

Quantification of Hydrologic Budget Parameters for the Vadose Zone and Epikarst in Mantled Karst

J. V. Brahana¹, Tiong Ee Ting², Mohammed Al-Qinna³, John F. Murdoch⁴, Ralph K. Davis¹, Jozef Laincz¹, Jonathan J. Killingbeck⁵, Eva Szilvagy⁶, Margaret Doheny-Skubic⁷, Indrajeet Chaubey⁴, P.D. Hays^{1,8}, and Greg Thoma²

¹Department of Geosciences, 113 Ozark, University of Arkansas, Fayetteville, AR 72701

²Department of Chemical Engineering, 3202 Bell, University of Arkansas, Fayetteville, AR 72701

³Faculty of Natural Resources and Environment, The Hashemite University, Zarqa 13115, Jordan

⁴Department of Biological and Agricultural Engineering, University of Arkansas, Fayetteville, AR 72701

⁵Department of Geology, Central Washington University, Ellensburg, Washington

⁶Department of Geology, Beloit College, 700 College St., Beloit, WI 53511

⁷Department of Geology, Carleton College, 300 N. College St., Northfield, MN 55057

⁸US Department of Agriculture, National Water Management Center, 44 Ozark, Fayetteville, AR 72701

ABSTRACT

Hydrologic studies at the Savoy Experimental Watershed initially focused on conduit-flow and transport in the karst aquifers that underlie the site. Recently, in the last two years, a new research focus has shifted to the shallower, more diffuse-flow pathways that contribute water to the fast-flow conduits. The extended residence time and exponentially-increased particle surface areas in the soil, regolith, and epikarst have been suspected to be active geochemical sites for microbe-soil-water-rock interaction. Preliminary chemical analyses indicate that the interface and interflow zones are indeed optimum locations for biogeochemical processing. To more fully document and provide needed data on fluxes, hydraulic parameters, and calibration quantities for numerical testing of hypotheses, an accurate characterization of hydrologic budget components within all aspects of the flow system was undertaken. This study briefly summarizes new infrastructure and presents preliminary results that have helped refine a coherent, integrated conceptual model.

INTRODUCTION

The Savoy Experimental Watershed (SEW) is a University of Arkansas property that encompasses about 1250 hectares typical of the karst terrane of the Ozark Plateaus of the mid-continent (Brahana et al., 1998). It is a long-term hydrologic research site that provides an opportunity to investigate processes of flow and contaminant fate and transport *in situ* at a well-characterized and well-instrumented site.

The surface-water/ground-water interface and the interflow zones in the vadose region in the southern part of Basin 1 (fig. 1) of SEW currently is an area of intensive hydrologic instrumentation and infrastructure buildup. A multidisciplinary research team of hydrogeologists, biologists, soil scientists,

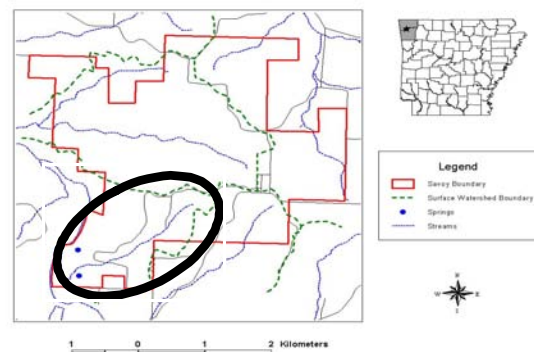


Figure 1. Basin 1 (ellipse), in Savoy Experimental Watershed.

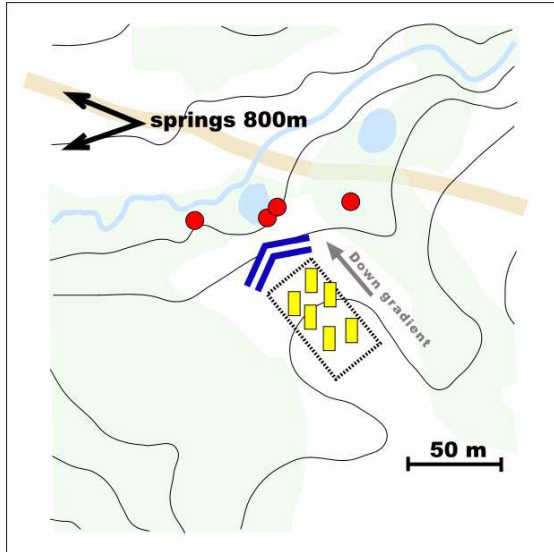


Figure 2. Vadose zone and epikarst research area showing geometry of infrastructure in Basin 1. Circles are weirs at springs, parallel lines identify the trench, and rectangles represent field plots. Details of the infrastructure are shown in figure 3.

chemical engineers, biological and agricultural engineers, stable-isotope geochemists, ecologists, hydrologists, animal scientists, karst tracers, and crop scientists have installed a suite of instrumentation that includes: 4 tipping-bucket rain gages; a full weather station; 6 suction lysimeters in the soil zone (fig. 2); 5 epikarst wells; one deep well; one 2-meter deep sampling trench (figs. 2, 3, and 4); 36 v-notch weirs measuring surface runoff and sheet flow from test plots (figs. 3 and 5); 3 H-flumes which capture and collect surface runoff from storms; 5 v-notch weirs and 1 H-flume on perched springs which drain the study site, 3 of which that are monitored continuously for discharge and temperature (fig. 2); 2 v-notch weirs on an overflow/underflow spring system that underdrains the shallow flow system through conduits in the shallowest phreatic carbonate aquifer; and periodic continuous autosamplers at selected sites during selected transient flow conditions.

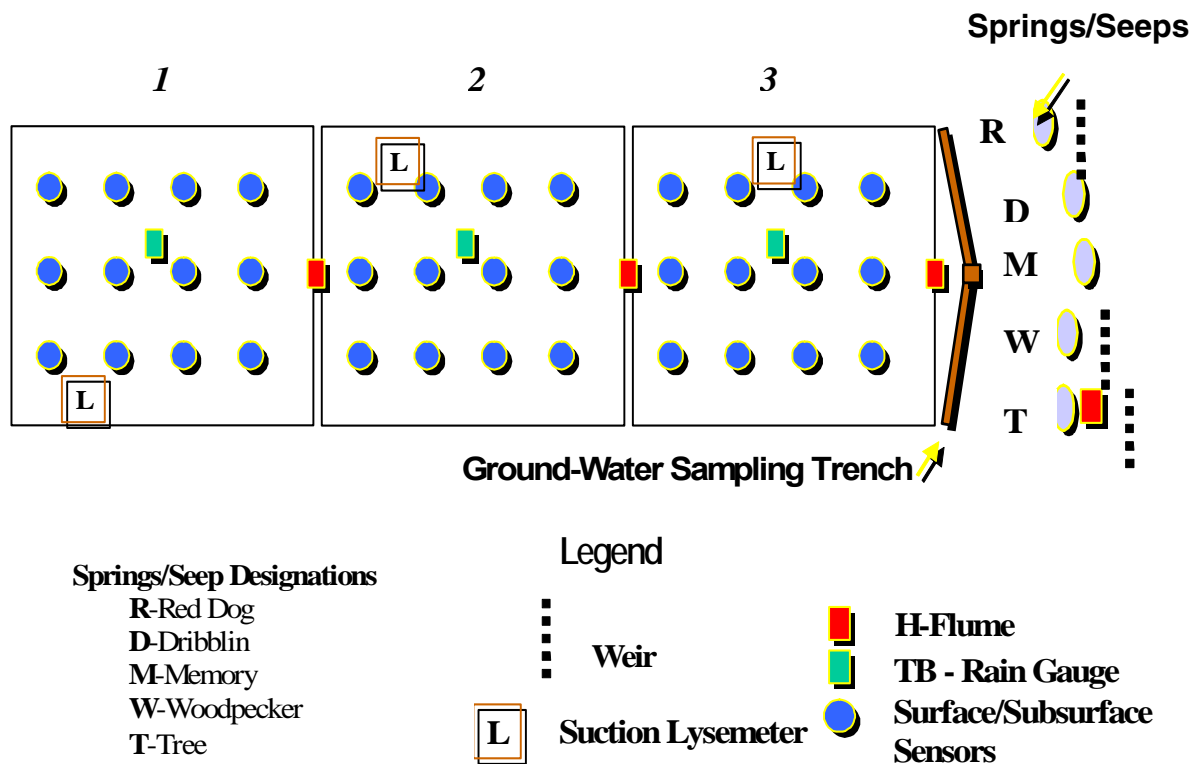


Figure 3. Numbered field plots of the vadose and epikarst research site. Note that the orientation of this figure has been rotated 120° clockwise from figure 2.

OBJECTIVES, METHODOLOGY, AND BACKGROUND

This report has two main objectives: 1) to provide a brief description of the type of infrastructure currently in place, including methodology, rationale, and expected accuracy; and 2) to synthesize data and make hydrologic interpretations based on those data. Inasmuch as space limitations preclude a detailed summary of results, information provided is not complete; the interested reader is directed to <http://www.uark.edu/depts/savoyres/index.html>.

Discharge at springs is determined by measuring the head in the pool behind 22.5° v-notch weirs. The stage-discharge data are represented theoretically by the equation:

$$Q = 274.4 H^{2.5} \quad (1)$$

where Q is discharge in liters per second, and H is head in meters above the bottom of the v-notch (Grant and Dawson, 1997). Below 0.06 meters, the stage discharge relation was determined empirically. Spring stage is monitored by transducers on a 5-minute interval, with an accuracy of 0.001 meter.

Precipitation is monitored by tipping-bucket rain gages, which are set to record increments (0.01 feet) of rainfall instantaneously. These are recorded with a time stamp, totalized every 5 minutes by the weather station, and recorded on digital data loggers powered by solar cells. Loggers also record other relevant digital data, and are periodically downloaded on approximately bi-weekly intervals.

Sensors attached to weirs measure the presence or absence of surface runoff during specific storms, and subsurface saturation sensors measure depth to soil saturation. There are 36 of each of these sensors; accuracy is 0.002 meters (m) for the surface runoff sensors, and about 0.050 m for the subsurface saturation sensors. Water level in wells is measured with pressure transducers, which have an accuracy of 0.001 meters. Total flow from each of the plots is measured by pressure transducers attached to stilling wells on H-flumes.



Figure 4. Redoximorphic and macropore features in the trench identify and provide access to preferred flow zones in the vadose zone above the epikarst.

The karst hydrogeology in SEW includes aquifers covered by a thin, rocky soil, and a variable thickness of regolith which mantles the bedrock (figs. 4 and 5). Below the regolith lies the Boone Formation, a layer of impure, cherty limestone of approximately 55 m thickness (Al-Rashidy, 1999). The Boone is widespread and is considered to be a karst-forming formation, but owing to its high concentration of insoluble chert and clay (as much as 70%) insoluble debris remaining from weathering mantles the surface of the carbonate rock and plugs voids in the developing conduits and bedding planes. The resulting overall karst nature of this formation typically is masked. Underneath the Boone Limestone is a relatively- pure, crystalline, chert-free St. Joe Limestone, about 6 m thick (Al-Rashidy, 1999). The St. Joe Formation is the predominant

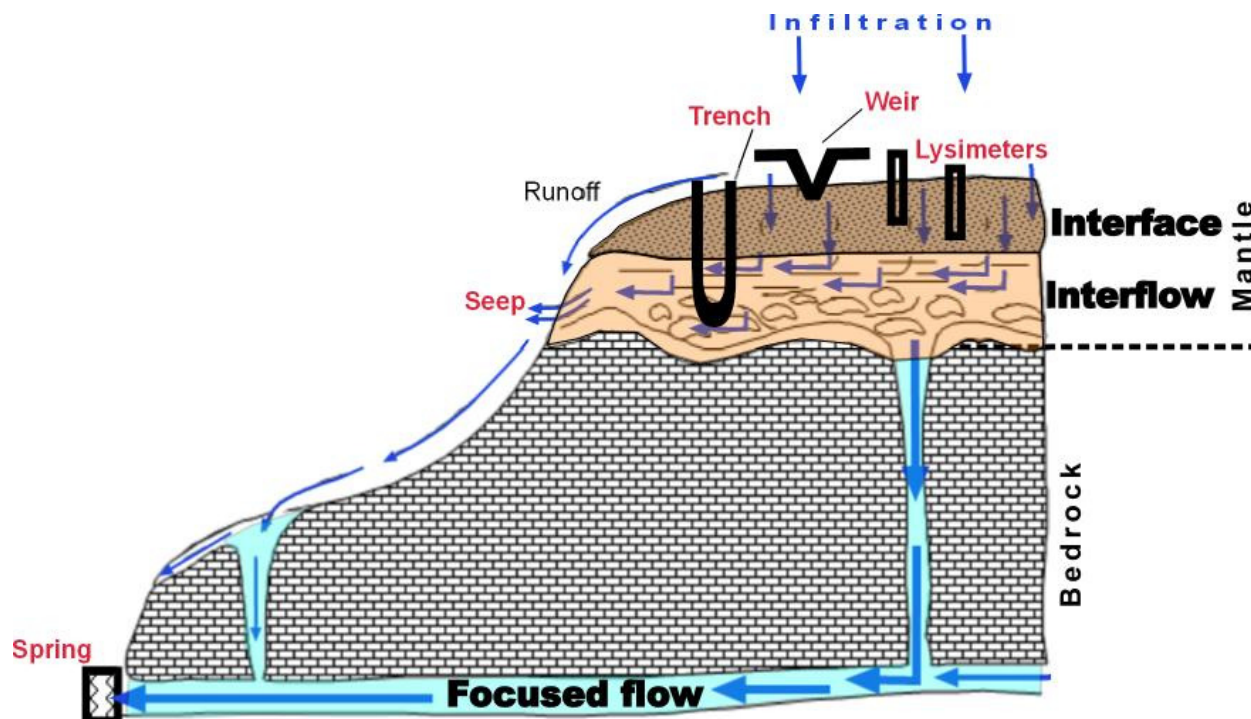


Figure 5. Schematic representation of environments in the shallow flow zone at the Savoy Experimental Watershed (figure modified from Laincz, 2005).

karst-forming unit in the area, and has most of the dominant zones in which the larger continuous springs, seeps, and caves occur. The ground-water flow in SEW and this part of the Ozarks is lithologically-controlled, with modification by structure (Brahana, 1997; Unger, 2004). The Chattanooga Shale (a black, relatively impermeable but highly fractured shale) forms the underlying impermeable boundary of the shallow carbonate aquifer at the SEW. The ground water flows westward and discharges directly into the nearby Illinois River, which flows on top of the Chattanooga Shale from the south to the north.

