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The Hydrology of the Carroll Cave-Toronto Springs System: Identifying and Examining Source Mixing through Dye Tracing, Geochemical Monitoring, Seepage Runs, and Statistical Methods

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CARROLL CAVE-TORONTO SPRINGS SYSTEM:
IDENTIFYING AND EXAMINING SOURCE MIXING THROUGH DYE TRACING, GEOCHEMICAL MONITORING, SEEPAGE RUNS, AND STATISTICAL METHODS

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Dedication

I'd like to dedicate this thesis to my parents Mike and Geri Miller, who have supported me in my dream and passion to study caves and karst. You have both always been there for me and I realize how lucky I am to have such supportive and loving parents. Thank you and I love you.

I would also like to dedicate this thesis to the Carroll Cave cavers, past and present, who have spent countless hours, days, and years surveying, documenting, and exploring this great cave system. Without your hard work and dedication the truly unique wonders of this amazing cave would remain unknown.

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In karst areas relationships between activities occurring on the surface and the overall health of the subsurface environment are often highly interconnected. However, the complex nature of karst flow systems can often make identification of these connections difficult. Carroll Cave, a large stream cave system located in the central Missouri Ozarks, is known for its biological and speleological significance. A dye tracing project to delineate a Carroll Cave recharge area through dye tracing has identified an area of 18.5 km^2 which contributes water to the cave. The water from Thunder River within Carroll Cave was positively traced to eight springs of the thirteen springs at a distributary spring system known as Toronto Springs. Through examination of the geochemistry of the individual springs, differences in water chemistry between the various outlets has become evident. Additional work with YSI Sonde dataloggers and consideration of carbonate chemistry relationships has sought to further define the variations in hydrochemical behavior, thus aiding in the discrimination potential spring sources. Primary sources thought to contribute water to the spring system include Carroll Cave and Wet Glaize Creek, with some minor influence from other losing streams in the vicinity. Seepage runs along Wet Glaize Creek have also identified major losing reaches, in close proximity to structural features, which may contribute water to Toronto Springs.

Examination of the measured parameters and derived have identified that Carroll Cave and Wet Glaize Creek are the primary end members for Ca^{2+}, Mg^{2+}, HCO_3^-, specific conductance, and temperature. Using these parameters a two end member mixing model has been developed which describes the mixing zone setting at Toronto Springs and calculates the average proportions of flow contributions by the end members. By using a multi-proxy approach of dye tracing, seepage runs, and geochemistry for the individual springs, the source waters and pathways for the springs at Toronto Springs have been identified.

Chapter 1 : Introduction

Karst is a landscape created by the dissolution of soluble bedrock by acidic water which creates unique features that allow drainage of water from the surface environment to the subsurface groundwater environment. Since up to 25% of the world's population relies on groundwater supplies, risks to groundwater contamination in karst areas must be avoided and local karst flow systems must be well documented and understood (Ford and Williams, 2007). Carroll Cave and Toronto Springs, located in the central Missouri Ozarks, represent the complex interactions that can occur between karst recharge areas and surface flow systems, resulting in mixing of distinct recharge sources and discharge from multiple springs.

In many karst areas the bedrock is commonly limestone, dolomite, or gypsum and landform features may include caves, sinkholes, springs, and losing streams. Often, surface drainage is diverted into the subsurface environment through a system of losing streams, sinkholes, and general infiltration. Because of the interconnectivity of the surface environment and the groundwater supply, any activities that occur on the surface may directly impact the water quality and the overall health of the subsurface environment (Vandike, 1982). Biological investigations of cave and karst systems show these environments are highly conducive to habitation by rare, endemic, and often troglomorphic biota (Christman and Culver, 2001). Therefore, in karst areas understanding the structure, functionality, and zones of influence on a karst area is critical. Rigorous investigation of the surface and subsurface interconnectivity provides information on the functioning of the groundwater systems of a region, and is important in order to maintain a high level of groundwater quality and protect potentially sensitive and rare biota (Vesper et al., 2000; Smith et al. 2003; Lerch, 2009).

Karst hydrology is the study of the movement of groundwater through karst terrain. In classical hydrology, movement of groundwater is examined through equations such as Darcy's Law. Darcy's Law describes the movement of a fluid through porous media, such as sands, loess, and various types of bedrock. However, Darcy's Law only deals with laminar flow, evenly distributed flow, which is often not the predominant flow type in karst areas. Since dissolution takes place within the soluble bedrock, karst areas display turbulent flow, which is concentrated along enlarged fractures, conduits, and openings. Due to this behavior, karst hydrology can often be difficult to model and can be extremely complex with regards to flow paths and behaviors. Field methods for studying karst hydrology include dye tracing, remote sensing, discharge measurements and water quality monitoring which allow hydrologist to study the complex and often hidden nature of karst hydrology.

Within the field of karst hydrology, concepts have been developed that help to describe the various ways by which water enters and leaves a karst system, the sources of this water, and the zones that the water moves through in a karst setting. Water acting as an input to the karst hydrologic system is known as recharge, which can enter through infiltration, sinkholes, and losing streams. Any water leaving or exiting from a karst system is known as discharge, and this occurs through discharge features such as springs and caves. Recharge can be further classified into discrete and diffuse recharge, depending on the rate or method by which the water enters the hydrologic system. Diffuse recharge enters a karst system by gradually infiltrating through soil, organic material and eventually into the epikarst. Discrete recharge usually enters more rapidly at specific recharge points, and provides an input that can, in many cases, accept much larger amounts of water. Karst systems can also have a vertical stratification of zones that help to classify each zone based on unique characteristics. At the base level of the karst zones is the phreatic zone, in which all openings are entirely water-filled, and this is also commonly referred to as the water table and the area below the water table. The vadose zone is just above the phreatic zone and consists of openings and passages that are partially to completely filled with air. Above the vadose zone is the epikarst zone which is an area where the bedrock is highly fractured, possibly in contact with soil material, and where conditions may exist that allow for a perched aquifer.

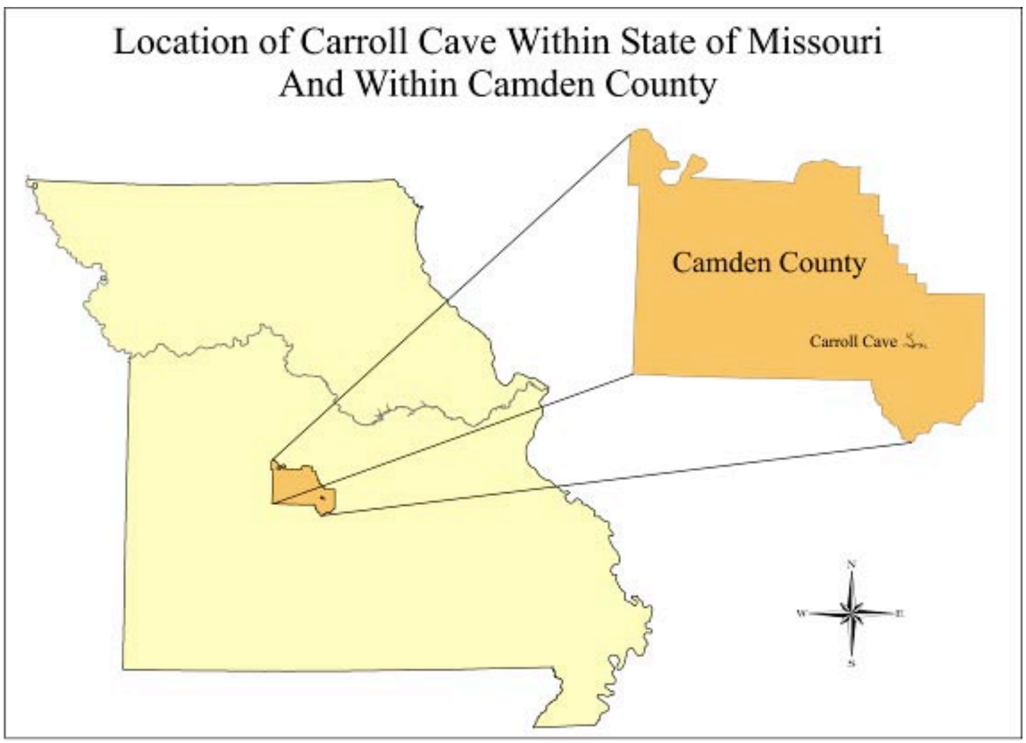


Figure 1: Map showing location of Carroll Cave within Missouri.

Carroll Cave is a large stream cave, approximately 28 km in length, located in central Missouri in the Ozarks ecoregion (Fig.1). Carroll Cave is known for the extensive nature of the passages, the high quality of speleothems, and for the biological diversity of the cave system. The water from Thunder River, within Carroll Cave, has been positively dye traced to eight spring outlets at Toronto Springs located four kilometers north along Wet Glaize Creek (Vineyard and Feder, 1974). Toronto Springs is a complex multiple outlet spring system located in an alluvial flood plain setting alongside Wet Glaize Creek.

Work began in October 2008 to delineate a recharge area for Carroll Cave, primarily focusing on identifying areas draining to Thunder River and discharge features associated with Thunder River. Delineation of a recharge area is a prerequisite for assessing land uses that may negatively impact the water quality of a karst aquifer and thus the biodiversity of the cave system (Jones et al., 2003). Knowing the recharge area also can help in future land acquisition for the protection of the cave system and allows one to examine land-use patterns and changes within that area over time. In identifying the Toronto Spring is a multiple outlet alluviated spring system in which multiple recharge sources contribute to the discharge of the springs. Some, but not all, of the springs have been shown to be connected to Carroll Cave which is hypothesized to be one of the two key recharge sources. The other probable recharge source is Wet Glaize Creek. A seepage run conducted from the upper portion of Wet Glaize Creek to below Toronto Springs, indicated a significant loss of flow in Wet Glaize Creek that apparently resurged at Toronto Springs. Previous research in this portion of the Missouri Ozarks has shown extensive sinking or losing streams that contribute water to springs located further downstream in the catchment area (Skelton, 1976; Harvey et al., 1983). Because of this hydrologic behavior of the surface streams, along with discharges at Toronto Spring which are larger than flow contributed by Carroll Cave it is believed that Wet Glaize Creek is a possible end member contributing flow to the spring outlets. While there may be other minor sources of recharge to Toronto Springs this research has studied the relationship between source waters contributed by Carroll Cave and flow contributed by Wet Glaize Creek.

