Journal of Geography and Geology; Vol. 7, No. 1; 2015
ISSN 1916-9779 E-ISSN 1916-9787
Published by Canadian Center of Science and Education

Nitrates in Karst Systems: Comparing Impacted Systems to a Relatively Unimpacted System

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Received: August 21, 2014 Accepted: August 27, 2014 Online Published: February 23, 2015

doi:10.5539/jgg.v7n1p65 URL: http://dx.doi.org/10.5539/jgg.v7n1p65

Abstract

Karst aquifers are highly susceptible to contamination because of the connection with surface water. Nitrate contamination is common; with most karst aquifers exhibiting some degree of impact. This work assesses the potential impacts of anthropogenic activities on the Horn Hollow Valley (HHV) in Carter County Kentucky. HHV is a karst aquifer system that appears to be minimally impacted by nitrate and chloride contamination. Sampling of the HHV area was conducted from June 2005 to November 2006. Nitrate as nitrogen (NO_3-N) concentrations were between 0.13 to 1.54 mg/L; chloride concentrations ranged from 1.43 to 66.3 mg/L. Impact from anthropogenic sources are observed at 1 mg/L for NO_3-N and 13 mg/L for chloride. Sources of nitrate are primarily soil organic matter and mineralized fertilizers. In addition to mineralized fertilizers, chloride appears to be contributed from road salts. Compared to waters from three other systems: the Mammoth Cave area, the southwestern Illinois sinkhole plain, and the Missouri Ozarks-Salem Plateau; waters from HHV exhibited lower concentrations of both NO_3-N and chloride. Waters from Mammoth Cave and the Missouri Ozarks tended to have higher NO_3-N concentrations and similar chloride concentrations. Waters from southwestern Illinois had higher NO_3-N concentrations and chloride concentrations. Overall, the karst aquifer of HHV appears to be a relatively pristine system, with minor human impacts.

Keywords: Carter Caves, water-quality, nitrate, chloride, Mammoth Cave, Ozarks

1. Introduction

Over a quarter of Earth's population utilizes ground water from karst regions that cover 20% of Earth's surface (Ford & Williams, 1989; A. N. Palmer, 1991). The reliance on karst aquifers for potable water requires that water quality of karst aquifers is clearly understood. In locations with human and agricultural development, contamination of karst ground water resources with human and animal wastes (Davis, Hamilton, & Brahana, 2005; E.W. Peterson, Davis, & Orndorff, 2000; Eric W Peterson, Davis, Brahana, & Orndorff, 2002; Eric W. Peterson, Davis, & Brahana, 2000; Wicks, Kelley, & Peterson, 2004), with agrichemicals from crop productions (Panno, Kelly, Weibel, Krapac, & Sargent, 2003), and with chemicals that are dumped or spilled on the ground (White, 1988) is common. Within the Appalachian Region, nitrate contamination is common as a result of the rapid interaction between surface water and the ground water and of the high proportion of landuse devoted to agriculture (Boyer & Pasquarell, 1995; Kastrinos & White, 1986; Knox & Moody, 1991)

Identifying karst areas that are not impacted by anthropogenic effects and are relatively pristine is difficult, but background levels of solutes have been calculated. From their work examining seasonal trends in nitrate concentrations in karst systems of Pennsylvania, Kastrinos and White (1986) extrapolated their data to calculate a background level of nitrate for the region. Using land use as the independent variable, Kastrinos and White (1986) found a linear relationship between agricultural land use and nitrate concentrations in the waters. Extrapolating the agricultural land use to zero percent, they predicted a background concentration of 5 mg/L nitrate (1.13 mg/L nitrate as nitrogen). Conducting a similar investigation in West Virginia, Boyer and Pasquarell (1995) reported in areas dominated by forest or grasslands (i.e. zero percent agricultural land use) nitrate concentrations ranged between 0.09 to 0.5 mg/L with a mean of 0.4 mg/L.

Rural areas are experiencing increased urbanization as residents of larger population centers move to quieter, more scenic locations. In areas underlain by karst, the potential for increased contamination of karst waters is significant. During construction of single-family dwellings and subdivisions, sediments are transported into karst systems via runoff, degrading water quality within the subterranean systems. Septic systems are common in rural areas where municipal wastewater treatment facilities are not available. Studies of on-site wastewater treatment systems in Illinois (Panno, Kelly, Hackley, & Weibel, 2007) and Missouri (Aley & Thomson, 1984) found that aeration-type systems are possible sources of nitrate, sodium, chloride, and enteric bacterial contamination within the underlying karst systems.

Geochemical research within the intensely karstified southwestern Illinois sinkhole plain (Panno & Kelly, 2004; Panno, Kelly, Weibel, Krapac, & S.L., 1998; Panno, Krapac, Weibel, & Bade, 1996; Panno, et al., 2003) has significantly contributed to our understanding of the effects of different land use practices on the quality of karst waters in cave conduits, springs, and surface streams. In the southwestern Illinois karst, nitrogen fertilizers and soil organic matter contributed the bulk of nitrate measured in the spring waters (Hackley, Panno, Hwang, & Kelly, 2007). Livestock and septic wastes were the dominant source for wells with high nitrate concentrations, while nitrogen fertilizers and soil organic matter were sources of low nitrate contaminations in other wells.

This study contributes to the science of karst hydrogeology by comparing chloride (Cl^-) and nitrate (NO_3^-) concentrations within karst waters in Horn Hollow Valley (HHV) of Carter County, Kentucky (Figure 1), a relatively unimpacted karst system, to concentrations in other karst systems. The opportunity to find and study a relatively pristine karst system is rare and provides initial data towards determining baseline ground water conditions in the eastern United States. Knowledge gained from this study can be utilized by state and local planning agencies to protect sensitive karst resources. Specifically, this work examines similarities and/or differences in NO_3^- and Cl^- concentrations between HHV and three other Midwestern karst regions. Comparison systems include Mammoth Cave, KY, the southwestern Illinois sinkhole plain, and the Salem Plateau of the Missouri Ozarks. Data from comparative systems were available for NO_3^- and Cl^-, major ion chemistry, and measured parameters.