To explain the controlling influences of the aspects of the regolith and soil matrix, macropores, burrows, tubes, hardpans, and other permeability contrasts in the nonindurated vadose zone (fig. 4) and epikarst of Basin 1 in SEW, we described a simple geometric conceptual model of the subsurface conduit network systems comprising three important flow zones: 1) interface (soil zone); 2) interflow (lateral flow zone); and 3) focused-flow (conduit-flow zone) (fig. 5). Sampling infrastructure for each of the zones includes the following: 1) inter-

face—**weirs and flumes** (occasional; runoff rare); **lysimeters** (soil-water samplers; common for intense storms); 2) interflow—**interceptor trench** (occasional; intense storms); seeps and springs at the intersection of the perching layer and the land surface —**weirs and flumes** (continuous flow); and 3) focused flow—**weirs** (continuous springs issuing from limestone at the terminus of the ground-water basin).

The interface is well-established as a zone where biogeochemical processing occurs, and the zone of focused flow is known for minimal processing, whereas the interflow zone is poorly understood. It is thought to be important for geochemical processing, especially for constituents such as nitrates and dissolved organic carbon (Laincz, 2005). The instrumentation to assess flow and storage through these zones is therefore critical to understanding the hydrologic budget at this and similar sites, owing to a longer residence time for water, and increased opportunity for enhanced biological activity.

DISCUSSION

The measurement of interflow through the weirs at the seeps and springs (Tree, Woodpecker, and Red Dog) provides insight into a component of the hydrologic budget that is seldom quantified. For the period 15 July through 20 July 2005, measurements of discharge were made in early morning and mid- afternoon using a graduated cylinder and a stopwatch. Ten measurements were averaged for each data point shown on the graphs (fig. 6). All plots show a diurnal reduction in flow during the period of maximum solar radiation, reflected also in the transducer measurements at each weir. This loss of water from the shallow ground-water system is interpreted to be to evapotranspiration, and is on the order of 5 to 25 milliliters per second over the course of a diurnal cycle for each spring. The period of record is not long, owing to the recent installation of the weirs this past spring, but preliminary results reflect consistent and reproducible records using multiple tools, and provide confidence that the quantities are accurate and reflect actual conditions in the subsurface.

Another suite of data from the epikarst site shows transient variations in stage of the H-flume at Tree Spring, and water levels in 3 epikarst wells (fig. 7) within the field plots. Three transient storm pulses are reflected in the water-level records starting on Julian date 112 (21 April 2004), with an obvious lag in the first record from plot 3 (fig. 3), reflecting the furthest downgradient well. This lag in water-level increase is interpreted to be caused by dryer conditions in a downgradient direction. Water level in the downgradient well does not rise until deficient soil moisture in the plot has been accommodated, after which time the water-level responses are rapid and coincident with the wells in plots 1 and 2. The delayed response of the H-flume at Tree Spring is explained by unsaturated conditions along the flow path initially requiring saturation. Once achieved, subsequent spring stage rises are almost instantaneous with precipitation occurrence and with ground water increases in wells (fig. 7).

Physical and chemical water-quality parameters are valuable tools that also hold clues for understanding the complexities of flow in karst terranes

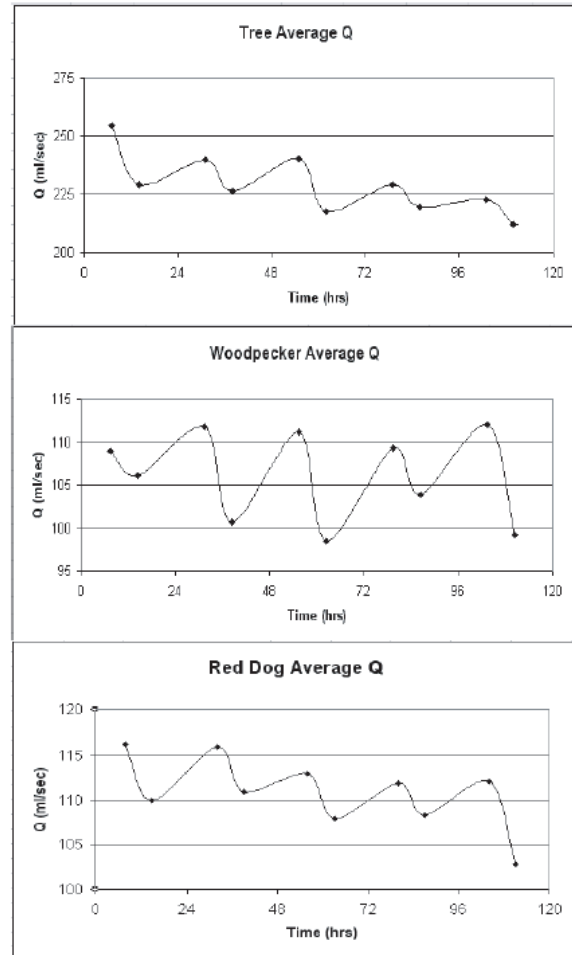


Figure 6. Diurnal variations in discharge (Q) in Tree, Woodpecker, and Red Dog Springs, interpreted to reflect increased transpiration during periods of maximum solar radiation. All springs are shallow and perched on chert in epikarst of lower 5 meters of the Boone Formation. 0 time is midnight, 15 July 2005.

(fig. 8). Continuous monitoring of two springs at the distal end of the ground-water flow path in Basin 1 provides an illustrative example. Langle Spring, the underflow part of the focused flow system, is about 3 centimeters lower than Copperhead, the overflow spring. During a 33-day period starting in December 1997, five major storms perturbed the stability of the temperature of these springs (fig. 8). These produced a general overall cooling in the discharge waters of Langle, although the trend was by no means linear or gradual. Water from Copperhead, on the other hand, showed both warming and cooling trends, numerous abrupt reversals in heating

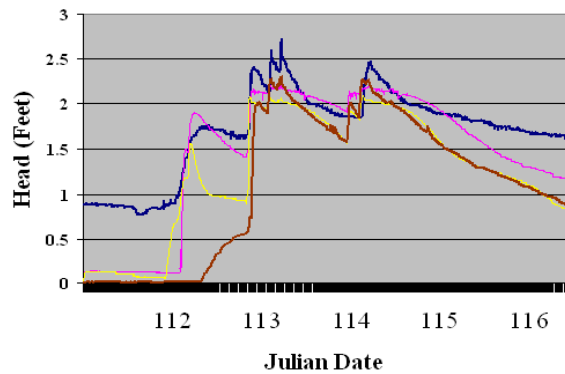


Figure 7. Transient variations in water levels in shallow wells in the epikarst research area and from continuously monitored stage in the H-flume at Tree Spring. Three storms are reflected in rapid water level rises in all records. Wells were constructed by augering to refusal in epikarst. Julian date 112 starts midnight, 21 April 2004; increasing dates are successive days of 24 hours.

and cooling, as well as many more fluctuations of about 1°C in the interval from December 13 through December 20. These diurnal variations were ultimately traced to a leaky, ephemeral surface pond that commonly stored water after periods of intense

rainfall. The pond was exposed to solar heating during clear weather following storms, and the heated water leaked into the karst aquifer and as it mixed with water from other sources, it imparted the diurnal thermal signature to Copperhead Spring. The signature was not obvious at Langle, owing to its much longer distance from the leaky pond.

The wider ranges of temperature in Copperhead Spring suggest that this part of the system is more open to surface water, and less thermally isolated than Langle. Cold water from the storm of 25 December obviously had an impact on the thermal regime of both springs, but the slope of the decrease at Langle supports the hypothesis that much of the water from the northern part of the spring system is more insulated from surface effects.

Near identical temperatures from the two springs on 8 December 1997 is interpreted to be caused by point-source input to each spring from fractures nearby the orifices. This effect is repeated on 25 December, and is thought to be a strong indication of the temperature of the precipitation at the time of coincident temperatures. Based on a preliminary assessment of all available data, the following

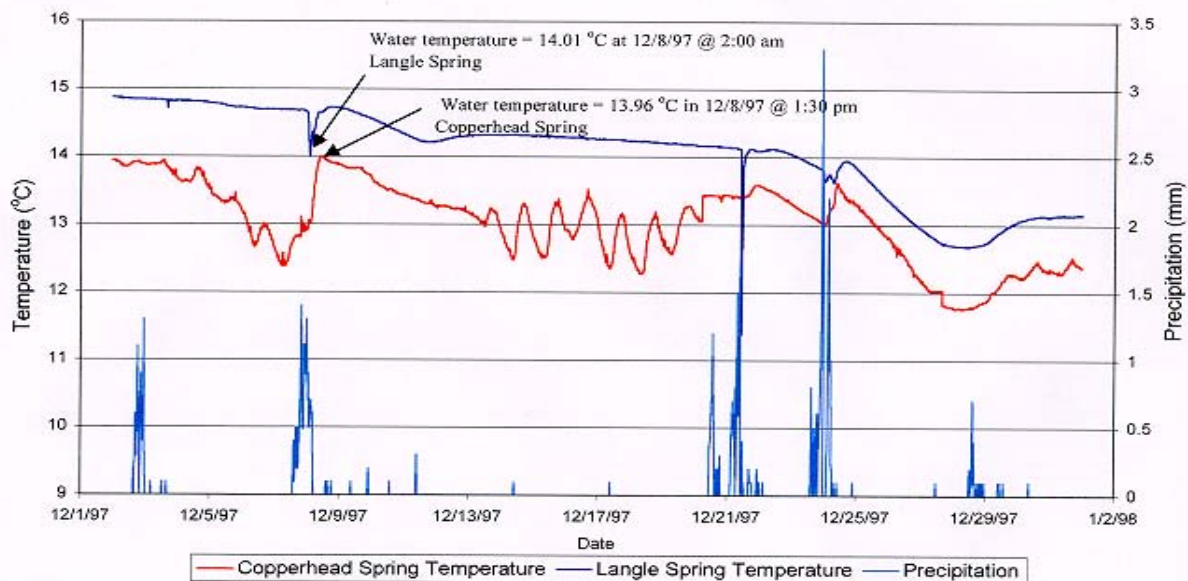


Figure 8. Temperature of two springs, Langle and Copperhead, that resurge from the St. Joe Limestone (focused flow, figure 4) at the distal end of the ground-water flow path in Basin 1. Comparing and contrasting the temperature variations in response to precipitation allows a detailed assessment of contributions to point sources of discharge in this indurated carbonate aquifer.

conceptual model is thought to describe the controlling influences of surface- and ground-water interaction within the SEW (fig. 9). Ground-water recharge (from precipitation) within SEW is distributed areally across the mantled aquifer, yet preliminary data suggest that runoff and recharge occur at discrete points. Lateral flow in the vadose zone, and temporal changes in directions of flow are a function of many factors which are highly variable, and can only be observed over long periods of observation that reflect the full range of hydrologic variability experienced at the site. Surface-water basins and ground-water basin boundaries do not coincide at SEW. This means that if a contaminant were spilled on the ground in one watershed, it may not necessarily show up in wells or springs in the same watershed; it may be “pirated” along unseen underground flow routes to discharge at another resurgence point. Permeability contrasts within the soil, at the soil-rock interface, and within the solid-rock aquifer concentrate flow and distribute it down gradient along the flow paths of least resistance. These preferred pathways are a reflection of many factors, and are a dominant control on the hydrology. Springs in Basin 1 represent the interception of flowpaths with

the land surface, and these range across a continuum of intermittent, infrequent flowing seeps that barely trickle to continuous springs that flow year-round. The epikarst developed on the Boone Formation, and the relatively-pure limestone of the St. Joe Formation represent the two most common zones in which continuous springs and seeps occur. Hydraulic gradients of the ground-water, which generally appear to follow the tilt (structural dip) of the rock formations, act independently (are decoupled) from surface-water bodies where confinement by chert layers in the Boone Formation is effective. This decoupling is also lithologically controlled, but in areas of faults and major joints, exhibits strong structural control. Stream piracy is one manifestation of combined lithologic and structural control that is obvious in Basin 1.

