CHARACTERIZATION AND COMPARISON OF THE GEOCHEMISTRY OF HORN

HOLLOW VALLEY KARST WATERS TO OTHER

MIDWESTERN KARST SYSTEMS

Julie C. Angel

88 Pages   December 2010

This study examined the geochemistry of karst waters to delineate flow paths within a karst valley and compared nitrate and chloride concentrations to other karst systems.

APPROVED:

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Date   Eric W. Peterson, Chair

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Date   Stephen J. Van Der Hoven

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Date   Toby J. Dogwiler

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Date   Dagmar Budikova

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Geochemical studies of karst aquifers provide information about
groundwater quality, flow paths, and the susceptibility of an aquifer to
environmental degradation. This study analyzed the geochemical evolution of
waters in Horn Hollow Valley (HHV), a relatively pristine karst system located
in Carter Caves State Resort Park in northeastern Kentucky.   The objectives of
this study were to examine the evolution of waters along the longitudinal
profile of Horn Hollow Creek (HHC), to relate geochemical signatures to
stratigraphic units for flow path analysis, and to compare Cl^- and NO_3^-
concentrations in HHV waters to three other karst systems. The hypotheses
were designed to identify potential differences in chemistry along HHC during
individual sampling events and between multiple sampling events, to
determine if ions yielded clues regarding flow paths, and to examine
similarities and differences in nitrate and chloride concentrations in three
other Midwestern karst systems. To accomplish the study objectives, water

samples were collected from 16 locations during four sampling events. Major ion chemistry and selected field parameters were analyzed during baseflow and high flow conditions to observe evolutionary trends. A piper plot was constructed to identify water types and Ca/Mg ratios were used to determine dominant rock lithology. Saturation indices (SI) were calculated for carbonate species. Background concentrations for Cl^- and NO_3^- were calculated using cumulative probability plots and sources of nitrate and chloride were identified for HHV and comparison karst systems. The analysis showed that water chemistry evolved down slope from an initial autogenic signature to a gradational allogenic signature. Waters were mainly Ca-Mg-HCO_3 with slight variations influenced by discharge conditions. Carbonate rocks were dominantly limestone with lesser amounts of dolostone and SI increased down gradient. Geochemical signatures allowed for identification of generalized flow paths. The analysis and comparison of Cl^- and NO_3^- indicated that HHV waters were relatively pristine.

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JULIE C. ANGEL

Thesis Submitted in Partial
Fulfillment of the Requirements
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2010

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CHAPTER I

INTRODUCTION

Definition of Karst

Karst forms in regions underlain by relatively thick carbonate rock; generally limestone or dolostone. These landscapes can be identified by the presence of distinctive surface and subsurface expressions such as springs, sinkholes, caves, disappearing streams and a general lack of surface rivers and streams. In most karst regions, slightly acidic recharge waters mix with acidic soil waters to become groundwater undersaturated with respect to calcite and move down-gradient through joints and fractures in soluble carbonate bedrock. Karst features develop as these acidic and undersaturated waters dissolve bedrock, creating and enlarging myriad flowpaths over hundreds of thousands to millions of years. Groundwater may develop flow paths along bedding planes, especially where one rock unit is less resistant to chemical weathering. As these input features enlarge, they are able to transmit larger volumes of water, eventually pirating water from the surface to create extensive underground drainage systems. The epikarst serves as a major recharge zone for waters entering karstified bedrock. Klimchouk (1997) defines the epikarst zone as "the uppermost zone of exposed karstified rocks, in which permeability due to fissuring and diffuse karstification is substantially greater and more uniformly distributed in area, as compared to the bulk rock mass below." Previous geochemical and isotopic studies of epikarst waters show residence times ranging from a few days to a few months (Gunn, 1983; Klimchouk and Jablokova, 1989; Williams, 1983). Rapid flow from the epikarst generally

occurs through well-developed shafts, while slower drip waters flow through sets of narrow fractures and fissures (Klimchouk, 2000). Epikarst waters can rapidly flush following precipitation events, resulting in short-term changes in chemistry within the system and at springs. Water can also enter the karst system via bowl-shaped depressions in the ground called sinkholes. These surface depressions form as soil is transported into fractures and joints in the epikarst or as underlying cave passages collapse. Disappearing streams provide water to the subsurface as water sinks beneath surface stream beds into underlying passageways. Caves and large conduits form in the subsurface, some large enough for humans to enter and explore. Karst waters discharge at the surface via springs as waters intercept layers of insoluble rock or reach the elevation of a local surface stream (Palmer, 2007).

Karst terrain occupies approximately 10-20% of earth's surface and greater than 25% of earth's population utilizes groundwater from karst regions (Ford and Williams, 1989; Palmer, 1991). Therefore, it is important to be able to identify and study karst areas and develop environmental best practices to protect karst system waters. In well-developed karst, thin soils allow rapid water recharge to the subsurface, preventing natural filtration and biodegradation processes that generally occur in non-karst areas (White, 1988). In locations with human and agricultural development, rapid drainage results in the contamination of karst groundwater resources with human and animal wastes, agrichemicals from crop productions (Panno et al., 2003), and chemicals that are dumped or spilled on the ground (White, 1988).

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 system. 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 et al., 2007) and Missouri (Aley and Thomson, 1984) found that aeration-type systems are possible sources of nitrate, sodium, chloride and enteric bacterial contamination within the underlying karst systems.

Purpose of Study

Geochemical studies of karst aquifers provide much needed information about groundwater quality, flow paths, and the susceptibility of an aquifer to environmental degradation from anthropogenic sources. Major ion chemistry and measured parameters provide information as to whether a system is largely open or closed, whether recharge occurs via conduit flow or diffuse flow, if system waters are from shallow or deep sources, the residence time of waters within the system, and may also yield flow path information based on dissolved species.

This study contributes to the science of karst hydrogeology by analyzing the geochemical evolution of karst waters as they move down slope in Horn

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Hollow Valley (HHV), a relatively pristine karst system, and by comparing NO_3^- and Cl^- concentrations from HHV to those in other karst systems. The opportunity to find and study a relatively pristine karst system is rare and may provide initial data towards determining baseline groundwater conditions in the eastern United States. Development forecasts indicate that land-use changes surrounding HHV are forthcoming, therefore, a current geochemical baseline of valley waters is needed for these and future studies to quantify changes in water quality as urbanization/development proceeds. Relating geochemical signatures to stratigraphic units within the valley will significantly increase understanding of flowpaths within the system and will aid long-term projects initiated at Carter Caves to study the origin of the Carter Caves systems and the effects of urbanization/development on karst terrains. Knowledge gained from this study can be utilized by state and local planning agencies to protect sensitive karst resources.

Comparison of NO^{3-} and Cl^- concentrations in Horn Hollow waters to those in other karst systems will contribute additional data towards our understanding of the environmental state of these midwestern karst waters. Comparison systems include Mammoth Cave, Ky, Southwestern IL sinkhole plain, and the Salem Plateau of the Missouri Ozarks. Data for comparative systems were available for NO_3^- and Cl^-, major ion chemistry, and measured parameters.

Hypotheses

The hypotheses for this study were designed to answer four main questions:

Question 1: Are there differences in Horn Hollow water chemistry parameters along the longitudinal profile of the stream?

Question 2: Are there differences in Horn Hollow water chemistry parameters between sampling events?

Question 3: Do the ions within Horn Hollow waters provide information regarding flow paths and water contact with specific geological units within the valley?

Question 4: Are there similarities and/or differences in NO_3^- and Cl^- concentrations between HHV and three other Midwestern karst regions?

Previous Work

Few karst studies have been conducted in the Carter Caves area, and there are no known published data of the geochemistry of HHV waters.

Groundwater resources in Carter County, KY have been studied by the Kentucky Geological Survey (Carey and Stickney, 2001), focusing on the topography and geology of the county, groundwater availability and quality, and karst regions within the county.

An investigation of the origin of several caves within CCSRP (Ochsenbein, 1974) examined the role of solutional and abrasive processes in the morphology of the caves and considered possible controls related to cross-

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bedding within the limestone layers. Solutional processes along bedding planes were identified as the initial mechanism for cave formation. As surface streams invade cave conduits, solution and abrasion provide duel mechanisms for cave enlargement. Well developed cross bedding was found to control both the shape and orientation of cave passages. The study found significant variation in the processes responsible for cave morphology, even in caves within close proximity.

A number of studies related to the biology and geology of Horn Hollow have been published by the Wittenberg University Speleological Society in their *Pholeos* publications (Hobbs and Pender, 1985).

Two pamphlets containing overviews of the stratigraphy, structure and hydrogeology of the Carter and Cascade caves area were published by the Kentucky Geological Survey (McGrain, 1954; McGrain, 1966), with sections devoted to caves within the Horn Hollow Valley (HHV).

Engel and Engel (2009) investigated the relationship of structural and stratigraphic features to formation of dominant cave passages in Carter County, KY. Examination of 13 caves showed passage orientations formed parallel to joint and fracture trends and drainage features in the area. Field evidence also showed horizontal water movement along bedding planes, with caves developing in similar lithologic units. Results of this study show that cave speleogenesis in the Carter Caves region was controlled by both stratigraphic and structural mechanisms.

Woodside (2008) conducted a thorough investigation of the longitudinal profile of HHV to determine if changes in grain size and channel morphology could be used to identify anomalies in the longitudinal profile of the valley. Anomalous concave-downward features were identified along the profile as indicators of current or past karst features within the Horn Hollow Creek channel. Increases in grain-sizes of stream sediments were also noted in four areas of the valley that exhibited the anomalous features, showing a correlation between the presence of the anomalies and changes in grain size. Geomorphic evidence showed that the upper valley experienced natural down cutting while the middle valley and portions of the lower valley channels were remnants of collapsed cave passages.

A GIS study by Harlan (2009) developed a database of the Carter Caves State Resort Park (CCSRP) area that included the locations and elevations of known caves, the location of sinkholes and lineaments, and a stream network model. These data were used to develop a conceptual model of the karst terrain within HHV and to determine if the system contains multiple levels of cave development. The study concluded that caves in the CCSRP region are present on four stratigraphic levels within specific lithologic units, similar to those in the Mammoth Cave area. Stream models also indicate that tributaries of Tygart's Creek are still down cutting through the carbonate units of the Newman Limestone.

Several studies have been conducted to determine the chemical evolution and groundwater origins of karst systems in the Ozark Plateau of

Missouri (Wicks, 1997; Wicks, 1999; Wicks and Engeln, 1997). Methods used in these investigations are of particular interest for the Horn Hollow geochemistry study, especially those related to determining flow patterns, observing geochemical changes within karst streams, and identifying source waters for karst systems.

Geochemical research within the intensely karstified southwestern Illinois (SWIL) sinkhole plain (Panno et al., 1996, Panno et al., 1998, Panno et al., 2003, Panno and Kelly, 2004) 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. Hackley et al., 2007, sampled 10 springs and 17 wells in the SWIL karst to identify dominant sources of nitrate by analyzing chemical, isotopic and bacterial parameters. Nitrogen fertilizers and soil organic matter contributed the bulk of nitrate concentration in the spring waters. 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.

Carter Caves State Resort Park (CCSRP) Study Location

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 and Stickney, 2001; Paylor and Currens, 2002). The study site, 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. 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 a tributary to Tygart's Creek. HHV terminates as a 14 m hanging valley above the aggressively down-cutting waters of Cave Branch (McGrain, 1954). Elevation change within the valley is ~30 m and the longitudinal profile is ~2000 m (Woodside, 2008).

CCSRP Stratigraphy and Structure

The complex lithostratigraphy of the Mississippian and Pennsylvanian rock units of northeastern Kentucky has been described and classified by a number of authors (Dever et al., 1977, Englund and Windolph, 1971, Ettensohn et al., 1984, Grabowski, 2001, Horne and Ferm, 1979, Horne et al., 1979). Stratigraphic units in CCSRP are Mississippian- to Pennsylvanian-aged consolidated sedimentary rocks and unconsolidated Quaternary-age sediments. These units formed in various depositional environments related to barrier and back-barrier island complexes. During the Paleozoic Era, large inland seas transgressed and regressed across the region, producing complex, intercalated layers of limestone, sandstone, shale, siltstone, dolostone, and coal

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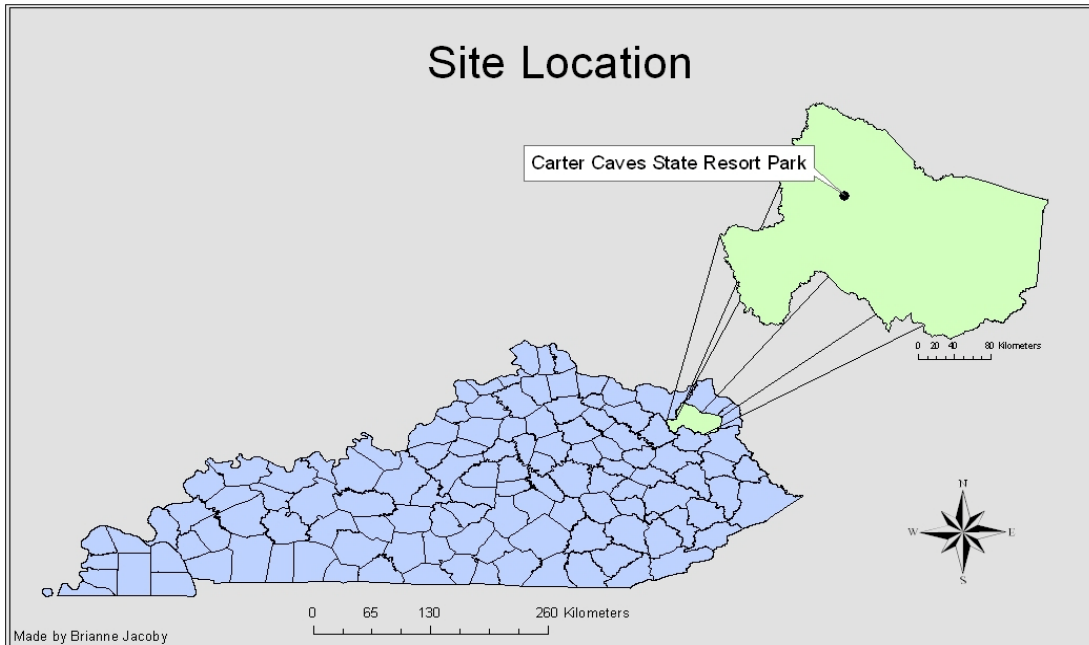
Figure 1. Site location of Carter County and Carter Caves State Resort Park.

(Dougherty, 1985; Tierney, 1985). These units correlate to those in other areas of Kentucky but are thinner in northeastern Kentucky from tectonic uplift along the Cincinnati and Waverly Arches to the west (McGrain, 1954; Tierney, 1985). Rocks dip gently to the east-southeast at 0.3° to 2° (McGrain, 1966).

A general stratigraphic column of the Carter Caves area (Figure 2) shows the relationship between Mississippian and Pennsylvanian rock units within the park. The Borden Formation is the oldest rock exposed in the CCSRP area and is approximately 90 m thick. The Borden consists of alternating sequences of red and green shales and siltstones and rests unconformably beneath the former Newman Formation limestones. The Newman limestones and the Renfro Member (formerly assigned to the Borden Formation) have

recently been designated as the Slade Formation (Ettensohn et al., 1984). The lowest unit within the Slade Formation is the Renfro Member, a thin-bedded crystalline dolostone with interbedded fine-grained limestone and lesser amounts of dolomitic siltstone, shale, and sandstone. The unit is generally ≤ 2 meters in northeastern Kentucky. The St. Louis Member rests conformably above the Renfro Member and is a series of light-gray fine-grained limestones, micritic limestones, cherts and greenish-gray shales. The St. Louis limestone formed during periods of marine advance during the late Mississippian in a subtidal environment. Uplift of the Waverly Arch during deposition resulted in erosion and alteration of the upper St. Louis. The Ste. Genevieve Member unconformably overlies the St. Louis Limestone. The unit consists of very light olive-gray to olive-gray oolitic and skeletal limestones with some intercalated shale and sandstone. The limestones are thin to thickly-bedded and cross bedded, indicating the presence of a high-energy, near shore, tidal-zone environment during deposition (McGrain, 1954; Wiggers, 1997); possibly as offshore carbonate islands. Above the Ste. Genevieve is the Upper Member of the Slade Formation containing cross bedded, thin to thick sandy limestones interbedded with shales and a thin layer of dolomitic limestone near the base. These units were deposited in tidal bar belt, tidal channel, and barrier environments. Joints are prominent in the Upper Member and Ste. Genevieve limestones, providing recharge sites for aggressive waters capable of dissolving carbonate rock (McGrain, 1954; Engel and Engel, 2009). Having formed in lagoon and tidal mud flats and open marine environments, the Pennington

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Formation sandstones, limestones and shales rest conformably above the Upper Member. The Carter Caves Sandstone, a unit within the Pennington, is an elongate deposit of fine- to medium grained, well-sorted quartz sandstone that extends from eastern Rowan County to southwestern Greenup County. Samples analyzed by Horne and Ferm (1979) at the CCSRP Lewis Caveland Lodge near HHV were fine-grained with calcareous cement, while Carter Caves sandstone at Echo Canyon was overlain by red and green shales and interbedded with dolomite. Pennington sandstones also contain plagioclase and microcline feldspars, along with biotite and chlorite (Connor, 1981). The undivided Lee and Breathitt Formations represent resistant, ridge-capping Pennsylvanian-aged rock in the CCSRP area. The lower Pennsylvanian Lee is dominantly a resistant, cross bedded, fine- to medium- grained quartzose sandstone with small amounts of siltstone and significant jointing and fracturing. Maximum thickness of the Lee Sandstone is approximately 41 m. The Breathitt Formation contains numerous beds of crossbedded sandstone, siltstone, shale, clays and coal. Most beds are 10-15 m thick. Shales in the lower Breathitt contain concretions of siderite, with sphalerite, galena and kaolinite found within shrinkage cracks. Sandstones in the upper Breathitt are fine- to medium grained and micaceous. The Tom Cooper Coal bed of the Breathitt can be identified in outcrop above the middle to lower valley segment of HHV on the Tygarts Creek Quadrangle Map (Sheppard, 1964).