2. Method

2.1 Area Description

2.1.1 Horn Hollow Valley - Carter Caves State Resort Park (CCSRP)

Karst terrain is prevalent in the state of Kentucky. Approximately 40% of the state contains carbonate bedrock suitable for karst formation, with 20% of the state exhibiting well-developed karst (Carey & Stickney, 2001; Paylor & Currens, 2002). The HHV karst system is located in northeastern Kentucky (Figure 1) in a relatively remote and intensely karstified region of north-central Carter County (McGrain, 1954). Drainage to the valley is primarily from park service land and forested private land in a relatively pristine area of CCSRP. However, headwater areas of HHV are located outside of the park boundaries and drain sparsely populated farmland with single-family dwellings. As waters move down gradient, they enter and exit the limestone subsurface several times before converging with Cave Branch, the main stream in the area and tributary to Tygart's Creek.

A conceptual model of the flow system (Angel, 2010) and a detailed description of the geology for HHV (Angel, 2010; Engel & Engel, 2009; B. Jacoby, Peterson, Kostelnick, & Dogwiler, 2013; Brianne S. Jacoby, Peterson, Dogwiler, & Kostelnick, 2011; Brianne Spence Jacoby, Peterson, & Dogwiler, 2011) have been previously published; here we summarize the relevant information. Under baseflow conditions, the upper and lower segments of the valley are underdrained. Allogenic surface waters are pirated at Horn Hollow Headwall (HHH) and Volcano Cave after water transitions from the siliclastic rocks to the underlying carbonate rocks. Waters reemerge at Bowel Spring and flow towards Cobble Cave. At Cobble Cave, the waters flow through the cave, exiting at the downstream entrance. The waters continue to flow on the surface until they enter Horn Hollow Cave. Waters flow through Horn Hollow Cave and upon exiting the cave, are directed to the subsurface until they discharge at the H_2O Cave Outlet above Cave Branch. Along the valley, there are a number of seeps and springs that supply water to the valley.

2.1.2 Descriptions of Comparison Systems

2.1.2.1 Mammoth Cave

The Mammoth Cave system is located in west-central Kentucky within the Western Pennyroyal Plateau and Chester Upland region (Paylor & Currens, 2002). The system is the longest known cave system in the world with over 215 km of interconnected caves developed within the same Mississippian-age limestones that are present in the CCSRP area. These cave-forming limestones are approximately 150 m thick in the Mammoth Cave region while only 38 m in the CCSRP area. Rocks dip gently to the northwest, exposing large areas of limestone to karst forming processes and the formation of widespread karst drainage basins (Arthur N. Palmer, 1981). The largest caves in the system form within a zone from the upper half of the St. Louis Formation through the Girkin Formation (Table 1) with Mississippian and Pennsylvanian impermeable sandstones and shales overlying the carbonate rock. Waters enter the massive system through sinkholes in the Pennyroyal Plateau and sinkholes that have breached the insoluble sandstones and shales of the Chester Upland, eventually discharging through springs along the Green River. Within MCNP, land cover is heavily forested. The land use outside of the park consists of farming and small urban centers. Water quality data were provided by J. Meiman, Mammoth Cave National Park (personal communication, 2009).

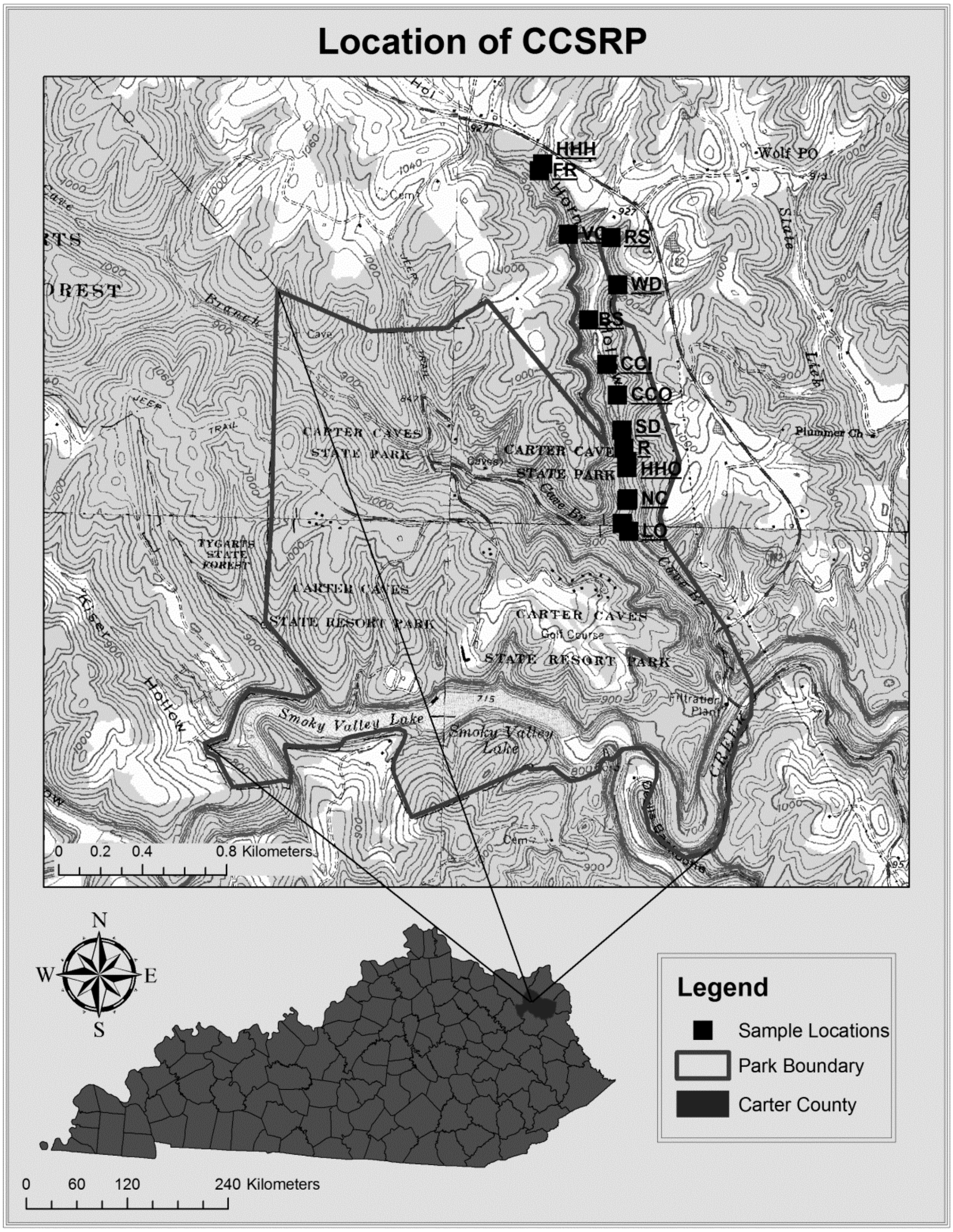

Figure 1. Location of Horn Hollow Valley (HHV), Carter Caves State Resort Park (CCSRP), Carter County, Kentucky with the positions of the sampling locations for reference