CONCLUSIONS

The wealth of karst understanding at SEW has benefited from long-term integrated research of a truly multidisciplinary flavor. Research projects have grown from basic descriptive studies of resource assessments to sophisticated

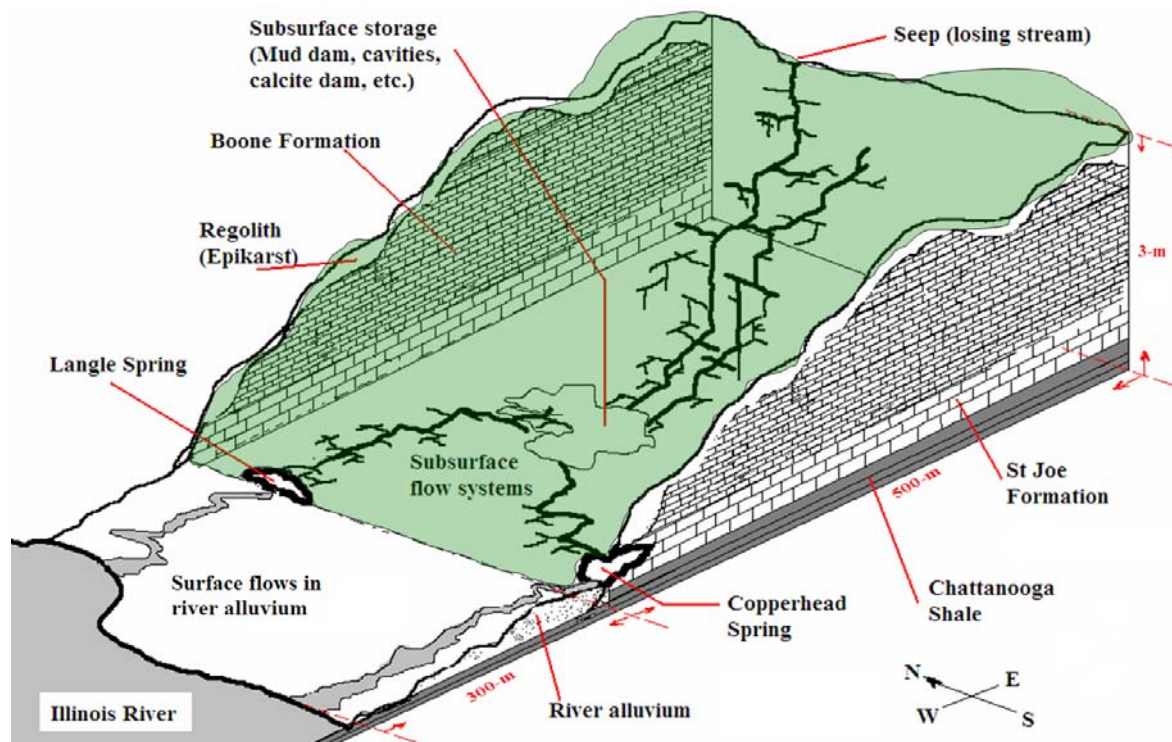


Figure 9. Conceptual model showing the relation between the karst flow components of Basin 1 in SEW (Ting, 2005).

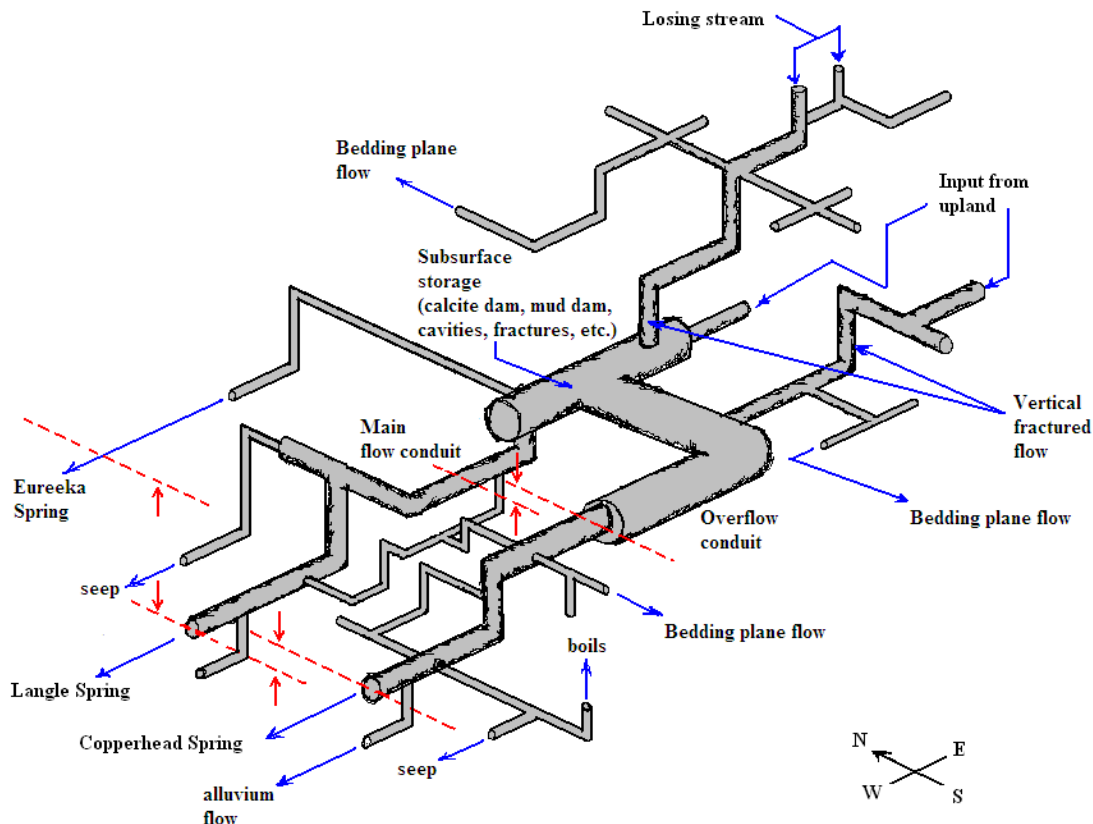


Figure 10. Proportional geometric model of the subsurface conduit network systems of Basin 1 in SEW. The storage unit is represented with a larger pipe in the conceptual conduit model, and is based on continuous flow data, tracing data, and long-term chemographs. (Ting, 2005)

process-oriented studies that cut across the boundaries of disciplines and draw from the community of many sciences. The conceptual models of flow have evolved from simple two-component mixing models to sophisticated three-dimensional models (fig. 10) that consider conservative and non-conservative constituents (Ting, 2005; Laincz, 2005; Al-Qinna, 2004). Numerical models of the site have been applied, and though not yet perfected, they provide insight and improving tools with which to test our hypotheses (Unger, 2004).

Hydrologic budget parameters are but one component of our recent emphasis, but such studies represent an essential part in gaining a thorough understanding of such complex systems. With our expanding infrastructure, burgeoning data bases, and our lengthening period of study, we feel that we are following the right path to finally get to solutions

that will allow us to provide meaningful answers to pressing land-use questions.

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Characterization of Nutrient Processing at the Field and Basin Scale in the Mantled Karst of the Savoy Experimental Watershed, Arkansas

By Jozef Laincz¹, P.D. Hays^{2,3}, Sue Ziegler⁴, Byron Winston⁴, J.F. Murdoch⁵, J.V. Brahana², K.F. Steele², Indrajeet Chaubey⁵, and Ralph K. Davis²

¹Program of Environmental Dynamics, 113 Ozark, University of Arkansas, Fayetteville, AR 72701

²Department of Geosciences, 113 Ozark, University of Arkansas, Fayetteville, AR 72701

³US Department of Agriculture, National Water Management Center, 44 Ozark, Fayetteville, AR 72701

⁴Department of Biological Sciences, 528 Science and Engineering, University of Arkansas, Fayetteville, AR 72701

⁵Department of Biological and Agricultural Engineering, 203 Engineering, University of Arkansas, Fayetteville, AR 72701

ABSTRACT

Animal production and associated pasture application of animal manures in vulnerable karst regions poses a significant threat to water quality. Balanced nutrient application presupposes an understanding of biogeochemical processes and controls on nitrogen transport, transformation, and sequestration—an understanding that is not well evolved for karst.

Concentration and bioavailability of dissolved organic carbon, and karst hydrogeological compartments were investigated as important factors controlling nutrient cycling and transport. Additionally, concentration and isotopic composition of NO_3^- was used to determine the extent of denitrification and immobilization of nitrate.

The study incorporated sampling events during two hydrologic regimes, storm and base flow, to characterize three components of a shallow system of a karst watershed: (1) surface-water/ground-water interface (soil/regolith) zone, (2) interflow over permeability contrasts zone, and (3) focused flow zone. The first two are presumably the zones with increased biogeochemical processing of nutrients due to longer retention time and greater matrix/water ratios. The importance of the soil zone in nutrient utilization and immobilization is well established. Conversely, the minimal degree of nutrient processing that occurs in the focused flow zone in karst is also well documented; however, the amount of nutrient processing that may occur in the interflow zone in karst setting has not been studied. The potential for nutrient processing that may occur in the interflow zone is important because of the lack of processing in thin soils and the focused flow zones that typify karst.

Study results indicate that dilution of dissolved nutrient species and flow bypassing the soil zone through macropores are two important controls on nitrogen behavior. A key finding of the study is that the decrease of nitrate concentrations observed within the interflow zone is greater than can be ascribed to dilution, indicating that microbial processing of nitrate is an important occurrence. Hydrologic conditions dictate flow-paths and affect biogeochemical processing of nitrate.

Once the biogeochemical mechanisms proposed are completely elucidated, the impact of agricultural practices on the integrity of these zones, and the way the processes occurring within these zones can be capitalized upon for nutrient management can be tested.

Transport Potential of *Cryptosporidium parvum* Oocysts in a Drinking-Water, Karstic-Limestone Aquifer: What We Have Learned Using Oocyst-Sized Microspheres in a 100-m Convergent Tracer Test at Miami's Northwest Well Field

Ronald W. Harvey¹, Allen M. Shapiro², Robert A. Renken³, David W. Metge¹, Joseph N. Ryan⁴, Christina L. Osborn⁴, and Kevin J. Cunningham³

¹U.S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303

²U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, Virginia 20192

³U.S. Geological Survey, 9100 NW 36th St., Miami, FL 33178

⁴Dept. Civil, Environ., and Arch. Eng., University of Colorado, Boulder, Colorado 80309

ABSTRACT

Aquifers characterized by karstic limestone are highly vulnerable to contamination by pathogens, in part because their solution-enlarged conduits and fracture systems can result in rapid and significant preferential flow. Contamination by *Cryptosporidium parvum*, a waterborne pathogenic protist, is of particular concern in areas where shallow karstic systems also serve as the drinking water supply. The vulnerability of Miami's Northwest Well Field (NWWF) to contamination by *C. parvum* oocysts was assessed in a large-scale, forced-gradient (convergent) injection and recovery test. The field study involved simultaneous pulse introduction to the Biscayne Aquifer of a conservative tracer (SF₆, an inert gas) and a polydispersed suspension of oocyst-sized (2-5 μm, diameter) carboxylated polystyrene microspheres. Estimated fractional recoveries for the microspheres at a municipal supply well 100-m downgradient from the injection borehole were inversely related to microsphere diameter and ranged from 2.8% for the largest to 5.6% for the smallest size classes or from 4.7% - 9.3%, respectively, if corrected for the incomplete (~60%) cumulative recovery observed for SF₆ in the same field test. Results from flow-through column studies with NWWF limestone cores housed in a modified triaxial cell indicated that microsphere surrogates may underestimate the transport potential of oocysts in Biscayne Aquifer by 4-6 fold, in part because of the microspheres' more-reactive surface (more negative zeta potential) under the calcium, ionic strength, and very slightly alkaline conditions of the Biscayne Aquifer. Our study suggests that, although the karstic limestone within the Biscayne Aquifer appears to have a substantive sorptive capacity for oocysts, it may take more than two hundred meters of transport to ensure even a 1-log unit removal of oocysts in the vicinity of the NWWF, depending upon the local-scale heterogeneity and factoring in a reasonable margin of safety. Flow-through column studies involving intact limestone cores housed within a modified triaxial cell suggest that considerable spatial variation in the transport behavior of microspheres relative to a conservative tracer may be expected because of the spatial variations in limestone structure beneath the NWWF.

