t_m = \left(1 + \frac{2}{P_e} \right) \tau \quad (7)$$

and

$$\frac{\sigma^2}{\tau^2} = \frac{2}{P_e} + \frac{8}{P_e^2} \quad (8)$$

The connection between Peclet number, $E(t)$, mean residence time and variance is accomplished by treating τ (space-time) in the above equations as an unknown and first calculating P_e based on the experimental RTD and then calculating for τ ($\tau = V/u$) (Bischoff and Levenspiel, 1962).

Adaptation of the RTD-Biodegradation Model for a Single-Well Injection

The fate of organic contaminants in a karst aquifer system also depends on their susceptibility to biodegradation. As a result, the application of the RTD alone is not sufficient to numerically predict the fate of contaminants in a karst aquifer. The karst-contaminant model developed here uses RTD coupled to a biodegradation rate reaction.

The chemical kinetics of biodegradation are assumed to be represented by a rate equation such as:

$$\frac{dC_A}{dt} = kC_AC_B \quad (9)$$

Equation 9 describes a changing concentration of contaminant A (dC_A) through time (dt) as a function of the biodegradation rate (k), the concentration of contaminant A in solution (C_A), and bacteria and electron-acceptors, (C_B). Since the rate is dependant upon two variables, the rate equation can be expressed as a second-order reaction. If the bacteria and electron acceptors, however, are assumed to be present at a relatively steady state, then (C_B) can be considered constant while the contaminant concentration (C_A) continually changes. In such conditions, C_B is treated as a constant and the second-order equation is re-written as a pseudo first-order equation:

$$\frac{dC_A}{dt} = kC_AC_B \Rightarrow k'C_A \quad (10)$$

where $k' = kC_B$ becomes a pseudo first-order rate constant, which can be obtained by fitting the experimental and field data.

The RTD function and biodegradation function can be coupled to develop the RTD-biodegradation function capable of quantifying biodegradable contaminants at a given time, $C(t)$. This function can be mathematically expressed as:

$$C(t) = C_0 \frac{4*a*e^{1/(2*(1/P_e))}}{(1+a)^2*e^{a/(2*(1/P_e))} - (1-a)^{\frac{a}{2*(1/P_e)}}} \quad (11)$$

where $a = \sqrt{(1 + k't(1/P_e))}$ and C_0 = initial contaminant concentration.

This RTD-biodegradation equation was used to predict and quantify benzene and toluene removal in a single karst well. This approach accounts for the non-ideal flow, axial dispersion, and biodegradation in the karst aquifer directly surrounding the injection well. The following section describes the results of applying this formula in a field study.

METHODS AND MATERIALS

A jet-fuel-contaminated karst site in south-central Kentucky was selected because of the availability of site history and previous research (Byl and others, 2002). An unknown quantity of fuel released over a 60-year period has slowly migrated down from the regolith into the bedrock aquifer. The geology at this site consists of approximately 25 meters of regolith composed of chert (fused silica), clay, silt, sand, and gravel. Underlying the regolith is 3 to 10 meters of epikarst (weathered bedrock embedded with clay). Below the epikarst is limestone bedrock that has water-filled conduit openings ranging from millimeters to 2 meters thick.

A contaminated well was screened in the interval from 38.4 to 41.5 meters below ground surface; the top of bedrock is at 38.7 meters below ground surface. A jet pump equipped with a clean Teflon[®] hose was lowered to a known conduit based on geophysical information (Gregg Hileman, U.S. Geological Survey, oral commun., 2005). A no-purge method (Puls and Paul, 1995) was used to pump water at a low, constant rate of 2.6 liters per minute. Periodic water-level measurements verified no decline in head while pumping occurred, indicating that the water was coming from the aquifer. The water temperature was a steady 14.1° C with a specific conductance of 685 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), and a pH of 10.5. A total of 378-liters (100 gallons) of contaminated aquifer water was pumped into containers and titrated to a pH of 6.5 with 0.1 molar HCl; then the treated water was returned to the aquifer system. A week following the pH adjustment, a 378-liter volume of aquifer water was pumped again and treated with 4 liters of 33 percent H_2O_2 . Sodium chloride (1.25 kg) was also

added for the quantitative tracer analysis. Benzene and toluene concentrations were stable at 6 micrograms per liter ($\mu\text{g/L}$) and 20 $\mu\text{g/L}$, respectively, prior to adding the HCl, and the H_2O_2 and NaCl.

Volatile organic compound (VOC) samples were collected from the test well and surrounding wells every few days using passive-diffusion bag (PDB) samplers. The PDB-sampling technique provided a 12-hour integrated sample of the well and did not show the temporal variability of grab samples. The dissolved oxygen and specific conductance were measured using a YSI-600 XLM datasonde that was placed in the well at the level of the conduit opening. Two additional karst wells within 100 yards of the injection well also were equipped with monitoring devices and were sampled for VOCs.

The first-order degradation rates (k') developed from the field data were 0.01357 per hour for toluene and 0.072 per hour for benzene biodegradation. The biodegradation rates were then coupled to the RTD equation that had been modified for a single-well system.

RESULTS AND DISCUSSION

A known amount of NaCl was dissolved in 100 gallons of water and injected as a single pulse, displacing an equal volume of water surrounding the injection well. A correlation between the NaCl concentration and the specific conductance was established. Thus, specific conductance data provided a measure of conservative tracer concentration with respect to time. Specific conductance was measured in the injection well and two nearby monitoring wells (fig. 1). The benzene concentration in the injection well is shown in figure 1 to illustrate the rapid decline in benzene as compared to NaCl. Dissolved oxygen levels

went from less than 0.1 milligrams per liter (mg/L) to a supersaturated concentration of 55 mg/L as a result of the H_2O_2 injection (data not shown). The dissolved oxygen declined slowly over a 6-week period.

A comparison of the RTD-biodegradation model predictions and measured field concentrations for toluene and benzene indicated close agreement between the two approaches (figs. 2 and 3). The graphs show the percentage of contaminants remaining in the water as calculated by the model and measured in the PDB samplers. The predictions of the RTD-biodegradation model and the measured amount of toluene and benzene removed through biodegradation were within 0.5 $\mu\text{g/L}$ at each sampling point.

CONCLUSION

The concept that a karst aquifer is analogous to a non-ideal flow reactor was tested, as well as H_2O_2 -enhanced fuel biodegradation. The results indicate that biodegradation was enhanced and the RTD-biodegradation model could be used to describe the process in a single well. This is the first known field application of the RTD-biodegradation model in conjunction with enhanced-fuel bioremediation in a karst aquifer. The numerical approach

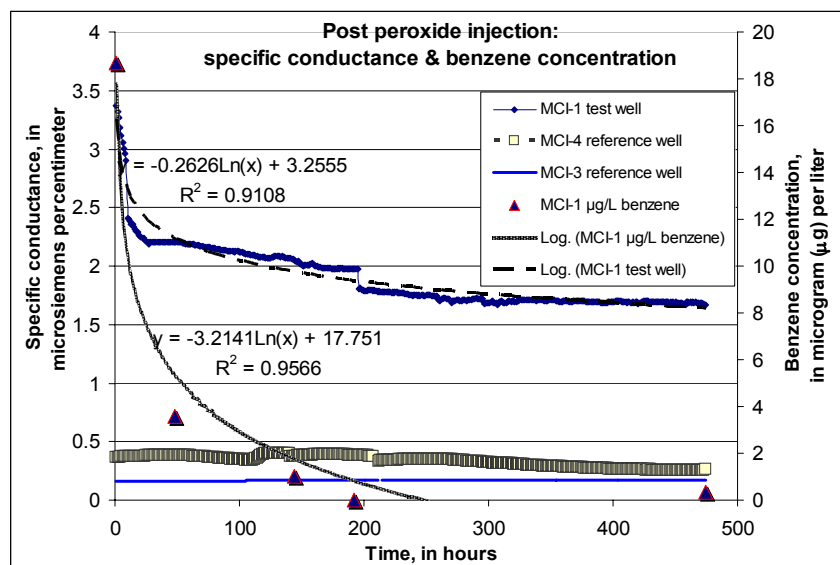


Figure 1. Specific conductance measured as a function of time in three karst bedrock wells. The benzene concentration is shown also with concentrations indicated on the second y-axis.

