

## **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 ft<sup>3</sup>/sec for Spring Creek and 50 ft<sup>3</sup>/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.

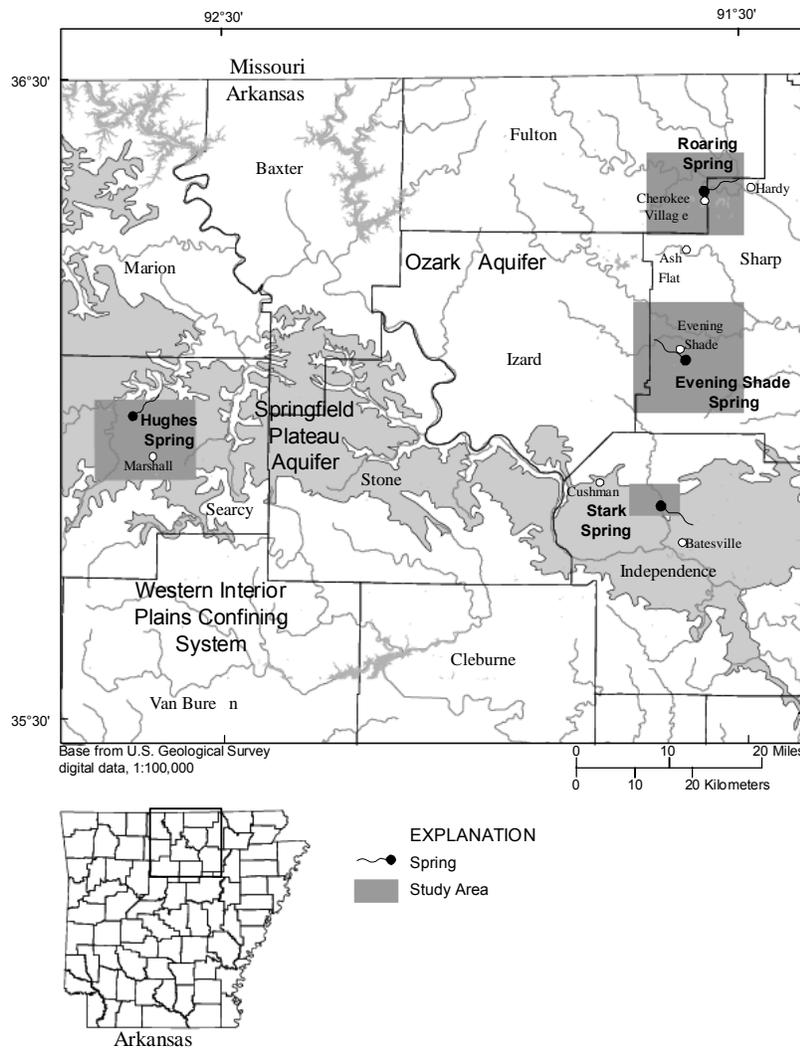


Figure 1. Location of springs and study areas.

## 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 Plattin 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 ( $\text{ft}^3/\text{s}$ ), respectively (Brossett and Evans, 2003). Mean daily discharge ranged from approximately 0.5 to 14  $\text{ft}^3/\text{s}$  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  $\text{ft}^3/\text{s}$ , respectively (Brossett and Evans, 2003). Mean daily discharge ranged from approximately 0.1 to 23  $\text{ft}^3/\text{s}$  for water year 2001 and from 0.1 to 49  $\text{ft}^3/\text{s}$  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