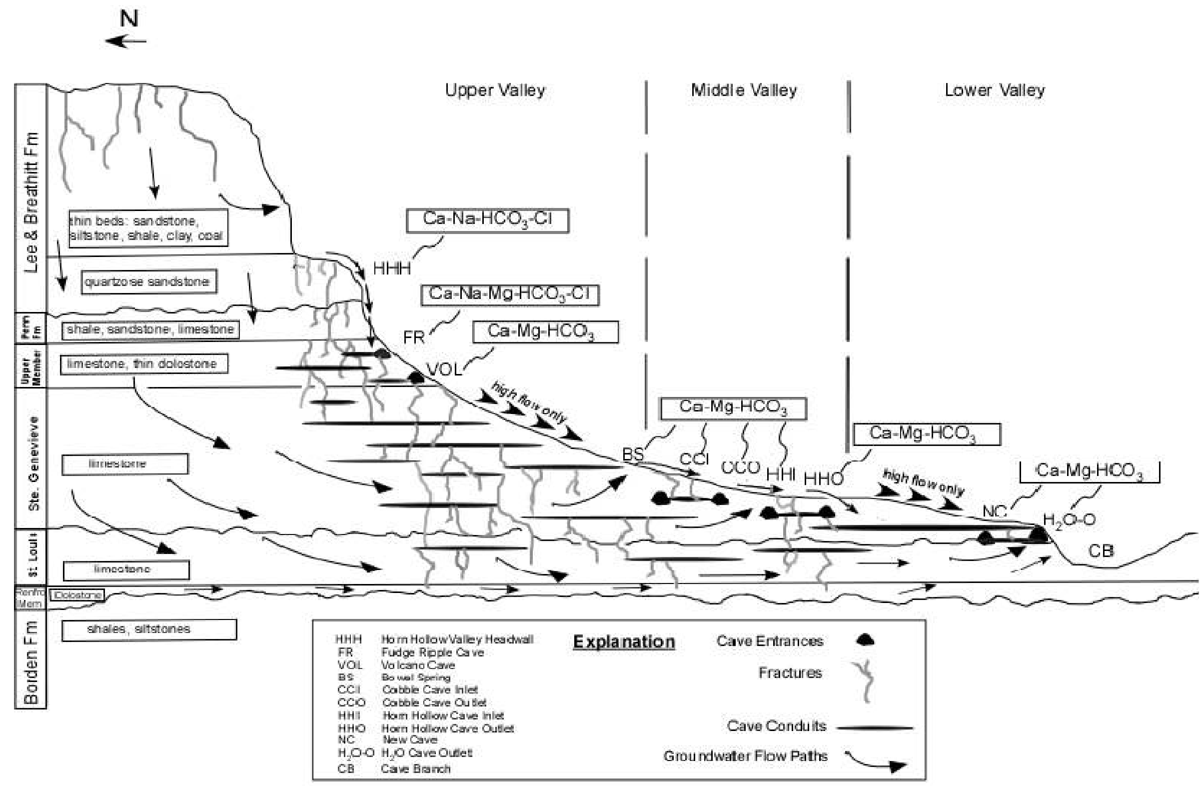

Figure 2. Conceptual Model of HHV including Geologic units, water types, flow paths and cave conduits

2.1.2.2 Southwestern Illinois Sinkhole Plain

The sinkhole plain of southwestern Illinois encompasses portions of St. Clair, Monroe and Randolph Counties and is part of the Salem Plateau Section of the physiographic provinces presented by Leighton et al. (1948). Over 10,000 sinkholes dot the landscape in this area along with disappearing streams, caves, and springs. Mississippian-age St. Louis and Ste. Genevieve Limestones and the Salem Limestone are the predominant karst-forming bedrock units (Table 1), exceeding 60 m in thickness in bluffs along the Mississippi River Valley (Panno, et al., 1996). Other units include Mississippian and Pennsylvanian sandstones, shales, claystone, coal and additional limestone. The development of karst terrane has been influenced by several anticlinal and synclinal features as well as the local bedrock topography. Waters enter the subsurface through sinkholes and fissures, forming caves as waters dissolve carbonate rock along bedding plane partings. The area contains two major ground water basins; the Fogelpole Cave Basin and Collier Spring Basin (Aley, Moss, & Aley, 2000; Panno, et al., 1998). Land-use within both basins is predominantly agricultural, but urban sprawl from the St. Louis area has increased the number of rural subdivisions and homes that rely on septic systems for waste removal. Anthropogenic contamination from septic and agricultural sources is widespread within this region. Water quality data were provided by S. V. Panno, Illinois State Geological Survey (personal communication, 2009).

2.1.2.3 Missouri Ozarks-Salem Plateau

The majority of Missouri's largest springs discharge from Cambrian and Ordovician-age dolomites (Table 1) within the Salem Plateau physiographic division of the Missouri Ozarks (McCracken, 1971; Vineyard & Feder, 1982). This region is known for rugged topography, with deep, narrow valleys, high ridges and significant karst development. Losing streams, caves, springs, and sinkholes are found throughout the plateau. The Jefferson City Dolomite and the Roubidoux Formation dominant the topography of the Salem Plateau uplands. Waters from the largest springs discharge through the Gasconade, Eminence and Potosi Dolomites, many along prominent rivers that course through the region. Recharge to karst ground water occurs through faults and fractures and within sinking stream segments of surface waters. Much of this region is heavily forested land, although some cattle and poultry operations are also present (Petersen et al., 1998). Water quality data were retrieved from Vineyard and Feder (1982) and United States Geological Survey (2010).

2.2 Sampling Procedure

Water samples were collected from 16 specific locations in HHV (Figure 1) during four field-sampling events. Three sampling events occurred during periods of baseflow, June 2005, June 2006 – pre storm, and November 2006, and one following a recharge event, June 2006 – post storm. Sampling locations included the HHV headwall, inlets and outlets of caves within the system, a valley drip, a dome within Horn Hollow Cave, drips in Rimstone Cave and Laurel Cave, and the springs discharging waters into Cave Branch. Samples were collected, stored in polyethylene bottles, and transported to the Illinois State University laboratory in ice-filled coolers. Chloride (Cl^-) and Nitrate as N (NO_3-N), were analyzed using a Dionex DX-120 Ion Chromatograph (IC).