Significant karst development has occurred within three subdivisions of the Late Mississippian Slade Formation: the St. Louis limestone, Ste. Genevieve

limestone, and the Upper Member limestone (Ochsenbein, 1974; Tierney, 1985), with the Ste. Genevieve acting as the major cave producing unit in the region. These cave-forming limestones are exposed in valley walls and floors in the Carter Caves area as a result of the down cutting of surficial streams. Rocks of the Borden Formation are more resistant to erosion than the overlying Mississippian limestones, therefore, they represent the lower boundary of limestone dissolution in the CCSRP area.

Local and Regional Hydrogeology

CCSRP resides within the Appalachian Plateaus sub region of the Appalachian Plateaus and Valley and Ridge Ground Water Region of North America (Heath, 1988). This sub region is characterized by uplifted, dissected plateaus that are capped by resistant Pennsylvanian-aged rock.   Most groundwater flow systems occur within 100 m of the land surface where jointing and fracturing have increased the permeability and porosity of rock units in valley walls and bottoms (Seaber et al., 1988). The longitudinal extent of groundwater flow paths in this region is relatively short, with many individual, self-contained systems draining into major streams (Parizek et al., 1971). Horn Hollow Creek conforms to this model, discharging into Cave Branch, a tributary stream to Tygart's Creek. Tygart's Creek is the main stream in the CCSRP vicinity and eventually discharges into the Ohio River to the north. Horn Hollow Creek and Cave Branch are still down cutting through soluble limestones; Tygarts Creek has incised into the insoluble shale and
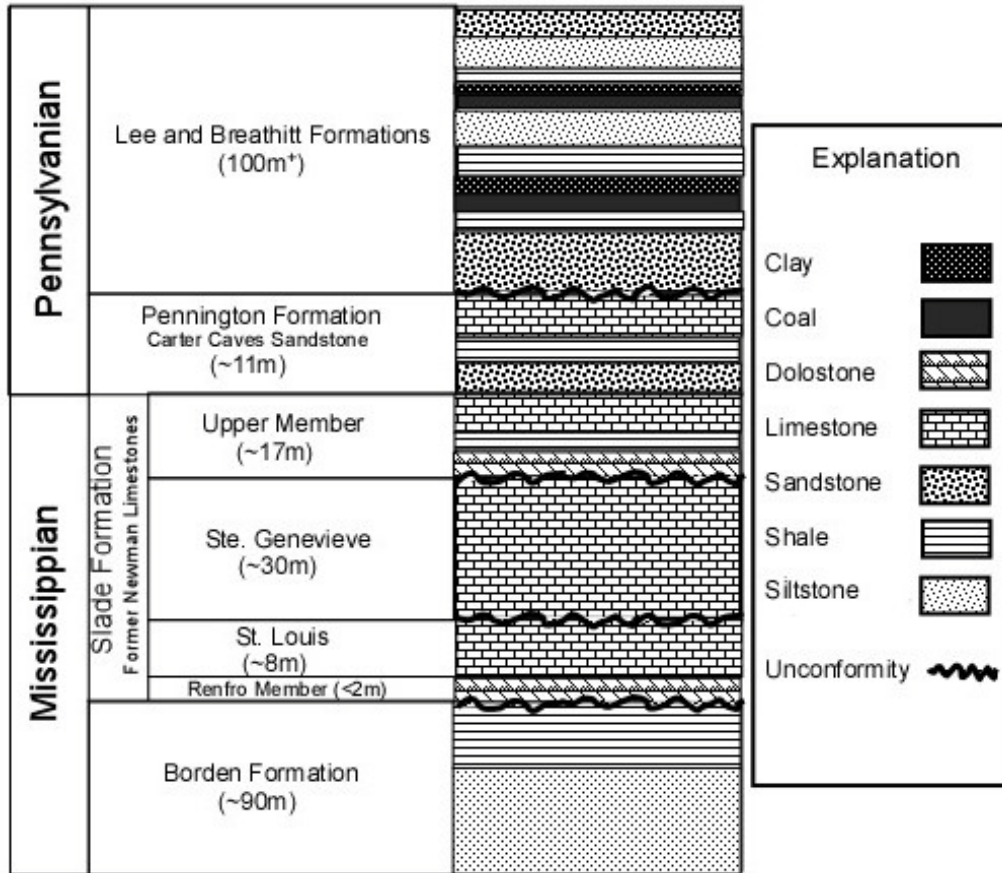
Figure 2. Stratigraphic column of CCSRP showing the cave forming Newman limestone units of the Slade Formation. Thickness of units modified from Ochsenbein (1974).

siltstone of the Borden Formation and is no longer down cutting. The aforementioned drainage system is part of the Little Sandy-Tygart's Creek Drainage Basin (Carey, 2009). Springs are common and can be seen flowing from carbonate units along valley walls. In the CCSRP area, many springs emerge at the contact between the Ste. Genevieve and St. Louis limestones (McGrain, 1954). Aquifers in the Appalachian Plateaus sub region form in sandstone, conglomerate, and limestone units, with water types in the

carbonate units dominantly Ca-Mg-HCO$_3$ type. The geochemistry of groundwater in this region is a reflection of the aquifer materials along flow paths (Seaber et al., 1988).

Most karst systems receive waters through a combination of allogenic and autogenic recharge (Palmer, 2007; White, 1988). Allogenic waters enter karst regions as surface flow or sinking streams from adjacent, insoluble rock units. These waters exhibit flashy responses to precipitation events and have variable discharge and flow rates. Well-developed conduits form in systems with solutionally aggressive allogenic recharge. Conduit flow dominates the flow regime and discharge is generally through a single, large spring (Schuster and White, 1971). Conversely, purely autogenic waters are derived from precipitation that falls directly on the karst landscape and enter the system as internal runoff and diffuse flow; collectively known as epikarst/drip waters. Karst systems dominated by autogenic recharge have smaller ranges in variability of flow rates, exhibit poorly developed conduits, and discharge through several smaller springs and seeps. Field observations of HHV during four sampling events revealed well-developed conduits, variable discharge rates and flashy responses to precipitation events and evidence of subsurface flow within inaccessible conduits. There were several drips from valley walls and cave domes and the majority of valley waters discharged through a single, large spring.   Therefore, the Horn Hollow karst system receives recharge through a combination of allogenic and autogenic sources, with significant

allogenic conduit flow and lesser amounts contributed by autogenic recharge as internal runoff or diffuse flow.

HHV can be subdivided into three segments based on flow characteristics of Horn Hollow Creek; the Upper Valley, Middle Valley and Lower Valley. The Upper Valley is an example of a valley that has been underdrained. White (1988) defines this morphology as one in which "the valley retains its fluvial shape, its gradient, and the surface channel is clearly visible, although it may frequently be dry." Allochthonous waters from the Lee and Breathitt formations are pirated to the subsurface a short distance downstream of the Horn Hollow headwall (HHH) (Figure 3) via well-developed, vertical joints and fractures. Fudge Ripple Cave (FR) is directly downstream of HHH, approximately 4 m beneath a narrow NW-SE trending fracture. Field observations indicate that FR may receive at least some of the pirated waters from HHH. Volcano Cave (VOL) is a short distance down gradient on the west side of Horn Hollow Creek. VOL waters are derived from subsurface conduits and from a perennial surface stream flowing into the horizontal entrance. Redbird Spring (RS) and Warrior Spring (WS) are located within two separate draws along the north side of the Upper Valley. Waters from these low-flow springs appear to discharge from bedding planes well above the dry stream channel. Bowel Spring (BS) is the resurgence of Upper Valley waters and defines the last sampling location within the Upper Valley. Upper Valley waters flow in the well-developed surface channel of Horn Hollow Creek only during significant rain events.

The Middle Valley of the Horn Hollow system is dominated by surface flow. Resurgence waters from BS enter a very large beaver pond created by a dam extending the full width (~120 m) of the valley. Waters flow over the top of the dam and enter Cobble Cave Inlet (CCI) ~30 m downstream on the east side of the valley. Cobble Cave extends into the valley wall as a horizontal phreatic conduit, meandering back to the surface a short distance downstream at Cobble Cave Outlet (CCO). Horn Hollow Creek widens and shallows for ~60 m until waters flow into the upstream inlet of Horn Hollow Cave (HHI). As waters enter HHI, the main trunk passage is met by a very small tributary stream flowing from the northeast. Surprise Dome (SD) is located approximately 10 m upstream and to the right of this stream and appears to receive epikarst waters that collect in a small pool at the base of the dome. Past the confluence of the main and tributary channels, water flows in a single conduit for ~159 m downstream (McGrain, 1954) until it exits the cave at the Horn Hollow Outlet (HHO), the furthest downstream sampling site within the Middle Valley. Creek waters flow along the base of a vertical rock face on the west side of the channel and enter the subsurface through a swallet. Rimstone Cave (RIM) is located in the valley wall to the west of Horn Hollow Cave. The caves are connected by a small crawlway, but RIM is not hydrologically connected to Horn Hollow Creek. RIM contains beautiful rimstone dams that form as drip waters enter through a dome.

Under baseflow conditions the Lower Valley is underdrained. Waters pirated by the HHO swallet remain in the subsurface until they discharge at the

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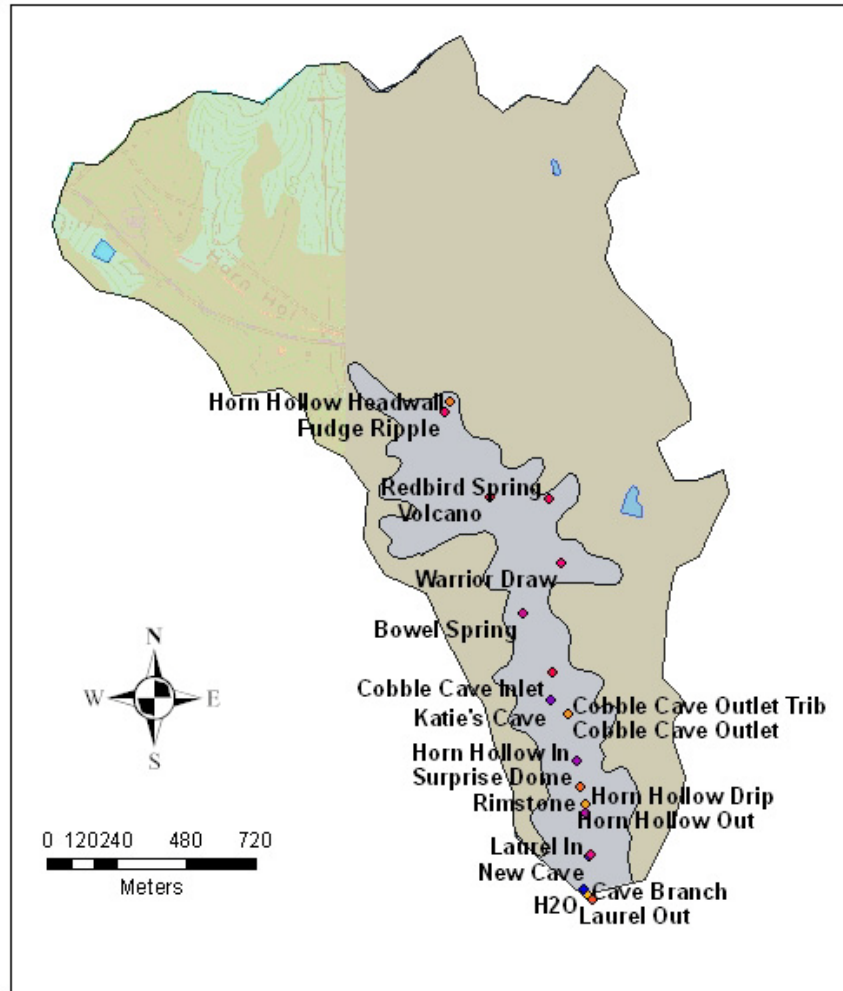
Figure 3. Sampling site locations within the Horn Hollow karst system. Tan area represents Pennsylvanian-age rock units; Gray area represents Mississippian-age rock units.

H$_2$O Cave Outlet (H$_2$O-O) above Cave Branch (CB). Between the swallet and New Cave (NC), the surface channel is dry and carries water only during high flow events, with the exception of a low-flow drip located on the east valley wall a short distance from HHO . Horn Hollow Drip (HHD) waters discharge from a small, 10 cm diameter conduit that likely formed along a bedding plane. Waters flow within an 8 cm by 10 cm dissolved bedrock channel for

approximately 1.5 m before cascading over the lip of the east bank and into the dry stream channel. NC was discovered during the June 2006 field season within the downstream left bank near the terminus of the dry surface channel. Observations of the NC stream suggest that these waters flow to the southeast towards H_2O-O. NC acts as a drain for waters flowing within the dry surface channel during high flow conditions. Directly above NC is the upstream entrance (LI) to Laurel Cave, a horizontal, multi-level cave with ~260 m of lower level traversable conduit. Water drips from a small conduit in the cave wall a short distance inside LI, forming a gravel-filled pool at its base. The lower level carries low volumes of water during baseflow and serves as an overflow channel for floodwaters within the upstream surface channel during high flow events. The downstream entrance of Laurel Cave is located approximately 10 m above Cave Branch within the north bluff and downstream from H_2O-O. Waters discharge from this large, dry entrance only during high flow events, while baseline waters appear to be pirated to lower, inaccessible conduits a short distance inside the entrance. The last Lower Valley sampling site is a perennial, low-flow seep labeled Laurel Out (LO). It is located ~3m above Cave Branch and directly beneath the Laurel Cave entrance.

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Descriptions of Comparison Systems

</div>

Mammoth Cave

The Mammoth Cave system is located in west-central Kentucky within the Western Pennyroyal Plateau and Chester Upland region (Currens, 2002). It

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 (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.

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 of 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, 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 groundwater basins; the Fogelpole Cave Basin and Collier Spring Basin (Panno, 1998, Aley et al., 2000). 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.

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 and 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. Deciduous forest dominates the plateau with pasture land of fescue and Kentucky bluegrass (USGS, 1995). Some cattle and poultry operations are also present in this region. (Petersen, et al., 1998). 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

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Table 1. Carbonate lithologies of comparison karst systems.

Karst Region	Primary Geologic Formations	Carbonate Lithology
Salem Plateau (Missouri Ozarks)	Ordovician: Roubidoux Formation and Gasconade Dolomite Cambrian: Eminence Dolomite and Potosi Dolomite (Feder, 1973; Imes and Emmett, 1994; Unklesbay and Vineyard, 1992)	*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
Salem Plateau (southwestern Illinois Sinkhole Plain)	Mississippian: St. Louis Limestone, Ste. Genevieve Limestone, and Salem Limestone (Willman, *et al.* 1975)	*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
Mammoth Cave, KY	Mississippian: Girkin Limestone, Ste. Genevieve Limestone, and St. Louis Limestone (Haynes, 1964)	*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.

Dolomites, many along prominent rivers that course through the region.

Recharge to karst groundwater occurs through faults and fractures and within

sinking stream segments of surface waters.

CHAPTER II

METHODOLOGY

To test hypotheses 1 and 2, the following methods and procedures were employed:

Water samples were collected during four field sampling events from 16 specific locations in Horn Hollow Valley to determine the evolution of waters from the upper to the lower portions of the valley. 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.

Field parameters were collected at the sampling sites during each event for dissolved oxygen (DO) (mg/L), specific conductance (SpC) (µS), temperature (°C), and pH using a YSI Model 63 pH meter and YSI Model 85 probe. *In situ* field titrations were performed with a Hach digital titration kit (Model 16900) to measure alkalinity (mg/L as $CaCO_3$)(method 8203), total hardness (mg/L as $CaCO_3$)(method 8213), and carbon dioxide (mg/L as CO_2)(method 8205).

Major cation and anion samples were collected, stored in polyethylene bottles, and transported to the Illinois State University laboratory in ice-filled coolers. Cation samples were passed through 0.45 micron filters and acidified with three drops of nitric acid in the field. Cations were analyzed in the Illinois State University laboratory using an Thermo-Jarrell Ash Inductively Coupled Argon Plasma Spectrometer (ICAP). K^+ concentrations for November 2006 were analyzed using Atomic-adsorption spectroscopy (AA). Anions were analyzed using an Dionex DX-120 Ion Chromatograph (IC). Cations and anions examined in

this study were calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), silica (Si), chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate as N (NO_3-N). Bicarbonate (HCO_3^-) values in mg/L were calculated using equation 1 (Basu, 2008):

Alkalinity(as $CaCO_3$) x 1.22 (1)

Several sample sites had charge balance errors (CBE's) of well over 15%. Most CBE's were positive, reflecting a shortage of anion charge. Bicarbonate makes up most of the anion charge within carbonate waters, therefore, it is likely that alkalinity error is responsible for the large CBE's. All field titrated alkalinity values were checked against values derived from the following linear regression equation developed by Panno (1998) from alkalinity titrations in the Ca-HCO_3-type waters of Illinois' sinkhole plain:

A = 0.48 [SpC - ([NO_3^-] + [SO_4^{2-}] + [Cl^-])] - 22.8 (2)

With only a few exceptions, titrated alkalinity values from samples with low CBE correlated well with calculated values from the equation 2. For the nine samples with high CBE, the calculated values were substituted for the actual titrations, resulting in acceptable CBE's. Human or equipment error may be responsible for the erroneous field titration values.

Stream gauging was completed at four locations within the middle to lower portion of the Horn Hollow system to determine total discharge during sampling events. Discharge was measured using the velocity-area method (Mosely and McKerchar, 1993), where velocity in a vertical section was measured at the 0.6 depth with an electromagnetic velocity meter.

Geochemical data were analyzed using AquaChem® and its component PHREEQC to produce piper plots to delineate water types and to derive saturation indices (SI) for aragonite, calcite, dolomite, gypsum and pyrite. Scatter plots were produced to identify evolutionary trends of dissolved species, to attempt to determine sources of rock-water interactions, and to identify the carbonate rock type (limestone or dolomite) contacted by karst waters along subsurface flowpaths using Ca/Mg ratios (White, 1988).