In karst settings, the carbonate chemistry of the water can indicate characteristics of the environment from which the water originated. Studies of karst springs have shown that variations in flow and geochemistry are related to conditions within the aquifer and can be used to examine the behavior of the karst aquifer (Shuster and White, 1971; Scanlon and Thrailkill 1987; Ryan and Meiman, 1996). Water with low concentrations of calcium and magnesium may indicate that the water originated from a surface stream setting which has not yet had an opportunity to dissolve a significant amount of bedrock. Water with high concentrations of calcium and magnesium may indicate water that has been in more sustained contact with limestone and/or dolomite bedrock, as in a cave setting. This research uses analyses of several water quality parameters to identify potential recharge sources for the multiple spring outlets at Toronto Springs. With two geochemically distinct sources (i.e. Carroll Cave and Wet Glaize Creek) a two end member mixing model for the springs at Toronto Springs was created using techniques similar those reported by Wilson et al. (2008) in which a two end member mixing models of soil isotopes was used to identify sediment sources in streams. Using a variety of water quality parameters (*e.g.* temperature, pH, specific conductivity and concentrations of cations), the objective of this research was to determine the specific proportion that each of the two end members contributes to the discharge at each of the 11 individual springs at Toronto Springs. An additional objective was to compare the various water quality parameters among the 11 springs to determine if spatial differences in recharge sources exist among the individual springs.

The goal of this research is to examine the hydrology of the Carroll Cave–Toronto Springs system with regards to identification of recharge areas for Carroll Cave, identification of end member sources for Toronto Springs, examination of geochemical variation between spring outlets, and the creation of a freshwater mixing model.

Hypothesis: Toronto Springs, a multiple outlet alluvial spring system, represents a mixing zone setting of whose primary source waters are Carroll Cave and Wet Glaize Creek.

Literature Review

Much of the work in karst areas over the last 50-60 years has focused on defining karst, examining the processes and influences on karst and the resulting impacts on karst landscapes, investigating the biological components of karst, and studying the sensitive nature of karst environments. However as research evolved in the field of karst and areas of specialization were created, scientists have identified difference in karst landscapes warranting further study.

Karst

Karst was defined by Ford and Williams (2007) as “comprising terrain with distinctive hydrology and land forms that arise from a contribution of high rock solubility and well developed secondary porosity”. This definition explains several of the aspects of karst landscapes, specifically that karst is a terrain or landscape with unique hydrology and the need for high bedrock solubility, which are established as a major components necessary for the formation of karst (Palmer, 1995). Within karst are three different zones of development which are vertically stratified based on the proximity of each zone to the water table. The zones (from water table up toward surface) are referred to as the phreatic zone, the vadose zone, and the epikarstic zone. Palmer (2007) defined each of the following; the vadose zone is “…above the water table in which water moves by gravity capillarity. Water does not fill all the openings…”, the phreatic zone is where “…all the openings are filled with water. Its top surface is the water table.” and the epikarst is “the highly porous upper-most zone of dissolution in soluble bedrock at the surface or just below the soil…Nearly all initial openings have been enlarged at comparable rates by highly under saturated water.”.

Karst hydrology has evolved to include studies of the conceptual framework of karst hydrology; including recharge and discharge relationships; geochemical investigations, evolution of conduit permeability, and the characterization of karst aquifers (White, 2002). In karst systems the characteristics of a recharge area directly impact the geochemical characterization of the waters discharging from a karst aquifer. The structure of a karst flow system, recharge area land use, and the geological conditions for an aquifer can also impact discharge behavior of springs as reflected in hydrograph studies (White, 1993; White, 2003; Florea and Vacher, 2006).

The biology of cave and karst systems is highly diverse and they have a high degree of endemism which varies greatly by the health and availability of habitat (Christman and Culver, 2001). Understanding the structure of a karst system and the hydrologic behavior can be necessary to examining the factors which may impact the unique biology present in these systems (Smith et al., 2003).

Due to the interconnected nature of karst flow systems, impacts from surface activities have the potential to contaminate groundwater supplies. Numerous case studies exist, documenting karst groundwater contamination from industrial, agricultural and anthropogenic sources (Field, 1988; Panno, 1996, 2001). Because of this interconnectivity, the sensitivity of groundwater resources and unique biota, understanding how karst systems function and what impacts these systems is critical to maintaining high quality groundwater and aquatic ecosystem integrity.

Dye Tracing/Tracer Tests

Dye tracing is one of the fundamental approaches used by hydrologists to study the complex surface-subsurface interactions of karst hydrology. Tracers allow researchers to study the movements of fluids in subsurface environments and can be used to understand or predict contaminant transport, delineate recharge basins for springs or caves, and to examine the many geochemical interactions that occur in the groundwater environment. Tracers have most commonly been non-toxic fluorescent dyes that have sufficient stability in the subsurface environment to be recovered from the aquifer, typically at or near points of resurgence, but other tracer such as bacterial spores, soluble salts, and even radioactive materials can be used as tracers (Aley and Fletcher, 1976). Specific use of dye tracer tests in karst areas and the considerations one must make in regards to dye selection and injection technique require specialized knowledge (Jones, 1984). Jones (1984) noted that various dyes may sorb to sediments or degrade rapidly due to photolysis from sunlight so the tracers must be selected for the conditions present. Because of the interconnectivity found in karst areas, between the surface and subsurface flow systems, care must be taken to use only non-toxic dyes or tracers when conducting groundwater traces as to not negatively impact delicate biota or endanger public health (Smart, 1984; Field, et al. 1995). Traces may be of a qualitative nature, determining specific hydrologic connections, or may be quantitative in nature where specific concentrations of the tracer are examined by intensive sampling at monitored discharge features. Tracer tests may help to describe the geometry of karst flow systems that are not humanly enterable or accessible by examining the variations in the shape and timing of breakthrough curves. Studies conducted by Smart (1988) definced the functioning and structure of a complex karst flow system at Castleguard Cave in Alberta, Canada using quantitative tracing techniques, sampling at multiple sites, and examining tracer travel time with concentrations.

Predicting or determining the transport of contaminants in karst areas has long been one of the primary applications of groundwater tracer tests, specifically using fluorescent dye as tracers. Frequently tracer tests are performed after an incident has occurred to determine the subsurface path that the contaminant may take and the area which will be affected from the contaminant. Vandike (1982) discusses a 1981 liquid fertilizer pipeline leak near Salem, Missouri that severely impacted a nearby first magnitude spring. During litigation following the spill dye traces provided the needed proof of a direct hydrologic connection between the spilled fertilizer and the spring eventually prompting further traces to delineate a recharge area for the spring (Vandike, 1996). Crawford and Ulmer (1993) detailed hydrological investigations and dye traces in the Lewisburg, Tennessee vicinity which were prompted by a contaminant spill and a desire to determine the source of a separate contaminant detected during the subsequent monitoring. Case studies such as these illustrate the need for delineating karst groundwater basins, via groundwater tracer tests, in order to maintain water quality, biological health of the subsurface environment, and to be prepared in the event of a contaminant spill/leak. Modern tracer tests also include using dyes, nutrients, and microspheres for tracing groundwater pathway. Researchers also use a variety of different analytical methods including continuous fluorescence monitoring instrumentation to tackle difficult problems such as diffuse recharge traces in the epikarst and conduit arrangements (Goldscheider et al., 2008).

Geochemistry

The study of karst hydrology is very much coupled with the study of the geochemistry of the waters flowing into, through, and discharging from karst aquifers.

Analysis of water samples from caves, surface streams, well waters, and soil waters within a karst aquifer have shown chemically distinct and statistically significant differences in water chemistry which can be used to identify the origin or path that water has taken to a specific site or discharge feature (Drake and Harmon, 1973; Harmon et al. 1975). Specifically, the geochemistry of karst waters in temperate climates is affected by factors of geology, land use, climate, and anthropogenic impacts (Troester and White, 1986). Troester and White (1986) examined the geochemistry of three adjacent karst drainages in Puerto Rico and found that the geochemistry of groundwater in stream basins with similar geology can vary depending on whether the groundwater recharge is fracture/diffuse flow or conduit/discrete flow. The geochemistry of karst waters in tropical climates is also more consistently saturated or supersaturated with respect to calcite in comparison to normal temperate springs. Land cover changes within an aquifer’s recharge area can have a major impact on the groundwater and affect both the flow and geochemical behavior of both karst and alluvial springs. Hydrological studies in the Lesser Himalaya region found that reductions in the forest cover of spring recharge areas decreased spring discharge by as much as 50-100 percent (Valdiya and Bartarya, 1991). Meiman (1993) found that discharge, turbidity, chloride, bacteria, and herbicide values varied for springs with different land uses in Mammoth Cave, Kentucky. The study also found a strong correlation between water quality and land use which could aid land managers in the protection and management of karst landscapes. In a similar study, Meiman (1996) found that contributions of recharge from zones of varying land use were detectable in the geochemical and bacterial values at an individual spring following precipitation events. Hess and White (1993) examined geochemical variations for local and regional springs, surface streams, and epikarstic springs in south-central Kentucky over a one year period. The saturation indices for calcite and dolomite appear to be similar for large springs and surface streams in the winter time; however in the summer surface streams become progressively more saturated than the springs eventually reaching supersaturation and remain so throughout the fall. Water from medium-sized springs and epikarstic springs are largely undersaturated with respect to calcite and dolomite and maintain this character throughout the entire year. Changes in saturation indices and CO_2 pressure from site to site were attributed to differences in source water origin and to flow path characteristics (i.e. fracture and shallow flow systems versus deeper open conduit flow systems).

Birk et al. (2003) used a small karst flow system between a sink and a spring in southwest Germany to test various techniques that can determine characteristics about a conduit supply system to spring based on discharge and geochemical responses to precipitation events. The research found that in a small and relatively simple karst flow systems it is possible to obtain information about a conduit system and the localized recharge supplying a spring system, however it was noted that in a larger, more complex karst system with multiple inputs these techniques might not be as effective. Spatial variability between springs in a karst aquifer can be an issue when considering a monitoring protocol for examining water quality and chemistry (Zhou et al., 2008). The variations in recharge sources, precipitation patterns, and the general heterogeneity of karst landscapes can create issues for comparison amongst sites. Because of this characteristic, when monitoring in karst, intra-spring variations in water chemistry and discharge, due to precipitation events and recharge area characteristics, must be accounted for in order to properly examine the characteristics of a given aquifer. Therefore, if comparing amongst sites draining similar recharge areas base flow conditions may be the only comparable conditions. However, according to Quinlan (1990) the only locations in karst that should be considered for monitoring are springs, caves streams, and water wells that have known recharge areas defined through groundwater traces (Quinlan, 1990).