During the June 2006- pre storm-sampling event, water samples were collected for nitrogen (N) and oxygen (O) isotopic analysis by the Illinois State Geological Survey. A total of 12.5 liters of water was collected at each of three sites; Bowel Spring (BS), Surprise Dome (SD) and Horn Hollow Outlet (HHO) and transported to the laboratory in ice-filled coolers. Isotopic analysis was performed at the Illinois State Geological Survey to identify values for $\delta^{15}N_{Air}$ (‰) and $\delta^{18}O_{SMOW}$ (‰). A scatter plot was produced for $\delta^{18}O_{SMOW}$ (‰) vs $\delta^{15}N_{Air}$ (‰) to identify different sources of nitrate using end-member delineations defined by Clark and Fritz (1997).

NO_3^- and Cl^- concentrations (mg/L) from waters collected in HHV were compared to NO_3^- and Cl^- concentrations (mg/L) from Mammoth Cave National Park, KY, the southwestern Illinois sinkhole plain, and the Ozark Plateau (locations in south-central Missouri). Data were plotted to analyze Cl^- vs NO_3^- in waters from selected springs and caves within the Horn Hollow system and comparison systems.

3. Results and Discussion

3.1 Chloride and Nitrate HHV Waters

Chloride is a negatively charged ion and is contributed to surface and ground waters from natural and anthropogenic sources. Naturally occurring chloride sources include sea water, basin brines, precipitation, and rock-water interaction, especially with shales. In other karst areas, background chloride concentrations are roughly 13 mg/L (Panno et al., 2006). Common sources of anthropogenic Cl^- are animal wastes, mineralized fertilizers, septic effluent, landfill leachate, and road salts (Panno, Hackley, et al., 2006).

Nitrate is a negatively charged, conservative ion and a common contaminant in shallow ground water and surface streams. The mineralization of natural organic nitrogen contributes nitrate to ground water systems while anthropogenic sources include livestock waste, mineralized fertilizer, and septic systems (Panno, et al., 1996; White, 1988).

In natural environments with little to no human impact, nitrate concentrations are relatively low. Nitrate as Nitrogen (NO_3-N) concentrations from natural sources are generally between 2.0 and 2.5 mg/L (Panno, Kelly, Martinsek, & Hackley, 2006). For HHV, NO_3-N values ranged from 0.13 to 1.54 mg/L with some of the highest values measured during baseflow conditions in June 2005 (Figure 3). The lowest NO_3-N values appear to result from dilution during the November 2006 sampling event. Samples collected during baseflow conditions reflect relatively pristine conditions with all waters having concentrations below those observed by Panno, Kelly, et al. (2006) . Peterson et al. (2002) found that ~74% of the nitrate within the regolith of an Arkansas karst region was transported during baseflow conditions. This same trend appears to occur within HHV.

Table 1. Carbonate lithologies of comparison karst systems

Karst Region	Formations Age	Carbonate Lithology
Mammoth Cave, KY[a]	Mississippian:	Girkin Limestone - fine to medium-grained, skeletal and argillaceous limestones with some oolitic limestone.
		Ste. Genevieve Limestone - crossbedded, massive, oolitic to skeletal limestone
		St. Louis Limestone - very fine-grained, some chert, argillaceous and dolomitic limestone. Some beds of skeletal limestone.
Salem Plateau (southwestern Illinois Sinkhole Plain)[b]	Mississippian:	St. Louis Limestone - fine-grained, cherty limestone with beds of dolomite, crystalline limestone, Fossiliferous limestone, and evaporites
		Ste. Genevieve Limestone - oolitic grainstone that contains peloidal and fossil grains, little chert, cross bedding evident
		Salem Limestone - white to light-gray grainstone with dolomite beds
Salem Plateau (Missouri Ozarks)[c]	Ordovician:	Jefferson City Dolomite - dolomite with chert, sandstone lenses, some shale. Pyritic
		Roubidoux Formation – fine-grained cherty dolomite with quartz sandstone beds
		Gasconade Dolomite – fine-course grained cherty dolomite
		Eminence Dolomite – medium-course grained, cherty dolomite
		Potosi Dolomite – fine-medium grained vuggy dolomite with quartz

[a] Haynes, 1964.

[b] Willman et al., 1975.

[c] Feder, 1973; Imes & Emmett, 1994; Unklesbay & Vineyard, 1992.

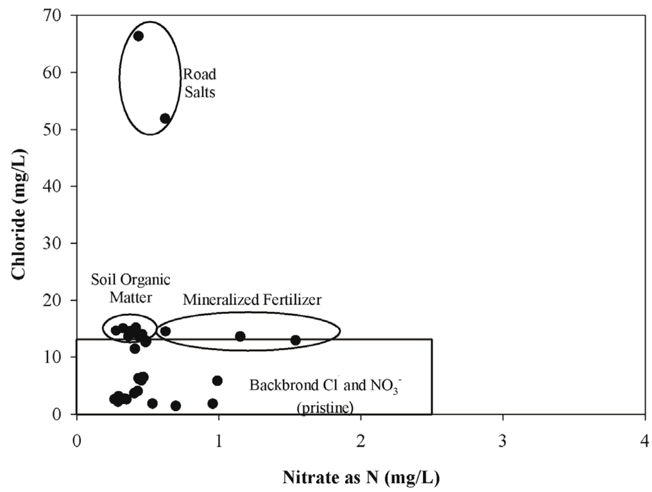

Figure 3. Nitrate and chloride concentrations for waters of Horn Hollow Valley. The classifications are based upon the values suggested by Panno et al. (2006b)

The isotopic composition of NO_3^- for three HHV samples, BS, SD and HHO, suggest mineralized fertilizer and soil organic matter are the potential source areas for NO_3^- (Figure 4). The NO_3^- present in BS and SD waters is derived from mineralized fertilizer, while NO_3^- at HHO comes from soil organic matter. Epikarst waters from SD represent allogenic drainage from the SR182 area where mineralized fertilizers may have been applied to fields. These waters probably entered the karst through myriad fractures and joints, quickly making their way along karstified bedding planes. Autogenic waters resurging at BS originate at the HHH and from other bedding plane sources in the Upper Valley (Angel, 2010). HHO waters are also autogenic, with soil organic matter that may be derived from fertilized and unfertilized crops. These results show that anthropogenic nitrate is present in both allogenic and autogenic waters in HHV.