During the June 2006 sampling event, water samples were collected for nitrogen (N) isotopic analysis by the Illinois State Geological Survey (ISGS). 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 ISGS laboratory in ice-filled coolers. Isotopic analysis was performed at the ISGS to identify values for $\delta^{15}N_{Air}$ (permil) and $\delta^{18}O_{SMOW}$ (permil). A scatter plot was produced for $\delta^{18}O_{SMOW}$ (permil) vs $\delta^{15}N_{Air}$ (permil) to identify different sources of nitrate using end-member sources from Clark and Fritz (1997).

Three qualitative dye traces were initiated in June 2006 to delineate flow paths within HHV. Background charcoal packets were installed at 16 locations within the valley to check for possible interferences with dye detection. The background packets were replaced with fresh packets prior to tracer injection. All tracer injections were performed in the upper portion of HHV; 2.14435 kg of NaCl solution was injected into Hillside Pit, 25 fl. oz. of fluorescein dye was injected into the stream approximately 15m above the

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inlet to Volcano Cave, and 20 fl. oz of rhodamine dye was injected at the Horn Hollow Head Wall. Two kg of NaBr was subsequently injected into the lower spring at Fudge Ripple Cave due to low flow conditions at the head wall. ISCO samplers were placed at three locations within HHV; HHO, NC, and H_2O, and were set to collect samples, temperature and specific conductance once per hour for 48 hours. Samples were analyzed at the Illinois State University laboratories for the presence of ions from the tracers. Dye packets were retrieved two days after tracer injection and qualitatively tested for dye absorption using a KOH elutriant.

To test Hypotheses 3 and 4, the following methods and procedures were employed:

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

Data for the comparison systems were obtained from the following sources:

Table 2. Data Sources for Comparison Karst System.

Karst Regions	Data Source
Ozark Plateau (Missouri)	Vineyard and Feder (1982) and United States Geological Survey (USGS) (2010)
Southwestern Illinois sinkhole plain	Illinois State Geological Survey S. V. Panno (2009)
Mammoth Cave, Kentucky	J. Meiman – Mammoth Cave National Park hydrologist (2009)

CHAPTER III

RESULTS AND DISCUSSION

Delineation of System Waters from Seep/Drip Waters

To observe the geochemical evolution of HHV waters, this study limits the sample representation to only system waters; those waters initially contributed by allogenic flow and represented by surface water or shallow subsurface conduit waters of Horn Hollow Creek. As these waters move down gradient and further into the HHV system, they interact with carbonate bedrock and become increasingly saturated with carbonate minerals. The chemistry of these system waters also changes as mixing occurs with autogenic waters that collect directly on the karst landscape.

Geomorphic observations and analyses of pH, hardness, temperature, water type and SI (calcite, aragonite and dolomite) were used to delineate the evolving allogenic system waters from relatively low flow allogenic seep waters and autogenic drip waters. Waters from the surface seeps generally flow onto the dry surface channel of Horn Hollow Creek, either evaporating or entering small fractures in the bedrock surface. Drips from domes and bedding plane partings within cave entrances appear to have little hydrologic connection to the bulk of evolving system waters. The low discharge from these sites would contribute negligible geochemical changes to system waters even with a direct hydrologic connection. Therefore, to observe the down gradient evolution of system waters on graphs and plots, it was necessary to remove these sites from the evolution database.   Several sites were sampled only once or twice,

therefore, more data are needed to make definitive conclusions regarding source waters.

Six sites were classified as seep/drip waters and removed from the geochemical evolution database. These sites were Redbird Spring (RS), Warrior Spring (WS), Surprise Dome (SDome), Horn Hollow Drip (HHD), Rimstone (RIM), and Laurel Cave Inlet (LI). Waters from RS and WS emerge along bedding planes within Upper Valley draws and receive their flow from shallow sources. As with many springs in Kentucky, RS and WS probably receive waters that flow downward through fractures and joints in the Pennington Formation and Upper Mississippian limestones. As waters reach more resistant rock units, they flow laterally and emerge as springs along valley walls. RS waters are Ca-Mg-HCO$_3$ type, suggesting flow paths intersecting interbedded limestones and dolostones of the Lee and Breathitt, Pennington and Upper Member Formations. The pH at RS is slightly acidic and waters are moderately hard as a result of relatively high concentrations of Ca^{2+} and Mg^{2+} (Figure 4). These allogenic waters are slightly undersaturated with respect to carbonate species (Figure 5) and are therefore, still capable of dissolving carbonate rock. RS temperature (Figure 6) is almost identical to that of surface waters entering the valley at the headwall (18.8 °C) and may be the result of short residence time in the subsurface or from seepage of very warm waters from a man-made pond above the draw. WS waters are Ca-HCO$_3$, indicating flow primarily through limestone. The sample from Warrior exhibits low pH and hardness values (Figure 4) and waters are highly undersaturated (Figure 5). Warrior Spring temperature (13.2°C) was

intermediate of surface water and groundwater temperatures from the same sampling event (Figure 6). Warrior source waters may be derived from the mixing of allogenic waters and groundwater, as mixing of waters with different SI's and temperatures reduces saturation levels of ions and temperature of the mixed solution. Warrior may also be receiving rapid input from the precipitation event that occurred the night before, resulting in dilution of waters and lower overall SI.

HHD waters are characteristic of allogenic seep waters and emerge from a small conduit developed within a bedding plane parting in the Middle Valley. These waters are undersaturated with respect to carbonate minerals, especially dolomite (Figure 5) therefore, flow paths are developed mainly within limestone. The acidic pH and low hardness (Figure 4) along with moderate variability of water temperature during all sampling events (Figure 6) suggests short residence times in the subsurface. These waters flow onto the dry bedrock surface of Horn Hollow Creek and appear to evaporate or flow into small fractures in the bedrock surface.

SDome and LI waters are Ca-HCO$_3$ type and very similar with respect to chemistry and field parameters. SDome waters drip from a bedding plane within a 5-6 m dome in Horn Hollow Cave with no evidence of secondary calcite formation within the dome. LI waters flow from an ~10 cm conduit formed within a bedding plane parting in the upstream entrance of Laurel Cave. Waters from both locations are acidic with low hardness, plotting in the same position on Figure 4. Temperatures at each site appear to have equilibrated

with bedrock temperatures, as they show little variance between sampling events (Figure 6). SI's were virtually the same for all carbonate species; undersaturated with respect to calcite and aragonite and highly undersaturated with respect to Mg^{2+} (Figure 5). These waters were probably not in contact with dolomite layers or shales due to the absence of significant Mg^{2+}.
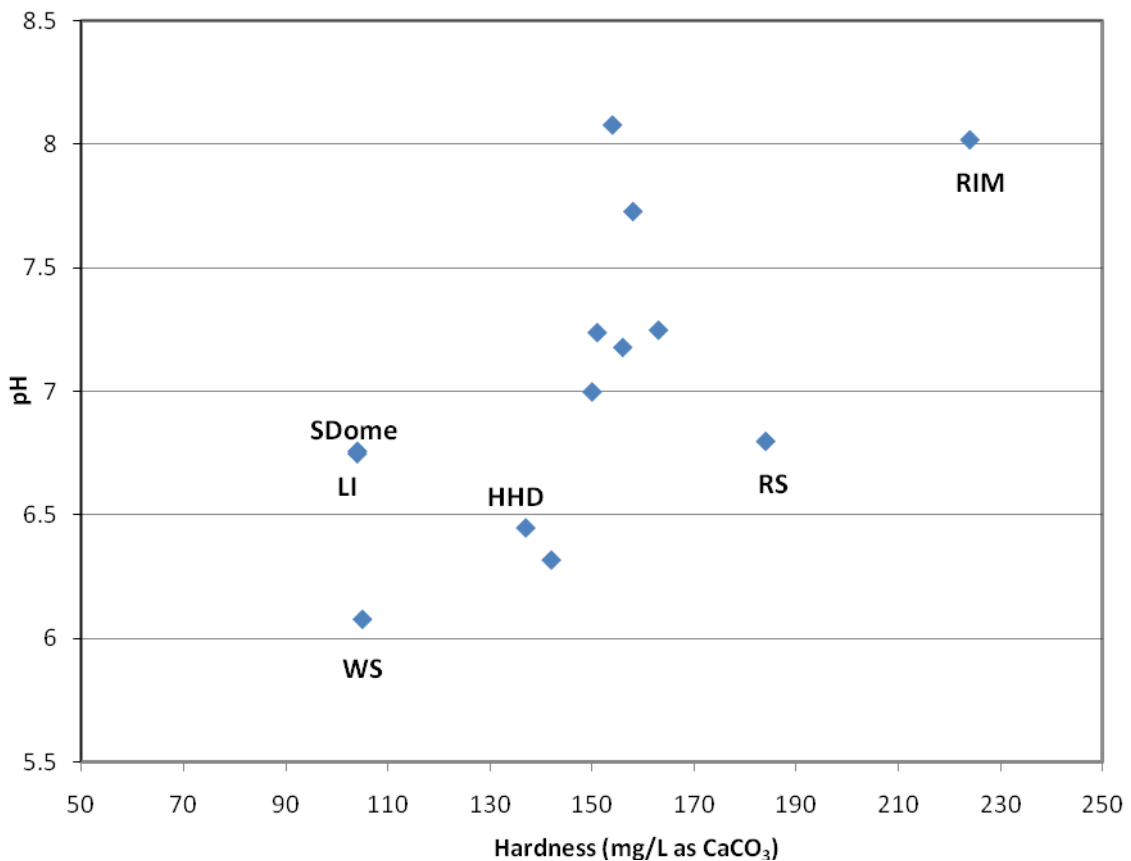
Figure 4. Hardness and pH of the seep/drip sites. Note that SDome and LI plot at the same location. Data points that are not labeled are system waters.

RIM waters exhibit the characteristics of diffuse drip waters that have spent longer residence time in the subsurface. Waters drip from flowstone

within a 5-6 m dome, and are supersaturated with respect to calcite and

aragonite (Figure 5). As these waters enter the cave atmosphere, reduced

atmospheric pressure causes degassing of CO_2 and concomitant precipitation of

calcite, forming rimstone dams. Temperatures are slightly lower than those

measured at LI and SDome (Figure 6) and show little to no variance between
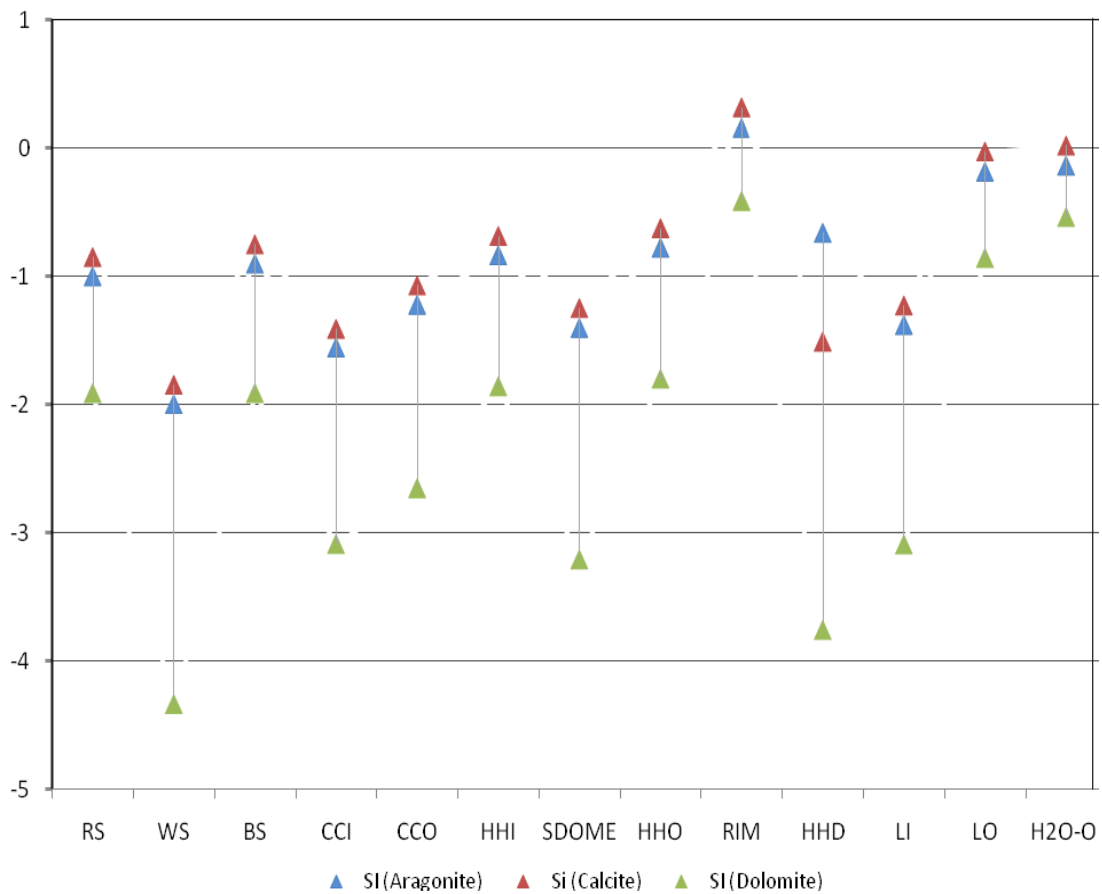
Figure 5. Saturation Indices for HHV sites on June 21, 2006. Vertical lines show
data ranges.

sampling events. Measured parameters show a very basic pH and relatively

high hardness when compared to other sites in HHV (Figure 4).

System water sites were identified as HHH, FR, VOL, BS, CCI, CCO, HHI, HHO, NC, LO and H_2O-O.
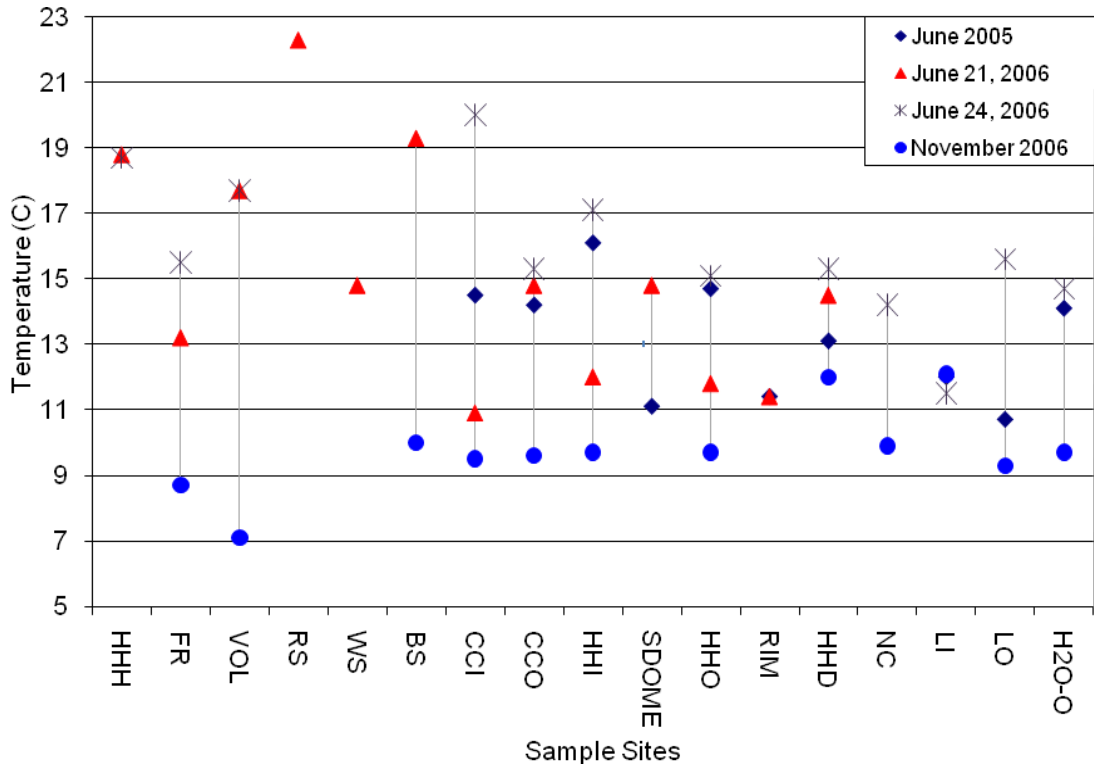
Figure 6. Temperatures of water for all HHV sampling sites during each sampling event. Vertical lines show data ranges.

Horn Hollow Valley Field Parameters

Stream Discharge and Precipitation Regimes

Precipitation events and resulting changes in discharge may produce noticeable changes in the measured and chemical parameters of a system as waters utilize different flow paths under changing flow conditions. Rain events are capable of flushing longer residence waters from the epikarst and bedding

planes, thereby increasing the concentrations of ions within system waters. Dilution of ion concentrations can also occur after high-intensity rains and rapid snow and ice melts. Therefore, it is important to measure stream discharge to classify flow conditions during sampling events. Stream discharge was measured at four locations within the Middle Valley during each sampling event (Table 3). Measured discharge for June 2005 and June 2006 were considered base flow with the exception of the June 2005 discharges at HHI and HHO, which were measured after a 1.5 cm rain during the overnight hours. November 2006 discharge was 27% greater than June 2005 and 36% greater than June 2006.

Climatological data were obtained for each sampling event to observe precipitation regimes during the four month period prior to sampling, during the month of the sampling event, and for the specific date of each sampling. Precipitation was normal for each observation period related to the June 2005 sampling event. June 2006 and November 2006 precipitation was also within normal ranges during the four month period prior to each sampling and during the month of each sampling event. Anomalous precipitation regimes were observed on June 24, 2006 where precipitation rates were above normal and on November 18, 2006 where precipitation was slightly above normal. These findings are in agreement with measured discharge and subsequent classification of flow regimes for HHV. These flow regimes may or may not be representative of base flow and high flow conditions over an entire year, but are an assessment of conditions observed during the specific sampling events.

Table 3. HHV discharge showing baseline and high-flow events.