Study Area

Toronto Springs and the Carroll Cave system are located within the Wet Glaize watershed. Wet Glaize Creek and Dry Auglaize Creek converge to form the Grandglaize Creek, a major tributary to the Osage River and Lake of the Ozarks. A study examining the low flow characteristics of Ozarks streams first examined the complex hydrology of the Grandglaize area by conducting seepage runs along the tributaries and various portions of the main streams (Skelton, 1976). This early seepage run largely examined the overall region's hydrology and did not examine any influence Toronto Springs might have on groundwater flow in the Wet Glaize watershed. The hydrology of the Grandglaize, Niangua, and Osage Fork basins were studied extensively by Harvey et al. (1983). Seepage runs, discharge measurements, groundwater behavior, and other field work were combined to study the hydrologic functioning of these basins. In the same report dye tracing and engineering geology of Conn's Creek were also examined by Dean (1969) who established a hydrologic connection from the upstream losing portions of Conn's Creek to Blue Hole Spring along Wet Glaize Creek. Toronto Springs, Carroll Cave, and the portions of Wet Glaize Creek between the two features were not studied in detail due to the large scale of the research.

Toronto Springs are first mentioned in the scientific literature by Beckman and Hinchey (1944) who described two springs at the site, mentioning that the springs rise in gravel beds then flowing along spring runs to Wet (Au) Glaize Creek. Vineyard and Feder (1982) discussed the geography of the spring(s), previous dye trace from Carroll Cave, and also include a discharge value of 163 L/s for Toronto Spring, as well as presenting some preliminary water chemistry data from one sampling period. Similar to most early documentation of the spring system, Vineyard and Feder (1982) only described two springs, Toronto Spring and Little Toronto Spring. Padgett (2001) was the first to describe the area as having multiple spring outlets, referring to the site in the plural sense as “Toronto Springs”. However, Padgett reported on the exotic and invasive aquatic plant communities of Toronto Springs, not the hydrology.

Helwig (1965) discussed the geology of the Carroll Cave system focusing on the sediments and their stratification throughout the system as well as the speleogenetic history of the cave. However, it is in this paper that the connection between Thunder River and Toronto Springs is first discussed in the description of a 1962 dye trace to “Toronto Spring” and of the unique character of the springs being located on the opposite side of the creek from Carroll Cave. In *Springs of Missouri*, Vineyard and Feder (1982) make note of the connection of Carroll Cave to the Toronto Springs system, the previous dye trace, and speculate on the speleogenetic history.

Biological investigations of Carroll Cave have examined both the paleo-fauna and unique troglobitic/stygobitic potential of the cave system. Carroll Cave has been studied for the diversity of Pleistocene fauna which has been found in some portions of the cave, notably Dire Wolf, *Canis dirus*, and Short-Faced Bears, *Arctodus simus* (Hawksley, 1965; Hawksley, 1981; Anyonge and Roman, 2006). Due to the large amount and variety of possible cave niche habitats found in Carroll Cave, there are conditions which are conducive to higher than average biodiversity. The current biological significance of Carroll Cave has been hypothesized to be significant in relation to many other Missouri Ozarks cave systems but has thus far received little study (Elliott, 2007).

Summary and work to be done

Karst hydrology has developed techniques that allow for the delineation of a recharge areas through groundwater tracer tests, the examination and impact of a recharge area upon the geochemistry of a spring or stream. However while much of the literature has examined individual spring variations or variations at springs with different land use, there has not been considerable work in examining mixing of sources between flow from cave/karst and flow from primarily surface streams. In the Wet Glaize Creek vicinity work has been conducted looking at the larger overall functioning of the watershed but the detailed complexity of the karst hydrology within the watershed has not been fully studied. Toronto Springs represents a unique karst hydrologic setting where karst water discharges from multiple alluvial spring outlets, but the determination of the recharge sources to these springs has not been studied. In addition, Carroll Cave requires more work to delineate the recharge area and to more closely examine the interactions between the cave and Toronto Springs. The geochemistry of Toronto Springs and a recharge area that might influence the springs remain to be examined in further detail, as well as documenting the unique geologic characteristics of the site. Study of the recharge to the various springs at Toronto Springs has not been previously conducted, and this site provides the opportunity to develop a generalized conceptual model for the karst hydrology of multiple outlet alluviated spring systems. Interactions that Wet Glaize may have with Toronto Springs need to be studied as well through the use of groundwater tracing and more closely refined seepage runs conducted along the streams of the study area. Karst hydrologists have studied the complex interactions between the surface and subsurface flow systems and this background of work will help to define and illustrate the unique mixing zone setting of Toronto Springs.

Study Area

The Wet Glaize Creek drainage basin is located in the central Missouri Ozarks region and is within the Grandglaize Basin which in turn is part of the Osage River Basin. The Wet Glaize Basin is approximately 331.3 km^2 in size including the drainage areas contributed by tributaries. The area is characterized by rolling hills dissected by meandering streams and local elevation varies from 213 m to 348 m above sea level with total vertical relief around 135 meters. The region is dominated by karst topography such that springs, caves, and sinkholes are common features and the majority of local surface drainages have losing streams. The underlying bedrock is dominated by Ordovician dolomites and sandstones, the cave and karst areas largely are within the Gasconade Dolomite with overlying Roubidoux Sandstone along ridgetops and Jeff City-Cotter Dolomite exposed in a few areas near the Montreal Fault Block (Middendorf, 1984). Land cover is dominated by grasslands and deciduous forests, which account for 91% of the total land cover in the watershed.

Wet Glaize Creek is composed of a fairly extensive network of first, second, and third order streams (Fig. 2). Wet Glaize is identified on topographic maps as the streamway below the confluence of Sellers Hollow and Conns Creek. Sellers Hollow is the combined flow of Sellers Hollow, Rocky Hollow, and Murphy Creek while Conns Creek has only one named tributary, Deberry Creek. Other large tributaries enter Wet Glaize below the confluence of Sellers and Conns Creeks, the largest of which is Mill Creek. By examining topographic maps of the study area, it becomes apparent that Conns Creek is the primary channel of Wet Glaize and for this reason it will be treated as the headwaters of Wet Glaize Creek. Numerous springs contribute significant amounts of flow to the streams with the largest series of springs being the Toronto Springs system.

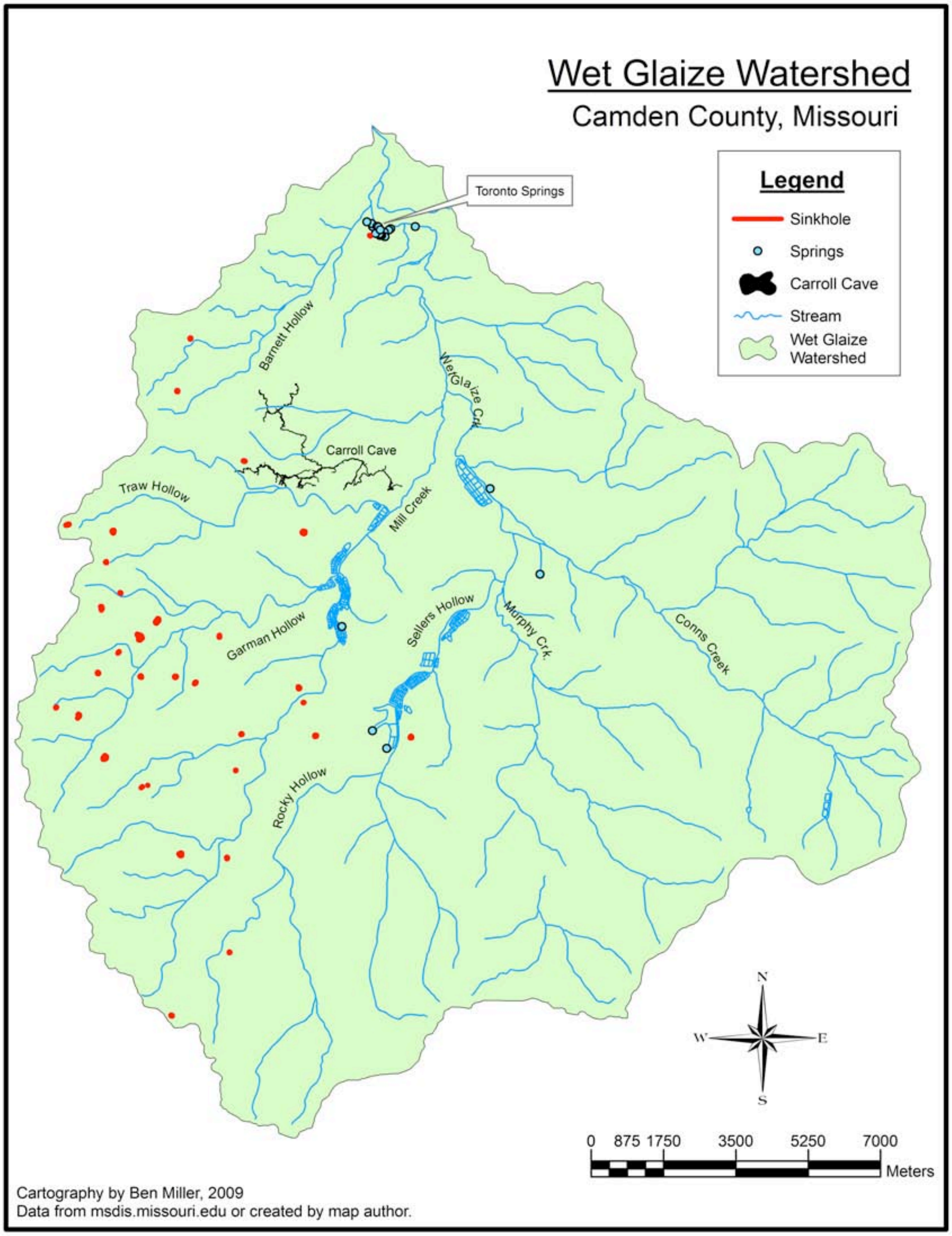


Figure 2: Map of Wet Glaize Creek Watershed

Carroll Cave is an extensive stream cave system, currently 28 km in length and still being explored. The cave is developed within the Gasconade Dolomite and located in the northwest portion of the Wet Glaize Creek watershed. The cave is known to have dense populations of the Southern Cavefish (*Typhlicthys subterraneus*) and the Grotto Salamander (*Eurycea spelaea*) both stygobitic species of special concern within the state of Missouri. The hydrologic behavior of the cave is controlled by three independent cave streams; Carroll River, Thunder River, and Confusion Creek/New River (Fig.3). Thunder River, the largest of the cave streams, has an average daily flow of 150 L/s and contains multiple tributaries along the 11 km course of the cave stream. Thunder River siphons at the downstream end and flows north to resurge at Toronto Springs. Carroll