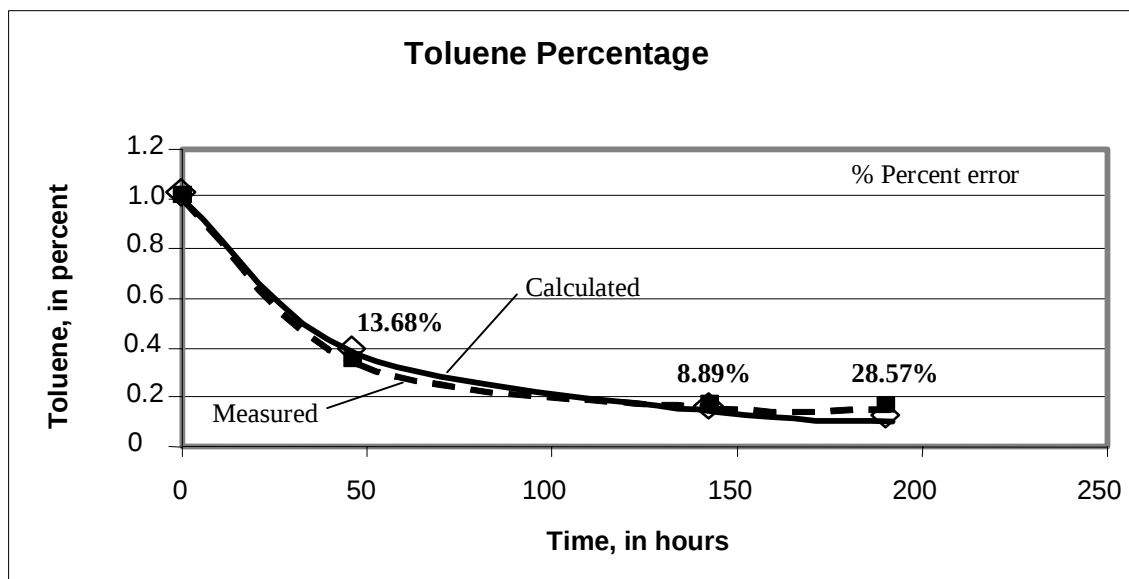


Figure 2. The RTD-biodegradation model prediction compared to the measured field toluene concentrations. The graph shows close agreement between the model calculation and measured concentration.

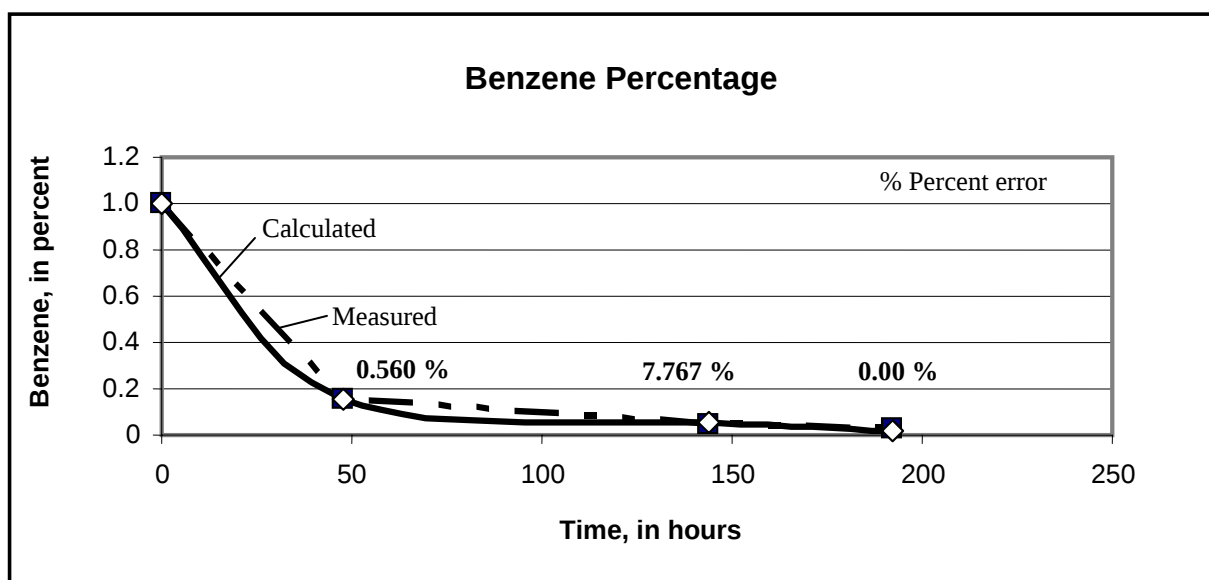


Figure 3. The RTD-biodegradation model prediction compared to the measured field benzene concentrations. Close agreement is indicated between the two approaches.

mathematically accounts for advection, dispersion, and biodegradation of a contaminant in a non-ideal flow system. These findings are important because they extend the potential for enhanced bioremediation to karst sites. This approach provides a method to predict and quantify biodegradation in a karst

aquifer possibly providing new remediation strategies for karst aquifers.

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Free-Living Bacteria or Attached Bacteria: Which Contributes More to Bioremediation?

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ABSTRACT

Researchers have implied that natural bioremediation in karst or fractured rock is unlikely to occur because of the lack of bacteria biofilm in karst aquifers. Hydrologic and geologic characteristics of fractured rock aquifers have been described as not being suited for natural bioremediation because of small microbial populations. If bioremediation in bedrock aquifers is dependent upon contact between surface-attached bacteria and contaminants, then bioremediation would be limited by the low surface area to volume ratio (SA/V) of karst aquifers. A quantitative basis, however, for accepting or rejecting the assumption that attached bacteria dominate the biodegradation process in karst conduits has not been shown. The objective of this research was to determine if free-living karst bacteria contributed as much to toluene biodegradation as attached bacteria. Two flow-through reactor systems were established to test the different biodegradation rates. Each reactor system consisted of four 1.24-liter cylinders connected together with glass tubing for a total open volume of approximately 5 liters. The second reactor system was similar to the open system except the cylinders were filled with acid-washed, circular glass spheres that increased surface area to volume ratio approximately fivefold compared to the open system. Rhodamine dye was used to calculate the different residence-time distributions in each system. A sterile control study established that less than 3 percent of the toluene was lost to abiotic processes. Next, raw water from a karst aquifer containing live, indigenous bacteria was pumped through each system for 5 days to establish a biofilm on the glass surfaces. Colonization of the surface was confirmed by microscope visualization before toluene was added to the systems. The resulting first-order rate constants were computed to be 0.014 per hour for the open system and 0.0155 per hour for the packed reactor system. If surface-attached bacteria were the main contributors to the biodegradation process and the SA/V ratio was increased fivefold, a significantly higher biodegradation rate should have occurred in the packed reactor. The results of this study indicate that the free-living bacteria indigenous to a karst aquifer contribute as much to the toluene biodegradation process as attached bacteria.