Location	June 2005	June 2006	November 2006
CCI	0.0018 m^3/s	0.0015 m^3/s	0.0221 m^3/s
CCO	0.0016 m^3/s	0.0014 m^3/s	0.0321 m^3/s
HHI	0.0037 m^3/s (rain)	0.0010 m^3/s	0.0368 m^3/s
HHO	0.0039 m^3/s (rain)	0.0012 m^3/s	0.0998 m^3/s
Mean Discharge	0.0017 m^3/s (base flow) 0.0038 m^3/s (rain)	0.0013 m^3/s (base flow)	0.0477 m^3/s (high flow)

Temperature

Temperature, SpC and pH measurements are essential for most groundwater studies. These parameters provide information regarding residence time of waters, mixing of end member waters, and dissolution of minerals within a system. HHV temperatures for system water sites ranged from 11.4°C - 22.3°C and showed wide variation between sampling events (Figure 6). Temperatures generally corresponded to surface temperatures, a trend common to systems with dominant open conduit flow. System water temperatures were highest during June 2005 and June 2006. The exception to this trend was at LO, where temperatures were much cooler than surface waters for June 2005 and June 21, 2006, ranging from 10.7°C - 11.4°C. LO waters appeared to be equilibrating with rock temperatures, suggesting longer residence time in the subsurface. Conversely, LO waters sampled on June 24, 2006 were much warmer and more in line with cave outlet temperatures in the

Middle Valley. Cooler, longer residence waters were likely flushed from subsurface conduits feeding LO during the June 20th rain event and replaced by warmer waters from precipitation on June 23rd.

Temperatures at cave inlets in the Middle Valley were warmer than cave outlet temperatures for all June sampling events. The inlet waters at CCI and HHI had sufficient time to warm during exposure to surface temperatures. Hackley et al. (2007) observed very rapid, significant temperature changes between samples measured at the top and bottom of Falling Spring in southwestern Illinois, indicating that water temperatures can be quickly affected by surface conditions. Cave outlet temperatures at CCO and HHO varied significantly from inlet temperatures, indicating mixing of warmer inlet waters with substantial volumes of cooler waters added from karstified bedding planes. June 24, 2006 samples also suggested mixing in the Upper Valley as very warm headwall waters mixed with colder subsurface waters feeding FR, and in the Lower Valley as HHO and NC waters mixed to produce an intermediate temperature at H_2O-O.

November 2006 temperatures were much cooler, ranging from 7.1°C to 10°C. Water temperatures were lowest at FR and VOL where surface waters initially enter the system, were warmer at BS after spending time in the subsurface, then remained constant through the remainder of the Middle and Lower Valley. Discharge was highest during November 2006, therefore, waters did not have time to equilibrate with rock temperatures. The temperature at

H_2O-O measured between those at NC and HHO, again suggesting mixing of the two waters.

pH

pH ranged from 5.98 - 8.19 for all sampling events (Figure 7). pH trends followed those of typical carbonate systems; waters were acidic and undersaturated as they entered the system and as limestone/dolomite dissolution occurred, they became more basic and closer to saturation. pH ranges were wider in the Upper Valley and narrowed through the Middle and Lower Valleys (Figure 7) as waters evolved toward basic solutions. In June 2006, Upper Valley waters running off the sandstone cap at HHH and VOL showed pH values of 6.1 and 5.98 respectively. By the time waters resurfaced at BS, pH had risen to a neutral 7.18 from carbonate dissolution in the Upper Valley. As waters moved downstream through the beaver dam pond, acidity was restored from exposure to atmospheric CO_2 and decaying plant material. This process was more prominent during warmer months due to actively growing/decaying plant material as compared to November 2006. pH at Middle Valley cave inlets was generally lower than at cave outlets during all June sampling events. Inlet waters flow for a short time in Horn Hollow Creek, allowing for slight CO_2 replenishment and, therefore, increased acidity. As waters moved through the short cave conduits within Middle Valley walls, a small amount of dissolution likely occurred as well as some mixing of surface waters with basic, diffuse subsurface waters.   As with temperature, H_2O-O pH

for June 24, 2006 and November 2006 reflected a balance between that of NC and HHO, suggesting mixing of the two waters. H_2O-O values were more basic on June 21, 2006 than June 24, 2006. Again, flushing of longer residence subsurface waters may have occurred with the first significant rain on June 20th, contributing saturated waters with a more basic pH. The subsequent rain
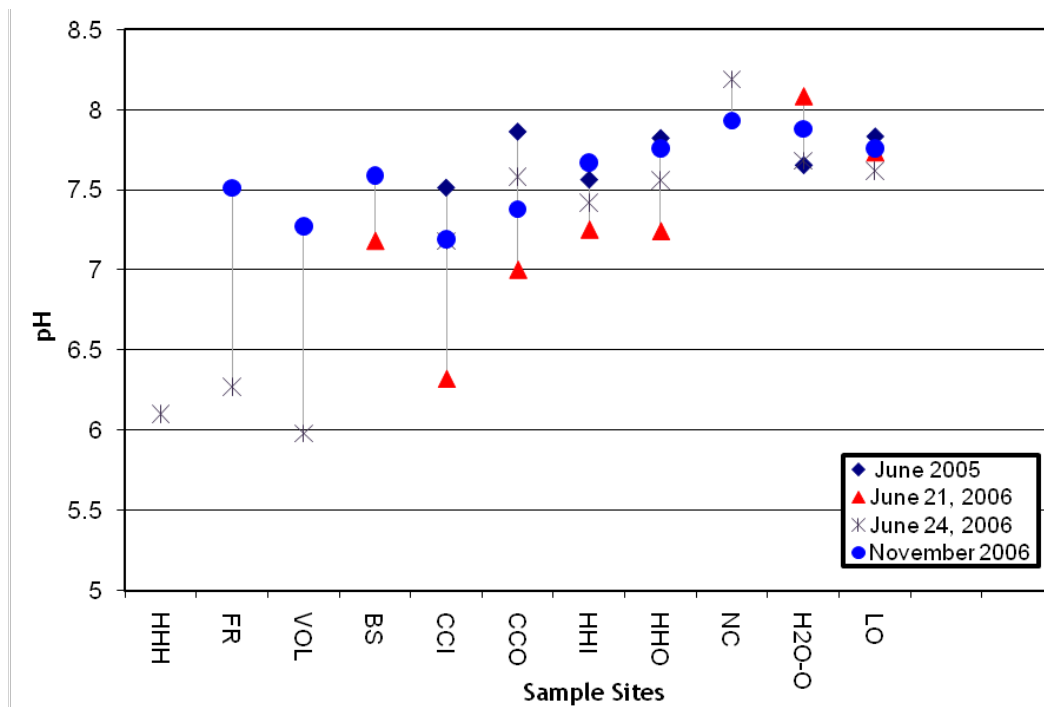
Figure 7. pH values of HHV system waters during all sampling events. Vertical lines show data ranges.

event on June 23rd may have flushed slightly more acidic, undersaturated waters that had not had time to dissolve carbonate rock. pH at LO remained relatively constant for all sampling events, an indication of longer residence time in the subsurface with significant carbonate dissolution. November waters recharging from the Upper Valley sandstone were very basic and changed very

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little throughout the system as high flow conditions provided rapid through-flow with little or no time for dissolution.

Specific Conductance

Specific Conductance (SpC) ranged from 146 to 371 µS/cm (Figure 8). Values were higher during baseflow conditions in June 2005 and June 2006 and lower in November 2006, probably from the dilution of waters and/or less dissolution during higher discharge conditions. The higher values at HHH and through the Middle Valley on June 24th correspond to higher concentrations of Na^+ and Cl^- . On this same sampling date, SpC was significantly reduced between HHH and FR, further supporting the premise of mixing of waters.
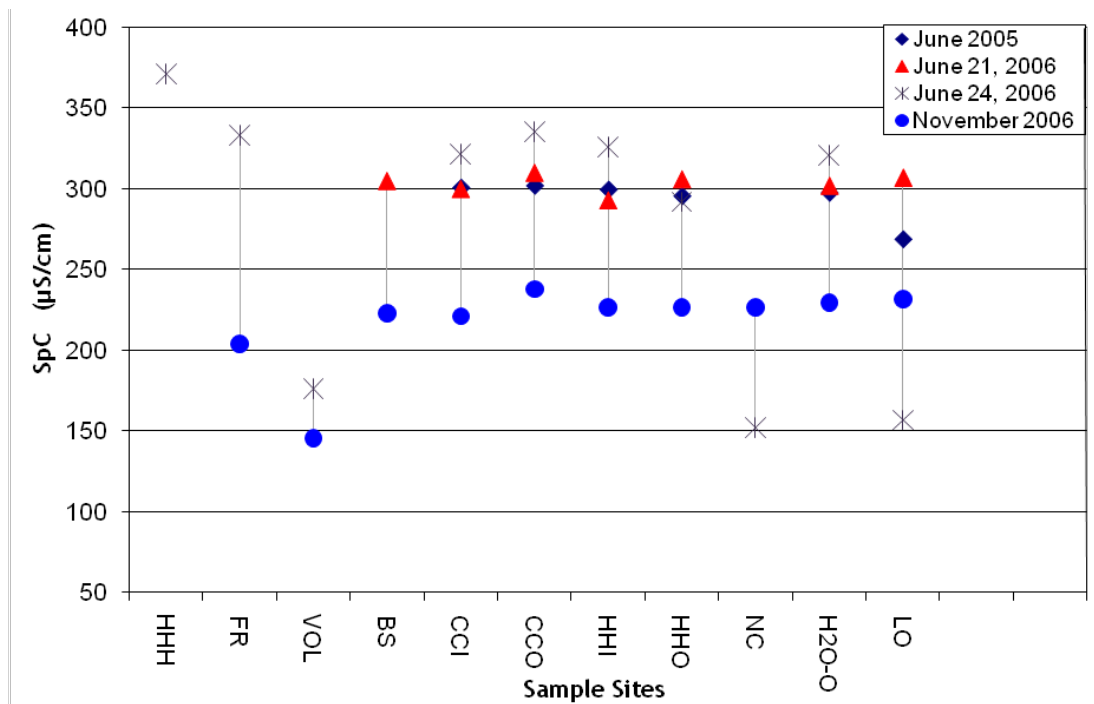
Figure 8. Specific conductance values for HHV system waters. Vertical lines show data ranges.

VOL had the lowest values in HHV as waters appeared to be flowing directly from the quartzose Lee sandstone. Values were virtually the same for base flow conditions in June 2005 and June 21, 2006, reflecting carbonate dissolution without the addition of significant Na^+ and Cl^- contributions as seen at HHH.   The NC sample collected on June 24, 2006 had a much lower SpC than system waters moving through the Upper and Middle Valleys. This suggests that NC waters were from a different source and were not being affected by the high Na^+ and Cl^- concentrations.   November 2006 SpC values were significantly lower and relatively constant, with the exception of an increase between FR and BS where carbonate dissolution was likely occurring in the phreatic zone, and CCI and CCO where there may have been some mixing with karstified bedding plane waters inside the cave.

Hardness

Field titrated hardness values were checked against values calculated in AquaChem®. AquaChem® calculates hardness by summing the "ions that can precipitate from water as hard particles", namely, Ca^{2+} and Mg^{2+} as meq/L or mg $CaCO_3$/L. The majority of field titrated values were higher than calculated values, and did not exhibit a slope of linear regression similar to those reported by Langmuir (1971) and White (1988) when plotted against SpC (Figure 9). Conversely, AquaChem® hardness correlated very well to SpC, with $r^2 = 0.79$ and a correlation coefficient (r) of 0.89. Two outlier samples from the June 24, 2006 sampling event (NC and LO) had very low SpC when compared to other

samples and were not included in the calculation of the regression coefficient. The regression coefficient results were very similar to those calculated by Wicks (1997) in a study of groundwater origins in the Bonne Femme Basin, MO. Therefore, hardness values calculated in AquaChem® were used in this study. Titration error may have been the result of missing the subtle indications of the initial endpoints.
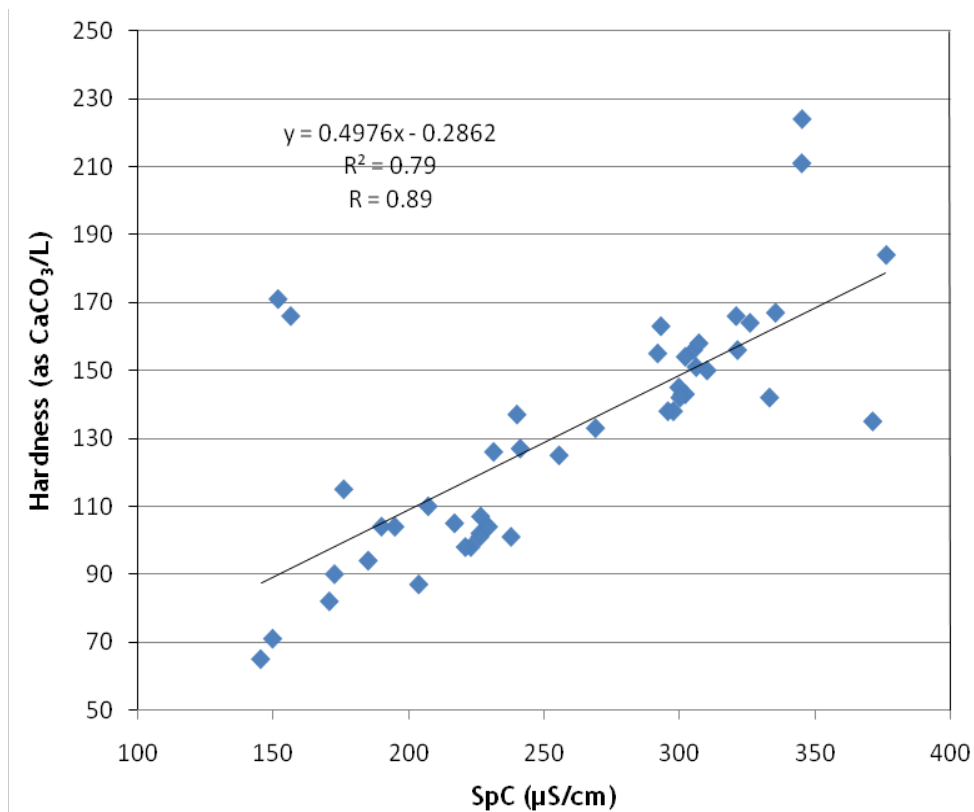
Figure 9. Hardness calculated in AquaChem® vs SpC for all samples.

Chemical Composition

Dissolution is a chemical weathering process that occurs as waters flow through geologic rock units and attempt to reach equilibrium with respect to reactive minerals in the solid phase and CO_2 in the gas phase (White, 1988). A reactive mineral is defined by Deutsch (1997) as "one that will dissolve into or precipitate from groundwater in a reasonable period of residence time for the water in the aquifer." As dissolution proceeds, solutions become increasingly saturated with ions from these reactive minerals, providing a history of rock/water interaction within the system. In most systems, it is possible to predict flowpaths from upper elevation recharge areas to lower elevation spring discharge areas through a combined analysis of measured parameters and ion chemistry at various sites within the system.

Calcium and Magnesium

Calcite and dolomite are the most common reactive minerals within carbonate systems and dissolve in the presence of acidic groundwater. Limestone is comprised mostly of $CaCO_3$, but may contain some $MgCO_3$, while dolostone is predominantly $CaMg(CO_3)_2$. Pure limestone and dolostone are end members within the carbonate system, with myriad combinations occurring in nature. Limestone is more soluble than dolostone, therefore, a bedding contact separating both rock units represents a plane of weakness. Waters invading this zone will rapidly dissolve the limestone along the contact, while dissolving dolostone at a slower rate. Ca^{2+} would be contributed to solution

along with lesser amounts of the Mg^{2+}. The complex interbedded layers of the Pennsylvanian and upper Mississippian units within HHV provide innumerable zones of weakness, not only between limestone and dolostone, but within a variety of impure sandstones, shales, clays, coal and siltstone. The ions contributed by dissolution of rock along these bedding planes should provide insight into possible flowpaths within HHV.