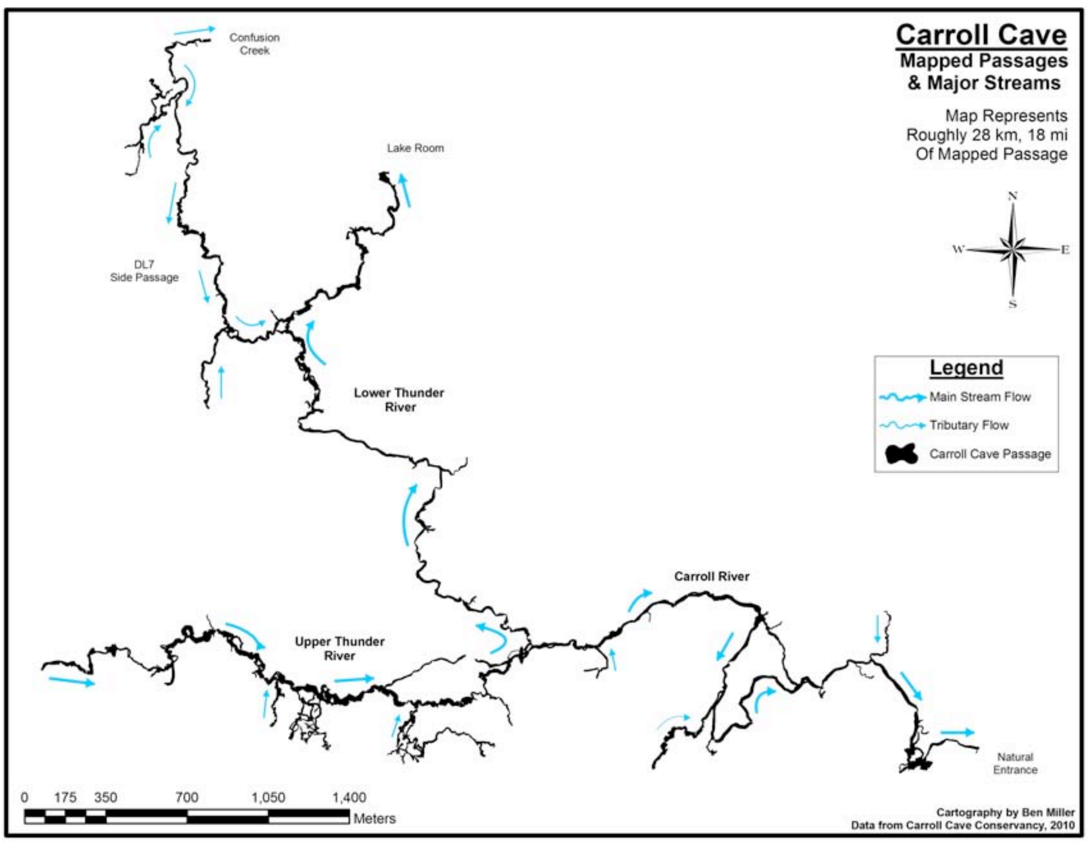


Figure 3: Map of Carroll Cave, showing flow direction of major streams.

River is a much smaller stream, which is the previous flow path of Thunder River, and exits via the cave's natural entrance. The flow to Carroll River has been abandoned due to the incision of Thunder River and today stream flow is from some side passage streams as well diffuse recharge via perennially dripping domes and speleothems. Confusion Creek, also referred to as the New River, is located at the extreme northern end of a side passage, DL7, in Lower Thunder River. A drainage divide is crossed and the new stream is accessed via a small tube which drops into the second largest stream in the cave, with about half the flow of Thunder River. This new stream has been traced to Toronto Springs as well, discharging from the same springs as Thunder River.

Toronto Springs is a multiple outlet alluvial spring system located along the north and south sides of Wet Glaize Creek (Fig. 4). The spring series is located approximately 4 kilometers north of the Thunder River siphon within Carroll Cave. The spring system consists of at least 13 spring outlets varying in discharge from approximately 14 liters per second (L/s) to 220 L/s. Dye tracing from within Carroll Cave has identified eight spring outlets which are connected to the Carroll Cave system. Interestingly, spring outlets that are connected to Carroll Cave are found on both sides of the base level stream, Wet Glaize Creek. The characteristic of having a discharge feature on the opposite side of a stream from the recharge area is somewhat of a unique feature of the Toronto Spring series compared to more typical fluvial karst springs. This aspect of the springs is especially unique in that there are no confining bedrock layers beneath Wet Glaize Creek. It is uniformly dolomitic bedrock under the stream channel, suggesting that existence of multiple confined conduits or fractures that allow for karst recharge to travel beneath the stream bed with no apparent interaction with the surface water.

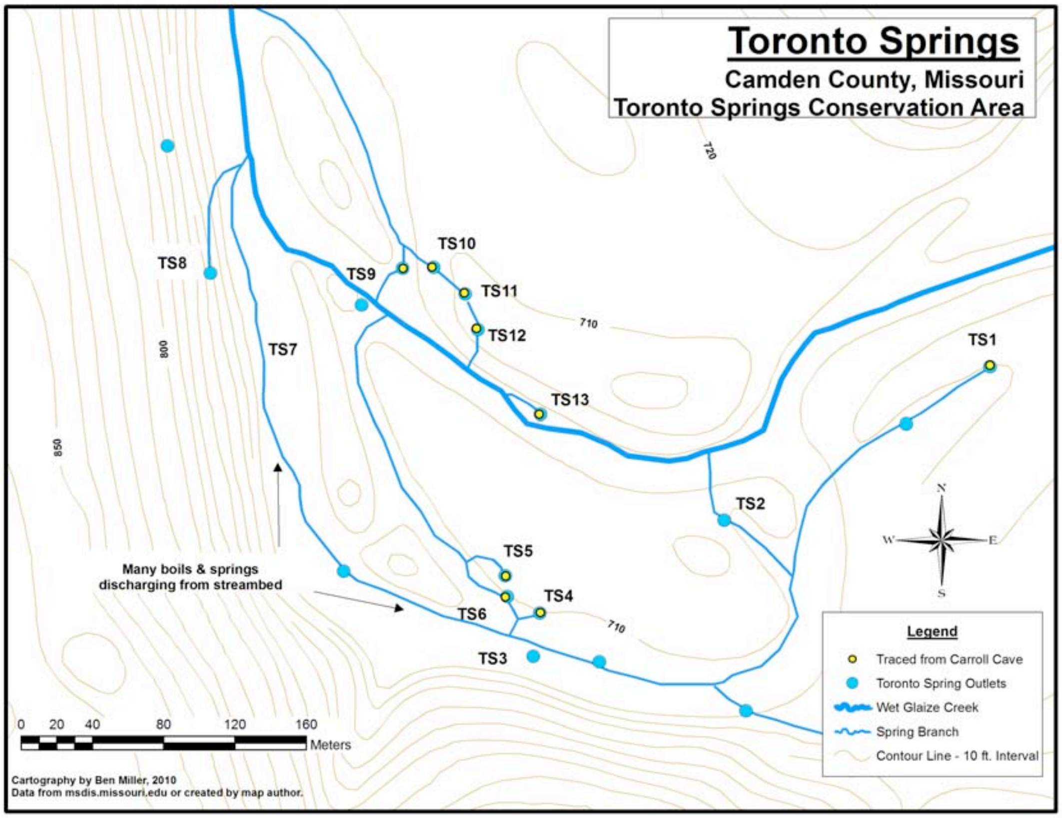


Figure 4: Map of Toronto Springs.

Chapter 2 : Methodology

Dye Tracing

Groundwater tracing with fluorescent dyes was used to delineate the recharge area for Carroll Cave and to attempt to confirm hydrologic connections between Wet Glaize Creek and various Toronto Springs outlets. Fluorescent dyes that were used for the groundwater tracing portion of the project included fluorescein, eosine, Rhodamine WT, sulphorhodamine B, and Tinopal OB. Each of these dyes has been used extensively in groundwater tracing experiments and has a toxicity level safe for use in karst terrains (Smart, 1984; Field et al., 1995). Dye was introduced into the hydrologic system by direct injection of dye into flowing water, dry sets, and flushing of dye with the aid of a fire tanker truck as the primary injection methods, depending upon the accessibility to an injection site and the flow conditions at the time of the injection. Injections focused on the large losing stream drainages of the surrounding area to Carroll Cave including Traw Hollow, Davis Hollow, and Barnett Hollow. Other drainages were also examined to determine the furthest possible bounds of the recharge area. Dye injection locations, the type of dye used, and mass of dye injected are summarized in Table 1. Monitoring sites were selected during a karst hydrologic inventory of the surrounding area, conducted in August 2008, as well as stream locations within Carroll Cave (Table 2). At each monitoring site, packets containing ~4 g of activated coconut charcoal (Thermo Fisher Scientific, Waltham, MA) were used to sorb the dyes from solution. Charcoal packets were attached to rocks or roots and placed in the direct stream flow of the discharge feature or location. Changeouts of packets occurred at semi-regular intervals in order to estimate travel time of the dye from injection site to recovery location. The packets were transported via coolers to the Crawford Hydrology Laboratory within 2-3 days of collection. In the laboratory the packets were rinsed, samples weighed out, eluted with a solution of 50% N-Propyl Alcohol, 30% De-Ionized Water, 20% NH_4OH, and then analyzed using a Shimadzu RF 5301-PC spectrofluorometer (Shimadzu Scientific Instuments Inc., Columbia, MD). The Shimadzu spectrofluorometer was calibrated before each analysis with samples of two known standard concentrations, 0.005 ppb and 0.1 ppb, for each dye analyzed. The receptors for this research were analyzed for up to five different dyes and thus a full scan was performed in which the spectrofluorometer analyzed fluorescence from 365-625 nm. If a receptor sample had high levels of dyes detected then a third standard, typically 1-10 ppb, was run in a higher scan mode before the packet was analyzed. Individual spectrofluorometer files were saved and can later be used in combination with the standards to determine the concentrations of dyes present within a receptor sample. Details of the spectrofluorometric analyses are reported in Karst Groundwater Investigation Research Procedures (Crawford Hydrology Laboratory, 2010). Interpretation and confirmation of the positive traces were made based on emission wavelength of dyes present in the eluted sample and the previously recorded background levels for that particular dye.