INTRODUCTION

The lack of studies examining biodegradation in karst aquifers may be due to the widespread perception that contaminants are rapidly flushed out of karst aquifers. In highly developed and well-connected conduit systems, the rate of contaminant migration is expected to be much faster than the rate of biodegradation. Field (1993) states that remediation techniques such as ground-water extraction or bioremediation are impractical in karst aquifers dominated by conduit flow; however, he also states that the belief that contaminants are rapidly flushed out of karst aquifers is a popular misconception. Large volumes of water may be trapped in fractures

along bedding planes and other features isolated from active ground-water flow paths in karst aquifers (Wolfe and others, 1997). In areas isolated from the major conduit flow paths, contaminant migration may be slow enough that biodegradation could reduce contaminant mass if favorable microorganisms, food sources, and geochemical conditions are present.

Researchers have implied that natural bioremediation in karst or fractured rock is unlikely to occur because of the microbiological characteristics of karst aquifers; small microbial populations and low surface area to volume (SA/V) ratio (Vogel, 1994). Typical microbial numbers for material from

unconsolidated aquifers have been reported to range from 1×10^4 to 1×10^7 cells per milliliter (cells/mL) (Ghiorse and Wilson, 1988). Studies have shown that water from bedrock (granite and karst) aquifers also may contain microbial populations within this range. For example, total microbial populations of 9.7×10^5 to 8.5×10^6 cells/mL and heterotrophic bacteria populations of 3.5×10^3 to 5.0×10^5 cells/mL were detected in ground-water samples collected from a gasoline-contaminated karst aquifer in Missouri (O'Connor and Brazos, 1991). The fact that greater than 70 percent of bacteria in consolidated aquifers are attached to solid surfaces (Harvey and others, 1984; Harvey and Barber, 1992) may have led to the assumption that natural bioremediation in karst conduits is negligible because contact between attached bacteria and contaminants would be limited by the SA/V ratio.

Research currently underway at Tennessee State University in cooperation with the U.S. Geological Survey focuses on modeling biodegradation of contaminants in karst systems. The research presented in this paper compares the biodegradation of toluene by attached and free-living bacteria in two laboratory karst systems. Conservative tracer studies, sterile controls and quantified toluene biodegradation were used to mathematically determine

biodegradation rates for two laboratory karst systems representing a different SA/V ratio. The toluene-biodegradation results from the laboratory karst systems were analyzed in terms of chemical reaction kinetics and mass transfer principles. The math used to calculate whether the degradation was predominantly a function of volume through free-living microbes or a function of surface area through attached bacteria is described in the Methods and Materials section of this paper.

METHODS AND MATERIALS

Flow-through microcosms were constructed using a 20-liter glass reservoir, a multi-channel peristaltic pump, 10-milliliters (mL) stirred injection cells, four 1-liter volumetric flasks (actual volume when full = 1,240 mL), and 3-millimeter (mm) inner-diameter glass tubing connecting the pieces (fig. 1). One system was packed with a sufficient number of flat, glass spheres to increase the surface to volume area fivefold in the packed system as compared to the unpacked system. Water was pumped into both systems by using a high-performance peristaltic pump. A stirred injection cell (10 mL volume) was placed at the entrance of each replicate system for the injection of dye or toluene. The water traveled from the stirred injection cell

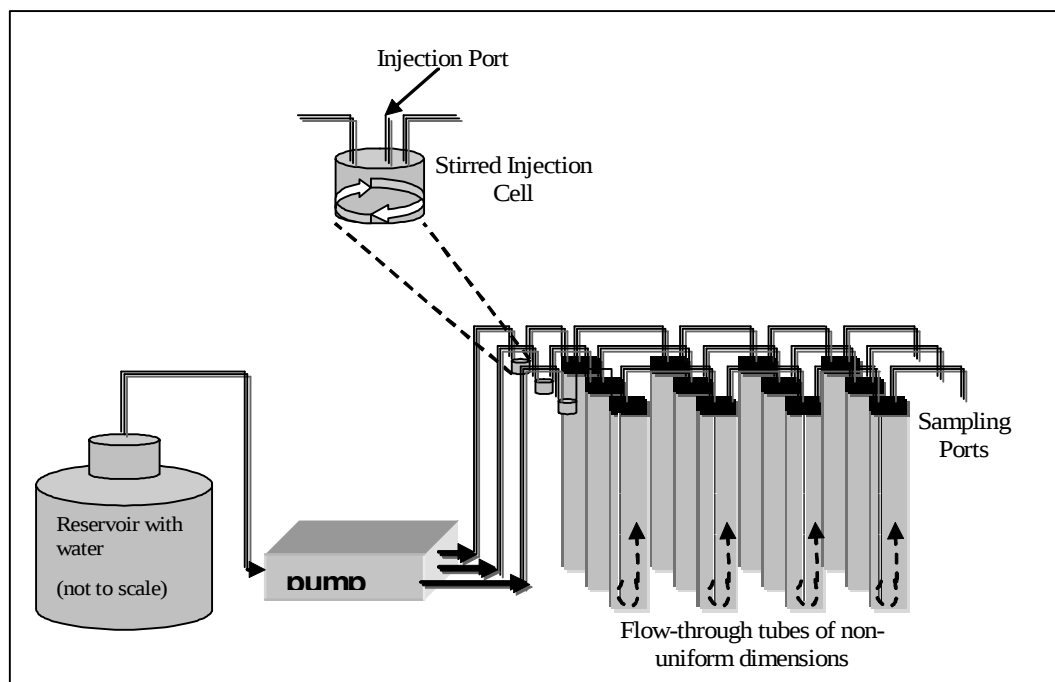


Figure 1. A schematic of the experimental karst systems.

through a thin glass tube to the bottom of graduated cylinders arranged in series. The water and injected constituents traveled through a series of nonuniform-size cylindrical glass tubes ranging from 3- to 56-mm in diameter. The non-uniform dimensions in the systems contributed to non-ideal flow conditions such as eddies and currents.

During the conservative dye tracer study, a constant flow rate of approximately 3 milliliters per minute (mL/min) was established for both systems. The pump was stopped at the beginning of the tracer study, 476 micrograms (μg) of Rhodamine dye was injected into each stirred injection cell, and the pump was restarted. The Rhodamine concentration at the discharge port was monitored through time by collecting samples at 1- to 2-hour time intervals over a 4-day period. A Turner 700[®] fluorometer was used to quantify the Rhodamine in the water samples. The lower detection limit on the fluorometer was established at 100 parts per trillion.

Before the toluene biodegradation study was initiated, the experimental systems were sterilized with bleach. The bleach was neutralized with sterile sodium thiosulfate. Filter-sterilized toluene (87 μg) dissolved in 100 microliters (μL) of methanol was delivered into the injection cell and pushed through the system with sterile water that had a pH of 10. Previous work indicated that elevating the pH to 10 to maintain an abiotic system.

Toluene concentration was monitored at the discharge port over the next 5 days. Water samples were collected in clean 40-mL volatile organic compound (VOC) vials every 1 to 4 hours. The water samples were immediately analyzed on a Syntex[®] gas chromatograph (GC) equipped with a purge-and-trap system, 30 meter (m) X 0.32 mm, 1.8-micrometer (μm) silica-film capillary column, argon-carrying gas, and micro-argon ionization detector. The lower detection limit for toluene on the GC was 0.5 microgram per liter ($\mu\text{g/L}$). Every fourth sample was either a duplicate sample or a standard of known toluene quantity, and a complete calibration curve was run every 6-12 hours.

The biodegradation experiments used water containing live bacteria collected from a 120-foot-

deep well completed in a karst aquifer in south-central Kentucky. An 87- μg aliquot of toluene was dissolved in 100 μL of methanol and placed in the stirred injection chamber at time zero. The flow rate used in all experiments was kept constant at approximately 3.0 mL/min. Data results from the tracer tests and the biodegradation studies were entered into a computer spreadsheet and all calculations regarding residence-time distribution (RTD) and biodegradation rates were documented in the spreadsheets.