Ca/Mg ratios are used to determine the dominant lithology of host rocks within carbonate settings. Ratios at or near unity represent waters controlled by dissolution of dolomite, while waters controlled by pure limestone dissolution exhibit ratios of 3 to 10. Ranges of 1.5 to 3 identify waters from both limestone and dolomite sources (White, 1988). Ca/Mg ratios for HHV waters ranged from 0.74 to 6.40 (Figure 10). The majority of HHV samples displayed Ca/Mg ratios above unity, indicating waters in contact with limestone or a combination of limestone and dolomite. The highest ratios occurred in June 2005 and June 2006, with samples clustering about the 3:1 trendline (Figure 10). This trend reflects the dominance of limestone dissolution during baseflow conditions with little to no Mg^{2+} contribution from karstified bedding planes. Rapid flow-through during the higher discharge conditions in November 2006 allowed little time for calcite dissolution and likely diluted calcite concentrations in the November samples. Concomitant flushing of bedding plane waters in contact with dolomitic layers in the Upper Valley increased Mg^{2+} concentrations in these samples. The dilution of calcite and increase in Mg^{2+} produced lower Ca/Mg ratios observed along the 1.5:1 trendline (Figure

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10). The November 2006 samples exhibited a trend of increasing Ca^{2+} and

decreasing Mg^{2+} down gradient, further supporting the premise that Mg^{2+} is

being flushed from Upper Valley karstified bedding planes.   November FR

waters also showed greater molar concentrations of Mg^{2+} than Ca^{2+} and the VOL

ratio was slightly less than 1:1, indicating significant contribution of waters in

contact with dissolving dolomite in the Upper Valley. Ca/Mg ratios plotted well

above the 3:1 trendline (Figure 10) for all samples collected at LO, suggesting

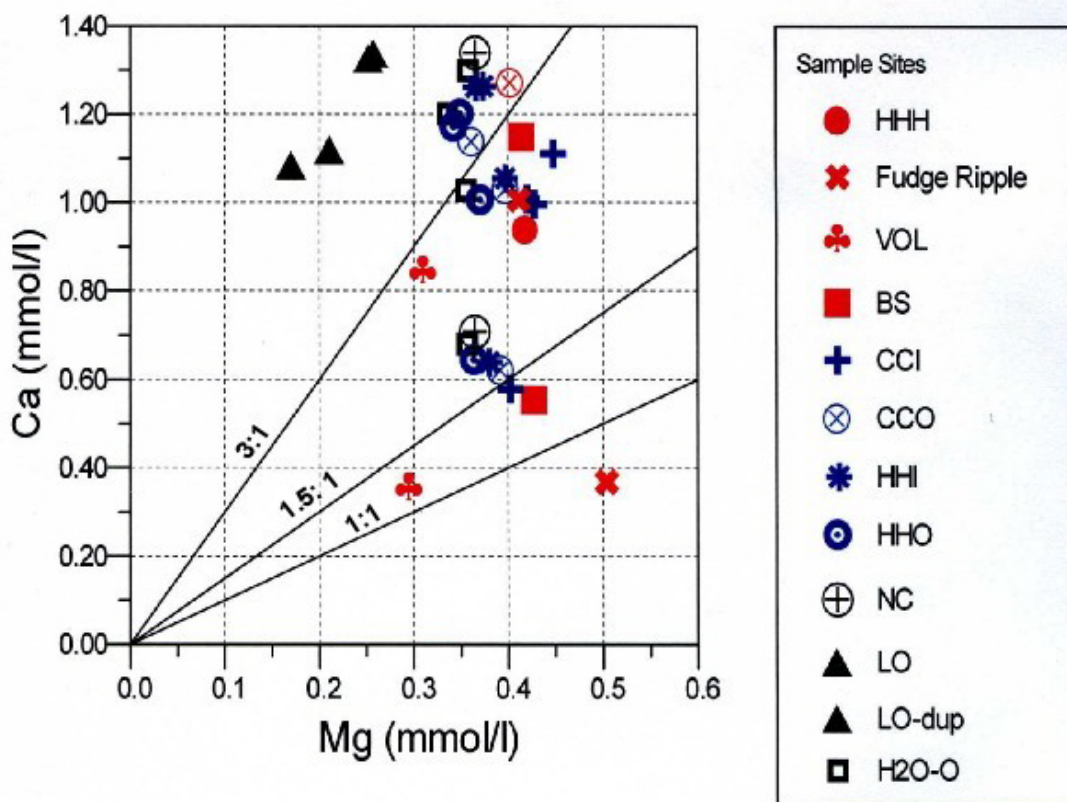little contact with dolomitic layers.

Figure 10. Ca vs Mg trends for HHV waters during sampling events.

Mg/(Ca + Mg) values were calculated in AquaChem® to determine the dominant sources of these ions in solution. All HHV samples had values < 0.5, indicating limestone weathering with some dolomite, with the exception of the November 2006 sample from FR. The FR value of 0.6 shows that dolomite dissolution was the dominant source of Ca^{2+} and Mg^{2+} in that location.

Saturation Indices

Saturation states of dissolved minerals within water samples are useful for predicting mineral presence and reactivity. SI calculates near zero for a reactive mineral that occurs in the aquifer environment and shows that the mineral is affecting solution composition. SI < 0 indicates that a sample is undersaturated with respect to a given mineral and will dissolve until equilibrium is reached. If significantly less than zero, the ratio shows that the mineral is not present in the aquifer environment or is not reactive. SI > 0 represents supersaturation of a mineral and potential precipitation from solution. A range of SI = 0 ± 0.5 is generally considered to be within the equilibrium range for a mineral (Deutsch, 1997, White, 1988).

Calcite controls the dissolution of carbonate minerals within HHV, although aragonite also contributes to calcite saturation (Figure 11a and 11b). Dolomite remains undersaturated for most sampling sites (Figure 11c). These carbonate minerals were highly undersaturated in the Upper Valley during all sampling events, as aggressive waters entered the karst system at HHH, FR and VOL. Dissolution within the subsurface increased the saturation levels of all

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three species within resurging waters at BS. Between BS and CCI, saturation levels dropped from dilution of waters within the beaver dam pond. As waters moved through the Middle Valley, there was an overall increase in all ion saturations. Waters at NC were from a different source than evolving system waters, as saturation levels were significantly higher on June 24, 2006 and significantly lower in November 2006 than waters leaving HHO. Calcium and aragonite were saturated and dolomite was very near saturation on June 24, 2006 at NC. Waters sampled in NC during November 2006 were significantly undersaturated as compared to evolving system waters, again suggesting a different source for these waters. For both events, NC waters mixed with those from HHO to produce intermediate solutions at H_2O-O.

Reactive minerals may remain slightly undersaturated in open conduit flow systems due to rapid flow-through and limited contact with aquifer materials, especially during high flow conditions. This trend is evident when observing saturation indices for carbonate species in HHV for November 2006.

The majority of Ca^{2+} is probably coming from limestone and aragonite dissolution within the Upper Member and Ste. Genevieve limestone as waters evolve down gradient, with smaller amounts from dolomite, anhydrite ($CaSO_4$), gypsum and clays within the Breathitt and Lee, Pennington and Upper Member Formations. Mg^{2+} concentrations are primarily contributed from dolostone and dolomitic limestones in the Pennington and Upper Member, with lesser amounts from clays and weathering of biotite found in the micaceous Pennsylvanian-age sandstones.
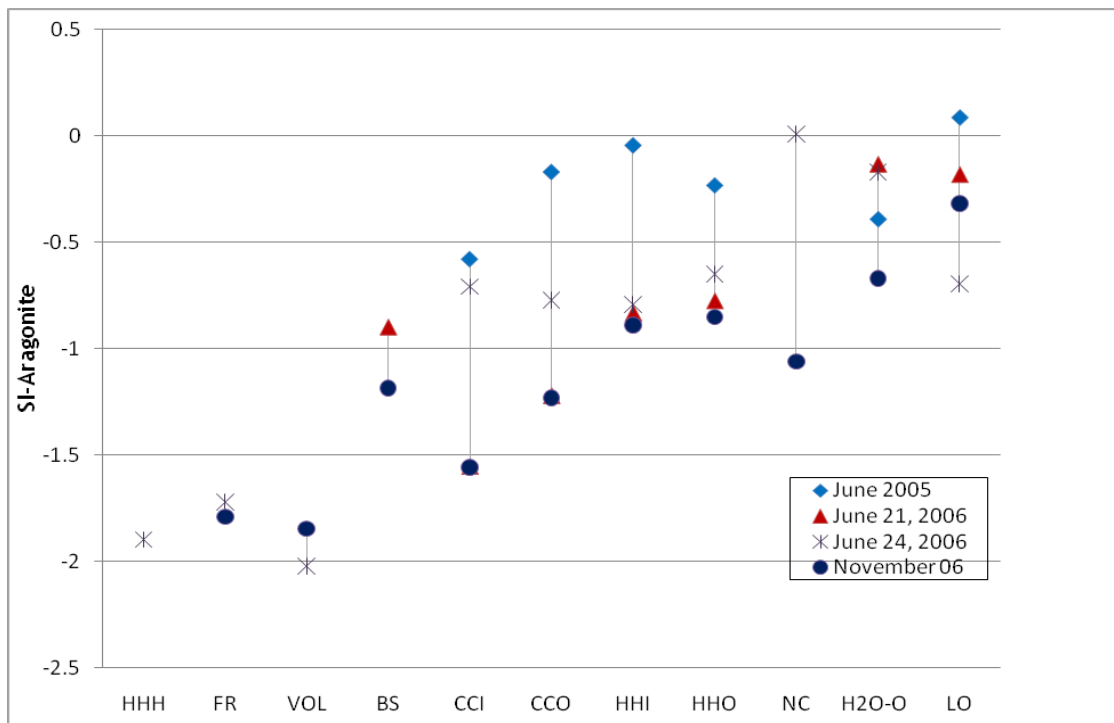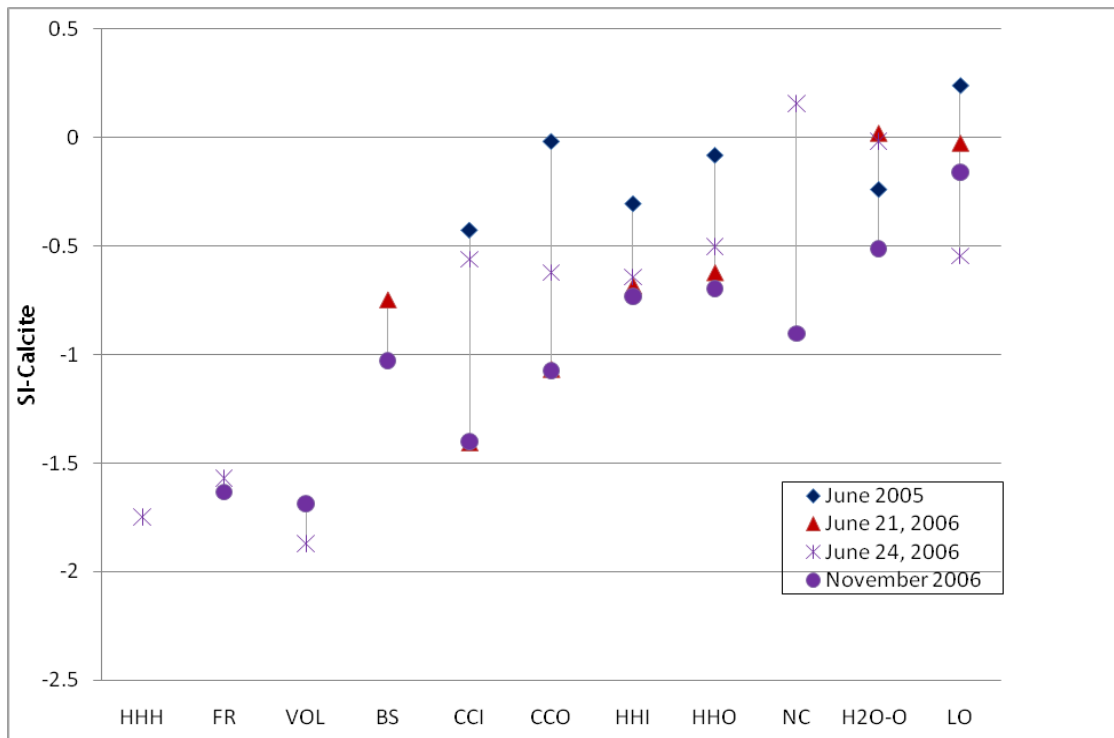
Figure 11. a) SI-calcite for all sampling events, b) SI-aragonite for all sampling events, c) SI-dolomite for all sampling events. Vertical lines show data ranges.
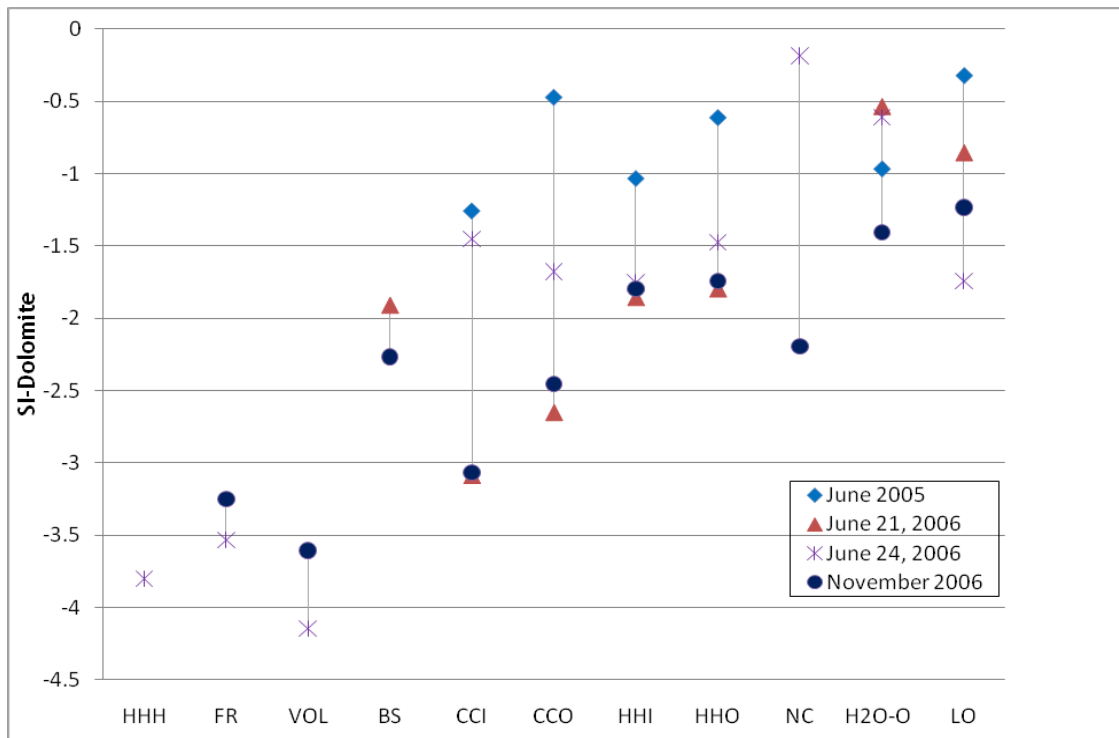
Figure 11 *continued*. a) SI-calcite for all sampling events, b) SI-aragonite for all sampling events, c) SI-dolomite for all sampling events. Vertical lines show data ranges.

Sodium

Na$^+$ concentrations in HHV waters ranged from 0.161 mmol/L to 1.765 mmol/L.   Figure 12 displays Na$^+$ trends for all sampling events. Na$^+$ concentrations were highest throughout the valley during the June 24, 2006 sampling event, with significantly higher concentrations measured at HHH (1.765 mmol/L) and FR (1.409 mmol/L). The higher concentrations may be the result of surface and bedding plane flushing from the June 21, 2006 recharge event. Dilution from the higher discharge conditions may have produced the lower concentrations during the November 2006 sampling event.

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There was a potential problem with excess Na^+ values from the ICP during the June 2006 sample processing, although Na^+ values did not look anomalous compared to other sampling events. A plot of Cl^- vs Na^+ (Figure 13) showed that all but 9 sampling sites had excess Na^+ relative to Cl^-, indicating that excess Na^+ may not have been an anomaly for June 2006 samples. Six of the nine samples with high CBE's were from June 21, 2006, with values plotting very close to the 1:1 line representing dissolution of NaCl, providing further evidence that alkalinity error was likely responsible for the high CBE's and not excess Na^+. The June 24, 2006 samples from HHH and FR plotted very near the 1:1 line and showed higher concentrations of both Na^+ and Cl^-, implying that road salts stored in soils near Rte. 182 may be the likely source. A study by Panno et al.,(2006) identified and characterized sources of Na-Cl within the midwestern U.S. and found that water samples enriched in Na^+ relative to Cl^- were derived from soils within uninhabited areas, ground water from relatively uncontaminated aquifers, and from precipitation samples. The study concluded that the additional Na^+ in these environments was likely derived from Na-clays and/or Na-feldspars within the soil zones and aquifer. These results suggest that sampling sites within the relatively pristine HHV system with excess Na^+ and lower concentrations of Na^+ and Cl^- may be derived from similar sources.

Na/(Na + Cl) values calculated in AquaChem® also indicated that there were additional sources contributing Na^+ to solution beyond NaCl. Values >0.5
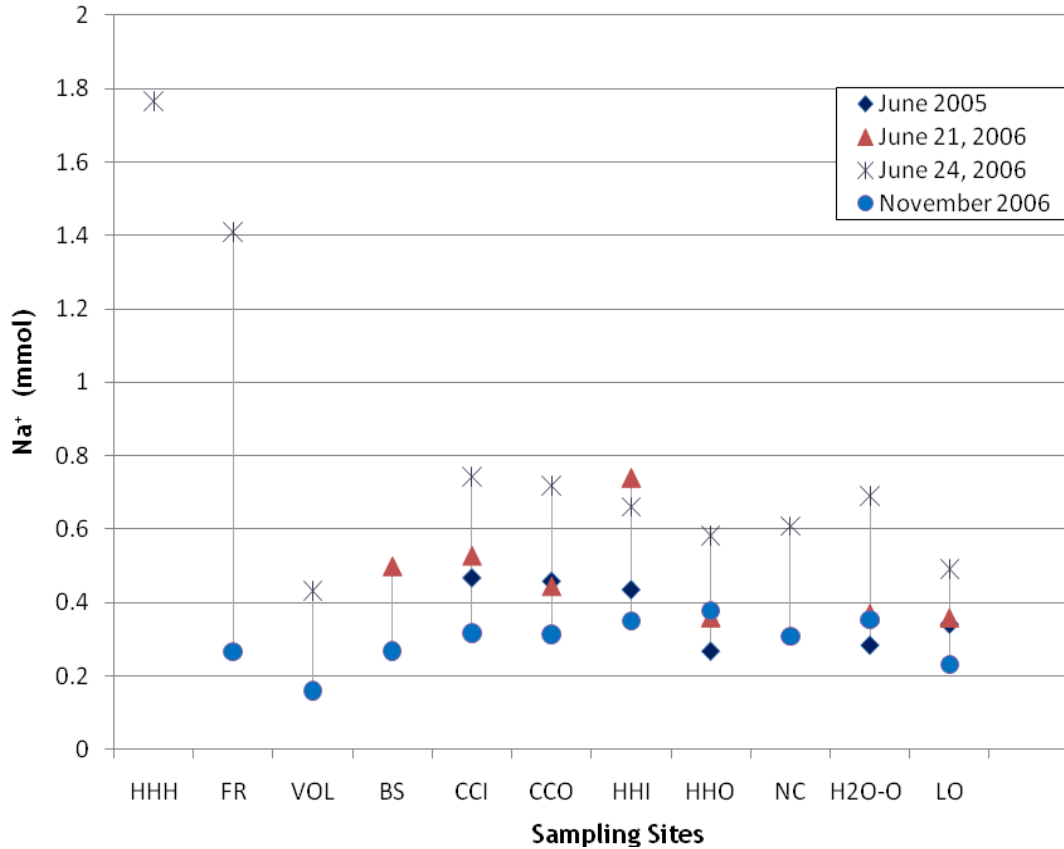
Figure 12. Na$^+$ concentrations in HHV system waters for all sampling events. Vertical lines show data ranges.