Table 1: Table of dye injection locations, elevations, dyes used, and dye amounts injected.

Round #: Injection #	Date	Location Description	UTM-NAD 83 Easting/Northing	Elev. (m)	Dye Injected	Dye Amt.
1:1	10/2/08	Carroll Cave - Thunder River just below DL7	E: 539751 N: 4201297	228.6	Fluorescein	1.8 kg (4 lbs)
1:2	10/3/08	Traw Hollow - north arm, directly south of Traw Hollow Rd. off Hwy BB	E: 535772 N: 4198913	310.9	Sulphorhodamine B	2.27 kg (5lbs)
1:3	10/3/08	Traw Hollow - south arm, off Hwy BB	E: 535754 N: 4197887	316.9	Eosine	2.27 kg (5lbs)
2:1	4/19/09	Traw Hollow - at Traw Hollow Rd.	E: 538459 N: 4198437	280.4	Rhodamine WT	1.36 kg (3 lbs)
2:2	4/19/09	side arm to Traw Hollow - off Hwy 7	E: 538185 N: 4200730	298.7	Fluorescein	0.91 kg (2 lbs)
2:3	4/19/09	Barnett Hollow - north arm	E: 537407 N: 4202731	277.4	Tinopal	1.8 kg (4 lbs)
3:1	9/19/09	Whirlpool Sinkhole - south arm of Barnett Hollow	E: 537245 N: 4201724	280.4	Fluorescein	1.36 kg (3 lbs)
3:2	9/19/09	Barnett Hollow - south arm at Bikkor Road	E: 537921 N: 4201770	280.4	Rhodamine WT	1.36 kg (3 lbs)
3:3	9/19/09	Mill Creek - at Seven Springs Rd.	E: 542961 N: 4199473	260.6	Sulphorhodamine B	1.8 kg (4 lbs)
3:4	9/19/09	Wet Glaize Creek - at Seven Springs Road	E: 545091 N: 4198929	234.7	Eosine	2.04 kg (4.5 lbs)
4:1	1/31/10	Garman Hollow - at Brown Way Rd.	E: 537377 N: 4195953	283.5	Sulphorhodamine B	1.8 kg (4 lbs)
4:2	1/31/10	Davis Hollow - at Mill Creek Rd.	E: 540585 N: 4200343	262.1	Eosine	2.27 kg (5lbs)
4:3	2/16/10	Pettijohn Hollow - at High Point Rd.	E: 533229 N: 4195604	322.2	Rhodamine WT	2.27 kg (5lbs)
4:4	2/16/10	"Hippie Shack" Sinkhole - south of Montreal	E: 534892 N: 4201042	313.9	Fluorescein & Tinopal	2.27 kg FL, 6.80 kg OB
5:1	4/28/10	Carroll Cave - Confusion Creek in DL7 Side Passage	E: 539335 N: 4202312	216.4	Tinopal	1.36 kg (3 lbs)
5:2	5/31/10	Davis Hollow - central branch	E: 540554 N: 4201225	253.0	Fluorescein	1.36 kg (3 lbs)
5:3	5/31/10	Whirlpool Sinkhole - south arm of Barnett Hollow	E: 537245 N: 4201724	280.4	Eosine	1.36 kg (3 lbs)
5:4	5/31/10	Barnett Hollow - north arm near Barnett Hollow Cave	E: 538661 N: 4202834	259.1	Sulphorhodamine B	1.36 kg (3 lbs)
5:5	5/31/10	Barnett Hollow - south arm at end of Thiess Property	E: 539107 N: 4202600	256.0	Rodamine WT	1.8 kg (4 lbs)
6:1	9/22/10	Wet Glaize Creek - at Seven Springs Road	E: 545091 N: 4198929	234.7	Fluorescein	1.36 kg (3 lbs)
6:02	10/28/10	Mill Creek - at Seven Springs Rd.	E: 542961 N: 4199473	260.6	Sulphorhodamine B	1.36 kg (3 lbs)

Table 2: Table of charcoal receptor monitoring sites.

ID #	Site Name	Feature Type	Elev. (m)
001	Carroll Cave - Thunder River @ Backdoor Entrance	In-cave stream	240.8
002	CarrollCave - Thunder River @ Horseshoe Falls	In-cave stream	223.4
003	Carroll Cave - DL7 side passage entrance	In-cave stream	223.1
004	Carroll Cave - UL2 side passage stream	In-cave stream	246.3
005	Carroll Cave - UL5 side passage stream	In-cave stream	251.5
006	Carroll Cave - Thunder River above UL5 side passage	In-cave stream	252.4
007	Barnett Hollow @ Hwy. A	Surface stream	222.5
008	TS1 - Toronto Springs #1	Spring	214.9
009	TS2 - Toronto Springs #2	Spring	214.9
010	TS3 - Toronto Springs #3	Spring	214.9
011	TS4 - Toronto Springs #4	Spring	214.9
012	TS5 - Toronto Springs #5	Spring	214.9
013	TS6 - Toronto Springs #6	Spring	214.9
014	TS7 - Toronto Springs #7/Reference site	Spring	214.9
015	TS8 - Toronto Springs #8 / Grote Hole Cave	Spring	214.9
016	TS9 - Toronto Springs #9	Spring	214.9
017	TS10 - Toronto Springs #10	Spring	214.9
018	TS11 - Toronto Springs #11	Spring	214.9
019	TS12 - Toronto Springs #12	Spring	214.9
020	Carroll Cave - Natural Entrance	Cave stream resurgence	238.1
021	Mill Creek Spring Cave	Cave stream resurgence	242.3
022	Mill Creek @ Seven Springs Rd.	Surface stream	234.7
023	Wet Glaize Creek @ Carroll Cave Rd.	Surface stream	225.6
024	Davis Hollow @ North Davis Hollow Rd.	Surface stream	243.8
025	Traw Hollow @ Carroll Cave Rd.	Surface stream	242.3
026	TS13 - Toronto Springs #13	Spring	215.8
027	Carroll Cave - DR1 side passage stream	In-cave stream	236.2
028	Carroll Cave - DR4 side passage stream	In-cave stream	231.7
029	Carroll Cave - DL7-L6 side passage stream	In-cave stream	228.6
030	Carroll Cave - DL7 side passage stream upstream of L6	In-cave stream	226.8
031	Carroll Cave - DL8 side passage stream	In-cave stream	211.8
032	Carroll Cave - Bear Claw side passage stream	In-cave stream	242.3
033	Carroll Cave - Turnpike side passage stream	In-cave stream	243.8
034	Carroll Cave - CR10 side passage stream	In-cave stream	242.3
035	Carroll Cave - DL7, Confusion Creek Tributary	In-cave stream	222.5
036	Carroll Cave - DL7, Confusion Creek	In-cave stream	217.9

Datalogger Use

Dataloggers were used to remotely collect various physical and chemical parameters for 11 of the 13 spring outlets at Toronto Springs, as well as in Thunder River inside Carroll Cave and Wet Glaize Creek. YSI 6600 Sonde dataloggers (YSI, Yellow Springs, OH) were placed in the stream flow of each monitoring site and collected pH, specific conductivity, temperature, and turbidity data at 15 minute intervals. Each datalogger was anchored to a stake placed into the sediments of the spring outlet channel in order to safeguard each datalogger and to ensure proper probe orientation. At the time of data collection, after two to three weeks, the probes on each of the dataloggers were calibrated to ensure quality control and accurate values for the measured parameters. Programming and calibration of the YSI 6600 Sonde dataloggers were performed using YSI EcoWatch software. A reference site was established at site TS7 on the south side of Wet Glaize Creek, where a datalogger remained throughout the duration of the experiment. Due to resource constraints dataloggers were not placed at the other 12 monitoring sites simultaneously and thus one to two dataloggers were used in addition to the reference site. The site at TS7 represents the combined flow for approximately six of the identified spring outlets and was used to create a ratio of variance for the other monitored sites. The ratio data from each datalogger monitoring location to the reference site was used to determine if the individual springs possess distinct geochemical and physical properties from one another through use of statistical analysis (see Statistical Analysis below).

Ion Sample Collection & Analysis

Bi-monthly water sampling for ion analysis was initiated in February, 2010 at each of the 11 monitored springs at Toronto Springs, Thunder River in Carroll Cave and Wet Glaize Creek. Ion sample collection consisted of collecting approximately 500 mL of water from each site while minimizing the head space of air in each bottle. After collection of the sample the lid and top of the bottle was wrapped with Parafilm and placed in a cooler for transportation to the laboratory. At the time of collection a YSI Professional Plus Handheld water quality probe took measurements of the pH, temperature, and specific conductivity which were recorded into a field book and transferred to electronic media (YSI, Yellow Spring, OH). The water quality probe was allowed at least five minutes to equilibrate with the surroundings and was calibrated at the beginning of each sampling round, with no more than three hours between instrument calibration and sample collection. For each sampling round a cation and bicarbonate sample was collected from every site, at least one anion sample was also collected per sampling round with the site which was selected randomly before sample collection.

Laboratory analysis of cations and bicarbonate were conducted at the University of Missouri Plant and Soil Diagnostics Lab. Sodium (Na^+) and potassium (K^+) concentrations in water were determined by flame photometry on filtered samples (Whatman #2 filter paper) within 24-48 hours of sample collection (Greenberg et al., 1992a). The instrument was calibrated using the external standard approach, and the method detection limit was 0.1 mg/L for both Na^+ and K^+. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations in water were determined by atomic absorption spectrometry on filtered samples (Whatman #2 filter paper) diluted 20:1 in a 1.11%

La_2O_3 using the direct air-acetylene flame method (Greenberg et al., 1992b). All samples were analyzed within 24-48 hours of collection. Method detection limits were 0.08 mg/L for Ca^{2+} and 0.007 mg/L for Mg^{2+}. Bicarbonate (HCO_3^-) concentration in water was determined by titration using 1% phenolphthalein indicator added to a 250 mL sample which was then titrated with a 0.5N H_2SO_4 until a color change occurred. If the solution turned colorless, from pink, then two drops of 0.5% methyl orange was added to create a yellow color and the sample titrated with 0.5 N H_2SO_4 until the sample became colorless. The amount of titrant is then used to calculate the total carbonate (CO_3^{2-}), if present, and total bicarbonate of the sample. Anions were analyzed by ion chromatography with electrolytic suppression (SM 4110D) on a Dionex DX600 system with detection by conductivity (Dionex Corporation, Sunnyvale, CA). The method used an AS14A-5 µm 3x150 mm column (with guard column) eluted with 8 mM carbonate, 1 mM bicarbonate buffer with a flow rate of 0.5 mL/min. A Dionex Anion Atlas suppressor was used with 28 mA current. Details of the methodology follow the methodology for ion chromatography as described in Standard Methods for the Examination of Water and Wastewater (Eaton et al. 2005).