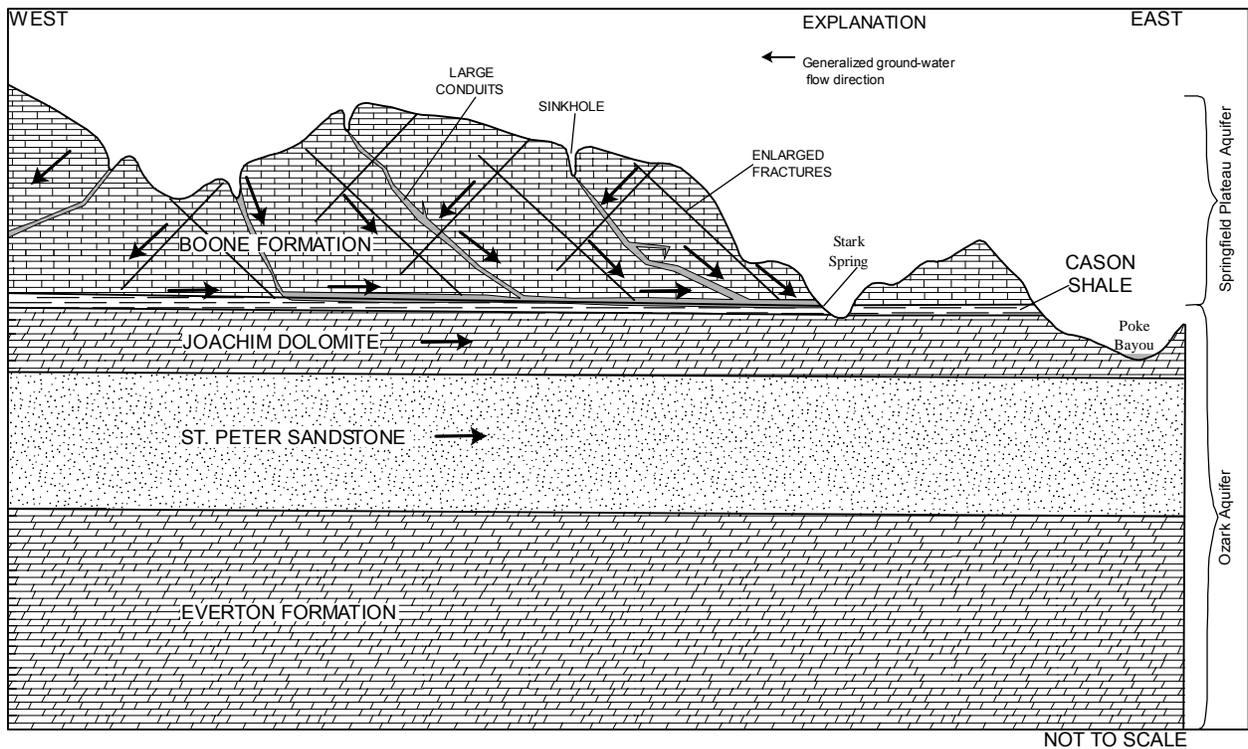
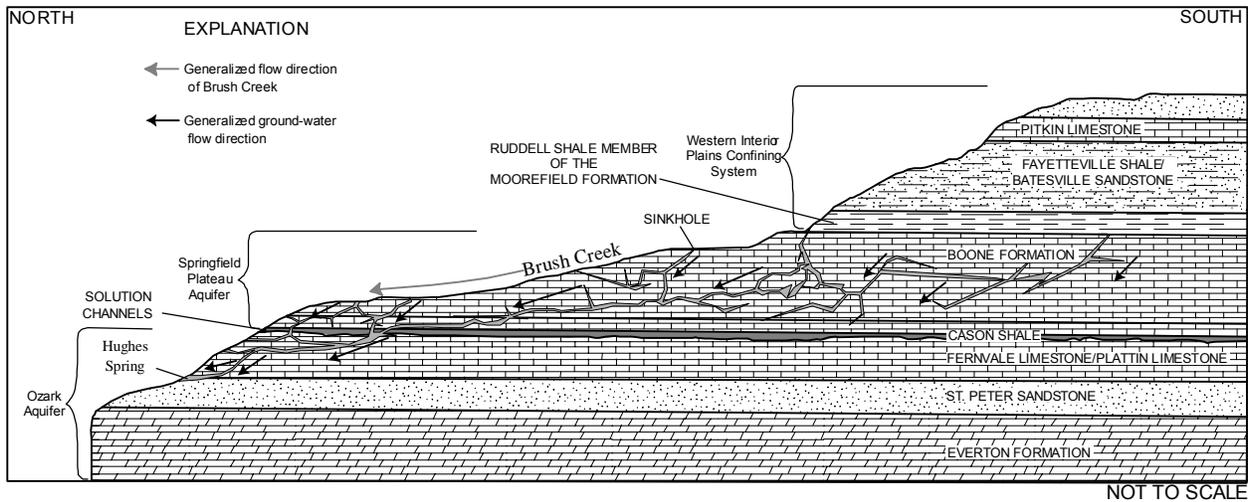


Figure 2. Conceptual model of ground-water flow to Hughes Spring and Stark Spring.