generally suggest that Na-plagioclase (albite) dissolution and/or ion exchange processes within clays and shales may be responsible for excess Na$^+$. Waters within flow paths intersecting the immature sandstones of the upper Breathitt and Pennington Formations come in contact with albite (Connor, 1981). The slow dissolution of albite produces kaolinite, an abundant clay mineral in the upper Pennsylvanian units of HHV, and releases Na$^+$ and Si to solution. This process, along with very slow weathering of biotite may also be responsible for the low concentrations of Si in HHV waters. Na$^+$ is a dominant ion within
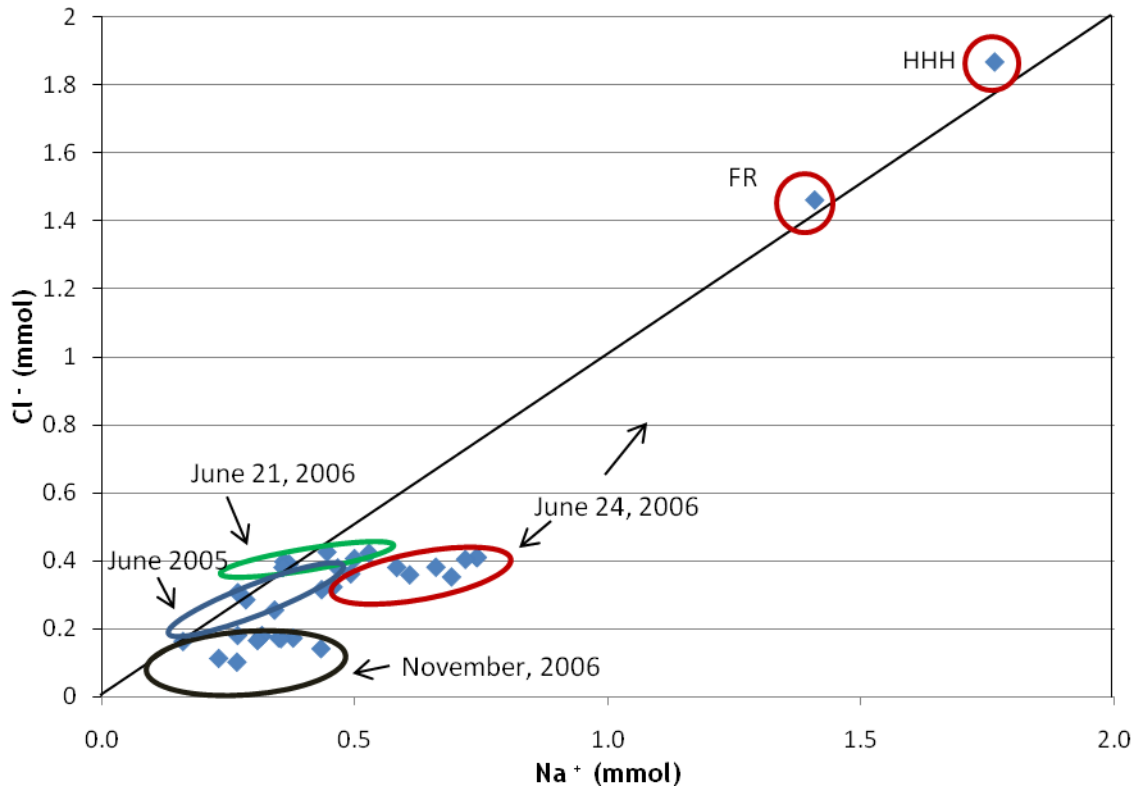
Figure 13. CI vs Na (mmol) showing excess Na for majority of system water samples.

waters draining shales and clays from the ion exchange of Ca^{2+} and Mg^{2+} for Na^+, therefore, this process may take place within the myriad shale and clay layers of the Breathitt and Lee and Pennington Formations. Ball clays are common in Carter County, KY, and are composed of kaolinite with a small amount of montmorillonite (Kentucky Geological Survey, 2010a). Montmorillonites have a high cation exchange capacity and, therefore, probably contribute some Na^+ to solution through ion exchange with Ca^{2+} and Mg^{2+}.

Sodium ions can be adsorbed to exchange sites within sandstones that

were originally deposited under marine conditions and subsequently intruded by sea water (Hem, 1985). As waters move through these sandstones, Na^+ can be exchanged for other ions. The back barrier island environment present during the formation of HHV stratigraphic units and the successive transgressive-regressive cycles of the inland sea suggest that some Na^+ may be derived from sandstone units in the upper Breathitt and Lee and Pennington Formations. Relict seawaters trapped within shales during deposition are also considered sources of Na^+ (Devers, 1988).

Ettazarini (2005) plotted samples from the Turronian limestone aquifer, Morocco, on a Ca + Mg versus SO_4 + HCO_3 diagram to verify the capture of Ca^{2+} and Mg^{2+} ions by Na-rich clays. A 1:1 relationship corresponded to simultaneous calcite, dolomite, gypsum dissolution, while the ion exchange process was characterized by an excess SO_4 + HCO_3 over Ca + Mg (values < 1). Reverse ion exchange had values >1. A similar plot of HHV system waters (Figure 14) shows that the exchange of Ca^{2+} and Mg^{2+} for Na^+ is a dominant process in HHV and may also account for excess HCO_3 produced during the weathering of silicate minerals.

Sulfate

Sulfate concentrations in HHV waters ranged from 0.105 mmol/L to 0.734 mmol/L (Figure 15). The highest concentrations of SO_4^{2-} were measured in November 2006, while the lowest were in June 2006. The highest overall concentration was at FR (November 2006) and the lowest overall was at LO
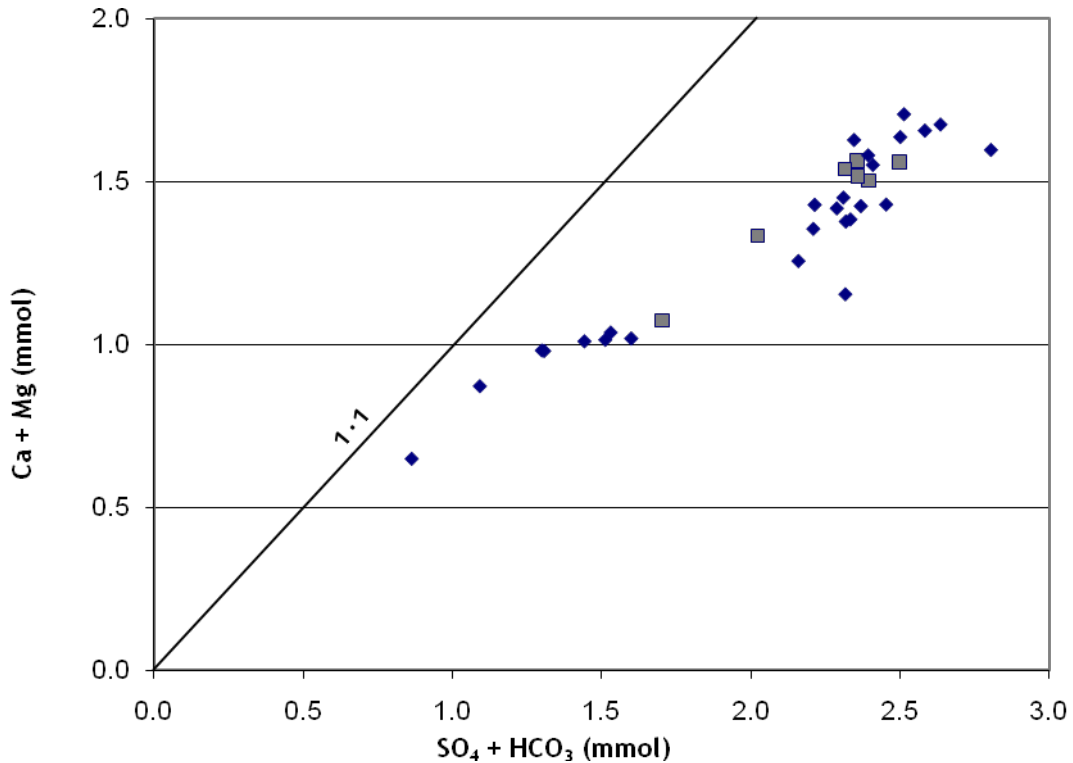
Figure 14. Plot of Ca + Mg versus SO4 + HCO_3 showing ion exchange as the dominant process responsible for excess Na+ in HHV. Note: HCO_3 values calculated from field titrated Alkalinity are noted as triangles and HCO_3 values from calculated Alkalinity using Equation 2 are noted as squares.

(June 2006). There was a slight decrease in SO_4^{2-} concentration down gradient during all sampling events.

In carbonate environments, sulfate is commonly present from pyrite oxidation, gypsum dissolution and from waters draining shales (Drever, 1997) in concentrations of tens of mg/L or higher (Panno, personal communication, 2009). In the southwestern Illinois sinkhole plain, Panno et al. (2001) reported that SO_4^{2-} may have been derived from fertilizer, oxidation of organic matter in field soils, oxidation of pyrite or the dissolution of gypsum.
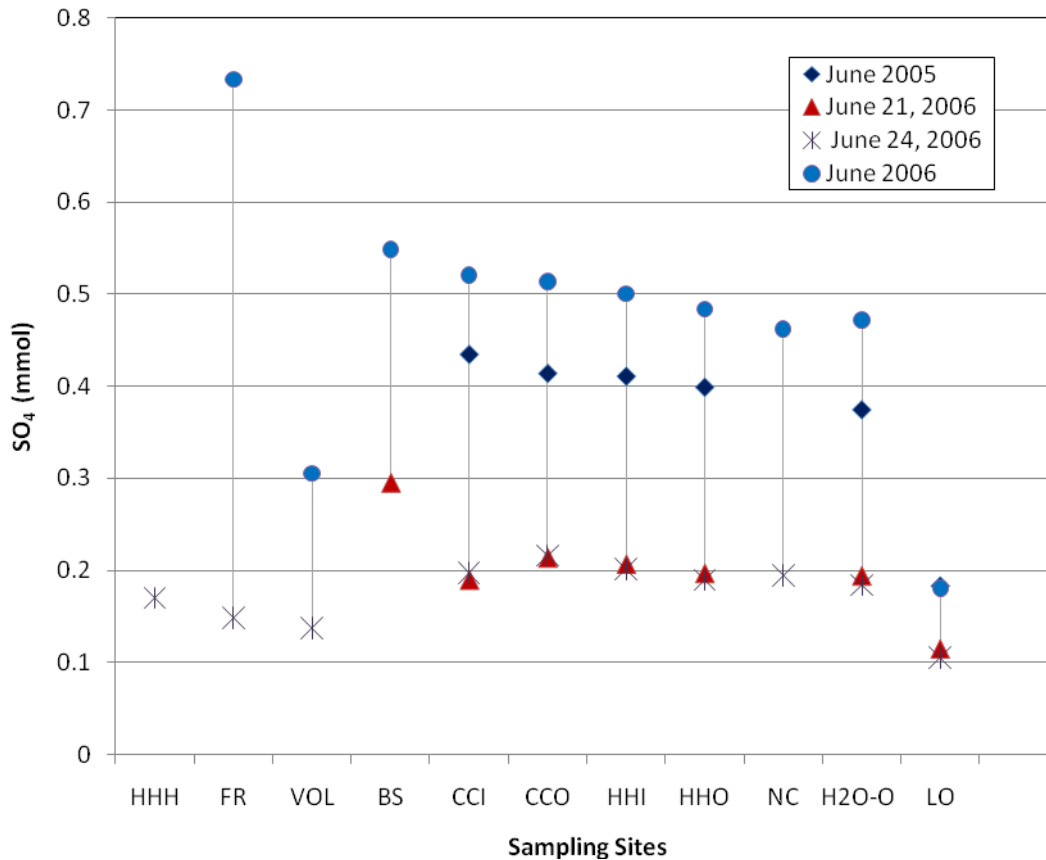
Figure 15. SO$_4$ concentrations in HHV System Waters. Vertical lines show data ranges.

The SO$_4$/Cl vs SO$_4$ plot (Figure 16) was constructed to determine possible sources of SO$_4^{2-}$ in HHV waters. Chloride is a nonreactive indicator of dilution and evaporation. If sulfate is being produced by the dissolution of gypsum, pyrite or anhydrite, SO$_4^{2-}$ will increase relative to Cl$^-$ and result in a positive slope. If sulfate is decreasing due to sulfate reduction, the SO$_4^{2-}$/Cl$^-$ value will decrease, yielding a negative slope on the plot. The slope is positive for HHV data, suggesting that the dissolution of gypsum, pyrite or anhydrite may be increasing SO$_4^{2-}$ concentrations.

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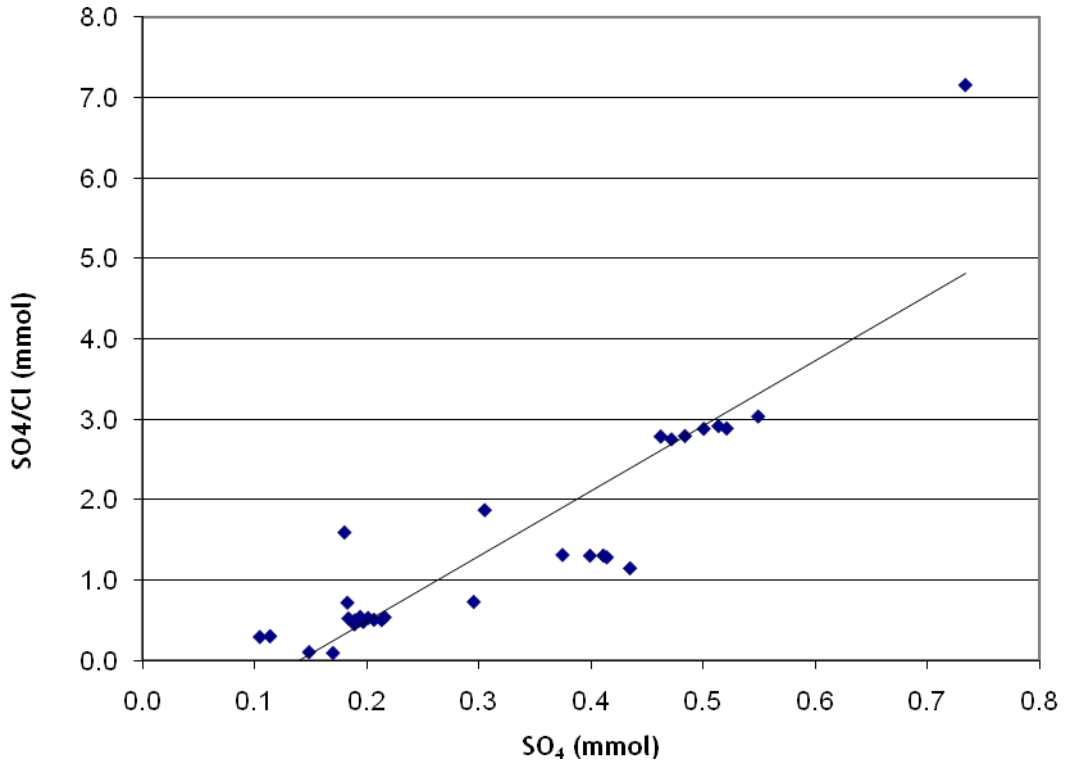
Figure 16. SO_4/Cl vs SO_4 to determine SO_4 sources in HHV waters.

Ca/(Ca + SO_4) values were calculated in AquaChem® to determine possible sources of sulfate. Gypsum dissolution yielded a value of 0.5 and was identified as the source of sulfate for four samples in the Upper and Middle Valleys during November 2006 sampling; VOL, BS, CCI and CCO. The remaining samples collected in November 2006, June 2005 and June 2006 had values >0.5, an indication that Ca^{2+} was being supplied by either carbonate dissolution or from silicate weathering.

Figure 17 plots SO_4^{2-} vs Ca^{2+} and shows distinct trends for SO_4^{2-} sources in HHV. The dissolution of gypsum yields a 1:1 ratio of Ca^{2+} and SO_4^{2-} in solution. Samples plotting along and very close to the 1:1 line represent the four
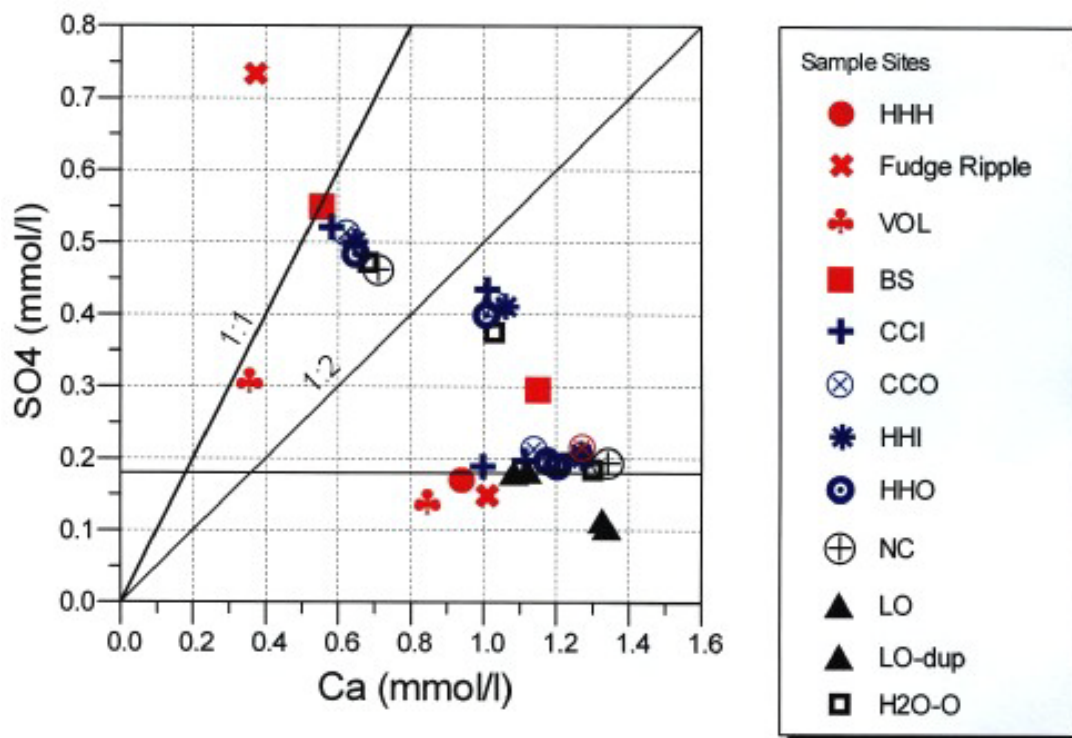
Figure 17. SO_4 vs Ca showing 1:1, 2:1 and horizontal trend lines to delineate possible sources in HHV waters

November 2006 samples in which gypsum was identified as the source for SO_4^{2-} in solution from AquaChem® calculations (VOL, BS, CCI and CCO). Gypsum veins are common within layers of flint clay in the Pennsylvanian strata of Carter County, Ky (McFarlan, 1943). Waters being flushed from these Upper Valley clays during the higher discharge conditions in November 2006 would contribute increased SO_4^{2-} to the system. The decreasing SO_4^{2-} concentrations for Middle- to Lower Valley sites in November 2006 were likely caused by dilution. There were no samples plotting along the 1:2 trendline (SO_4/Ca) representing the input of SO_4^{2-} from the oxidation of pyrite. SI calculations from Aquachem® were in agreement with these results, with pyrite ranging

from -79.7 to -111.8. Therefore, there appears to be little to no pyrite in the

HHV system. Samples from June 2006 and all sampling events for LO follow a

trend of increasing Ca^{2+} and relatively constant SO_4^{2-} values. A similar

horizontal trend was observed by Panno et al, (2001) in a study of karst spring

chemistry. The results of their study indicated that there was an initial input

of SO_4^{2-} from pyrite and gypsum dissolution followed by continued limestone

dissolution with no additional input of SO_4^{2-} to the system.