Seepage Runs

A series of three seepage runs were conducted along Wet Glaize Creek and major tributaries. The seepage run consisted of multiple stream gauging measurements taken along a stretch of streamway within a twenty four hour time span. In the case of Wet Glaize Creek, multiple stream flow measurements were taken upstream of Toronto Springs as well as a site located downstream of all the spring outlets. The gauging measurements were gathered via the use of a measuring tape, pygmymeter, and wading rod. At each location the stream channel width was divided into multiple subchannels, each approximately one meter in width, the depth at the center of each subchannel is recorded and a series of four recordings are taken at 40% of the subchannel depth. These measurements were then translated into discharge values for each subchannel and summed for the discharge of the channel. Once discharge calculations were plotted on a map any portions of the streamway that have a discharge measurement less than the last upstream measurement indicate stream flow loss into the streambed. Any areas where significant flow loss occurred were more closely refined on subsequent seepage runs. All seepage runs were conducted in base flow conditions in order to accurately assess the amount of stream flow loss.

DataCollection

Two to three YSI Sonde dataloggers were deployed to measure water chemistry data every 15 minutes at each of the 13 sites (11 springs, Wet Glaize Creek, and Thunder River in Carroll Cave). One site was chosen as a reference site (TS7) at which the YSI datalogger was continuously deployed while one or two other dataloggers were rotated among sites at 2-4 week intervals (see Methodology for details). The data collected was pH, specific conductivity (SpC, μs/cm), temperature (^{o}C), and turbidity (NTU). The data were then examined for baseflow periods and statistical analyses (see Methodology, Statistical Analysis) were then used to determine if individual springs are significantly different in these basic water quality parameters. Only baseflow conditions were examined as inundation of the springs by Wet Glaize Creek during high flow periods invalidates comparisons among the springs under high flow conditions. Base-flow YSI data were chosen based on four main criteria:

1. The datalogger has equilibrated to the surrounding spring water.
2. No erratic readings exist or acceptable replacement data can be used
3. Specific conductivity, pH, and turbidity readings are stable or are asymptotically approaching equilibrium following a runoff event.
4. After baseflow dates are identified, randomly choosing a 3-day interval.

The data selected represents 288 individual data points (3days x 15 min-intervals = 288 measurements) for each site and were used to create ratios to the reference site at TS7 as well as being used to help create a mixing model and to calculate various statistics. Each site in the study, where possible, had a datalogger period during a cool month (October-March) and a warm month (April-September) to examine possible seasonal variations, however due to time constraints and resource limitations four sites have two warm periods and no cool periods.

Ion analysis from bi-monthly water samples yielded the third type of primary data which were used in the research. These analyses included Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and HCO_3^- at all 13 sites. One site was randomly chosen for each sample set for anion analyses (NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-, F^-) to ensure charge balance occurred (within 10%) for the ion analyses. Coincident with the samples collected for ion analysis, *in situ* measurement of pH, Temperature (^oC), and Specific Conductivity (µs/cm)were conducted. The pH and temperature were used in conjunction with the Ca^{2+}, Mg^{2+}, and HCO_3^- data to compute temperature-dependent saturation indices (relative to dolomite) for each site. These data were also used to calculate the saturations indices for dolomite, and CO_2 partial pressure of each sample.

Statistical Methods

Several different statistical tests were used in the research to determine if differences exist among the springs and to determine if seasonal differences in geochemistry exist within a given spring (Fig. 5). Datalogger data were examined and a dataset of three days worth of data was selected from an individual sampling period. These datasets consisted of 288 individual measurements for a spring in a given season, with warm months designated as April through September and cool months designated as October through March. Due to the sampling periods, datalogger maintenance, and the time span of the research some sites may only have two warm seasons of data and some statistical methods were required to deal with these datasets. Differences for two warm season were examined through the use of Mann-Whitney or U-tests, if sites showed statistically significant differences ($\alpha < 0.05$) the two warm season datasets then the dataset closest to the mid-point of the season was chosen.

Due to resource constraints, it was not possible to monitor all thirteen sites simultaneously. In order to eliminate temporal variations in the hydrologic conditions present at the sites, a ratio was created for data for each individual spring or site 1zto the reference site at TS7. The ratio data allowed for comparisons between sites assuming that the sites were examined only during base flow conditions. Both raw data and ratio data were tested to determine whether the data was normally distributed, which dictated which statistical tests were used to determine seasonal differences by site. Both raw and ratio data values from the datalogger data were not normally distributed and as such non-parametric statistical methods were used for determining seasonal differences and

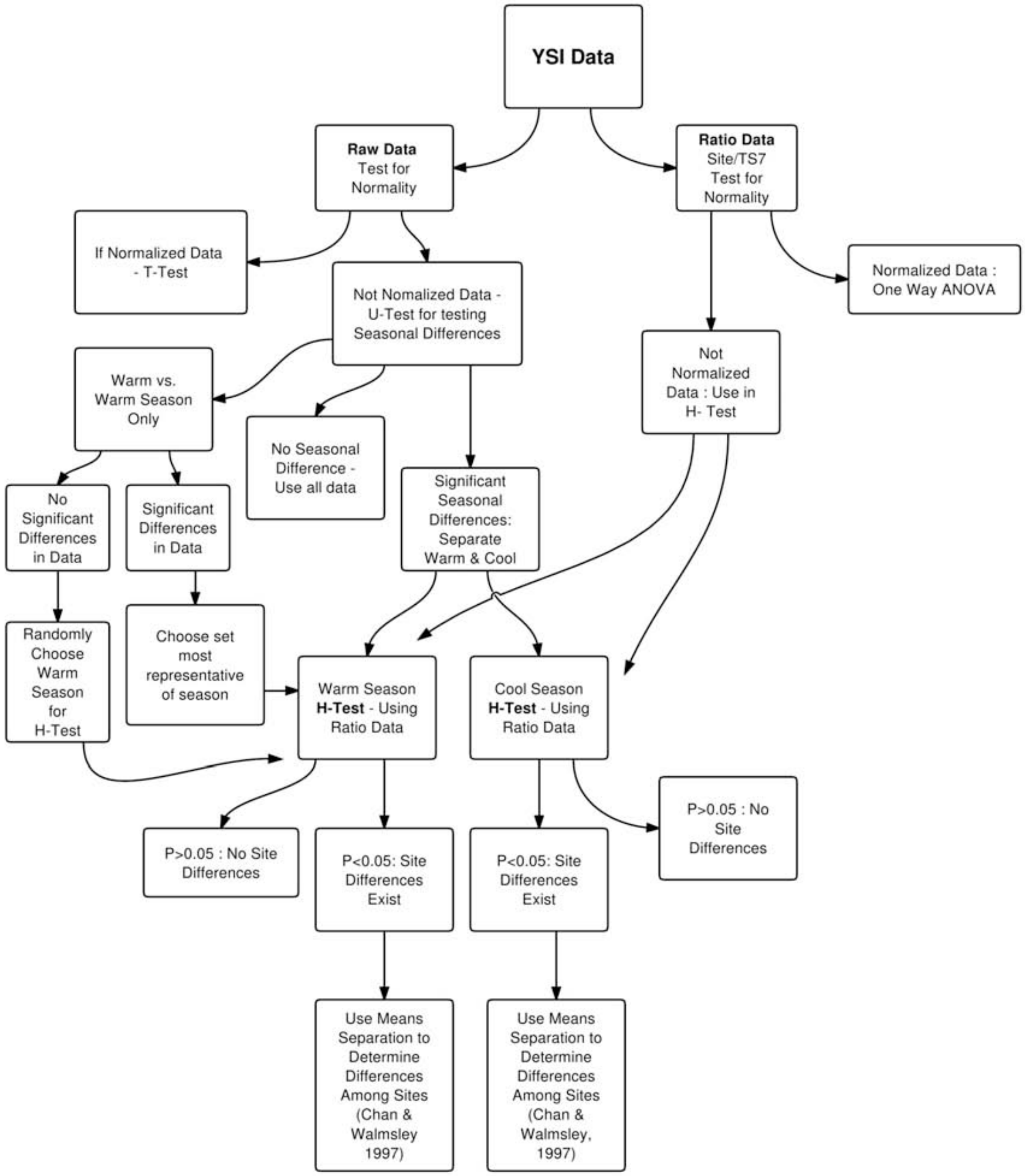


Figure 5: Flow chart of datalogger data statistical analysis methods.

differences between sites. Regardless of the test used to determine seasonal differences, the *a priori* level of significance used was $\alpha = 0.05$

Mann-Whitney or U-tests were used to determine seasonal differences for a site, which compared cool and warm season data for a site. U-test results for pH, temperature, and specific conductivity indicated significant seasonal differences with the majority of P-values being zero. The four sites with only warm season data were also tested using the U-tests and were found to have significant differences between warm season datasets for a single site. Thus the warm season datasets with a time span closest to the center of the sampling period were selected, with the only exception being Spring TS6 which appeared to be recovering from a precipitation event in the mid-season data based on extremely low SpC values.

After the U-tests determined significant seasonal differences for individual site, ratio data for each site by season was used to determine differences between sites for the parameters of pH, SpC, and temperature. The use of ratio data instead of the raw data values allowed for comparisons between sites, assuming base flow conditions, which was necessary since the sampling periods for the monitored sites were not concurrent. Since the time series data had been examined, base flow periods identified and these data retrieved from the overall sampling period this assumption of base flow conditions is valid. The ratio data for all of the sites was tested for normal distribution and, similar to the raw data values, the majority of the ratio data was found to not be normally distributed. Because the ratio data was not normally distributed, the non-parametric Kruskel-Wallis test was used to create a mean rank of the sites for each season by parameter. In order to determine significant differences among sites by mean rank a critical difference was calculated using a method developed by Chan and Walmsley (1999). The critical differences for each season are a function of the number of observations for a site as well as the number of sites used in the test. Therefore critical differences calculated for the cool season were smaller, compared to the warm season critical difference, due to the fact that less overall sites were monitored due to time constraints. Through the use of H-tests differences among sites were able to be examined for water chemistry parameters by season.