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.

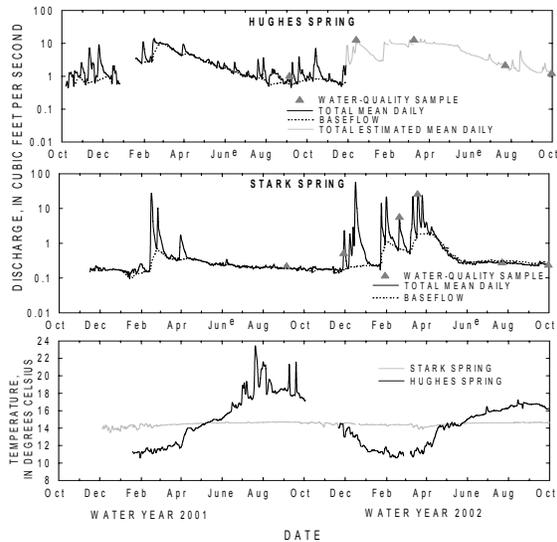


Figure 3. Daily discharge and water temperature recorded at Hughes Spring and Stark Spring.

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 ( $SI_{\text{calcite}}$ ) (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  $SI_{\text{calcite}}$  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 ( $\text{mi}^2$ ). 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 mi<sup>2</sup>. An average computed recharge area of 0.79 mi<sup>2</sup> 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).