Potassium

K^+ values calculated from November 2006 samples ranged from 0.028

mmol/L to 0.061mmol/L. K^+ can enter solution through several processes

including albite weathering, ion exchange with clays, and from the weathering

of micas. The presence of K^+ suggests that illite, montmorillonite or glauconite

may be present (Hem, 1985) although the low cation exchange capacity of

these clays suggests lower contributions of K^+ than other sources. Immature

sandstones within the Upper Valley may be contributing the bulk of K^+ to

solution through the slow weathering of albite and biotite mica.

Water Types

Piper diagrams are useful for defining water types and identifying mixing

that may be occurring between end member waters. Pipers were constructed

for HHV waters by plotting relative concentrations of cations and anions as

percentages. If mixing is present, samples plot along a straight line between

each end member field of the diagram. If samples cluster within a field, they

are not controlled by mixing. HCO_3 for LO (June 2005), BS, CCI, CCO, HHO, H2O-O (June 2006) and NC (November 2006) were calculated from Alkalinity derived from Equation 2.

A piper plot of HHV system waters shows different water types for each sampling event (Figure 18). Waters sampled in June 2005 clustered as Ca-Mg-HCO_3-SO_4 type with the exception of LO which was Ca-HCO_3 type. Mg^{2+} and SO_4^{2-} were entering solution in the Upper Valley with concentrations (mmol)
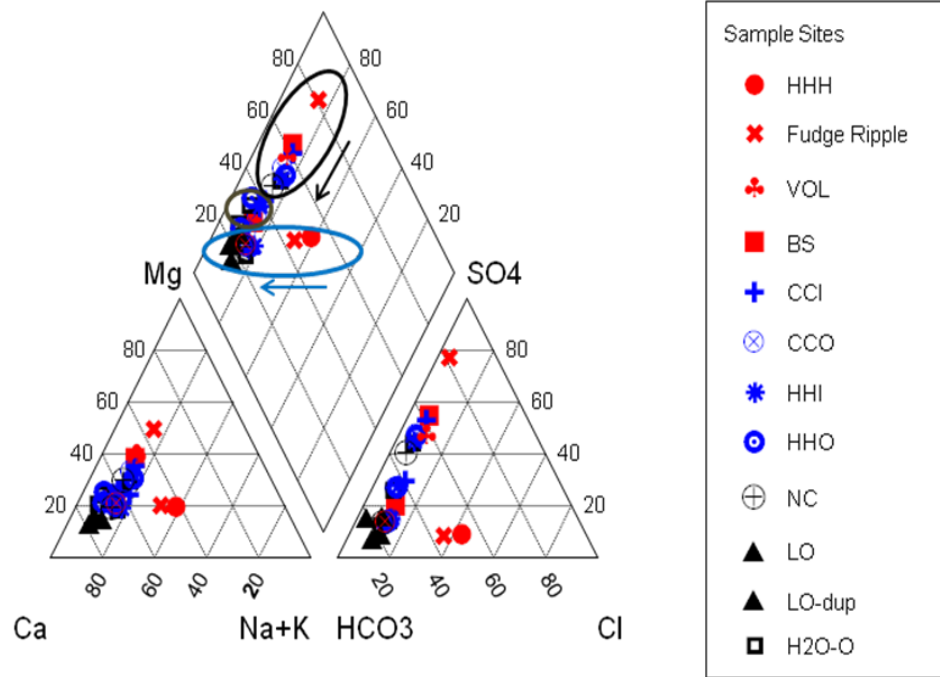

Figure 18. Piper diagram showing water types based on percentages of cations and anions for all sampling events. The blue arrow shows evolution of waters on June 24, 2006, the black arrow shows evolution of waters during November 2006.

decreasing slightly as the waters evolved downgradient. June 2006 waters were mostly Ca-Mg-HCO_3 type, suggesting dominance of carbonate dissolution

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at that time. HHH and FR showed large percentages of Na^+ and Cl^- during the June 24, 2006 sampling. These species appear to have originated from sources outside HHV. November 2006 waters were predominantly $Ca-Mg-SO_4-HCO_3$ type in the Upper and Middle Valleys, evolving to $Ca-Mg-HCO_3-SO_4$ type in the Lower Valley. The very high SO_4^{2-} in the Upper Valley may have resulted from flushing of bedding plane waters in contact with gypsum or dissolving silicates.

Conceptual Model of HHV

A conceptual model of HHV system waters (Figure 19) provides an overall summation of hydrologic flow paths, cave locations, and water types.

Allochthonous waters enter the Upper Valley via fractures and joints within the undivided Lee and Breathitt Formation and from pirated surface waters that flow from the Lee sandstone at the HHH and at VOL. Groundwater flows downward through the fractures and joints, with some flowing laterally along bedding plane partings as waters come in contact with resistant shales, clays and carbonate units of the Pennington and Upper Member Formations. These waters may eventually emerge along valley walls as seeps or small springs. Aggressive waters enter the subsurface at HHH via a plunge pool beneath the falls, moving downward through joints and fractures within the Upper Member limestone and dolostone units. During the June 24, 2006 sampling event, these waters exhibited relatively high concentrations of Na^+ and Cl^- as indicated by the $Ca-Na-HCO_3-Cl$ water type. Na^+ and Cl^- may have been stored in the soils following application of road salt to SR 182 the previous

winter, contributing to higher dissolved concentrations. The Ca-Na-Mg-HCO$_3$-CI waters at FR suggest dissolution of Ca^{2+} and Mg^{2+} between HHH and FR. A significant 3.2°C decrease in water temperatures between the two sites during the June 24, 2006 sampling suggests possible mixing of HHH waters with cooler subsurface waters. FR temperatures were similar to those measured at cave outlets in the Middle Valley during that same event, providing additional evidence for mixing. A concurrent decrease in SpC of 38 μS/cm between HHH and FR also implies mixing of different source waters. At VOL, the Ca-Mg-HCO$_3$ waters were very aggressive and significantly undersaturated with respect to calcium, aragonite, and dolomite. Temperatures were comparable to surface waters at the HHH and SpC conductance was very low. These parameters suggest that waters were mainly from surface flow off the quartzose Lee sandstone, with lesser contributions from seeps or spring waters that have been in contact with subsurface Pennsylvanian-age clastics. The Mg^{2+}, Ca^{2+} and SO$_4$$^{2-}$ in VOL waters were probably contributed to solution by ion exchange processes within shales and clays of the Lee and Breathitt Formation, dissolution of gypsum within flint clays, weathering of silicates, and dissolution of carbonates from the limestone unit within the Pennington Formation. BS is a resurgence site for Upper Valley waters during low flow and high flow conditions. The Upper Valley is underdrained during base flow conditions, but waters may flow within the dry stream channel between FR and BS during high flow events. Waters at BS were Ca-Mg-HCO$_3$ type with higher SI values for calcite, aragonite and dolomite, neutral pH values and lower temperatures than the other Upper

Valley sites. These parameters imply that carbonate dissolution occurred between HHH, FR, VOL and the resurgence of the waters at BS and that waters were in the subsurface long enough to begin equilibrating with bedrock units.

Ca-Mg-HCO$_3$ waters were dominant at all Middle Valley sampling sites as carbonate dissolution proceeded down-gradient within the Ste. Genevieve limestone. Temperature, pH and SI for carbonate species changed significantly between BS and CCI as waters flowed through the large beaver dam pond. As a result, water temperatures appeared to equilibrate with surface temperatures, pH became highly aggressive as additional CO$_2$ entered solution, and SI values dropped significantly from dilution with pond waters. Water temperatures were higher at cave inlets than at cave outlets in the Middle Valley as subsurface waters mixed with waters entering the caves from Horn Hollow Creek. pH values were lower at cave inlets than at cave outlets as CO$_2$ gas was replenished during surface flow and as carbonate dissolution occurred within the cave segments. The dissolution process also produced a general increase in SI values for aragonite, calcite and dolomite as waters flowed through the Middle Valley. Waters entered the subsurface through a swallet a short distance downstream from HHO.

The Lower Valley is under-drained during low flow conditions with waters flowing in the dry bed of Horn Hollow Creek only during high flow events. Water types at NC and H$_2$O-O were Ca-Mg-HCO$_3$ and at LO were Ca-HCO$_3$. NC waters may originate from alternate flow paths, as SpC was significantly lower than waters at HHO during baseflow conditions. NC waters
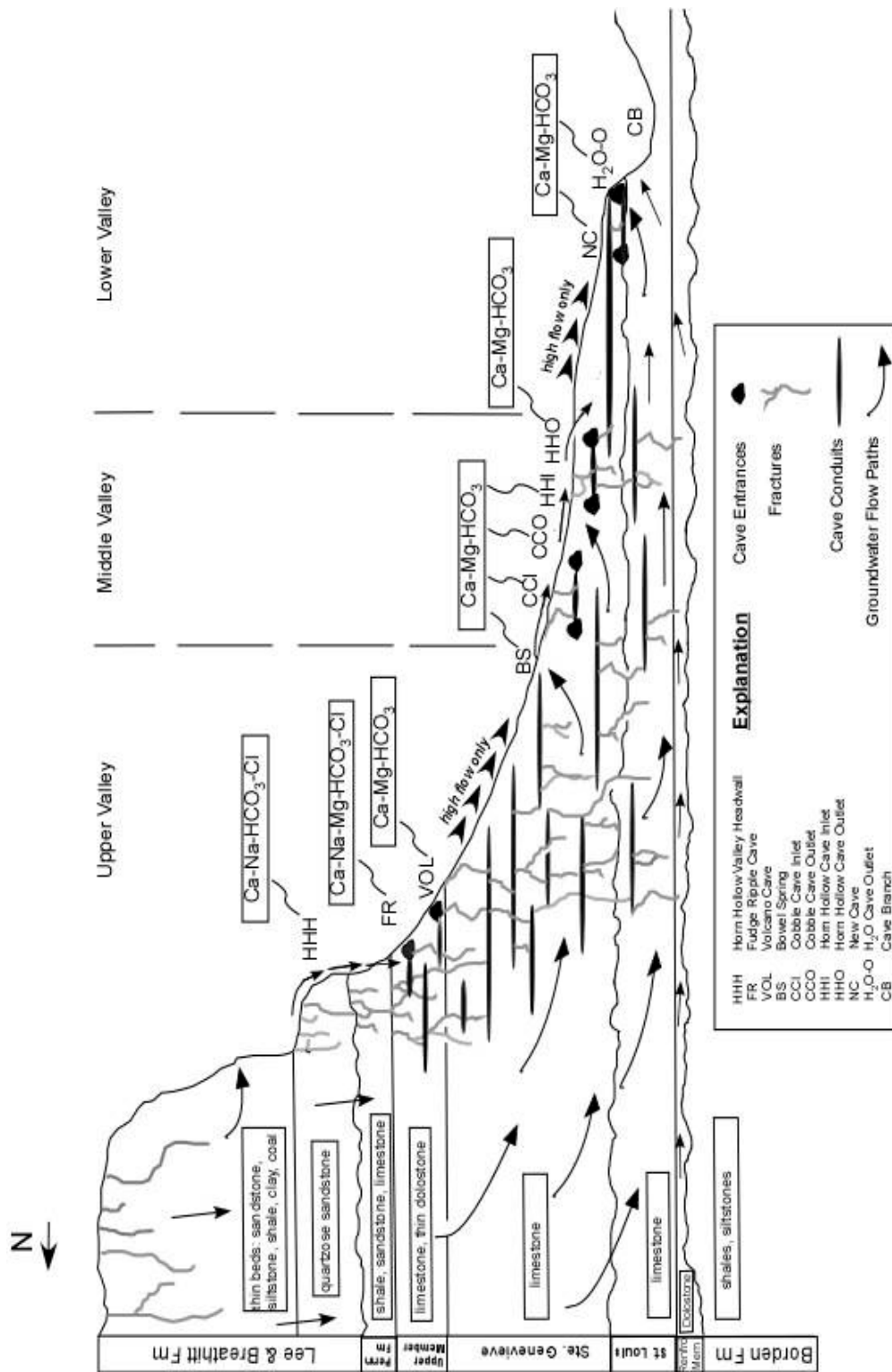
Figure 19. Conceptual Model of HHV including Geologic units, water types, flow
paths and cave conduits.

were very basic and were saturated with respect to calcite and saturated with respect to aragonite and dolomite. Waters discharge HHV at H_2O-O, and appeared to be a mixture of waters from HHO and NC. Temperature, pH and SpC values from H_2O-O measured between the values at HHO and NC. LO is a low-flow seep beneath the Laurel Cave entrance and directly above Cave Branch. Waters at this site generally have lower temperatures than system waters, suggesting a longer residence time in the subsurface. These waters may flow along the bedding plane parting between the Ste. Genevieve and St. Louis limestones, as concentrations of non-carbonate ions appear to be lower than at other sampling sites. Flushing of cooler subsurface waters appears to occur at this site in response to precipitation events, causing SI values to fluctuate between saturation and undersaturation and temporary discharge of warmer waters. Waters from LO and H_2O-O flow into CB, a tributary to Tygart's Creek.

Tracer Test

Three tracer tests were performed on June 26, 2006 to identify hydrologic connections between the caves and springs in HHV. Rhodamine dye injected into the plunge pool at the HHH was observed within FR, establishing a connection between the two sites. Sodium Bromide was injected as a second tracer into the lower spring within FR, establishing a connection between FR, BS, HHO, NC and H_2O-O. A third dye trace was conducted upstream of the VOL entrance using fluorscene dye. The fluorscene was detected at VOL, BS, HHO,

NC and H_2O-O. These results are in agreement with the geochemical analysis of flow paths within HHV and with the conceptual model of system waters.

ISCO samplers were placed at HHO, NC and H_2O-O to collect samples once an hour for 48 hours following the tracer injections. Bromide concentrations were detected in ISCO samples at each location and showed a minimum residence time of 7 hours as waters flowed down gradient from FR to H_2O-O. These results show that residence times for HHV waters are relatively short. Residence time is difficult to quantify with results from a single tracer test and limited knowledge of all potential flowpaths. It is possible that bromide moved through the system within unknown flowpaths at a quicker rate. Therefore, future tracer tests may yield different residence times as additional flowpaths are identified.

Potential Contaminants in HHV Waters

Nitrate

Nitrate is a negatively charged, conservative ion and a common contaminant in shallow groundwater and surface streams. The mineralization of natural organic nitrogen contributes NO_3^- to groundwater systems while anthropogenic sources include livestock waste, mineralized fertilizer and septic systems (Panno et al.,1996; White, 1988). Nitrogen from organic sources is converted to ammonium (NH_4^+) in the soil zone, and the NH_4^+ is subsequently oxidized to NO_3^- (Freeze and Cherry, 1979).

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In natural environments with little to no human impact, nitrate concentrations are relatively low. Nitrate as Nitrogen concentrations (NO_3-N) from natural sources are generally between 2.0 and 2.5 mg/L (Panno et al., 2006a). Nitrate as N values for HHV ranged from 0.13 to 1.54 mg/L with some of the highest values measured during baseflow conditions in June 2005. The lowest NO_3-N values were a result of dilution during the November 2006 sampling event, although samples collected during baseflow conditions still reflect relatively pristine conditions. 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.

The Illinois State Geological Survey analyzed the isotopic composition of NO_3^- for three HHV samples collected on June 24, 2006; BS, SD and HHO. Figure 20 is a plot of $\delta^{18}O$ versus $\delta^{15}N$ and shows potential source areas for NO_3^- for the three sample sites. The NO_3^- present in BS and SD waters is derived from mineralized fertilizer, while NO_3^- at HHO comes from soil organic matter. Seep 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. HHO waters are also autogenic, with soil organic matter that may be derived from fertilized and unfertilized crops (Panno et. al, 2006). These results show

that anthropogenic nitrate is present in both allogenic and autogenic waters in HHV.

Background Concentrations of Nitrate and Chloride

Delineating background and anthropogenic sources of contaminants may also be useful 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. Following the technique described in Panno et al., 2006a, data were plotted on cumulative probability plots to delineate background and anomalous populations of chloride and nitrate from samples collected in Horn Hollow Valley. 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.