Ground-Water Quality Near a Swine Waste Lagoon in a Mantled Karst Terrane in Northwestern Arkansas

Christopher M. Hobza¹, David C. Moffit², Danny P. Goodwin³, Timothy Kresse⁴, John Fazio⁴, John V. Brahana⁵, and Phillip D. Hays¹

¹U.S. Geological Survey Arkansas Water Science Center, Fayetteville, AR

²Natural Resources Conservation Service National Water Management Center, Ft. Worth, TX

³Natural Resources Conservation Service National Water Management Center, Little Rock, AR

⁴Arkansas Department of Environmental Quality, Little Rock, AR

⁵University of Arkansas Department of Geosciences, Fayetteville, AR

ABSTRACT

Livestock production is generally the predominant agricultural practice in mantled karst terranes because the thin, rocky soils associated with carbonate bedrock are not conducive to crop production. Unfortunately, livestock production in karst areas can create environmental problems because of rapid, focused flow through soil and regolith. A study was conducted by the U.S. Geological Survey in cooperation with the Natural Resources Conservation Service National Water Management Center, the University of Arkansas, and the Arkansas Department of Environmental Quality to examine a swine waste storage lagoon in a mantled karst terrane at the University of Arkansas' Savoy Experimental Watershed to evaluate the effects of a swine waste lagoon on ground-water quality. The Savoy Experimental Watershed is a long-term, multi-disciplinary research site, which is approximately 1,250 hectares and encompasses parts of six drainage basins. An anaerobic swine waste lagoon was constructed at the Savoy Swine Facility in compliance with U.S. Department of Agriculture Natural Resources Conservation Service Conservation Waste Storage Practice Standard no. 313 in one of the drainage basins. An inventory of springs, seeps, sinkholes, and losing streams was conducted in the basin where the waste lagoon was constructed. Based on the inventory, nine shallow monitoring wells were augered to refusal in the regolith. Shallow ground-water from wells, springs, and an interceptor trench was sampled and analyzed for nutrients, major cations, and major anions during high-flow and low-flow conditions. Results from ground-water sampling indicate concentrations of chloride and nitrate were higher than concentrations from non-agricultural land-use areas in the Ozarks, but were comparable to concentrations near the site prior to the construction of the swine facility. A sample collected from an interceptor trench indicated that nutrients are able to pass through the clay liner. The results of an electromagnetic geophysical survey indicated that there were no preferred flow paths from the swine waste storage lagoon. Based on these results, it appears that the swine waste lagoon built using the Natural Resources Conservation Service Conservation Practice no. 313 is minimally affecting the ground-water quality of the area.

INTRODUCTION

Animal production in northwestern Arkansas is the predominant agricultural practice because the thin, rocky soils are unsuitable for sustainable crop production. Nationally, Arkansas ranks 2nd in broiler production, 16th in cattle, and 17th in swine production (U.S. Department of Agriculture, 2003). Animal waste generated from these agricultural operations typically is applied to local pastures, often in excess of nutrient requirements. These excess nutrients have little opportunity for natural attenuation in a mantled karst setting because of thin soils and underlying karst geology that allow rapid, focused flow resulting in contaminated ground and surface waters. Adamski (1987) compared nutrient concentrations in springs in an intensely farmed area with a minimally affected forested area and reported that the areas of intense livestock production had elevated concentrations of nitrate and chloride.

One potential source of ground-water contamination is from animal waste stored in anaerobic lagoons generated from confined animal feeding operations. These lagoon structures are designed to store animal waste for a specified time period until the waste is ready to be applied as liquid fertilizer to adjacent pastures or cropland. If not properly located, designed, constructed, and maintained, animal waste lagoons can adversely affect water quality through the introduction of excess nutrients and bacteria (Ham and DeSutter, 2000).

The Natural Resources Conservation Service (NRCS) has developed several Best Management Practices (BMPs) to reduce this risk of ground-water contamination. Waste Storage Practice no. 313 was created to allow producers to safely and effectively store animal waste while protecting ground-water resources in environmentally sensitive areas across a variety of hydrogeological environments (Natural Resources Conservation Service, 2003). Ideally, these structures are located in areas with thick soils, over deep or confined aquifers, and away from domestic water supplies. When this is not possible, the NRCS provides options that allow an additional measure of safety such as an impermeable geosynthetic membrane liner or a compacted liner con-

structed from native soil with a specific permeability.

This BMP has been successful in protecting ground-water resources in other hydrogeologic settings, (David Moffit, Natural Resources Conservation Service, oral commun., 2004) but its effectiveness has not been evaluated in areas with thin soils such as a mantled karst setting. To address this need, the U.S. Geological Survey in cooperation with the Natural Resources Conservation Service National Water Management Center, the University of Arkansas, and the Arkansas Department of Environmental Quality designed a study to determine the effectiveness of Waste Storage Practice no. 313 for storing swine waste in a mantled karst setting. The purpose of this report is to describe ground-water quality near the swine waste lagoon.

STUDY AREA

The Savoy Swine Facility is located within the Savoy Experimental Watershed (SEW) in northern Washington County in northwestern Arkansas (fig. 1). The SEW serves as a long-term, multi-disciplinary research site to examine water-quality problems associated with livestock production in a mantled karst setting. The SEW offers a unique opportunity to test and evaluate the environmental effects of different animal agricultural practices. In 2002 the University of Arkansas constructed the Savoy Swine Facility to improve planned large-scale swine production. The Savoy Swine Facility is managed as a demonstration farm to provide a long-term model for environmentally friendly management of animal nutrition, animal waste and odors (Maxwell and others, 2003).

The Savoy Swine Facility is located within the Springfield Plateau (Fenneman, 1938), which is underlain by nearly flat lying Mississippian-age cherty limestones and limestones. These sedimentary sequences have been incised by streams to form dendritic drainages and rolling hills. Karst features such as springs, sinkholes, losing streams, caves, and conduits are present in the study area (Little, 1999).

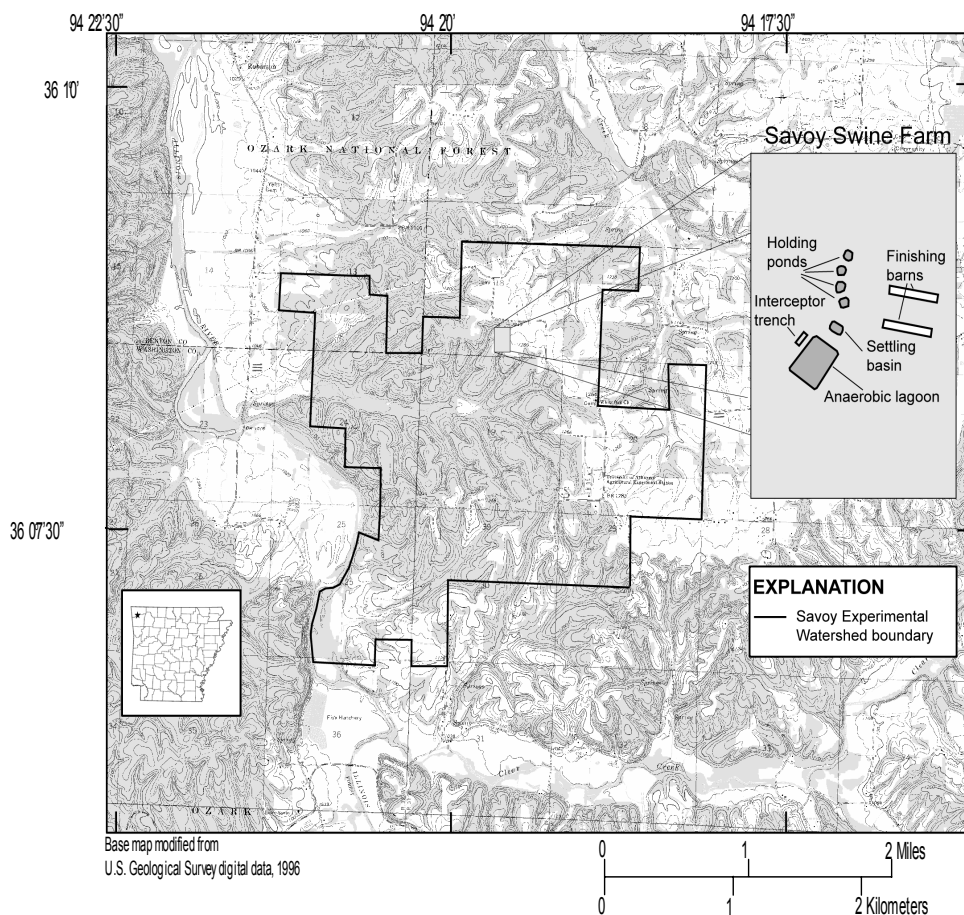


Figure 1. Location of the Savoy Swine Farm and diagram of waste storage infrastructure within the Savoy Experimental Watershed.

The major geologic units present in the study area are the Chattanooga Shale, the St. Joe Limestone Member of the Boone Formation, and the Boone Formation. The Chattanooga Shale is a black, Devonian-age shale that is approximately 45 feet thick within the SEW (Little, 1999) that unconformably underlies the St. Joe Limestone Member. The Chattanooga Shale acts as a regional confining unit where it is present in the Ozarks separating groundwater flow between the Mississippian-age limestones which compose the Springfield Plateau aquifer and the underlying Ordovician-age dolomites and sandstones which compose the Ozark aquifer (Imes and Emmett, 1994). The St. Joe Limestone Member, which is part of the Boone Formation is a relatively pure limestone, is conformably overlain by cherty limestone. The Boone Formation consists of Mississippian-age cherty limestones and is thickest beneath the uplands throughout the study area. The bedrock in the study area is overlain by regolith that is the weathering product of the cherty lime-

stone of the Boone Formation that creates the mantled karst topography. The soils formed from the regolith are composed of silt loams and the associated subsoils are silty clay loam or cherty silt loam (Harper and others, 1969).

The waste storage infrastructure at the Savoy Swine Facility was constructed in compliance with Waste Storage Practice no. 313 (Natural Resources Conservation Service, 2003). Because the swine facility was constructed over an unconfined limestone aquifer, more stringent design options were considered for the waste lagoon. The most economical solution was to construct a compacted clay liner from sieved native soil with a target coefficient of permeability of 1.0×10^{-7} centimeters per second (Stan Rose, Natural Resources Conservation Service, oral commun., 2004). Because of budget constraints during the construction, the Savoy Swine Facility is only able to house half the animals it was initially designed for. As a result the waste storage

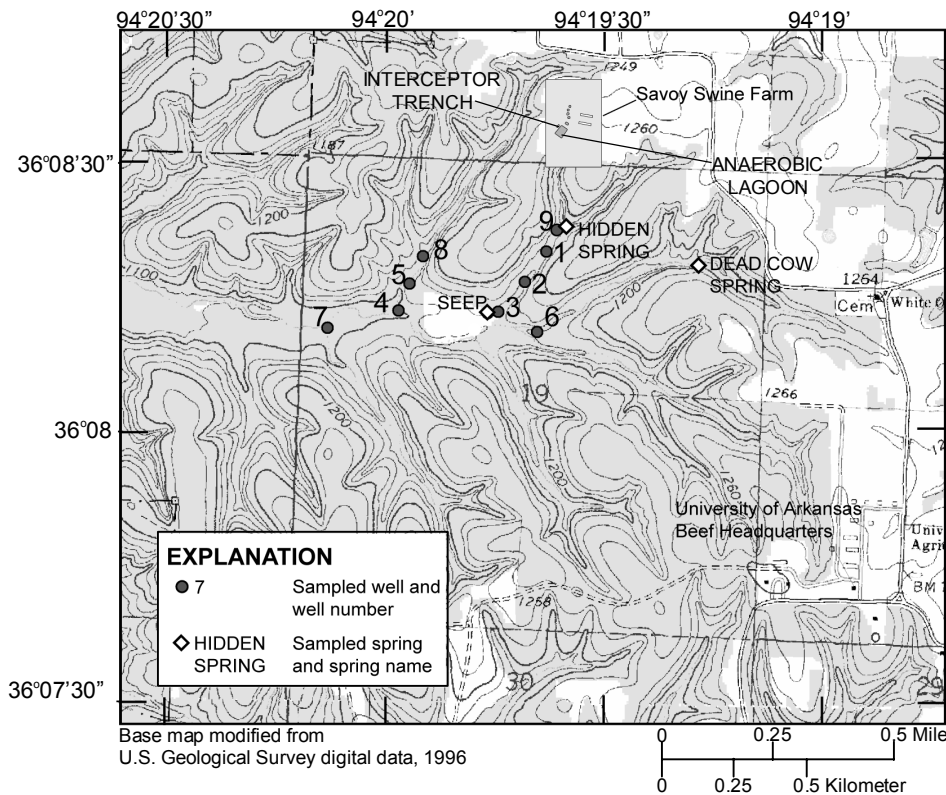


Figure 2. Location of water-quality sampling points within study area.

infrastructure is substantially oversized with respect to the number of animals served (Karl VanDevender, University of Arkansas, oral commun., 2004). The Savoy Swine Farm has a unique project-specific design constructed with four holding ponds each designed to store animal waste for a set of animals with a specific diet (fig. 1).