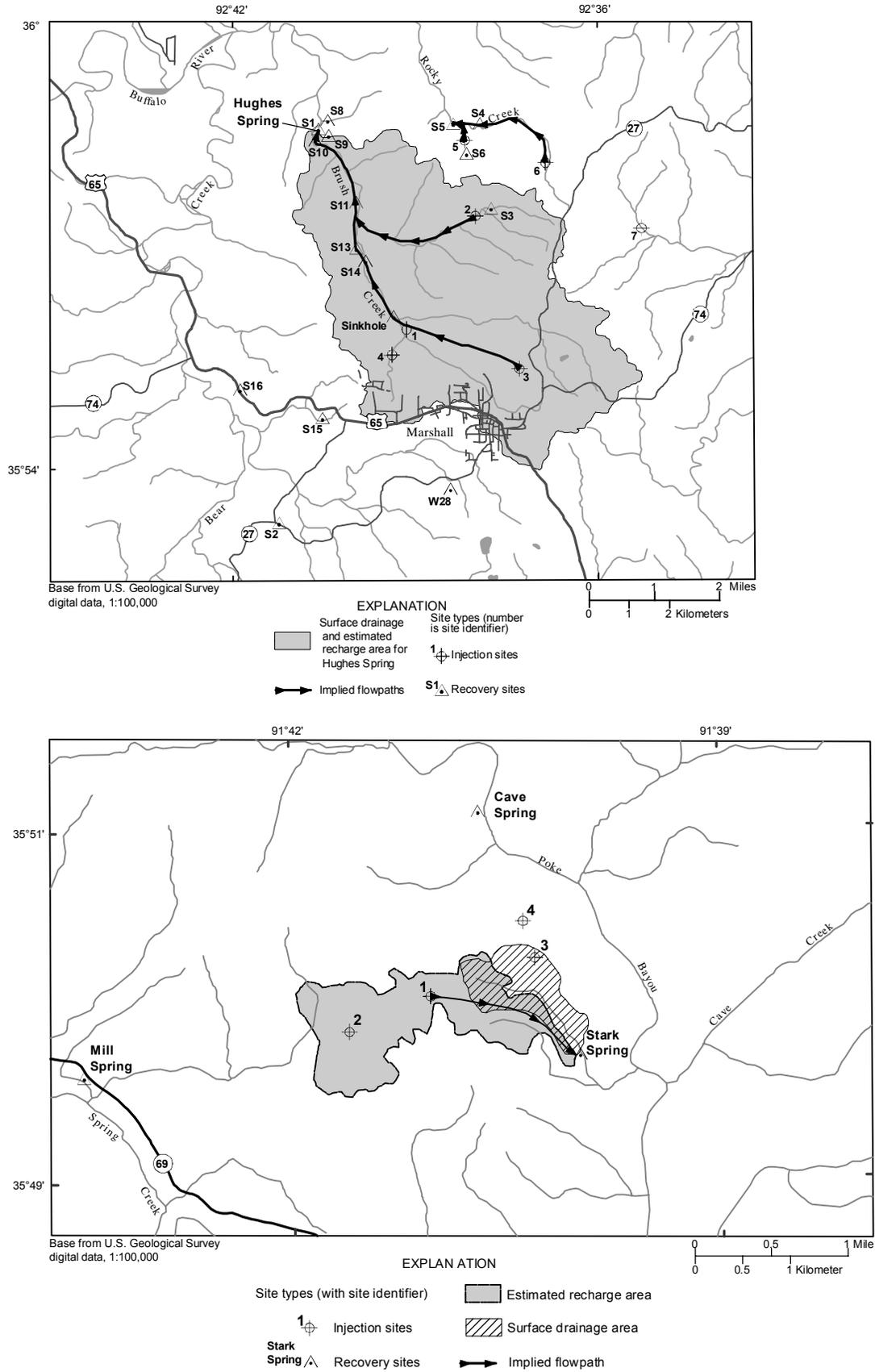


Figure 4. Locations of tracer injection and recovery sites with implied flowpaths of tracers and delineated recharge areas for Hughes and Stark Springs.