Two End Member Mixing Model Analysis

The creation of a two-end member mixing model for Toronto Springs primarily involved the use of the ion data along with the values of temperature, pH, and Specific Conductivity measured during sample collection. The two-end member mixing model assumes that Carroll Cave and Wet Glaize Creek are the primary end-members of the monitored springs at Toronto Springs and that any other recharge sources to the springs are negligible. The average values for ion concentrations, calculated values, and measured *in situ* values for each of the sites are calculated in order to give a mean representation of the data for the mixing model, since the proportions of each member should vary from date to date based on hydrologic conditions within the system. Once the mean values are calculated for each site and for each parameter, then the higher and lower end members can be established and the proportion of each end member to an individual site can be determined using a simple equation (Equation 1).

Equation 1: Equation for creating a two-end member mixing model.

$$P_{iHM} = (S_{ij} - LM_j)/(HM_j - LM_j)$$

Where P_{iHM} = the proportion of the highest valued end member flow contributed to the spring, i; S_{ij} is the ith spring for parameter j, where j = cation or anion value (in mg/L), temperature (^{o}C), and SpC (µS/cm); HM_j is the highest end member value for parameter j; and LM_j is the lowest end member value for parameter j). Note that P_{iHM} is a proportion, not a ratio, with the proportion of flow contributed by the highest end member, the proportion to the lowest end member is the difference between the high end member proportion and one. The proportion then can be converted to percentages to indicate the mean percent of flow contributed by an end member to a particular spring of the 11 monitored springs at Toronto Springs. If a spring has a negative percentage or is over 100% then Carroll Cave or Wet Glaize are not the end members for that particular site.

Chapter 3 : Results

Dye Tracing & Recharge Area Delineation

Dye tracing was initiated in October, 2008 and continued throughout the duration of the research project with the last round of dye injections occurring in late-October, 2010. In all a total of 22 dye injections, in six rounds of traces, took place in the study area in order to both delineate a recharge area for Carroll Cave and to confirm possible hydrologic connections between upstream portions of Wet Glaize and Mill Creek to springs at Toronto Springs. Dye traces are summarized in Table 3, maps showing the results for each round accompany descriptions of the individual rounds (Figs. 6-11), and a map showing all dye injections, monitoring sites, and positive traces shown in Figure 11.

Dye traces in the first round focused on establishing a link between Thunder River and Toronto Springs and between Traw Hollow and Thunder River. As part of the first round of traces two dyes, eosine and Rhodamine WT were injected into the upper reaches of Traw Hollow in an attempt to positively connect Traw Hollow to Thunder River inside Carroll Cave. A trace was also conducted in-cave from Thunder River to Toronto Springs to reproduce the 1965 injection performed by Vineyard (1974) and to establish which of the 13 identified springs might receive recharge from Carroll Cave. Eight of the springs at Toronto Springs were traced from Thunder River, and these springs were termed the "Carroll Suite" because all subsequent traces shown to enter Thunder River would show fluorescence at these same eight springs (Fig. 4). This trace was fundamental to documenting that some springs at Toronto Springs are connected to Carroll Cave while other springs appear to have independent recharge areas. One other interesting characteristic that was identified as a result of the trace is that water from Thunder River passes under Wet Glaize Creek to resurge from as many as four springs on the north side of the stream. Given that the bedrock below the stream valley is all Gasconade Dolomite with no known confining layer, this finding provides support for the existence of distinct conduits that traverse under the stream channel and resurge from the springs on the north side of the Creek. In addition, the injections in upper Traw Hollow were positively traced to Thunder River (Fig. 6). This finding was expected given the

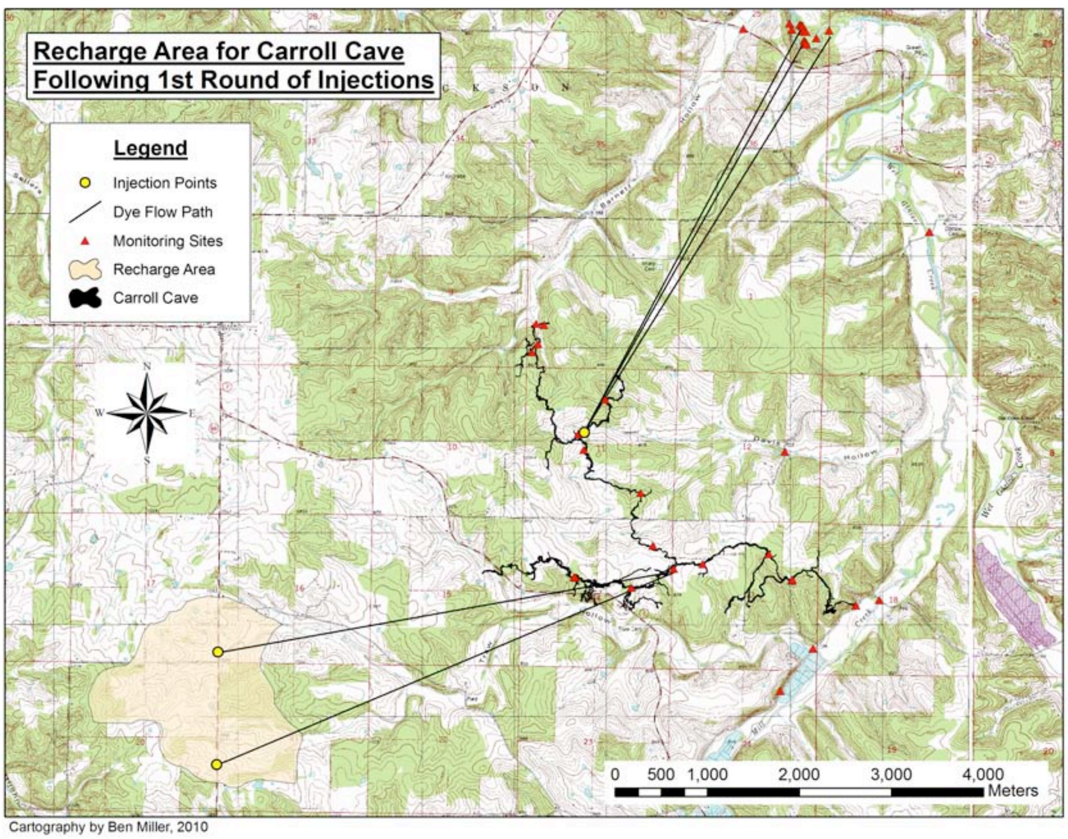
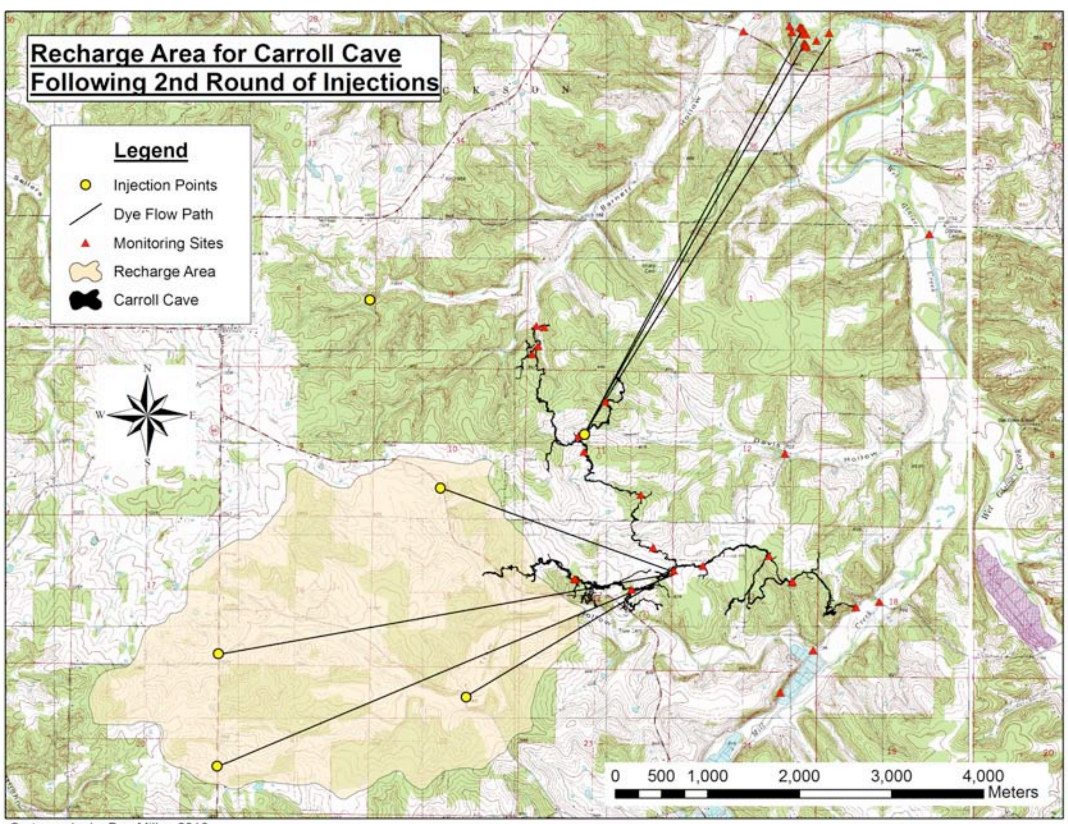


Figure 6: Recharge area map for Carroll Cave, after first round of injections.

close proximity of the Upper Thunder River arm of Carroll Cave to Traw Hollow. However, the travel time of 10 weeks was longer than expected, based on the proximity to the cave, due to an extended dry spell directly after the injection date.