3.2 Background Concentrations of Nitrate and Chloride

Delineating background and anthropogenic sources of contaminants provides information necessary for identifying water sources and flow paths in karst regions. Background concentrations of dissolved species can be defined as the concentrations derived specifically from naturally occurring processes within a given environment. Insufficient data are present to apply the land use extrapolation methods used by Boyer and Pasquarell (1995) and Kastrinos and White (1986). To approximate background concentrations and identify anomalous populations the technique described in Panno et al. (2006) was employed in which Cl^- and NO_3-N concentrations were plotted on cumulative probability plots (Figure 5). Inflection points or changes in the slope of the graph line represent thresholds separating the data populations; one being background and the remainder representing the anomalies or anthropogenic inputs of the observed ions (Panno, Hackley, et al., 2006).

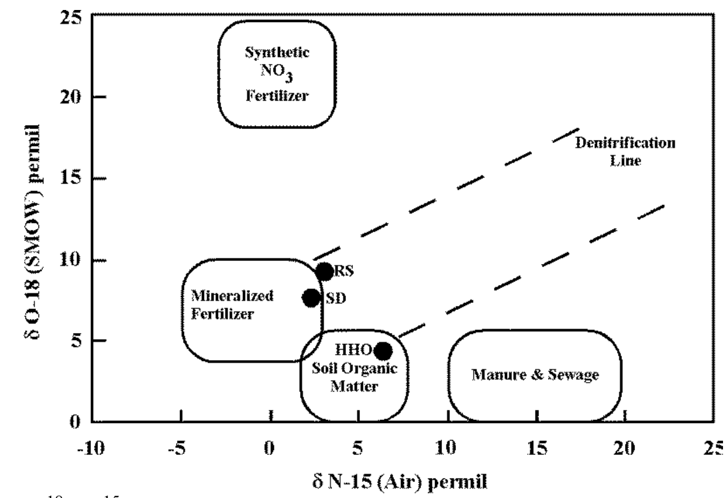

Figure 4. Results from $\delta^{18}O/\delta^{15}N$ isotopic analysis for selected samples collected on June 24, 2006. The boxes represent typical ranges of common end-members as presented by Clark and Fritz (1997)

The chloride cumulative probability plot (Figure 5a) has one inflection point along the curve at 13 mg/L Cl^-, yielding two populations of data. Therefore, background concentrations for HHV range from 0-13 mg/L Cl^-. One anomalous (anthropogenic) population was present from 13-66 mg/L Cl^-. Sixty-eight percent (68%) of the samples from HHV fell within the range of background concentration. These samples were mainly from Lower Valley sites. Thirty-two percent (32%) of the samples, all representing Middle and Upper Valley sites, plotted within the 13-66 mg/L anthropogenic population. These results suggest that anthropogenic contamination of Cl^- is highest in the Upper Valley and diminishes down gradient, a likely result of dilution by autogenic waters originating in the forested areas of CCSRP.

The nitrate cumulative probability plot (Figure 5b) has one inflection point at 1 mg/L NO_3-N yielding two populations of data. Background nitrate for HHV ranges from 0-1 mg/L NO_3-N, with an anomalous (anthropogenic) population present from 1-1.54 mg/L NO_3-N. The background level of 1 mg/L is similar to the value reported by Kastrinos and White (1986), but slightly elevated from the upper limit of 0.5 mg/L reported by Boyer and Pasquarell (1995). With the exception of six samples (three samples collected in June 2006; one from the Upper Valley and two from the Lower Valley), waters from the HHV sites had NO_3-N concentrations below background levels of 1 mg/L Surprisingly, the three samples within the anomalous population were not the BS, SD and HHO samples identified as anthropogenic NO_3-N sources through isotopic analysis. NO_3-N concentrations from BS, SD and HHO were well within the background population range. The data indicate that these three sites receive anthropogenic NO_3-N, but concentrations are so low that they fall within the background population, supporting the position that waters from the park are low nitrate and dilute waters from outside the park area.

3.4 Sources of Nitrate and Chloride

A two-lane blacktop road, CR182, borders the northeastern perimeter of HHV. Farms with homes and livestock are present along both sides of the road. Small ephemeral (intermittent) streams, which flow into HHV via draws, flow beneath the road or have headwaters near the road. Subsequently, the land use near the road serves as non-point, anthropogenic source of NO_3-N and Cl^-. Possible sources of nitrate and chloride can be delineated by plotting Cl^- vs NO_3-N (Figure 3), identifying samples that fall within the background concentration ranges and observing the relationships between NO_3-N and Cl^- for those samples falling outside of background.

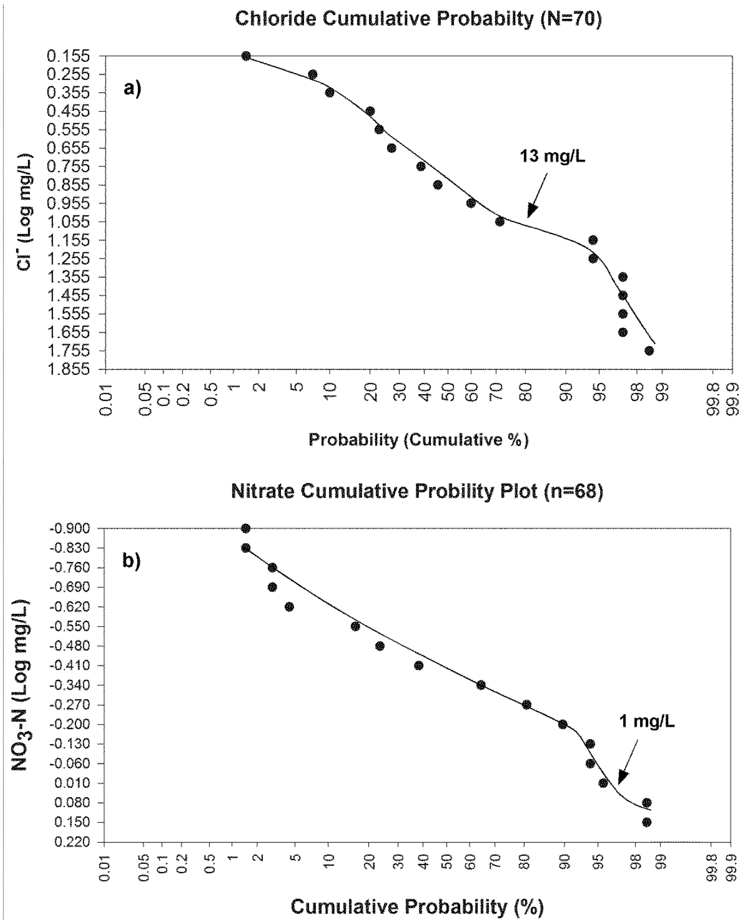

Figure 5. a) Chloride cumulative probability plot (%) showing a single inflection points yielding three populations of data. Background ranges from 0-13 mg/L Cl-. b) Nitrate cumulative probability (%) showing a single inflection point yielding two populations of data. Background ranges from 0-1 mg/L NO3-N