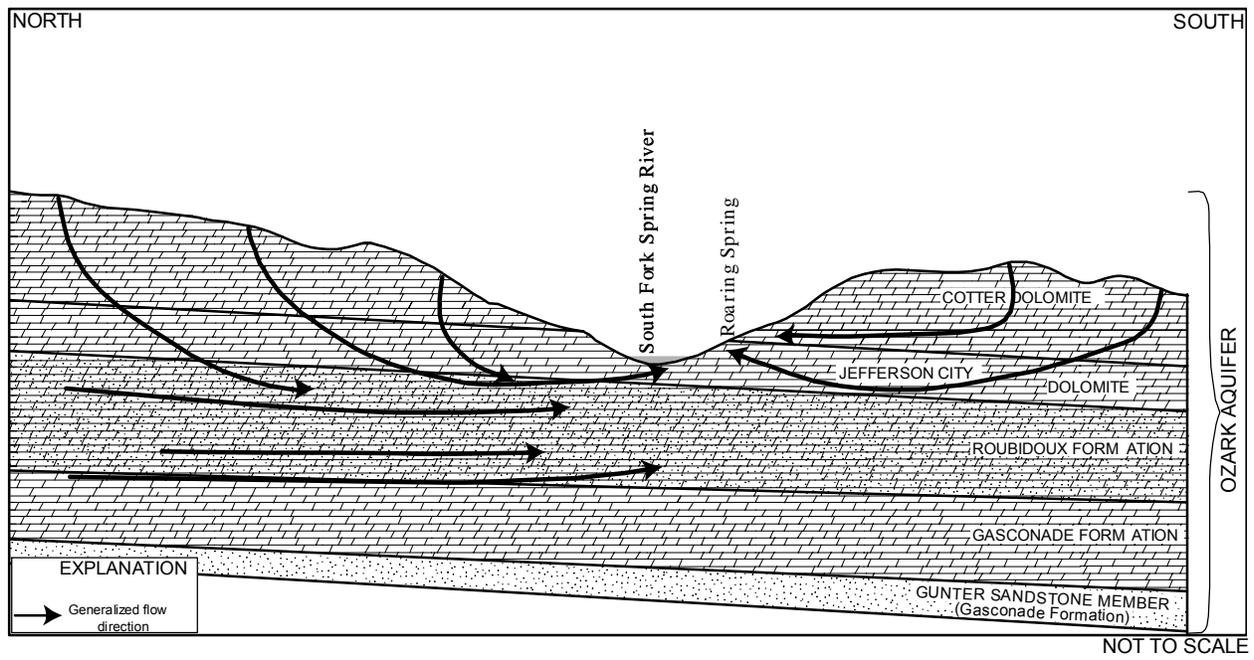
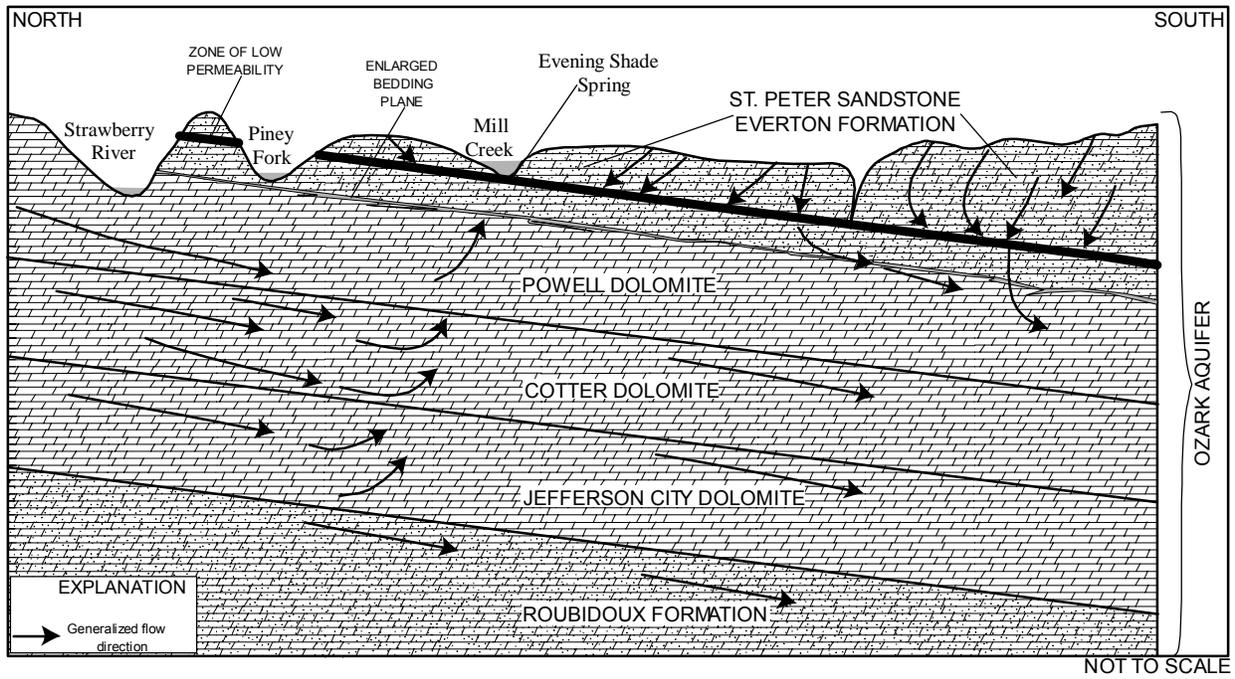


Figure 5. Conceptual model of ground-water flow to Evening Shade and Roaring Springs.

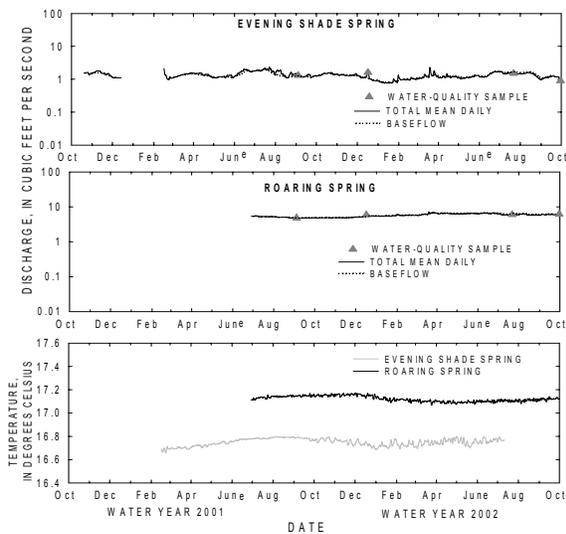


Figure 6. Daily discharge and water temperature recorded at Evening Shade Spring and Roaring Spring.