METHODS

A karst inventory was conducted in the area of the swine farm to gain a better understanding of the ground-water system prior to sampling point selection and well drilling. An inventory of springs, seeps, sinkholes, and losing and gaining reaches of streams was compiled. Nine shallow monitoring wells were augered to the depth of drilling refusal in the regolith. All wells were constructed with 2-inch polyvinyl chloride (PVC) casing and slotted PVC screen sections. A sand filter pack was installed surrounding the screened section with 2 feet of bentonite overlying the filter pack to prevent surface

contamination. An interceptor trench was installed west of the anaerobic lagoon on the swine farm and was excavated with a backhoe to the bedrock surface to allow collection of lagoon leachate moving down-gradient from the anaerobic lagoon after a storm event (fig. 1).

Sampling points consisted of monitoring wells, springs, seeps, and the interceptor trench. Water-quality samples were collected (fig. 2) during high-flow conditions in April 2004 and low-flow conditions in October 2004. The interceptor trench was sampled after one storm event on July 27, 2004. All samples were analyzed for nutrients including nitrate plus nitrite, ammonium, total Kjeldahl nitrogen, total phosphorus, and orthophosphate, major cations and major anions by the Arkansas Department of Environmental Quality (ADEQ) Water Quality Laboratory in Little Rock, Arkansas. Nitrate plus nitrite concentrations are reported as nitrate for this report because nitrate is the dominant form of nitrogen for this analyte. Fewer monitoring wells

were sampled during low-flow conditions because some of the wells were dry or did not yield water for sampling.

An electromagnetic geophysical survey was conducted near the waste storage infrastructure to determine any areas of preferential seepage from the lagoon and to assess the selection and placement of the sampling points. An EM-31 is a frequency domain electromagnetic instrument that is capable of determining subsurface conductivity (Geonics, 1984). Electromagnetic surveys have been successful in the past locating areas of preferred seepage from animal waste lagoons. Areas of lagoon seepage result in anomalously high subsurface conductivities compared to unaffected areas (Brune and Doolittle, 1990). Conductivity data were collected with a horizontal dipole instrument orientation providing an average depth of investigation of 6 meters. Global Positioning System (GPS) data and subsurface conductivity data were collected simultaneously. These data were plotted and contoured using the computer program Surfer (2002) for visual interpretation of results.

Table 1. Concentrations of nitrate and chloride for low-flow and high-flow sampling events

[Background concentrations of nitrate and chloride are from relatively pristine, forested areas of the Ozarks. Source sample collected from anaerobic lagoon]

Sampling point	High-flow sampling (concentrations in mg/L)			Low-flow sampling (concentrations in mg/L)			
	Date	Nitrate as N	Chloride	Date	Nitrate as N	Chloride	Ammonium as N
Well 1	4-12-04	1.08	14.8	-	-	-	-
Well 2	4-12-04	2.10	6.96	10-5-04	1.37	18.4	-
Well 3	4-12-04	1.23	9.97	10-5-04	1.07	18.9	-
Well 4	4-12-04	0.32	5.87	10-5-04	0.98	14.4	-
Well 5	4-12-04	0.46	3.95	-	-	-	-
Well 6	4-12-04	0.75	5.87	10-6-04	0.84	15.2	-
Well 7	4-12-04	0.27	3.95	10-6-04	0.99	14.1	-
Well 8	4-12-04	0.62	14.3	10-5-04	2.22	29.1	-
Well 9	4-12-04	1.99	12.9	-	-	-	-
Hidden Spring	4-12-04	2.39	11.5	10-5-04	3.41	30.2	-
Dead Cow Spring	-	-	-	10-5-04	2.59	19.8	-
Seep	4-12-04	1.32	8.90	10-5-04	1.15	16.0	-
Interceptor Trench	7-27-04	23.5	10.5	-	-	-	1.19
Anaerobic lagoon	6-13-05	-	-	6-13-05	0.44	462	40.0
Background ¹	-	0.5	5.0	-	-	-	-

¹ From Steele (1983)

GROUND-WATER QUALITY

Concentrations of nitrate and chloride for both high-flow and low-flow sampling events were above background concentrations, but were low compared to other areas in the Ozarks affected by livestock production (table 1). Background concentrations for nitrate plus nitrite in forested, relatively pristine areas of the Ozarks are typically less than 0.5 milligrams per liter (mg/L) as nitrogen (N) and 5.0 mg/L for chloride (Steele, 1983). Data collected in this study indicate that local livestock production probably is affecting the ground-water quality of the area. Concentrations of nitrate ranged from 0.27 to 2.39 mg/L as N during high-flow conditions and 0.84 to 3.41 mg/L as N during low-flow conditions. Chloride concentrations ranged from 3.95 to 14.8 mg/L during high-flow conditions and 14.1 to 30.2 mg/L during low-flow conditions. Concentrations of both nitrate and chloride were higher during the low-flow sampling event probably because of mixing and dilution that occurs during high-flow conditions.

These results were comparable to a previous study conducted prior to the construction of the Savoy Swine Facility. Little (1999) collected water-quality samples from springs, seeps, and wells proximal to the study area under high-flow and low-flow sampling conditions. Nitrate concentrations ranged from 0.06 to 4.64 mg/L as N and chloride concentrations ranged from 2.89 to 27.0 mg/L as N. The elevated concentrations suggest that the basin probably was affected by local livestock production prior to the construction of the Savoy Swine Facility. The highest concentrations of nitrate and chloride were detected near the University of Arkansas Beef Headquarters towards the eastern portion of the study area (fig. 2).

The results from the interceptor trench sample indicate that nitrogen is seeping through the anaerobic lagoon liner as ammonium with nitrification converting the ammonium into nitrate. The interceptor trench sample had concentrations of nitrate at 23.5 mg/L as N and ammonium concentrations at 1.19 mg/L as N. A water-quality sample was collected from the anaerobic lagoon on June 13, 2005. The form of nitrogen within the anaerobic lagoon is predominantly ammonium, with concentrations at 40.0 mg/L as N. Nitrate concentrations were 0.44 mg/L as N and chloride concentrations were 462 mg/L in the lagoon sample (table 1). The lagoon

leachate is probably mixing with other waters resulting in lower concentrations of nitrate and chloride in downgradient sampled wells and springs. Based on these ground-water quality data, the swine waste lagoon built using the Natural Resources Conservation Practice no. 313 is minimally affecting the ground-water quality of the area.

ELECTROMAGNETIC GEOPHYSICAL SURVEY

The results of the EM-31 survey did not identify any areas of preferential seepage from the holding ponds, settling basin, or anaerobic lagoon. Subsurface conductivities ranged from 0.6 to 21.0 millimhos per meter. It appears that most of the leakage is from the anaerobic lagoon and the leachate is migrating from the source in a fairly uniform pattern (fig. 3). There is very little leakage from the waste holding ponds and settling basin. This is probably because the animal waste stored in both the holding ponds and settling basin contains a much higher proportion of solid animal waste compared to the anaerobic lagoon. The solid waste is able to create a seal that decreases liner permeability (Natural Resources Conservation Service, 2003). Based on the results of the EM-31 survey it appears that the oversizing of the waste storage infrastructure is having a negative impact on the effectiveness of the anaerobic lagoon.

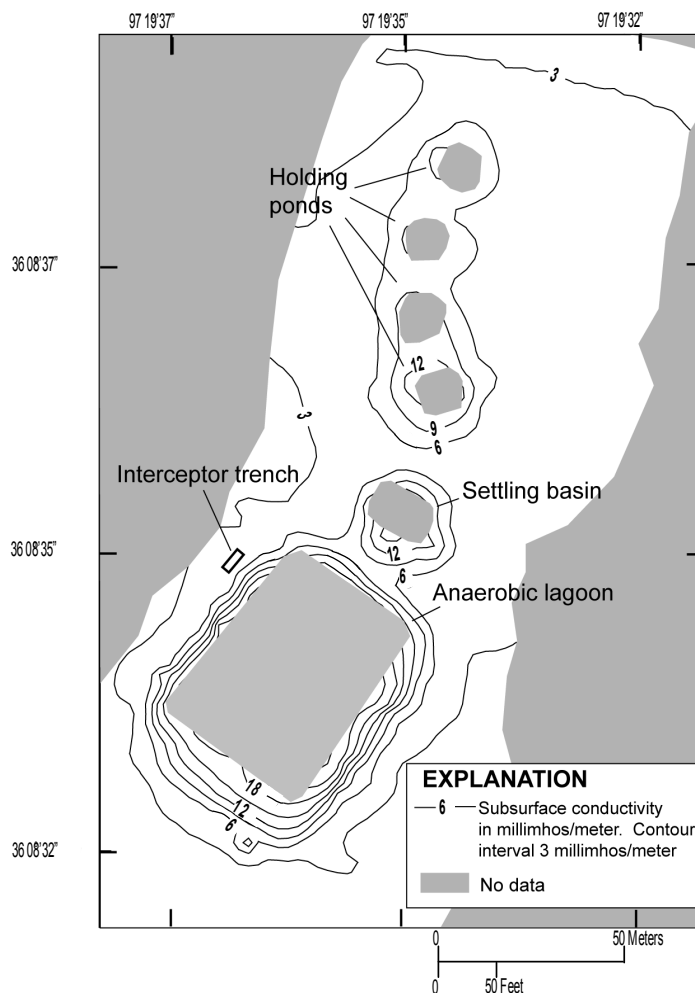


Figure 3. Results of EM-31 electromagnetic survey.

SUMMARY

A study was conducted to evaluate the effects of a swine waste lagoon on ground-water quality in a mantled karst terrane at the University of Arkansas' Savoy Experimental Watershed. An anaerobic swine waste lagoon was constructed at the Savoy Swine Facility in compliance with U.S. Department of Agriculture NRCS Conservation Waste Storage Practice Standard no. 313. An inventory of springs, seeps, and losing streams was conducted in the basin where the waste lagoon was constructed. Based on the inventory, sampling sites were selected and nine shallow monitoring wells were augered to the depth of drilling refusal in the regolith. Shallow ground-water from wells, springs and an interceptor trench was sampled for nutrients, major cations, and major anions during high-flow and low-flow conditions.

Data collected in this study indicate that the ground-water quality of the area is probably being affected by local livestock production. The concentrations of nitrate and chloride for both high-flow and low-flow sampling events were above background concentrations, but were low compared to other agriculturally affected areas in the Ozarks. Concentrations of nitrate plus nitrite ranged from 0.27 to 2.39 mg/L as N during high-flow conditions and 0.84 to 3.41 mg/L as N during low-flow conditions. Chloride concentrations ranged from 3.95 to 14.8 mg/L during high-flow conditions and 14.1 to 30.2 mg/L during low-flow conditions. Concentrations of both nitrate and chloride were higher during the low-flow sampling event probably because of mixing and dilution that occurs during high-flow conditions.

These results were comparable to a previous study conducted prior to the construction of the Savoy Swine Facility. Water-quality samples were collected from springs, seeps, and wells within near the study area under high-flow and low-flow sampling conditions. Nitrate concentrations ranged from 0.06 to 4.64 mg/L as N and chloride concentrations ranged from 2.89 to 27.0 mg/L. The elevated concentrations suggest that ground water in the basin has been affected by local livestock production prior to the construction of the Savoy Swine Facility.

A water-quality sample collected from an interceptor trench after a storm event on July 27, 2004 had concentrations of nitrate at 23.5 mg/L as N and dissolved ammonium concentrations at 1.19 mg/L as N. The results from the interceptor trench sample indicate that nitrogen is seeping through the anaerobic lagoon liner as ammonium with nitrification converting the ammonium into nitrate. The lagoon leachate probably is mixing with other waters resulting in lower concentrations of nitrate and chloride in downgradient sampled wells and springs.

The results of an electromagnetic geophysical survey identified no areas of preferred seepage from the holding ponds, settling basin, and anaerobic lagoon. Most of the leakage appears to be from the anaerobic lagoon and the leachate is migrating from the source in a fairly uniform pattern. Very little leakage from the waste holding ponds and settling basin occurs. This is probably because the animal waste stored in both the holding ponds and settling basin contains a much higher proportion of solid animal waste compared to the anaerobic lagoon. Based on these results, the swine waste lagoon built using the Natural Resources Conservation Service Conservation Practice no. 313 is minimally affecting the ground-water quality of the area.