On the plot. For example, the two data points representing high Cl^-/low NO_3-N (HHH and Fudge Ripple (FR)) are likely from road salt as there was high Cl^- with little to no NO_3-N. The Cl^- may have been retained in the soil following road salt application to CR182 the previous winter and released during the June 2006 sampling. From a Cl^- retention study in southeastern Sweden, Bastviken et al. (2006) concluded that soils can act as sources or sinks for Cl^-, with storage ranging from months to years. Lax and Peterson (2009) reported that road salts migrate through the vadose zone, providing a long term source of chloride to ground water. Values with low Cl^-/low NO_3-N represent background concentrations of both ions and are considered pristine waters. Cl^- is a dominant ion in waters draining shales; therefore, the Cl^- in these waters may be derived from the Upper Valley shale layers. Based upon classifications presented by Panno et al. (2006), the two populations with slightly higher Cl^- but low NO_3-N represent sources of mineralized fertilizer and soil organic matter. The mineralized fertilizer cluster contains the BS-1 and SD-1 samples that were identified using δO-18/δN-15 isotopes (Figure 3), while the soil organic matter cluster contains the HHO-1 sample included in the isotopic analysis.

3.5 Comparison of Cl and NO_3-N Concentrations between Systems

Nitrate and chloride concentrations for HHV samples were compared to those from three other karst regions in the Midwestern U.S. to assess the potential pristine nature of HHV waters. Comparison data were selected based on sites that were representative of karst waters from the comparison areas.

Echo River Spring, Turnhole Spring, and Pike Spring are three major sites that discharge water from several drainage basins encompassing the extensive Mammoth Cave karst system and Mammoth Cave National Park (MCNP). Sample data were collected between July 2002 and September 2005 by MCNP personnel (Meiman, personal communication, 2009). Samples from the southwestern Illinois sinkhole plain were collected at various sites within Illinois Caverns by the Illinois State Geological Survey during five sampling trips in 1996 and 1997 (Panno, personal communication, 2009). Samples from the Salem Plateau region of the Ozark Plateau of southern Missouri include Alley Spring, Maramec Spring, and Big Spring. Data from these three sites were available from the 1950's and 1960's and from the mid 1990's (United States Geological Survey, 2010; Vineyard & Feder, 1982).

Figure 6 shows Cl^- vs NO_3^- for HHV and comparison systems. Samples plotting within the black box represent background concentrations of <13 mg/L for Cl^- and < 1 mg/L for NO_3-N, which are consistent to other background concentrations for Cl^- (Panno, Hackley, et al., 2006) and NO_3-N (Panno, Hackley, et al., 2006). HHV system water contained background concentrations of chloride with the exception of the June 2006 sampling event. The high Cl- from road salts at HHH and FR produced Cl- concentrations of 66.3 mg/L and 51.9 mg/L respectively. Waters resurging at BS showed significant decrease in Cl- during the same sampling event and were only 2-3 mg/L above background. This may be the result of dilution within the subsurface conduits between the HHH and BS. HHV samples that cluster near the origin of the graph are probably the result of contaminant dilution during the higher discharge conditions in November 2006.

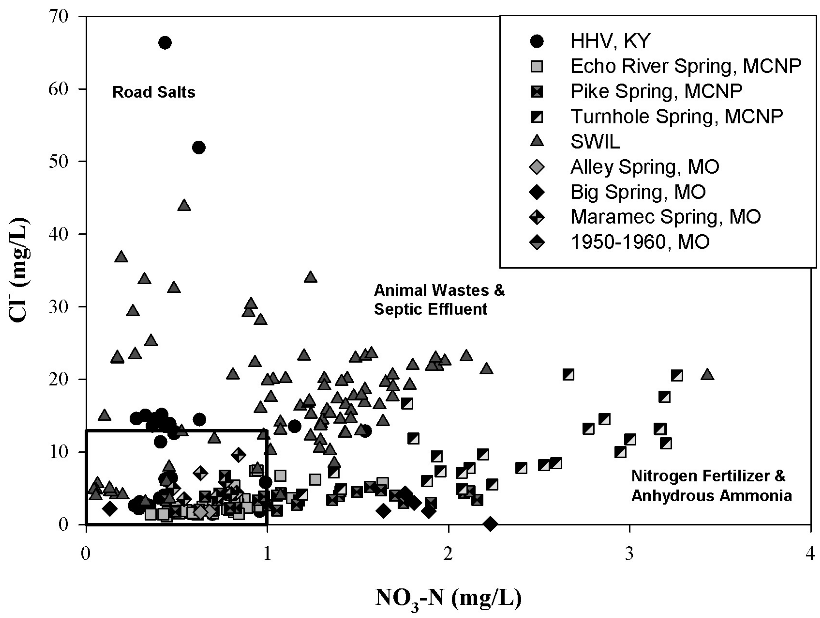

Figure 6. Nitrate and chloride concentrations for waters of HHV and the comparison systems. The pristine box is based upon the background concentrations as illustrated in Figure 5

The majority of samples from MCNP also exhibit background concentrations for Cl^- , but NO_3-N concentrations from all three MCNP springs are higher than background concentrations calculated from HHV. Pike Spring NO_3-N values are closer to those measured at HHV as this spring drains the heavily forested Flint Ridge and portions of MCNP (Quinlan, Ewers, & Aley, 1991). Turnhole Spring receives a large volume of drainage from the Pennyroyal Plateau to the southeast of MCNP. The Pennyroyal Plateau contains fertile soils that are ideal for row-crops and is also more heavily populated than the other two spring basins. Figure 6 shows that samples from Turnhole Spring have NO_3-N concentrations above background, suggesting anthropogenic contamination. Nitrate sources are likely from nitrogen fertilizers. Echo River Spring drains heavily forested park land, but dye tracing results from Quinlan et al (1991) show that subsurface drainage reaches the spring from sinkholes as far away as Park City, KY and Cave City, KY along the I-65 corridor. The same study also showed that the Echo River Spring drainage basin is breached by flow from the Pennyroyal drainage basin during high flow events. These sources may explain the increased NO_3^- values at Echo River Spring.