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 ft<sup>3</sup>/s for water year 2001 and from 0.76 to 2.25 ft<sup>3</sup>/s for water year 2002 (fig. 6). The mean annual discharge for water years 2001 and 2002 was 1.44 and 1.24 ft<sup>3</sup>/s, respectively (Brossett and Evans, 2003). The spring discharge periodically measured in the channel of Mill Creek ranged from 3.6 to 9.0 ft<sup>3</sup>/s during water years 2001 and 2002 (fig. 6). The mean daily discharge for Roaring Spring ranged from 4.8 to 7.2 ft<sup>3</sup>/s, and the mean discharge was 5.7 ft<sup>3</sup>/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.  $SI_{\text{calcite}}$  values from samples collected at Evening Shade Spring and Roaring Spring showed the waters are supersaturated with calcite. Values for  $SI_{\text{calcite}}$  appeared to have an inverse relation with the quantity of discharge at the time the sample was collected. At higher discharges, the  $SI_{\text{calcite}}$  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 mi<sup>2</sup>) 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 mi<sup>2</sup>) is larger than the surface-drainage area (0.34 mi<sup>2</sup>). 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 ( $\mu\text{g/L}$ ) 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,  $\Delta t$ , is so small, the  $C(t)$  is essentially constant. Therefore, the amount of the tracer ( $\Delta M$ ) 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 ( $\sigma^2$ ) 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  $\sigma^2$  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  $\tau$  (space-time) in the above equations as an unknown and first calculating  $P_e$  based on the experimental RTD and then calculating for  $\tau$  ( $\tau = V/u$ ) (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:

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

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:

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

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<sup>®</sup> 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  $\text{H}_2\text{O}_2$ . 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  $\text{H}_2\text{O}_2$  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

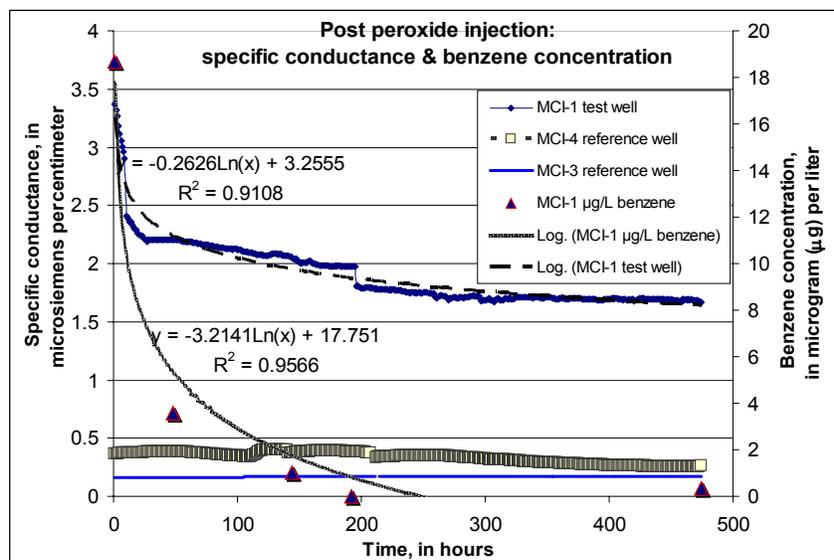
A known amount of NaCl was dissolved in 100 gallons of water and injected as a single pulse, displacing an equal volume of water surrounding the injection well. A correlation between the NaCl concentration and the specific conductance was established. Thus, specific conductance data provided a measure 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  $\text{H}_2\text{O}_2$  injection (data not shown). The dissolved oxygen declined slowly over a 6-week period.