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

By Scott L. Miller, Dr. Arden D. Davis, and Dr. Alvis L. Lisenbee

South Dakota School of Mines and Technology, Department of Geology and Geological Engineering, 501 East St. Joseph Street, Rapid City, SD 57701

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

By Joel M. Galloway

U.S. Geological Survey, 401 Hardin Road, Little Rock, AR 72211

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.

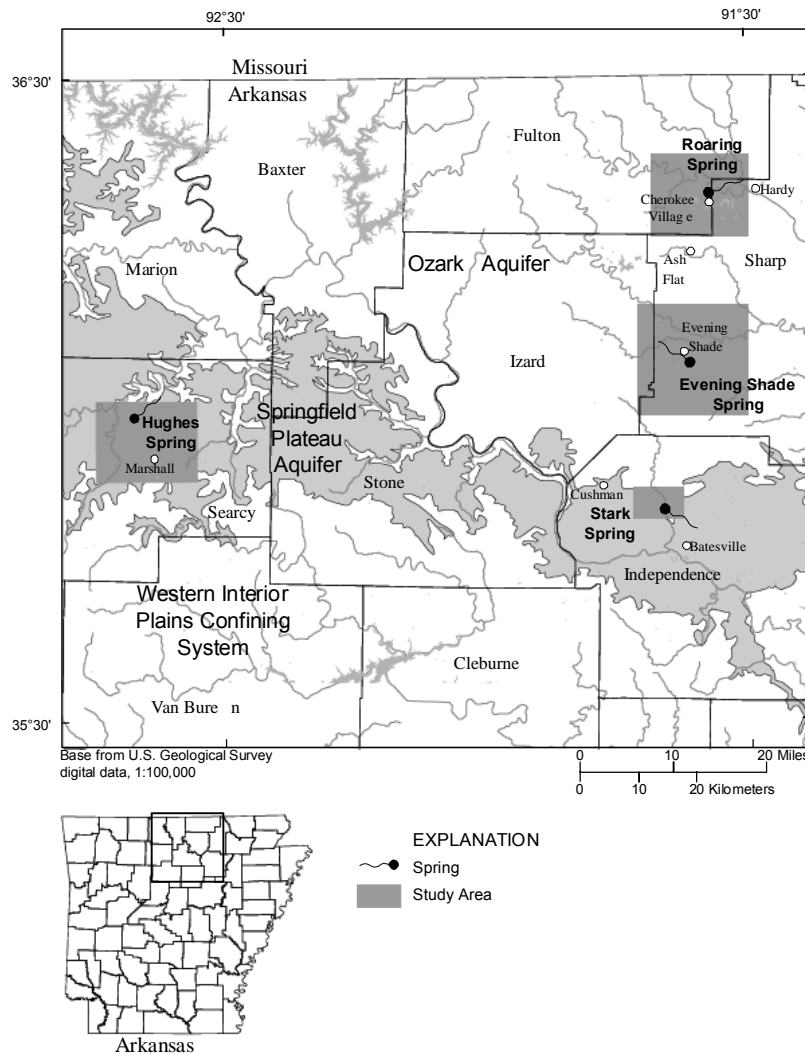


Figure 1. Location of springs and study areas.

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 (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

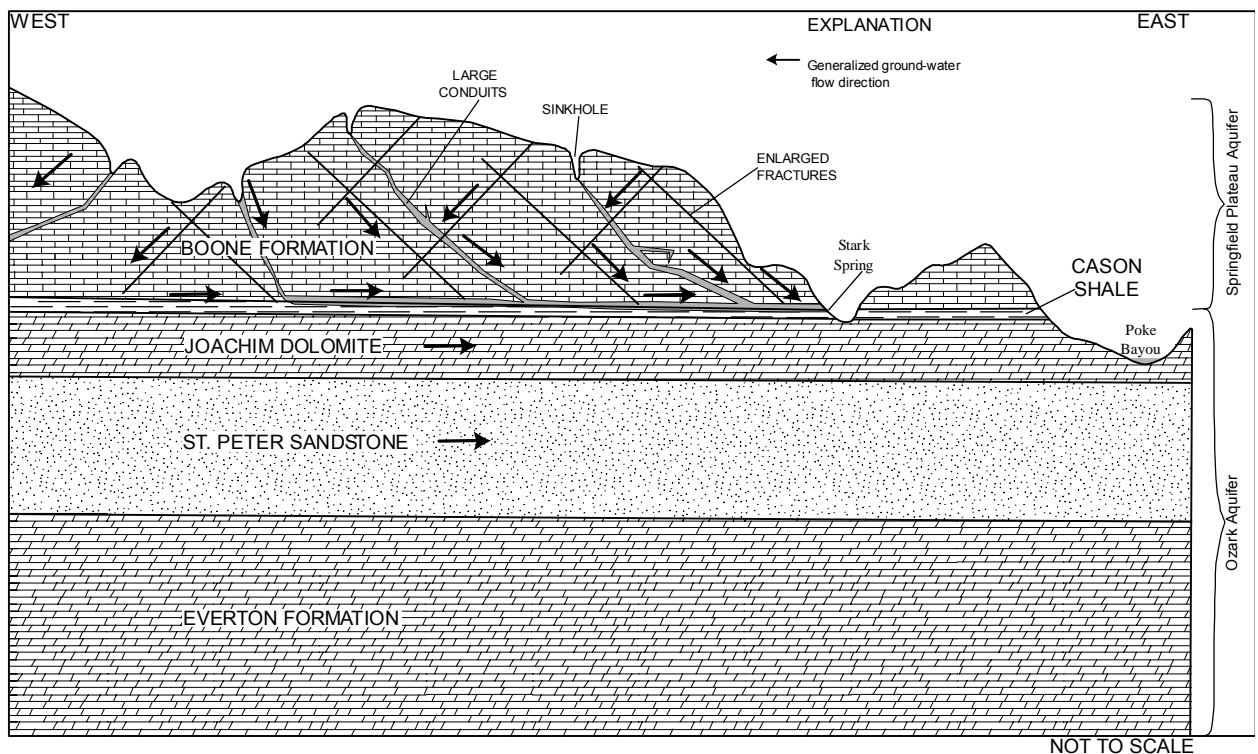
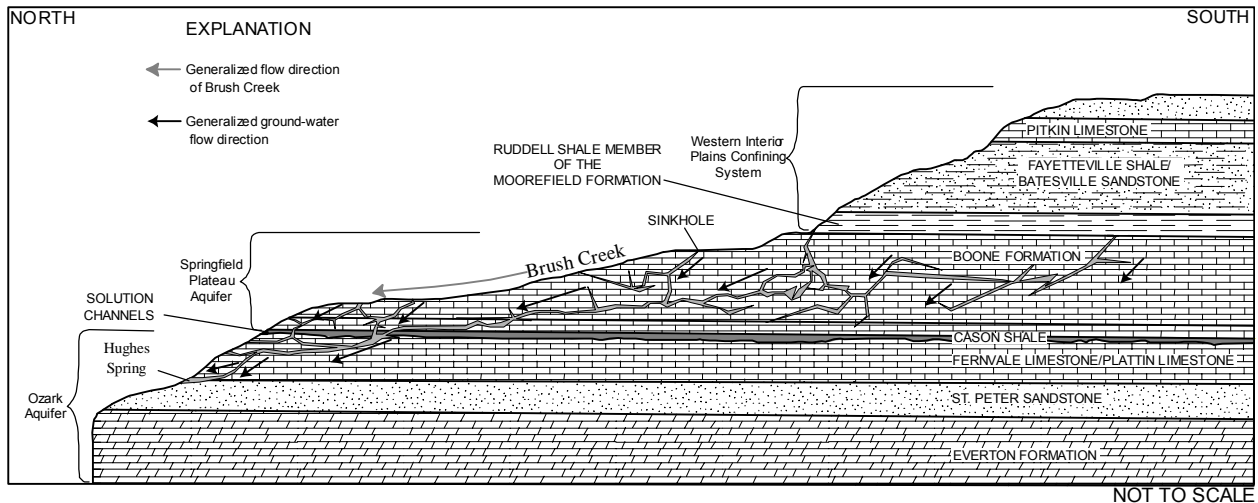


Figure 2. Conceptual model of ground-water flow to Hughes Spring and Stark Spring.

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.

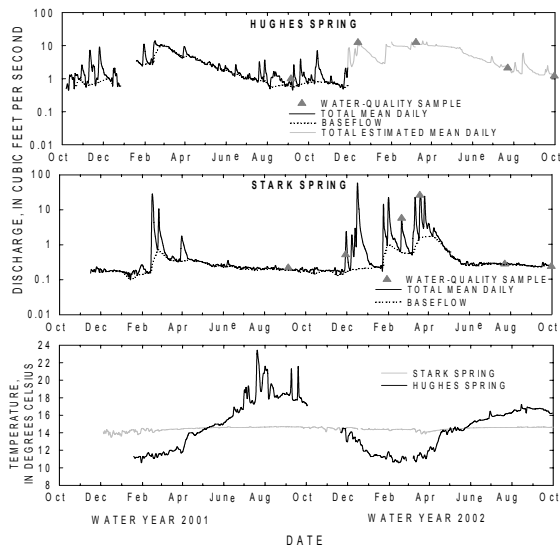


Figure 3. Daily discharge and water temperature recorded at Hughes Spring and Stark Spring.

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).

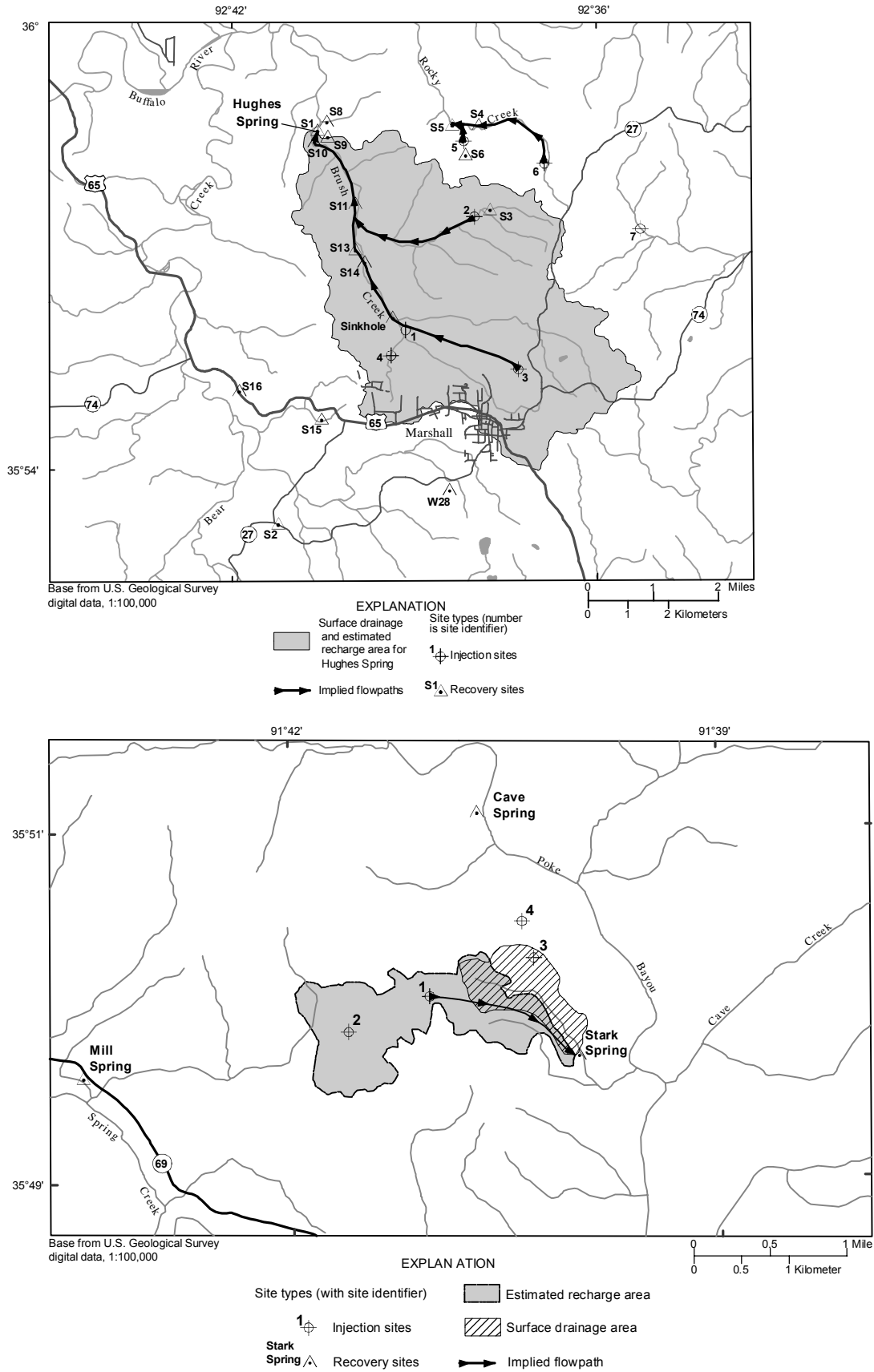


Figure 4. Locations of tracer injection and recovery sites with implied flowpaths of tracers and delineated recharge areas for Hughes and Stark Springs.