Experimental runs consisted of running the packed system and an unpacked system in parallel under similar conditions. In order to document the presence of attached bacteria, glass slides were suspended in both the packed and unpacked systems. The suspended slides were removed prior to and at the end of the experiments and viewed using an epifluorescent microscope and the direct-count method (Eaton and others, 1995).

Toluene was selected as the experimental contaminant because it is a component in most fuels and because previous work indicated *Pseudomonad* bacteria, which are heterotrophic aerobic bacteria (HAB), from the Kentucky site could grow using toluene as a food source (Byl and others, 2001; Byl and others, 2002). The concentration of HAB in the water was determined by using the most probable number (MPN) method (Eaton and others, 1995). The MPN bacteria concentrations in the abiotic systems were less than one colony-forming unit per 100 millimeter. The bacteria concentration in ground water from the karst aquifer ranged from 600,000 to 700,000 HAB/mL at the beginning and end of the experiment.

DESCRIPTION OF THE MATHEMATICS USED TO CALCULATE BIODEGRADATION RATES

The fate of biodegradable contaminants in a karst aquifer system is dependant upon the rate of their biodegradation and the amount of time they spend in the system with the bacteria (referred to as residence-time distribution or RTD). As a result, the difference in amount of toluene that is biodegraded in each of the systems is not sufficient to numerically predict the fate of contaminants in a karst

aquifer. The biodegradation-rate equation must be coupled to the RTD formula since the removal of the contaminant is a function of RTD and biodegradation reaction rate. Once the equation is established, it can be re-arranged to solve for the biodegradation rate using the experimental data. Following is a description of how the biodegradation rate and RTD equation were coupled.

For a sparingly soluble contaminant (A) reacting with a rate-limiting constituent (B), which may be the microbes themselves or different electron acceptors, the reaction may be second order (symbols are defined in Appendix):

$$\frac{dC_A}{dt} = kC_AC_B$$

In a situation where the microbes are acclimated and at steady state and electron acceptors are not limiting the concentration, the reaction, C_B may not change appreciably while C_A changes. Treating C_B like a constant, the equation can be rewritten as a first-order equation:

$$\frac{dC_A}{dt} = kC_AC_B \Rightarrow k'C_A$$

where $k' = kC_B$ is the pseudo first-order rate constant. Oxygen and microbes were assumed to be not limiting in this laboratory system because the initial water was saturated, allowing use of the pseudo first-order equation.

In this context, the relative contributions of surface and volumetric biodegradation to the observed biodegradation rate can be determined by experiments with varying SA/V. If free-living bacteria dominate, the biodegradation reaction is volumetric and the observed pseudo first-order rate constants for the packed and unpacked reactors will be of similar magnitude. If, on the other hand, attached bacteria dominate, then the reaction is surface controlled and the observed pseudo first-order rate constants will not be of similar magnitude. If attached bacteria dominate the biodegradation reaction, the rate constant will be directly proportional to SA/V ratio.

The non-ideal hydraulic and mass transfer characteristics for systems with different SA/V ratios would lead to different lengths of residence time in

each system. The dissimilar residence times in the packed and unpacked systems used in this study can be offset by using the RTD formula (Bischoff, and Levenspiel, 1962). The RTD of solutes in each system was determined using a conservative dye study to compensate for the shorter residence time in the system with less volume (that is, packed with glass spheres). The residence time (τ) is related to the mean residence time obtained from the RTD as:

$$t_m = \left(1 + \frac{2}{P_e}\right)\tau.$$

The Peclet number (Pe) is obtained from the variance of the RTD according to:

$$\frac{\sigma^2}{P_e^2} = \frac{2}{P_e} + \frac{8}{P_e^2}.$$

The Peclet numbers and the amount of toluene biodegraded (X_m) obtained from the biotic experiments in the packed and unpacked systems were used to obtain the rate of biodegradation by re-arranging the following:

$$X_m = 1 - \frac{4qe^{(P_e/2)}}{(1+q)^2 e^{(P_e q/2)} - (1-q)^2 e^{(-P_e q/2)}}$$

where:

$$q = \sqrt{1 + 4D_A/P_e}$$

The Damkohler number (D_A) incorporates the biodegradation reaction rate (k') and time. The equation can be rearranged and solved for k' .

RESULTS AND DISCUSSION

The RTD for each system was calculated from the conservative dye study. The data were numerically integrated to determine the mean residence time (t_m) and the variance (σ^2) for the packed and unpacked laboratory karst systems. These parameters were then used to calculate the Peclet numbers, which are an indicator of the dispersion as the solute moves through the system. The results of the conservative dye study are shown in figure 2. After the dye study, the reactor systems were sterilized and toluene was injected to measure the amount of removal by abiotic processes. A mass balance was done on the toluene injected and recovered from the sterile

systems. Approximately 3 percent of the injected toluene was lost to abiotic processes in each of the experimental systems during the sterile run.

In the third phase of the study, water containing live bacteria was pumped through the laboratory systems for 4 days to establish a biofilm on the glass surfaces. Bacteria counts using MPN and microscopic methods were used to confirm that bacteria covered the glass surfaces and were suspended in the water at the beginning and end of the experiments (photos 1 and 2). A solution containing $87.0 \mu\text{g}$ of toluene was injected into each system. Numerical integration of the resulting effluent toluene concentration and time (fig. 3) indicated recovery of $61 \mu\text{g}$ toluene from the unpacked reactor and $69 \mu\text{g}$ toluene from the packed reactor. The resulting observed toluene biodegradation value (X_m) for the packed and unpacked systems was 0.21 and 0.31, respectively.

These X_m values were used in the equation listed above to calculate the observed reaction rate constants (k'_{observed}). The values of k'_{observed} were 0.014 per hour and 0.0155 per hour for the packed and unpacked systems, respectively. The above results for conversion and rate constants for the packed and unpacked systems seem counter-intuitive at first glance; that is, the packed system has lower conversion and higher reaction rate of the two systems. This occurs because of the complex relation between hydraulic and chemical reaction kinetics in a non-ideal flow system. When the residence time is taken into consideration in each system, however, the rate of biodegradation for the free-living bacteria alone, or volumetric rate, $k'_{\text{volumetric}} = 0.0135$ per hour for both systems.