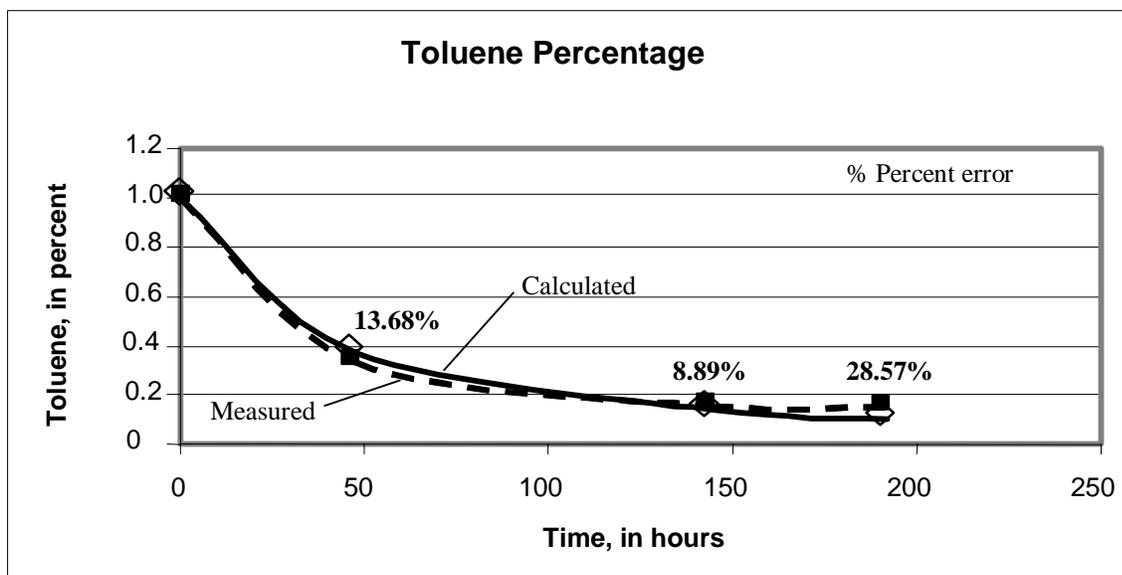
A comparison of the RTD-biodegradation model predictions and measured field concentrations for toluene and benzene indicated close agreement between the two approaches (figs. 2 and 3). The graphs show the percentage of contaminants remaining in the water as calculated by the model and measured in the 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

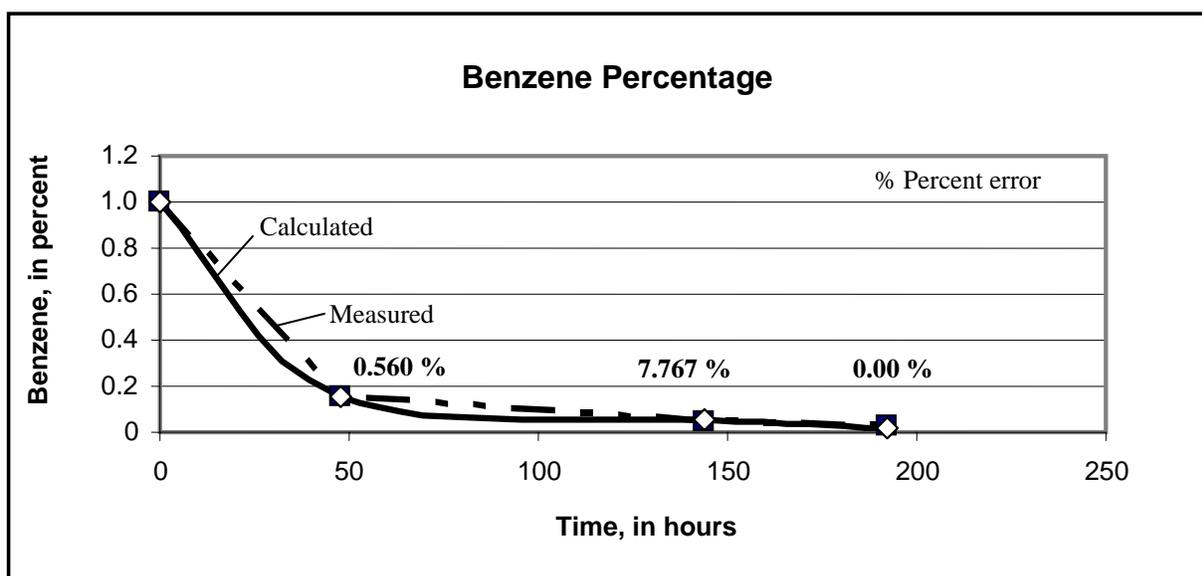
The concept that a karst aquifer is analogous to a non-ideal flow reactor was tested, as well as  $\text{H}_2\text{O}_2$ -enhanced fuel biodegradation. The results indicate that biodegradation was enhanced and the RTD-biodegradation model could be used to describe the process in a single well. This is 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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