Samples from the southwestern Illinois sinkhole plain plot along a trend indicating contamination from animal wastes and septic effluent. Agricultural land-use is dominant in this area and includes row-crops and small livestock operations (Panno, Hackley, et al., 2006). A study by Hackley et al. (2007) concluded that nitrogen fertilizer and soil organic matter were the major sources of NO_3-N in spring waters in the southwestern Illinois sinkhole plain. The Illinois samples had the highest overall chloride of all comparison systems with the exception of the June 24, 2006 samples from HHH and FR. The highest Cl^- values in this area were found near livestock operations and in shallow wells (Hackley, et al., 2007).

The three comparison springs from the Salem Plateau region of the Missouri Ozark Plateaus reside in the unconfined portion of the Ozark Aquifer and are, therefore, not protected from surface drainage. Waters in this region drain predominantly forested land, although there are some pasture-land agricultural operations in this area (Eric W Peterson, et al., 2002). Despite the presence of some agricultural land-use, samples collected from these three springs plot well within the background concentration ranges for both Cl^- and NO_3-N. The median NO_3-N concentration for samples collected at these three springs in 1993 was 0.62 mg/L. In comparison, the median NO_3-N concentration for the limited samples collected during the four HHV sampling events in 2005 and 2006 was 0.45 mg/L. Data were available from the 1950's and 1960's for Alley Spring, Maramec Spring and Big Spring, MO and were included on the Cl^- vs NO_3-N graph. The same data trends exists when comparing the current Missouri samples to the 1950's/1960's samples, but current levels are slightly elevated for both Cl^- and NO_3-N. This may result from increased agricultural land-use in this region. Median NO_3-N concentration from the three Missouri springs in the 1950's/1960's was 0.44 mg/L. This is virtually identical to 0.45 mg/L median NO_3-N value for the 2005 and 2006 HHV samples.

These comparisons show that HHV waters are relatively pristine, especially for NO_3^- concentrations, and contained slightly elevated Cl^- concentrations from road salt contamination in June 2006.

4. Conclusions

The examination of NO_3-N and Cl^- sources within HHV indicated that samples with concentrations above background levels might have been derived from organic soil matter, mineralized fertilizers and road salts stored in soils. A comparison of HHV NO_3^- and Cl^- concentrations with other Midwestern karst systems showed very low NO_3-N and relatively low Cl^- concentrations in HHV, supporting the overall pristine nature of HHV waters. The exception was the high Cl^-/low NO_3^- waters derived from stored road salts sampled at HHH and FR in June 2006.

While more data are needed to confirm the findings of this study, the results can be used as an initial baseline analysis of the system, as there have been very few studies in this area.

Acknowledgements

The authors wish to thank the Carter Caves State Resort Park and the Kentucky State Parks System for permission and access to HHV and its unique caves and karst features. We thank Toby Dogwiler, Sam Panno, anonymous reviewers for their critical and helpful reviews of manuscript. Thank you to Hue Hwa Hwang of the Illinois State Geological Survey for conducting the $\delta^{18}O/\delta^{15}N$ isotopic analysis.

References

Aley, T., Moss, P., & Aley, C. (2000). Delineations of recharge areas for four biologically significant cave systems in Monroe and St. Clair County. Protem, Missouri: Ozark Underground Laboratory.

Aley, T., & Thomson, K. C. (1984). Septic fields and the protections of groundwater quality in Greene County, Missouri (pp. 85). Springfield, Missouri: Ozark Underground Laboratory.

Angel, J. C. (2010). *Characterization and comparison of the geochemistry and evolutionary controls of Horn Hollow Valley karst waters to other karst systems.* M.S., Illinois State Unviersity, Normal, IL.

Bastviken, D., Sandén, P., Svensson, T., Ståhlberg, C., Magounakis, M., & Öberg, G. (2006). Chloride Retention and Release in a Boreal Forest Soil: Effects of Soil Water Residence Time and Nitrogen and Chloride Loads. *Environmental Science & Technology, 40*(9), 2977-2982. http://dx.doi.org/10.1021/es0523237

Boyer, D. G., & Pasquarell, G. C. (1995). Nitrate concentrations in karstsprings in an extensively grazed area. *Water Reseources Bulletin, 31*(4), 729-736.

Carey, D. I., & Stickney, J. F. (2001). *Ground-Water Resources of Carter County, Kentucky*. Kentucky Geological Survey.

Clark, I. D., & Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. New York: Lewis.

Davis, R. K., Hamilton, S., & Brahana, J. V. (2005). *Escherichia coli* survival in mantled karst springs and streams, northwest Arkansas Ozarks, USA. *Journal of the American Water Resources Association, 41*(6), 1279-1287.

Engel, A. S., & Engel, S. A. (2009). A field guide for the karst of Carter Caves State Resort Park and the surrounding area, northeastern Kentucky. In Annette Summers Engel & Scott A. Engel (Eds.), *Field Guide to Cave and Karst Lands of the United States, Karst Waters Institute Special Publication 15* (pp. 154-171). Karst Waters Institute.

Feder, G. I. (1973). *A conceptual model of the hydrologic system supplying the large springs in the Ozarks*. Ph.D., University of Missouri, Columbia, MO.

Ford, D. C., & Williams, P. W. (1989). *Karst Geomorphology and Hydrology*. London: Unwin Hyman.

Hackley, K. C., Panno, S. V., Hwang, H. H., & Kelly, W. R. (2007). *Groundwater Quality of Springs and Wells of the Sinkhole Plain in Southwestern Illinois*. Champaign, IL: Illinois State Geological Survey.

Haynes, D. D. (1964). *Geology of the Mammoth Cave Quadrangle, Kentucky*. Kentucky Geological Survey.

Imes, J. L., & Emmett, L. F. (1994). *Geohydrology of the Ozark Plateaus aquifer system in parts of Missouri, Arkansas, Oklahoma, and Kansas*. United States Geological Survey.

Jacoby, B., Peterson, E. W., Kostelnick, J. C., & Dogwiler, T. (2013). Approaching Cave Level Identification with GIS: A Case Study of Carter Caves. *ISRN Geology, 2013*(160397), 7. http://dx.doi.org/10.1155/2013/160397

Jacoby, B. S., Peterson, E. W., Dogwiler, T., & Kostelnick, J. C. (2011). Estimating the Timing of Cave Level Development with GIS. *Speleogenesis and Evolution of Karst Aquifers, 11*, 52-61.