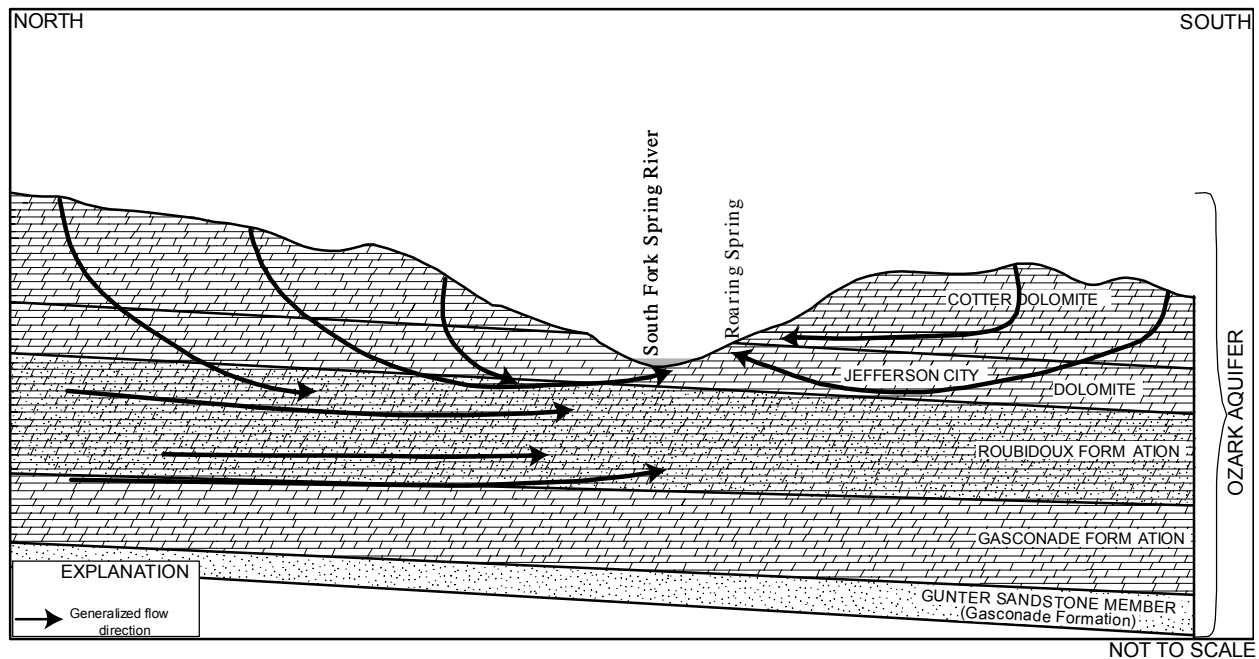
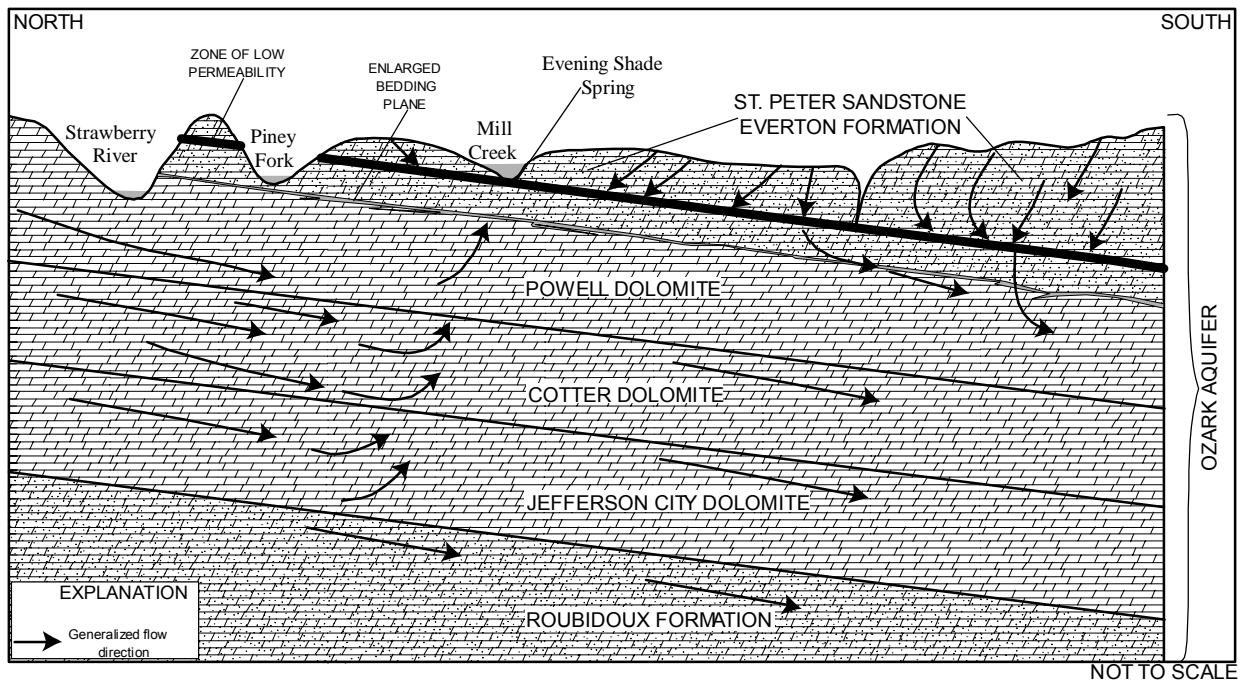


Figure 5. Conceptual model of ground-water flow to Evening Shade and Roaring Springs.

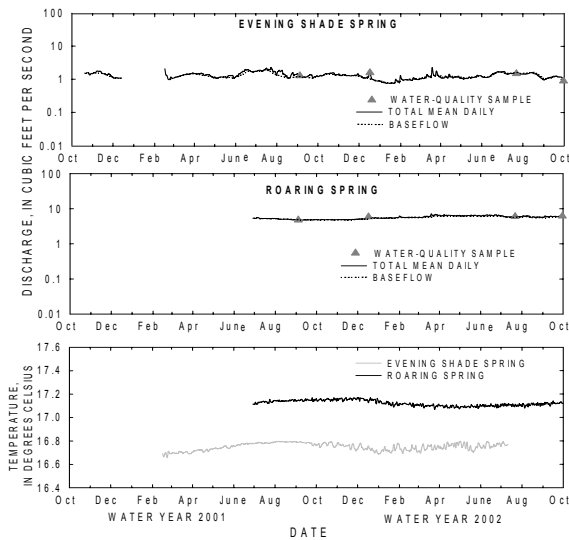


Figure 6. Daily discharge and water temperature recorded at Evening Shade Spring and Roaring Spring.

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

Lashun K. King¹, Roger D. Painter¹, and Tom D. Byl^{1,2}

¹Dept. of Civil & Environmental Engineering, Tennessee State University, Nashville, TN 37209

²U.S. Geological Survey, 640 Grassmere, Suite 100, Nashville, TN 37211

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, 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:

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

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[®] 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

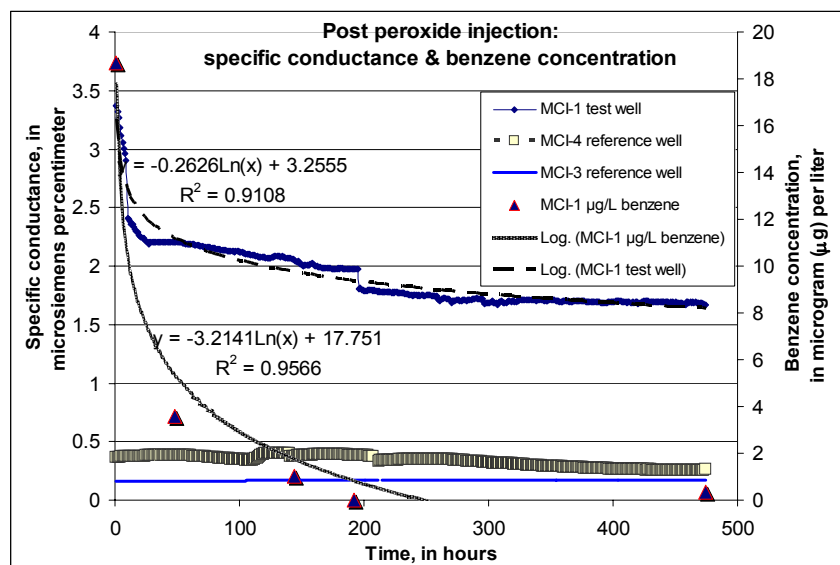


Figure 1. Specific conductance measured as a function of time in three karst bedrock wells. The benzene concentration is shown also with concentrations indicated on the second y-axis.

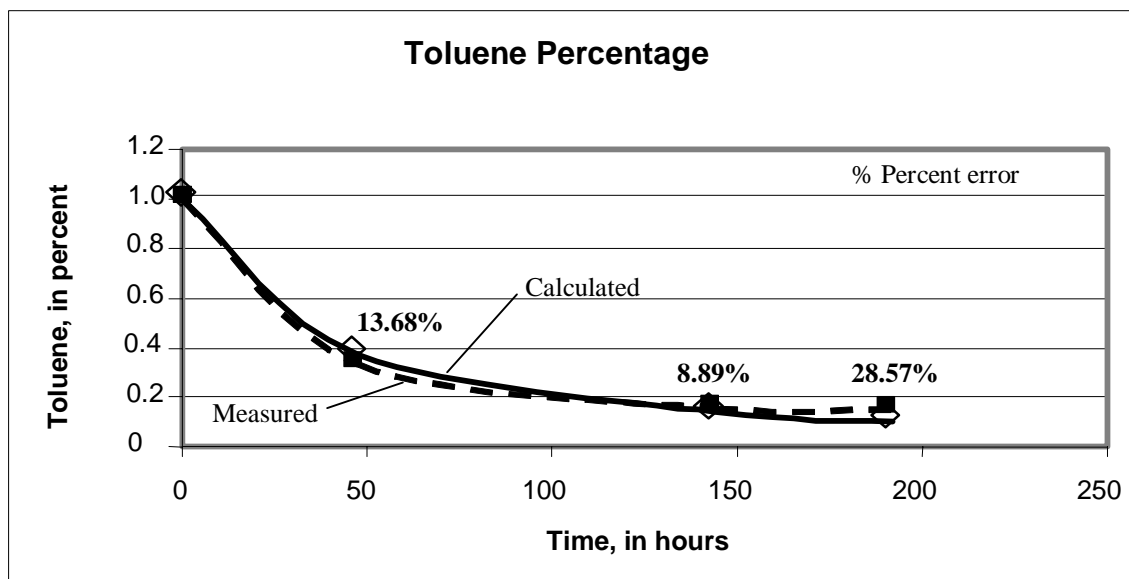


Figure 2. The RTD-biodegradation model prediction compared to the measured field toluene concentrations. The graph shows close agreement between the model calculation and measured concentration.

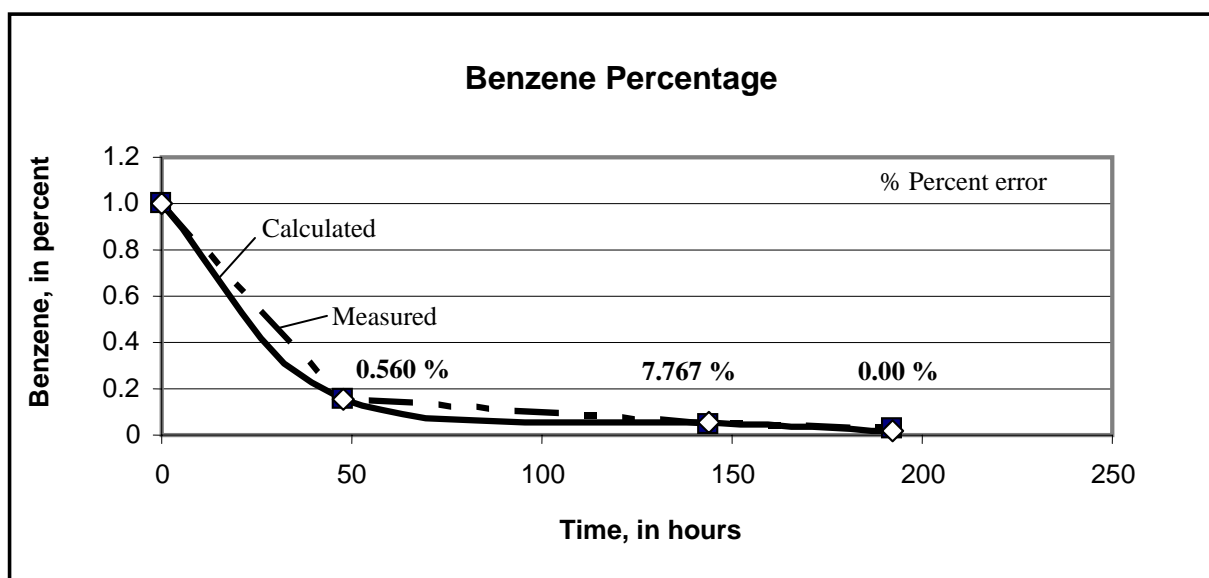


Figure 3. The RTD-biodegradation model prediction compared to the measured field benzene concentrations. Close agreement is indicated between the two approaches.