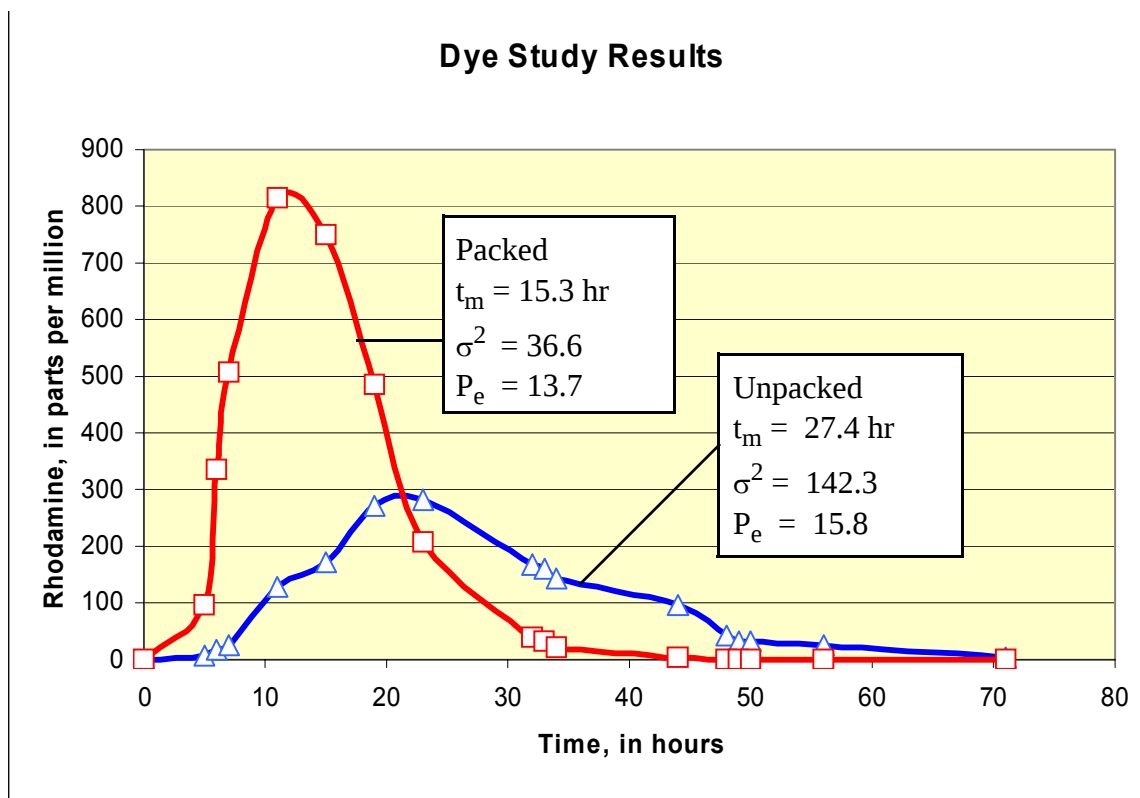
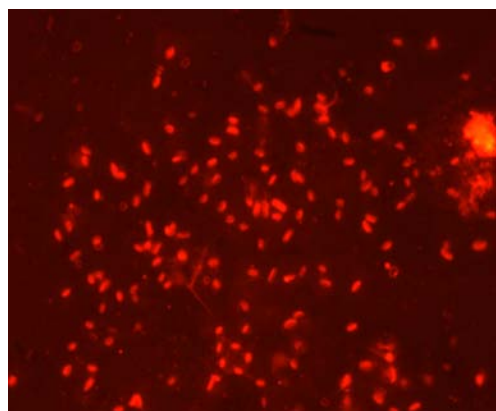
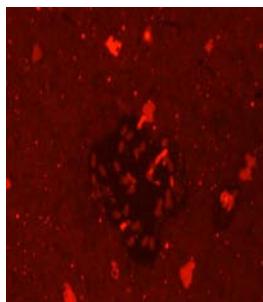


Figure 2. Rhodamine concentration at the end sampling port as a function of time for the high-surface area (packed) system and low-surface area (unpacked) system and the mean residence time (t_m), variability (σ^2) and Peclet value (P_e) for each system.

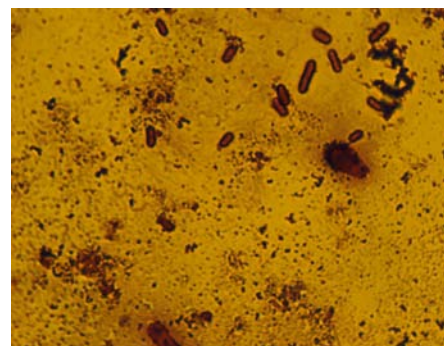
(A)



(B)



Photograph 1. (A) Bacteria (white objects) attached to the surface of the glass after 3 days of pumping water through the system (400x magnification, epifluorescent), and (B) close up of a bacteria cluster on the surface of the glass (800x magnification, epifluorescent).



Photograph 2. Free-living bacteria (dark objects) collected from the water column after 3 days. Flagella can be observed attached to the rod-shaped bacteria (1,000x magnification, bright field).

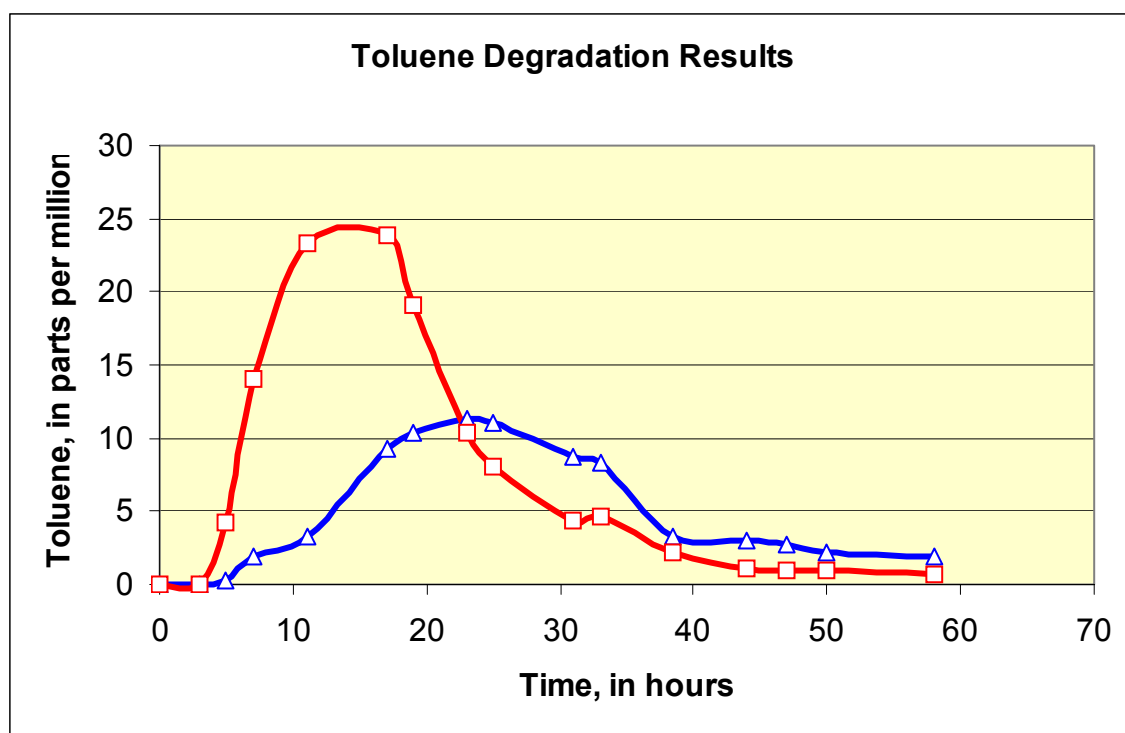


Figure 3. The concentration of toluene as a function of time in the packed system and unpacked systems. The X_{observed} refers to the amount biodegraded, and the K_{observed} refers to the first-order exponential rate of biodegradation calculated from the experimental data.

SUMMARY AND CONCLUSION

Biodegradation of toluene in flow-through laboratory karst systems of varying SA/V indicated that

the observed biodegradation of toluene was a function of free-living and attached bacteria. This was evidenced by the fact that the system with fivefold greater surface area had only a 10-percent increase

in biodegradation. If attached bacteria were primarily responsible for biodegradation, a proportional increase in biodegradation with an increase in surface area would be expected; however, the free-living bacteria appear to contribute as much to biodegradation processes as attached bacteria. The volumetric reaction rate constant ($k'_{\text{volumetric}}$) of 0.135 per hour corresponds to a half-life for toluene of approximately 51 hours without consideration of surface bacteria. Thus, dissolved toluene that resided for several days in a karst conduit with characteristics similar to those in this study could experience substantial biodegradation regardless of interaction with the surface area.