Jacoby, B. S., Peterson, E. W., & Dogwiler, T. (2011). Identifying the Stream Erosion Potential of Cave Levels in Carter Cave State Resort Park, Kentucky, USA. *Journal of Geographic Information Systems, 3*(4), 323-333. http://dx.doi.org/10.4236/jgis.2011.34030

Kastrinos, J. R., & White, W. B. (1986). *Seasonal, Hydrogeologic, and Land-Use Controls on Nitrate Contamination of Carbonate Ground Waters.* Paper presented at the Proceedings of the Environmental Problems in Karst Terranes and Their Solutions Conference, Bowling Green, KY.

Knox, E., & Moody, D. W. (1991). Influence of hydrology, soil properties, and agricultural land use on nitrogen in groundwater. In R. F. Follett, D. R. Keeney, & R. M. Cruse (Eds.), *Managing nitrogen for groundwater quality and farm profitability* (pp. 19-57). Madison, WI: Soil Science Society of America.

Lax, S., & Peterson, E. W. (2009). Characterization of chloride transport in the unsaturated zone near salted road. *Environmental Geology, 58*, 1041-1049. http://dx.doi.org/10.1007/s00254-008-1584-6

Leighton, M. M., Ekblaw, G. E., & Horberg, L. (1948). Physiographic Divisions of Illinois. *The Journal of Geology, 56*(1), 16-33.

McCracken, M. (1971). *Structural features of Missouri*. Missouri Geological Survey.

McGrain, P. (1954). *Geology of the Carter and Cascade Caves area*. Kentucky Geological Survey.

Palmer, A. N. (1991). Origin and morphology of limestone. *Geological Society of America Bulletin, 103*(1), 1-21.

Palmer, A. N. (1981). *A geoglogical guide to Mammoth Cave National Park*. New Jersey: Zephyrus Press.

Panno, S. V., Hackley, K. C., Hwang, H. H., Greenberg, S. E., Krapac, I. G., Landsberger, S., & O'Kelly, D. J. (2006). Characterization and identification of Na-Cl sources in ground water. *Ground Water, 44*(2), 176-187. http://dx.doi.org/10.1111/j.1745-6584.2005.00127.x

Panno, S. V., & Kelly, W. R. (2004). Nitrate and herbicide loading in two groundwater basins of Illinois' sinkhole plain. *Journal of Hydrology, 290*(3-4), 229-242. http://dx.doi.org/10.1016/j.jhydrol.2003.12.017

Panno, S. V., Kelly, W. R., Martinsek, A. T., & Hackley, K. C. (2006). Estimating background and threshold nitrate concentrations using probability graphs. *Ground Water, 44*(5), 697-709. http://dx.doi.org/10.1111/j.1745-6584.2006.00240.x

Panno, S. V., Kelly, W. R., Weibel, C. P., Krapac, I. G., & Saragent, S. L. (1998). The effects of land use on water quality and agrichemical loading in the Fogelpole Cave groundwater basin, southwestern Illinois. *Proceedings of the Illinois Groundwater Consortium Eighth Annual Conference. Research on Agricultural Chemicals in Illinois Groundwater, April 1-2*, 215-233.

Panno, S. V., Krapac, I. G., Weibel, C. P., & Bade, J. D. (1996). *Groundwater contamination in karst terrain of southwestern Illinois.* Champaign, IL: Illinois State Geological Survey.

Panno, S. V., Kelly, W. R., Hackley, K. C., & Weibel, C. P. (2007). Chemical and Bacterial Quality of Aeration-Type Waste Water Treatment System Discharge. *Ground Water Monitoring & Remediation, 27*(2), 71-76. http://dx.doi.org/10.1111/j.1745-6592.2007.00138.x

Panno, S. V., Kelly, W. R., Weibel, C. P., Krapac, I. G., & Sargent, S. L. (2003). *Water quality and agrichemical loading in the two groundwater basins of Illinois' Sinkhole Plain*. Champaign, IL: Illinois State Geological Survey.

Paylor, R. L., & Currens, J. C. (2002). *Karst Occurrence in Kentucky*. Kentucky Geological Survey.

Petersen, J. C., Adamski, J. C., Bell, R. W., Davis, J. V., Femmer, S. R., Freiwald, D. A., & Joseph, R. L. (1998). *Water Quality in the Ozark Plateaus, Arkansas, Kansas, Missouri, and Oklahoma, 1992-95*. United States Geological Survey.

Peterson, E. W., Davis, R. K., & Orndorff, H. A. (2000). 17 b-estradiol as an indicator of animal waste contamination in mantled karst aquifers. *Journal of Environmental Quality, 29*, 826-834.

Peterson, E. W, Davis, R. K., Brahana, J. V., & Orndorff, H. A. (2002). Movement of nitrate through regolith covered karst terrane, Northwest Arkansas. *Journal of Hydrology, 256*(1-2), 35-47.

Peterson, E. W., Davis, R. K, & Brahana, J. V. (2000). The use of regression analysis to predict nitrate-nitrogen concentrations in springs of Northwest Arkansas. In Ira D. Sasowsky & Carol M. Wicks (Eds.), *Groundwater flow and contaminant transport in carbonate aquifers* (pp. 43-63). Rotterdam, Netherlands: A.A Balkema.

Quinlan, J. F., Ewers, R. O., & Aley, T. (1991). *Practical Karst Hydrology, with Emphasis on Ground-Water Monitoring. Field Excursion: Hydrogeology of the Mammoth Cave Region, with Emphasis on Problems of Ground-Water Contamination*. Dublin, OH: National Ground Water Association.

Seyfried, W. E. J., Janecky, D. R., & Mottl, M. J. (1984). Alteration of the oceanic crust; implications for geochemical cycles of lithium and boron. *Geochimica et Cosmochimica Acta, 48*(3), 557-569.

United States Geological Survey. (2010). Water Quality Data for Missouri, Retrieved October 26, 2010, from http://nwis.waterdata.usgs.gov/usa/nwis/qwdata

Unklesbay, A. G., & Vineyard, J. D. (1992). *Missouri Geology*. Columbia, MO: University of Missouri Press.

Vineyard, J. D., & Feder, G. L. (1982). *Springs of Missouri*. Rolla, MO: Missouri Department of Natural Resources.

White, W. B. (1988). *Geomorphology and Hydrology of Karst Terrains*. New York: Oxford University Press.

Wicks, C. M., Kelley, C., & Peterson, E. W. (2004). Estrogen in a karstic aquifer. *Ground Water, 42*(3), 384-389.

Willman, H. B., Atherton, E., Buschbach, T. C., Collinson, C. F., Hopkins, M. E., & Simon, J. A. (1975). *Handbook of Illinois Stratigraphy* Champaign, IL: Illinois State Geological Survey.