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?

Roger D. Painter¹, Shawkat Kochary¹, and Tom D. Byl^{2,1}

¹Civil and Environmental Engineering, Tennessee State University, Nashville, TN 37209

²U.S. Geological Survey, 640 Grassmere Park, Suite 100, Nashville, TN 37211

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-milliliter (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

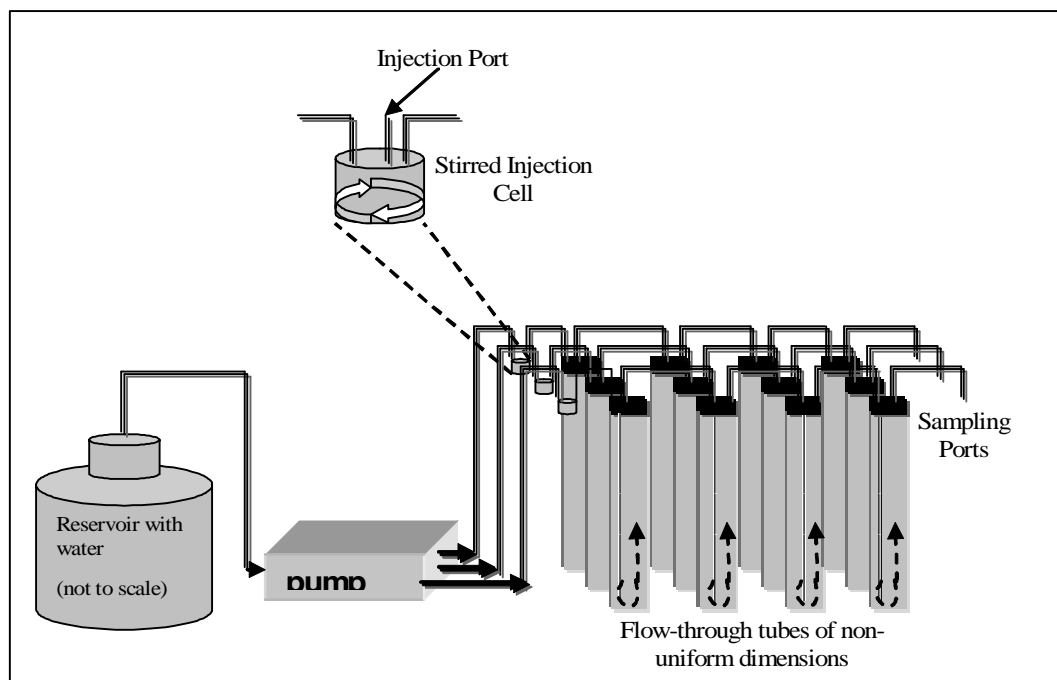


Figure 1. A schematic of the experimental karst systems.

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 ($\mu\text{g}/\text{L}$). 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):

$$\frac{dC_A}{dt} = kC_A C_B$$

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:

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

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.

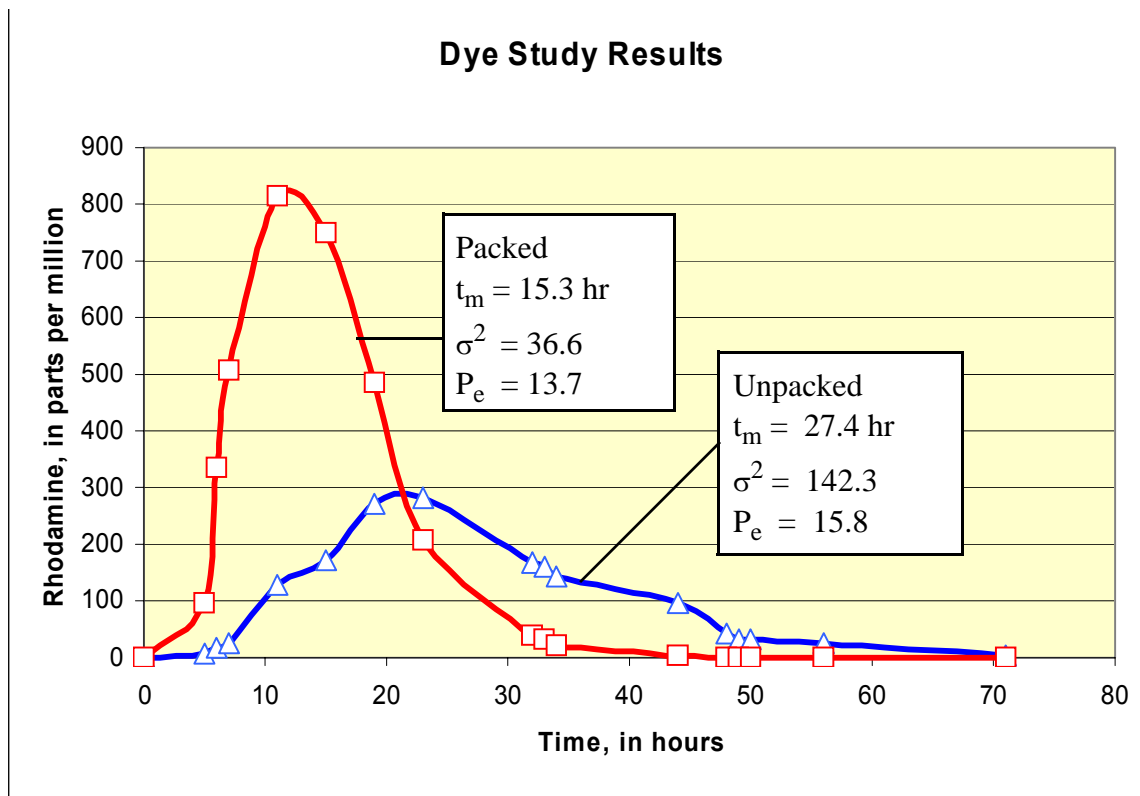
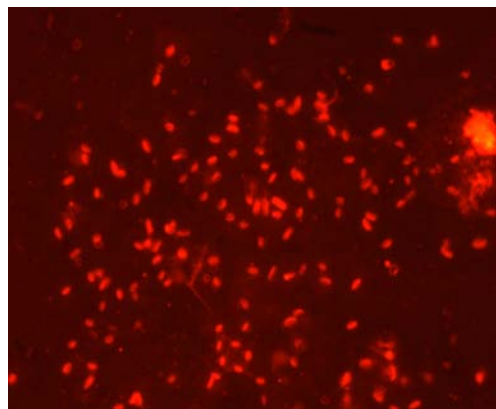
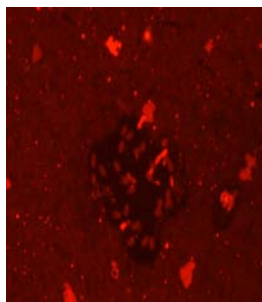


Figure 2. Rhodamine concentration at the end sampling port as a function of time for the high-surface area (packed) system and low-surface area (unpacked) system and the mean residence time (t_m), variability (σ^2) and Peclet value (P_e) for each system.

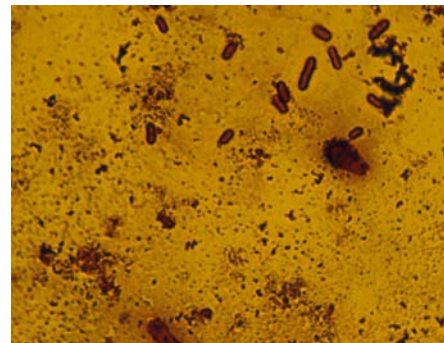
(A)



(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).

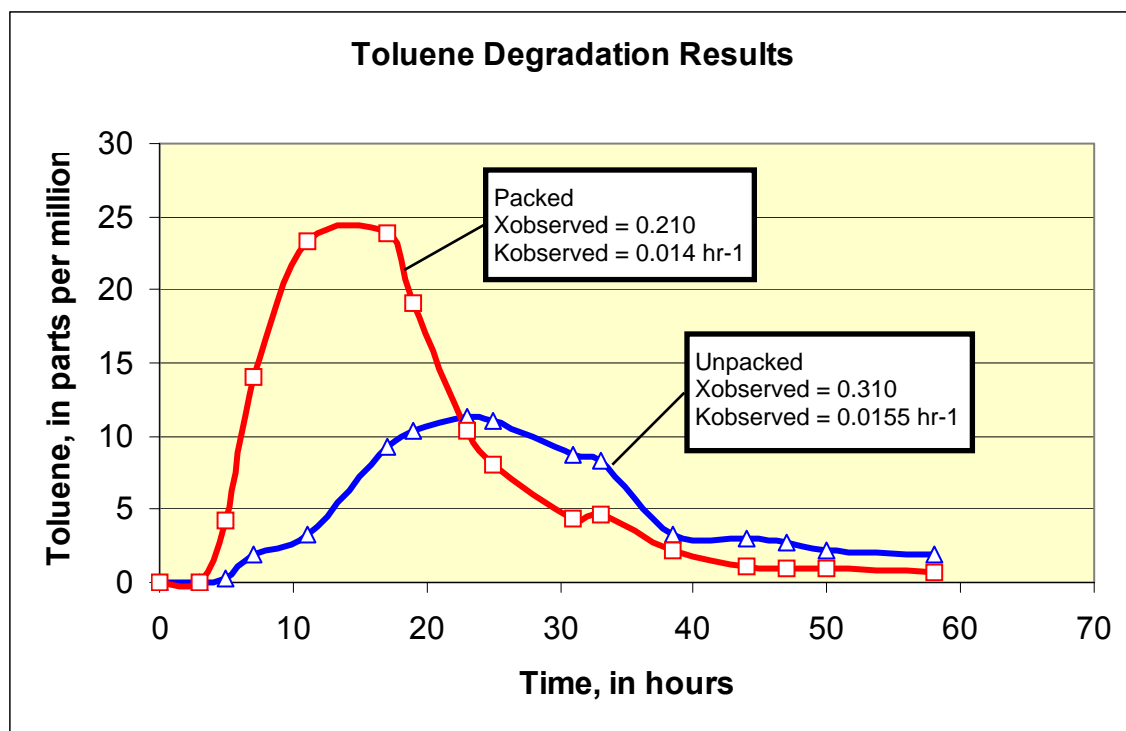


Figure 3. The concentration of toluene as a function of time in the packed system and unpacked systems. The X_{observed} refers to the amount biodegraded, and the K_{observed} refers to the first-order exponential rate of biodegradation calculated from the experimental data.

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

Mario Beddingfield¹, Khalid Ahmed¹, Roger Painter¹, and Tom D. Byl^{2, 1}

¹Dept. of Civil and Environmental Engineering, Tennessee State University, Nashville, TN

²U.S. Geological Survey, Nashville, TN

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

Ryan Fitzwater¹, Roger Painter¹, Valetta Watson¹, and Tom D. Byl^{2, 1}

¹Dept of Civil and Environmental Engineering, Tennessee State University Nashville, TN;

²U. S. Geological Survey, Nashville, TN 37211

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

LyTreese Hampton P.D. Hays¹, Roneisha Graham¹, and Tom D. Byl^{2, 1}

¹ Dept. of Civil and Environmental Engineering, Tennessee State University, Nashville, TN

² U.S. Geological Survey, Nashville, TN

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

Fuzail Faridi¹, Roger Painter¹, and Tom Byl^{2,1}

¹Dept. of Civil and Environmental Engineering, Tennessee State University, Nashville, TN

²U.S. Geological Survey, Nashville, TN

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

Serge Mondesir¹, and Tom D. Byl^{2,1}

¹Dept. of Civil & Environmental Engineering, Tennessee State University, Nashville, TN 37209

²U.S. Geological Survey, Nashville, TN 37211

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.

This work was supported in part by the U.S. Army Corps of Engineers DACW62-00-H-0001 contract.