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Appendix. Symbol notation and unit of measure

C	solute concentration, moles per liter [M/L]
C_A	initial contaminant concentration [M/L]
C_B	bacteria-electron-acceptor concentration [M/L]
$C(t)$	concentration of tracer as a function of time [M/L]
D_A	Damkohler Number
k'	pseudo first-order rate constant [T^{-1}]
P_e	Peclet Number [VL/D]
τ	space time [T]
t	time [T]
t_m	mean residence time [T]
$X(m)$	observed or calculated value of chemical biodegraded [M/L]
σ^2	variance [T^2]

Desorption Isotherms for Toluene and Karstic Materials and Implications for Transport in Karst Aquifers

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ABSTRACT

Karst aquifers dominated by conduit flow are extremely vulnerable to fuel contamination such as from leaky underground storage tanks or spills. Direct flow paths through fractures and sinkholes often allow contaminants to move rapidly into the conduit system. Not much is known about how the fuel will interact with the carbonate rock in the conduit system. The objective of this research was to bridge this information gap by measuring sorption and desorption of fuels to karst materials. The first phase of this study involved the dissolution and desorption processes. Initial experiments (n=5) used karst bedrock fragments of known size soaked in toluene for 24 hours. Then the sterile toluene-soaked rocks were placed in sterile distilled water. The concentration of toluene dissolved in the water was measured over increasing time periods. These data were used to derive a first-order exponential rate of desorption [$C_w(t) = C_i e^{kt}$]. The empirical value for k was 0.8958. The toluene concentration in the water reached a maximum carrying capacity in approximately 3 weeks. The second phase of this project involved sorption studies using limestone fragments of known size and water containing a known concentration of dissolved toluene. The empirical value for the sorption k was 1.006. These results show that sorption is faster than desorption and have implications for designing a model that predicts the fate and transport of fuels in karst aquifers.

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A Computer Program that Uses Residence-Time Distribution and First-Order Biodegradation to Predict BTEX Fate in Karst Aquifers

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ABSTRACT

Approximately 40 percent of the United States east of the Mississippi River is underlain by karst aquifers. Karst ground-water systems are extremely vulnerable to contamination; however, the fate and transport of contaminants in karst areas are poorly understood because of the complex hydraulic characteristics of karst aquifers. Ground-water models developed using Darcy's Law coupled to rates of biodegradation are useful for predicting the fate of fuels in unconsolidated aquifers, but have little utility in karst conduits. Conceptual models developed for karst aquifers have a consistent theme of non-ideal flow, storage, and active flow components. This research used a residence-time distribution (RTD) model approach that integrated residence times of contaminants isolated in storage areas with the residence time of contaminants moving through conduits coupled to a pseudo-first order rate of biodegradation. The microcosms consisted of four 1-liter chambers connected with small glass tubing. A peristaltic pump provided a consistent flow of karst water from a 10-gallon reservoir. First, a quantitative dye study was done to establish the residence-time distribution of the three systems. This was followed by a sterile toluene run to measure sorption of toluene to the microcosm systems. The third microcosm run incorporated karst bacteria and toluene. The removal of toluene predicted by the RTD-biodegradation model and the experiment were within 2 percent agreement (n=3). The RTD-biodegradation model was transformed into a user-friendly program that utilizes MS Excel® with Visual Basic interfaces. The input sheet of this prototype program requires site information, a biodegradation rate, and the results of a quantitative tracer study. The results, or output pages, provide residence-time distribution graphs and various statistical calculations. The output pages also report the calculated amount of BTEX removed during transport through the karst aquifer based on RTD and biodegradation. Additional work is needed to incorporate dilution into the model.

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Lactate Induction of Ammonia-Oxidizing Bacteria and PCE Cometabolism

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ABSTRACT

Water containing bacteria was collected from a PCE-contaminated karst aquifer in north-central Tennessee to establish liquid, 1-liter microcosms. The microcosms were spiked with known concentrations of perchloroethylene (PCE) and 11 different formulations of lactic acid. The ammonia-lactate formulation caused a rapid removal of PCE and oxygen (O₂). Similar results that were achieved by using a second set of microcosms spiked with ammonia-lactate to re-test the removal rate of PCE and O₂ indicated a possible cometabolic PCE-removal process. Although only one report of PCE-cometabolism was found in the literature, ammonia-oxidizing bacteria indigenous to the karst aquifer were hypothesized to be capable of cometabolizing PCE with the ammonia mono-oxygenase (AMO) pathway. To test this hypothesis, microcosms were established using different forms of ammonia (ammonia-lactate, ammonia-chloride, ammonium plus sodium lactate), reference controls (sterile, live without food, sodium lactate, sterile + ammonia lactate), and ammonia mono-oxygenase inhibitors [2-chloro-6-(trichloromethyl) pyridine, azide, and allylthiourea]. Microcosms treated with ammonia-lactate had the most rapid reduction of PCE and O₂, followed by the ammonium + sodium-lactate treatment. The other live microcosms treated with ammonia also experienced significant drops in PCE and O₂ after 24 hours. The control (sterile and live without food) microcosms did not experience a significant drop in PCE in the same time period. After 24 hours, the rapid PCE removal in all the ammonia-treated microcosms decreased due to the consumption of the oxygen. Tests with the AMO inhibitor in the presence of ammonia-lactate did not prevent the PCE removal or O₂ consumption. Lactate may stimulate AMO or protect the enzyme from inhibition. Additional tests need to be conducted to prove that AMO is responsible for the removal of PCE. These preliminary results provide strong evidence that karst bacteria indigenous to this aquifer can cometabolize PCE.

Biodegradation of Toluene as It Continuously Enters a 5-Liter Laboratory Karst System

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ABSTRACT

Contamination releases can occur as slow, long-term spills rather than as instantaneous spills. These continuous releases can result in a steady state of contaminants that can last months to years. Predicting the fate and transport of these contaminants in a karst aquifer is especially challenging because of the complex hydrogeology and uncertainties in residence time. The objective of this research was to adapt the residence-time distribution (RTD) biodegradation model, which was developed to predict the biotransformation of a single spill in a karst aquifer, for a continuous input of contaminants. Theoretically, the RTD for a karst system calculated from either a pulse- or a continuous-input tracer study would be identical, but mathematical manipulation of the data for the two approaches is quite different. Determination of the RTD from a continuous input requires numerical differentiation of tracer response data as opposed to numerical integration for the pulse approach. Three experimental runs were conducted involving the application of a continuous input: (1) rhodamine dye alone to establish RTDs for the systems, (2) sterile toluene (25 micrograms per liter) to quantify abiotic sorption, and (3) toluene with karst bacteria to quantify biodegradation. The three replicate karst systems were each 5 liters and had a continuous flow rate of 3.3 milliliters per minute. The difference between the RTD-based model prediction and the experimental toluene conversions was 17 percent. The continuous-input approach (numerical differentiation) had the tendency to magnify experimental and random errors in the tracer response data as compared to the pulse-input method (numerical integration).

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Bacteria Induced Dissolution of Limestone in Fuel-Contaminated Karst Wells

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ABSTRACT

Karst landscapes are formed in water-soluble geologic formations, such as limestone, in which dissolution processes have enlarged water-transmitting openings. Approximately 20 percent of the United States is underlain by carbonate rocks and is classified as karst, and 40 percent of the United States east of the Mississippi River is underlain by karst aquifers. Karst ground-water systems are extremely vulnerable to contamination. Many organic contaminants such as fuels can stimulate bacteria biodegradation and the production of carbon dioxide (CO₂). The increased respiration by bacteria in contaminated karsts aquifers can lead to a significant increase in CO₂ production and formation of carbonic acid.