The chloride cumulative probability plot (Figure 21) 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⁻.

Forty-two samples from HHV fell within the range of Cl⁻ background concentration. These samples were mainly from Lower Valley sites. Twenty samples from Middle and Upper Valleys plotted within the 13-66 mg/L anthropogenic population. Two of these samples within the second population
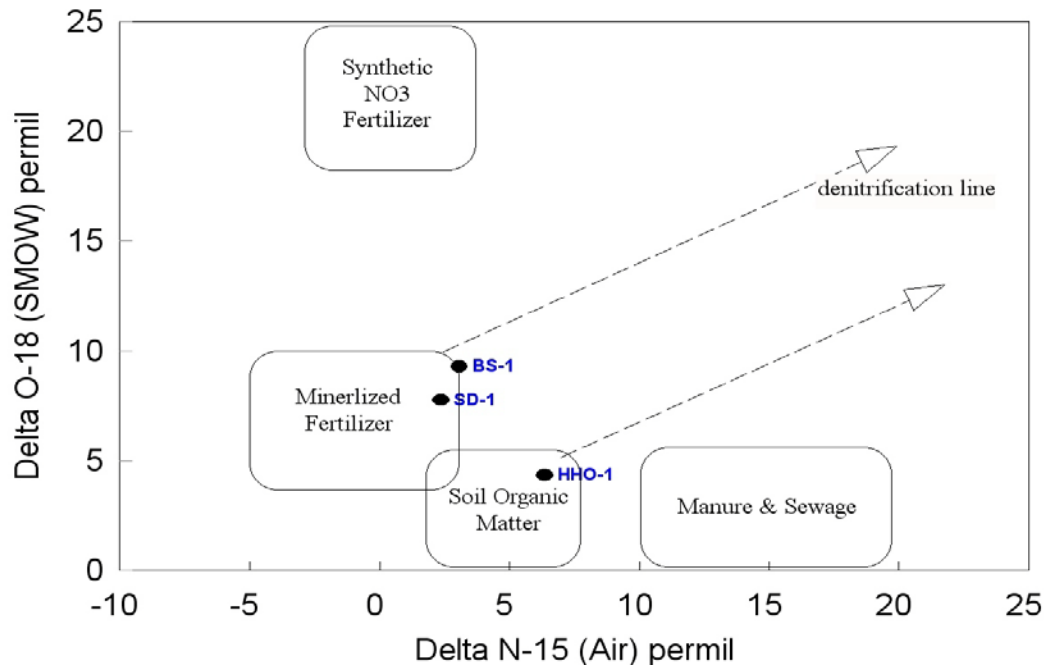
Figure 20. **Results from δO-18/δN-15** isotopic analysis conducted at the Illinois State Geological Survey. Samples were collected on June 24, 2006. Note: Typical ranges of common end-members were obtained from Clark and Fritz (1997).

were the high Cl^- samples from stored road salts sampled in June 2006. These results suggest that anthropogenic contamination of Cl^- is highest in the Upper Valley and diminishes down gradient.

The nitrate cumulative probability plot (Figure 22) has one inflection point at 1 mg/L NO3-N yielding two populations of data. Background nitrate for HHV ranges from 0-1 mg/L NO_3-N, with one anomalous (anthropogenic) population present from 1-1.54 mg/L NO_3-N. HHV sites showed background levels of NO_3-N, with the exception of three samples collected in June 2006; one from RS in the Upper Valley and two from LO in the Lower Valley. Sources

of NO_3-N at these sites may be mineralized fertilizer from the SR182 area. 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. It is possible that these three sites receive anthropogenic NO_3-N, but concentrations are so low that they fall within the background population.

Sources of Nitrate and Chloride

CR182 borders the northeastern perimeter of HHV. Farms with homes and livestock are present along the east and west sides of this two lane blacktop road. Small ephemeral (intermittent) streams flow into HHV via draws, possibly carrying NO_3^- and Cl^- from anthropogenic sources. Possible sources of nitrate and chloride can be delineated by plotting Cl^- vs NO_3^- (Figure 23), identifying samples that fall within the background concentration ranges and observing the relationships between NO_3^- and Cl^- for those samples falling outside of background on the plot. For example, the two data points representing high Cl^-/low NO_3 (HHH and FR) are likely from road salt as there was high Cl^- with little to no NO_3. 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. Bastviken et al. (2006) conducted a Cl^- retention study in southeastern Sweden and concluded that soils can act as sources or sinks for Cl^-, with storage ranging from months to years. Lax and

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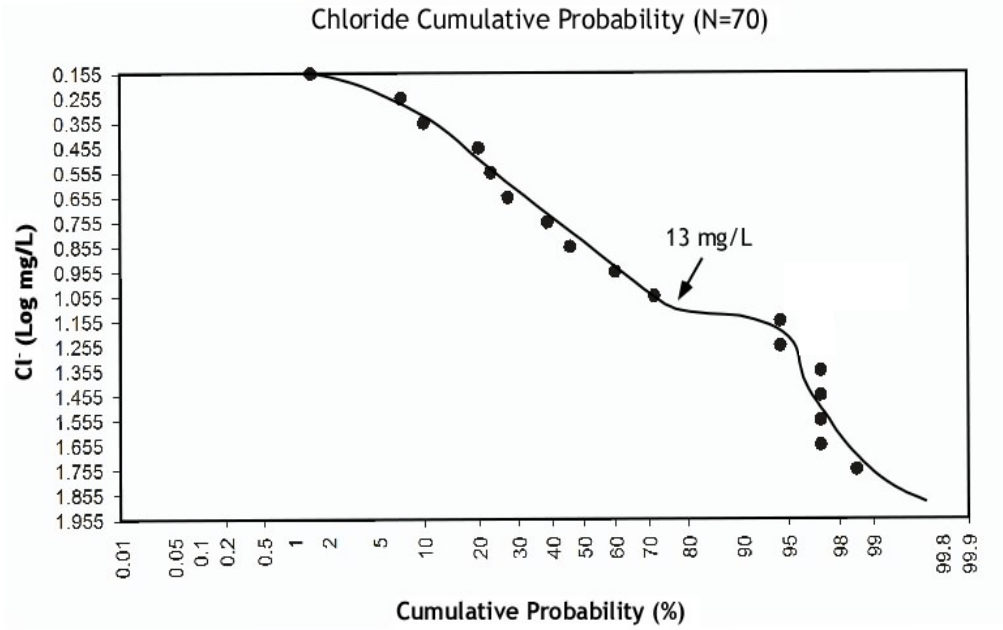Figure 21. Chloride cumulative probability plot (%) showing inflection points yielding three populations of data. Background ranges from 0-13 mg/L NO$_3$-N.
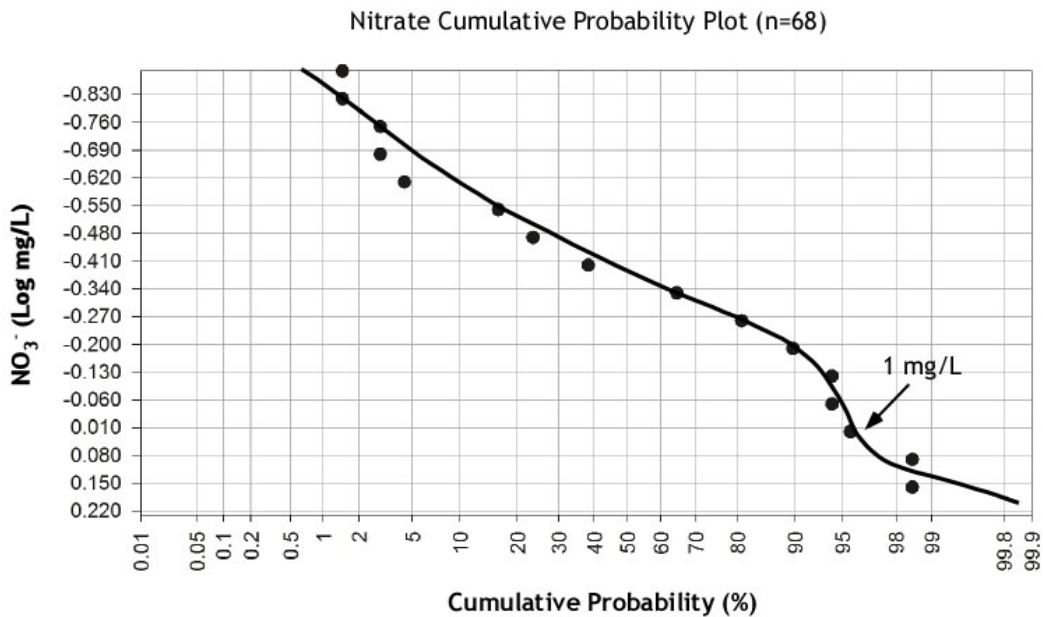

Figure 22. Nitrate cumulative probability (%) showing a single inflection point yielding two populations of data. Background ranges from 0-1 mg/L.

Peterson (2009) reported that road salts migrate through the vadose zone, providing a long term source of chloride to groundwater. Values with low Cl^-/low NO_3^- 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. The two populations with slightly higher Cl^- but low NO_3^- represent sources of mineralized fertilizer and soil organic matter (Panno et al., 2006b) . The mineralized fertilizer cluster contains the BS-1 and SD-1 samples that were identified using δO-18/δN-15 isotopes (Figure 20), while the soil organic matter cluster contains the HHO-1 sample included in the isotopic analysis.

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. Samples from the southwestern Illinois sinkhole plain were collected at various sites within Illinois Caverns by the Illinois State Geological Survey (ISGS) during five sampling trips in 1996 and 1997. Samples from the
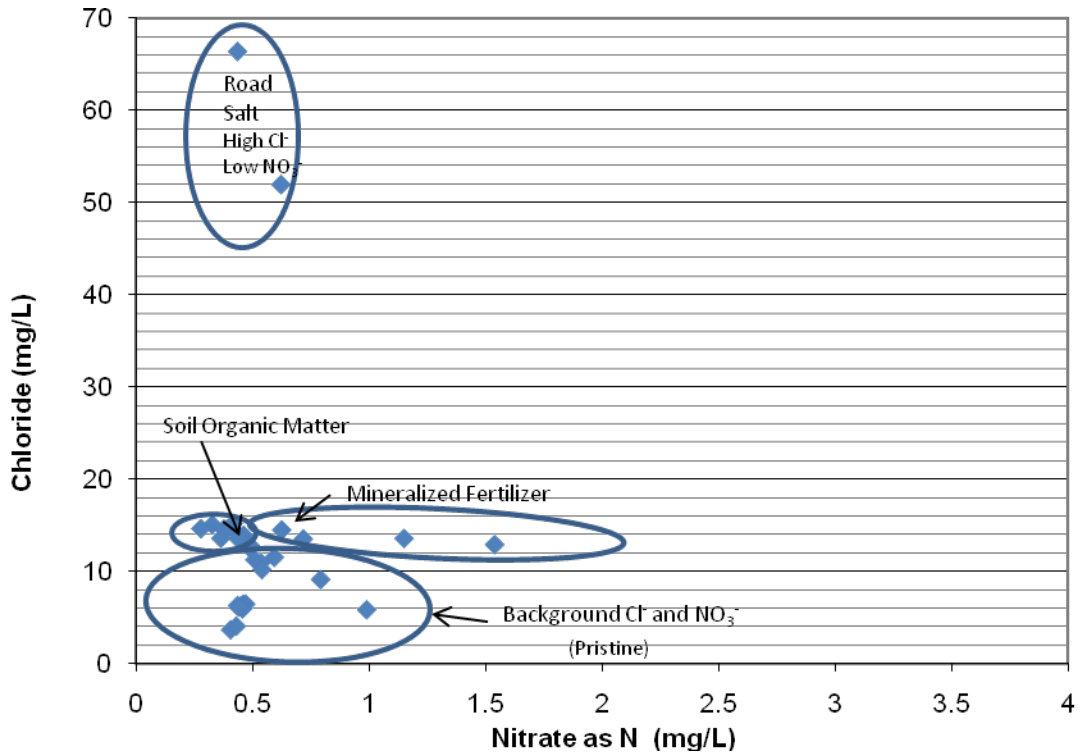
Figure 23. Cl⁻ vs NO₃-N (mg/L) showing sources of these constituents.

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.

Figure 24 shows Cl⁻ vs NO₃⁻ for HHV and comparison systems. Samples

plotting within the blue box represent background concentrations of <13 mg/L

for Cl⁻ (Panno et al., 2006b) and < 2.5 mg/L for NO₃-N (Panno et al., 2006a).

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

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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 24. NO_3-N and Cl^- concentrations for HHV and comparison systems.

The majority of samples from the MCNP database also exhibit background

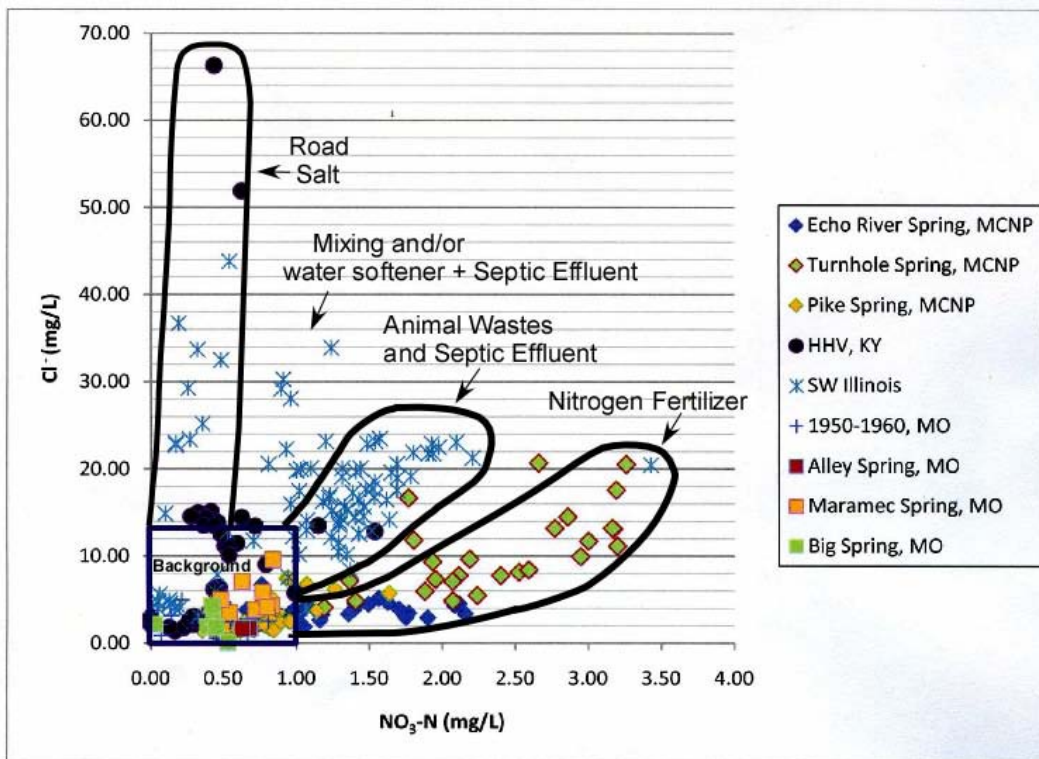concentrations for Cl^- and NO_3^-, although concentrations of NO_3^- at all three

MCNP springs are higher than those in HHV. Pike Spring NO_3^- values are closer

to those measured at HHV as this spring drains the heavily forested Flint Ridge

and portions of MCNP (Quinlan et al., 1991). Turnhole Spring receives a large volume of drainage from the Pennyroyal Plateau to the southeast of MCNP. The Pennyroyal contains fertile soils that are ideal for row-crops and is also more heavily populated than the other two spring basins. Figure 24 shows that some samples from Turnhole Spring have NO_3^- 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) showed 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 plotted along a trend that suggests contamination from animal wastes and septic effluent. Agricultural land-use is dominant in this area and includes row-crops and small livestock operations (Panno et al., 2006a). A study by Hackley et al. (2007) concluded that nitrogen fertilizer and soil organic matter were the major sources of NO_3^- 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 (Petersen et al., 1998). 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 exist 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 concentrations from the three Missouri springs in the 1950's/1960's were 0.44 mg/L. This is virtually identical to 0.45 mg/L median NO_3-N value for 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.

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CHAPTER V

CONCLUSIONS

The overall goals of this study were to analyze the geochemical evolution of karst waters within the Horn Hollow Valley (HHV), to determine general flow paths within the system, and to compare NO_3^- and Cl^- concentrations from HHV to three other midwestern karst systems.

Water chemistry data showed changes along the longitudinal profile of Horn Hollow Creek during individual sampling events and with comparison of multiple sampling events. The allochthonous waters entering the Upper Valley were aggressive and undersaturated with respect to carbonate minerals. These waters moved down gradient through the Pennington and Upper Member Formations, dissolving Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, and Si. These species allowed for the identification of generalized flow paths within the Upper Valley by relating the geochemical signatures to interbedded shale, clay, limestone, dolostone and sandstone units. Waters emerging from the Upper Valley at BS showed increased saturation with respect to carbonate species and waters began to display a more autochthonous signature. Waters flowing through the Ste. Genevieve limestones in the Middle and Lower Valleys showed increased saturation of carbonate minerals from continued dissolution of limestone. The chemistry of cave outlet waters indicated mixing of system waters with waters from karstified bedding planes. Waters discharging at the H2O-O were saturated with respect to carbonate minerals.

Overall, Ca/Mg ratios showed that HHV waters came in contact with a combination of limestone and dolostone and water types were generally Ca-Mg-HCO_3. Concentrations of most species changed slightly under the influence of

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changing discharge conditions and the November 2006 samples showed effects of significant dilution.

Finally, the examination of NO_3^- and Cl^- sources within HHV indicated that samples with concentrations above background levels may 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^- 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.

Future studies would benefit from a much larger data set, preferably from continuous sampling using a data logger. The public nature of this area presents significant challenges for installing and maintaining data loggers. A larger data set would also provide the opportunity for mixing model analysis. Expanded δO-18/δN-15 isotopic analysis would provide additional information regarding NO_3^- sources at other sampling locations within HHV.

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