A quantitative study was conducted to determine the effect of elevated concentrations of carbonic acid due to bacteria action on limestone dissolution. Sealed flasks were set up that contained 250 milliliters of distilled water, limestone fragments of known size and weight, and varying concentrations of CO₂. The flasks with elevated CO₂ concentration had a 3-fold increase in the rate of calcium carbonate dissolution. Water with elevated CO₂ concentrations had a slightly lower pH than water with the lower CO₂ concentrations, but the difference in pH was not statistically significant at the 0.05 confidence level. Further tests were done to determine if these lab results applied to field conditions. Water samples were collected from wells completed in karst aquifers. The CO₂ concentrations in water samples collected from fuel-contaminated wells were higher than in samples collected from wells with no fuel contamination. Also, the dissolved calcium was usually two or three times greater in the fuel-contaminated wells. The results have implications for redesigning geochemical models that predict conduit enlargement when fuel contaminants are present in karst aquifers.

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INTRODUCTION TO THREE FIELD TRIP GUIDES: Karst Features in the Black Hills, Wyoming and South Dakota- Prepared for the Karst Interest Group Workshop, September 2005

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This years Karst Interest Group (KIG) field trips will demonstrate the varieties of karst to be seen in the semi-arid Black Hills of South Dakota and Wyoming, and will offer comparisons to karst seen in the two previous KIG trips in Florida (Tihansky and Knochenmus, 2001) and Virginia (Orndorff and Harlow, 2002) in the more humid eastern United States.

The Black Hills comprise an irregularly shaped uplift, elongated in a northwest direction, and about 130 miles long and 60 miles wide (figure 1). Erosion, following tectonic uplift in the late Cretaceous, has exposed a core of Precambrian metamorphic and igneous rocks which are in turn rimmed by a series of sediments of Paleozoic and Mesozoic age which generally dip away from the center of the uplift. The homoclinal dips are locally interrupted by monoclines, structural terraces, low-amplitude folds, faults, and igneous intrusions. These rocks are overlapped by Tertiary and Quaternary sediments and have been intruded by scattered Tertiary igneous rocks. The depositional environments of the Paleozoic and Mesozoic sedimentary rocks ranged from shallow marine to near shore-terrestrial. Study of the various sandstones, shales, siltstones, dolomites and limestones indicate that these rocks were deposited in shallow marine environments, tidal flats, sand dunes, carbonate platforms, and by rivers. More than 300 ft (91 m) of gypsum and anhydrite were deposited at various times in evaporite basins.

Erosion of these uplifted rocks produced the landscape we see today. Rocks of the Pahasapa Limestone (Madison of some reports), Minnelusa Formation and older sediments form a limestone plateau that rims the central Precambrian metamorphic core. Erosion of weak red siltstones and shales of the Spearfish Formation has formed the "Red Valley", the main area of present and proposed future housing and industrial development. White gypsum caps many of the hills in the Spearfish and is a conspicuous landform in the overlying Gypsum Spring Formation. Resistant sandstones that are interbedded with other rocks lie outboard from the Red Valley and form the hogback that encircles the Black Hills and defines its outer physiographic perimeter.

Relatively soluble rocks, including dolomite, limestone, gypsum and anhydrite, comprise about 35 percent of the total stratigraphic section within the topographic Black Hills, that is, the area including and within the "Dakota sandstone hogback" (fig. 1), comprising rocks of the Inyan Kara Group (fig. 2). Karst is significant in many formations in the limestone plateau and Red Valley (fig. 2). World-class caves, sinking streams, and other features are found in the Pahasapa Limestone. Lesser karst features are found in the other carbonate units. Evaporite karst has developed extensively in the anhydrite and gypsum in the Minnelusa, Spearfish, and Gypsum Spring Formations. Solution of soluble evaporate and carbonate rocks at depth has produced collapse in non-soluble bedrock and surficial deposits at the surface, which in several places extends many hundreds of feet above the soluble rocks.

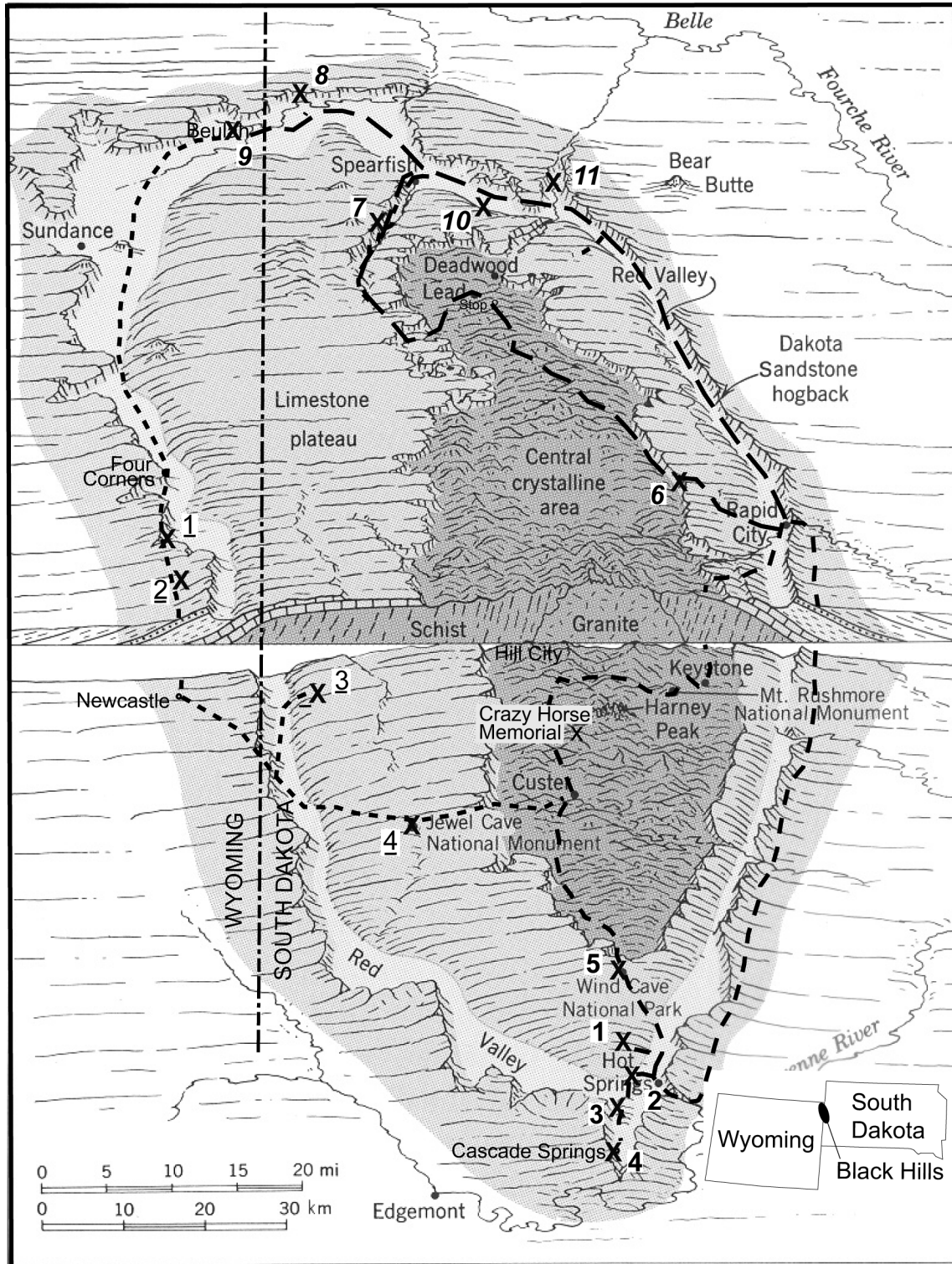


Figure 1. Generalized diagram showing the geology and geomorphology of the Black Hills and route of three 2005 Karst Interest Group field trips (southern trip, regular numbers; Northern trip, italics; western trip, numbers underlined). Most of the urban development and karst features are in the Red Valley, underlain by Triassic red beds and in the lime-

AGE			FORMATION	LITHOLOGY (Thickness in feet) (thicknesses mostly from DeWitt and others, 1989)	KARST FEATURES	FIELD TRIP STOP
CENOZOIC	QUATERNARY	Holocene/ Pleistocene	Terrace deposits, alluvium, colluvium, landslide deposits, sinkhole fill, spring deposits	Gravel, sand, silt, clay, and calcareous tufa	Collapse sinkholes due to dissolution of evaporites and carbonates in formations below; spring deposits; paleontologic animal traps	<u>2, 8, 9, 11</u>
MESOZOIC	CRETACEOUS	Upper	Hell Creek Formation	Shale and sandstone, lignite (425+)		
			Fox Hills Sandstone	Sandstone (25-200)		
			Pierre Shale	Dark-gray and black shale (1,200-2,700)		
			Niobrara Formation	Calcareous shale and impure chalk (80-300)		
			Carlile Shale	Light- to dark-gray shale (325-750)		
			Greenhorn Limestone	Shaly limestone and calcareous shale (225-400)		
			Belle Fourche Shale	Gray shale with limestone concretions and bentonite (150-850)		
			Mowry Shale	Gray siliceous shale (125-250)		
			Newcastle Sandstone	Brown and white sandstone (0-100)		
			Skull Creek Shale	Dark-gray to black shale (150-270)		
	JURASSIC	Lower	Fall River Sandstone	Massive to slabby sandstone (10-200)		
			Lakota Formation	Cross-bedded, conglomeratic sandstone, shale, clay and local impure limestone (35-700)		
		Upper	Morrison Formation	Green to maroon shale and thin sandstone (0-220)		
			Unkpapa Sandstone	Fine-grained sandstone (0-275)		
		Middle	Sundance Formation	Greenish-gray shale, yellow sandstone, and reddish sandstone and siltstone (250-475)		
			Gypsum Spring Formation	Gypsum, red siltstone, limestone, dolomite (0-45)		
	TRIASSIC	Lower	Spearfish Formation	Red shale, siltstone, fine-grained sandstone and gypsum (250-900)		
PALEO.	PERMIAN	Upper	Minnekahta Limestone	Laminated, purplish-gray limestone (30-65)		

↑ Breccia pipes extending down to the Minnelusa Formation

Gypsum karst: sinkholes; contorted gypsum.

Gypsum karst: sinkholes; probable caves at depth in several stratigraphic intervals; contorted gypsum; gypsum stringers; springs.

Minor carbonate karst: solution-enlarged fractures; few sinkholes; color leaching in Opeche below.

Figure 2. Generalized stratigraphic section showing known karst features in sedimentary rocks in the Black Hills, South Dakota-Wyoming. Numbers indicate formations visited during the formal conference. Underlined numbers indicate stops in the supplementary western field trip.

stone plateau, underlain by a variety of Pennsylvanian and Permian rocks. Modified from Strahler and Strahler (1987) with permission.

PALEOZOIC	PERMIAN	Up.	Opeche Shale	Red shale, siltstone, and fine-grained sandstone and scattered gypsum (25-150)	Possible minor dissolution of gypsum	10
		Lower	Minnelusa Formation	Yellow, red, cross-bedded sandstone, gray cherty limestone, dolomite, red shale and siltstone, and anhydrite in subsurface that is mostly absent at the surface due to dissolution. (350-1,500)	Intrastratal anhydrite karst in upper half; advancing dissolution front at depth; disrupted bedding, caves, collapse breccia; breccia pipes, some extending upwards as much as 1,000 feet into the Lakota Formation; paleokarst sinkhole fill at base.	1
	PENNSYLVANIAN	Upper				
	MISSISSIPPIAN	Lower	Pahasapa Limestone (Madison Limestone)	Massive, gray limestone that is locally dolomitic, with an irregular upper contact due to pre-Pennsylvanian karst weathering. (300-630)	Carbonate karst: world-class caves in upper part; swallow holes; resurgent springs; sinking streams; paleokarst; few surface sinkholes, if any.	5, 6, 7 Evening Cave Trips to Wind and Jewel Caves
		Upper	Englewood Formation	Gray to lavender limestone with shale at base (30-60)		
	DEVONIAN	Upper	Whitewood Formation	Gray dolomite and limestone (0-150)		
		Lower	Winnipeg Formation	Green shale and siltstone (0-110)		
	ORDOVICIAN	Upper	Deadwood Formation	Brown sandstone, green glauconitic shale, basal conglomerate and limestone-pebble conglomerate (4-700)		
		Lower				
	CAMBRIAN	Middle				
PRECAMBRIAN			Precambrian rocks	Schist, slate, quartzite, sandstone, intruded by amphibolite, granite, and pegmatite.		

Figure 2. Generalized stratigraphic section showing known karst features in sedimentary rocks in the Black Hills, South Dakota-Wyoming. Numbers indicate formations visited during the formal conference. Underlined numbers indicate stops in the supplementary western field trip -continued.

Two major aquifers are located in formations that include karstic rocks water in the Black Hills--carbonate karst in the Pahasapa Limestone, and evaporite karst in the Minnelusa formation. The Madison and Minnelusa aquifers are two of the most important aquifers in the Black Hills area and are used extensively for water supplies. Headwater springs originating in the limestone plateau, streamflow losses to the Madison and Minnelusa outcrops, and large artesian springs in the Red Valley are important hydrologic features that are associated with karst processes in these aquifers. Locally, secondary porosity has developed in the lower Spearfish formation due to gypsum dissolution. Sinkhole collapse in gypsum-bearing rocks is common. Sinkholes, of the type's common in the eastern United States are rare. Solution in carbonate rocks has produced the third and sixth largest known recreation caves in the world, Jewel Cave and Wind Cave. A sinkhole in Hot Springs is one of the world's greatest vertebrate paleontologic occurrences. Finally, carbonate rocks are the major aggregate resource in the Black Hills.

Three field trips are offered this year. They are not duplicative; each stop has something different to offer, demonstrating the wide variety of evaporite and carbonate karst in the Black Hills. The trip in the Southern Black Hills will examine evaporite karst in the Minnelusa Formation, artesian springs due to both carbonate and evaporite dissolution at depth, sinkholes and fracturing in the Minnekahta raising the question of the definition of karst, a large sinkhole that trapped Pleistocene animals, and a visit to Wind Cave. The northern trip will discuss dye tracing in carbonate rocks, hydrology in Spearfish Canyon that made the famous Black Hills gold mining possible, a variety of collapse features and gypsum intrusion in the lower Spearfish Formation creating a strong secondary porosity, effects of leaching in the Minnekahta, and a proposed sewage lagoon in a precarious area of evaporite karst. A third trip to the western Black Hills is offered for those wishing to do it on their own. Highlights are an overlook of the steeply dipping rocks in flatirons in a major monocline, a sinkhole in non-soluble rocks extending more than 800 feet down to the source of collapse, the most spectacular cliff exposure of caves, sinkholes, brecciation, and disrupted bedding in the Minnelusa formation, and a trip to Jewel Cave. Two guided evening trips are also planned to Jewel and Wind Caves.

Each field trip guide not only has detailed information for driving instructions and text for each stop, but also, provides comments about sites to see from the vehicle window and the text of historic markers and plaques along the way. The total miles and miles between driving directions, comments, markers, and stops have been noted on each field trip guide.

Parts of the field guide itineraries were borrowed freely from many excellent published guides to the Black Hills (Fahrenbach and Fox, 1996; Gries, 1996; Lisenbee and others, 1996; Martin and others, 1996; Rahn and others, 1977; Rahn and Davis, 1996; Redden and Fahrenbach, 1996). Additional sources of information about the Black Hills or engineering geology are found in Darton (1909) and Rahn (1986).

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