The second round of injections, April 2009, sought to extend the recharge area further downstream in Traw Hollow and began work on delineating the recharge areas of tributaries to Thunder River in Carroll Cave. Specifically dye injections attempted to delineate a recharge area for the main stream of DL7 in Carroll Cave, a large side passage in Lower Thunder River approximately five kilometers in length, with a perennially flowing stream. Injections were made from Traw Hollow Road and along Highway 7 into Traw Hollow as well as in a dry stream channel in the northern arm of Barnett Hollow, a potential source for the DL7 stream due to the proximal location of the hollow to the cave. Each of the injections in Traw Hollow were successfully traced to Thunder River, establishing that Traw Hollow is the largest sub-basin, with an area of 12.9 km^2,



Cartography by Ben Miller, 2010

Figure 7: Recharge area map for Carroll Cave, after second round of injections.

within the Carroll Cave recharge area (Fig. 7). The northern Barnett Hollow injection was not traced to the cave nor was the dye detected at any of the monitored sites within the study area.

The third round of injections in September, 2009 endeavored to connect southern Barnett Hollow to the DL7 side passage stream as well as prove a connection between Mill Creek and Wet Glaize Creek to the springs at Toronto. A dry set, a PVC pipe with powdered dye staked to a streambed, was placed in a large sinkhole on the north-side of the southern arm of Barnett Hollow, the sinkhole is known to cavers and locals as the Whirlpool Sink for the large amounts of water the sink receives following a rain event. The sinkhole represents one of the deepest and most dramatic sinkholes in the Carroll Cave region and had long been speculated to be related to the cave. The dry set utilized fluorescein powdered dye and was staked to the streambed entering the sinkhole. During a storm event less than a month later approximately 100 L/s were observed flowing through the dry set and the dye had definitely been injected in the system. The second dye injection required the use of a fire tanker truck to flush the dye into the upper portions of the south arm of Barnett Hollow.

The third and fourth injections were along Seven Springs Road (Fig.12) into Mill Creek and Wet Glaize Creek. Following the injections a large storm event passed through the area with over 15 centimeters of rain received in the study area. The dye from Mill Creek and Wet Glaize Creek was detected at all of the springs at Toronto Springs, believed to have been caused by the waters from Wet Glaize Creek rising and inundating all the sites creating false positives. The dye from the dry set in the sinkhole was detected in the Carroll Suite of springs at Toronto Springs and dye injected in the south arm of Barnett Hollow was positively traced to the main stream in DL7 side passage (Fig. 8).

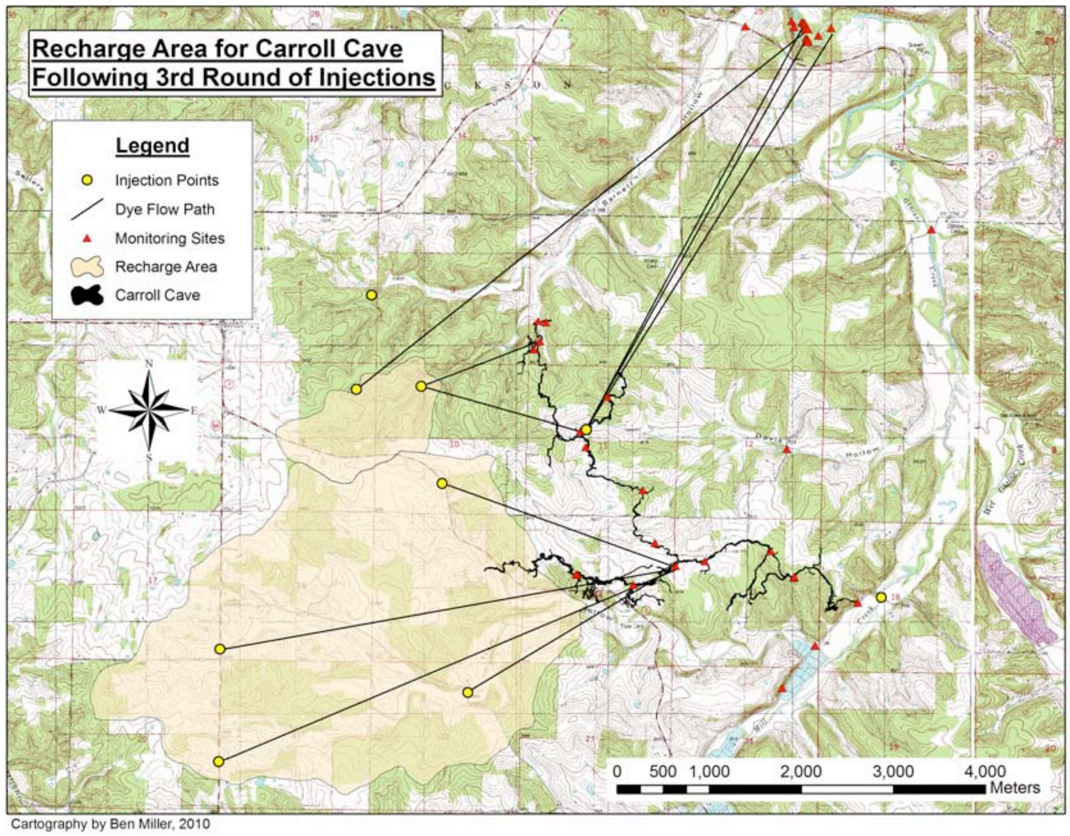


Figure 8: Recharge area map for Carroll Cave, after third round of injections.

The fourth round of injections, January and February 2010, was coordinated with the Missouri Department of Natural Resources Division of Geology and Land Survey (MODGLS). Injections were planned for Garman Hollow, south of Traw Hollow, to potentially extend the recharge area further south as well as an injection in Davis Hollow which overlies portions of Thunder River. The injections planned by MODGLS planned were part of an effort to delineate the boundary between the recharge areas for the Carroll Cave-Toronto Springs system with that of Ha Ha Tonka Spring, the 12th largest spring in

Missouri located 20 kilometers northwest of the study area along Lake of the Ozarks. The MODGLS traces focused on the sinkhole plain south of the town of Montreal and in Pettijohn Hollow, west of Traw Hollow. Because of the closeness of the traces, efforts were coordinated in determining injection times, locations and monitoring sites. Successful traces from the fourth round of injections included a trace from the sinkhole south of Montreal, hereafter referred to as the "Hippie Shack" Sink, to the Carroll Suite of springs at Toronto Springs and a trace from Davis Hollow to Thunder River (Fig. 9). The injection in Pettijohn Hollow was inconclusive as to whether the dye was detected at Ha Ha Tonka and the dye placed in Garman Hollow was not detected at the monitored sites in either study area.

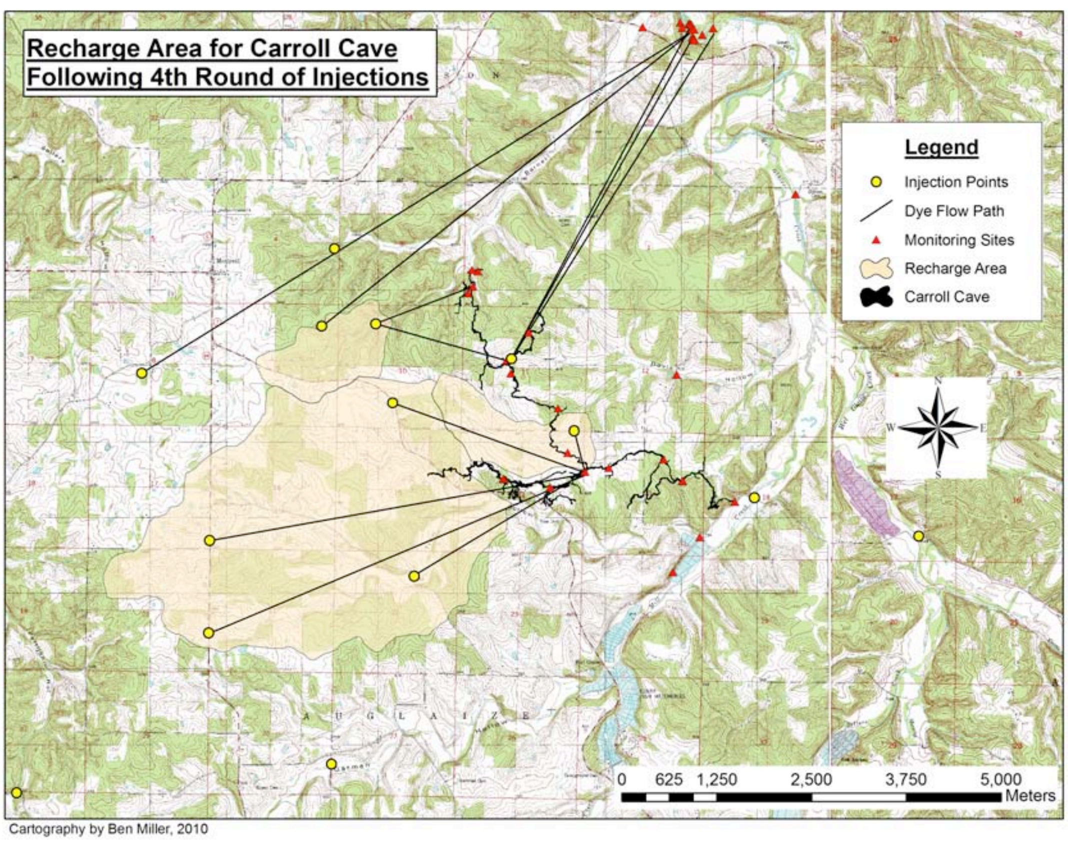


Figure 9: Recharge area map for Carroll Cave, after fourth round of injections.

Prior to the fifth round of traces an important discovery was made in the Carroll Cave system which affected the planning and scope of upcoming dye injections and changed the interpretation of previous traces. In the winter of 2009-10 a new river was discovered in Carroll Cave far upstream in the northern reaches of the DL7 side passage where a drainage divide was crossed in-cave (Fig 3). The new stream, termed Confusion Creek, has an estimated discharge of 100 L/s and was much larger than the main stream of DL7. The stream and its corresponding sump appear to be located between the sump of Thunder River at the Lake Room and Toronto Springs. Prior to an April 2010 dye injection performed in Confusion Creek, a charcoal packet was placed in the stream of Confusion Creek for a period of six hours in order to gather background fluorescence. The following analysis of the charcoal receptors showed Confusion Creek to have high levels of fluorescein, indicating a positive trace from the MODGLS injection into the "Hippie Shack" Sink, south of Montreal, that previously was traced to the Carroll Suite at Toronto Springs. A dye trace was also performed from Confusion Creek in April 2010 to establish a connection to Toronto Springs. Based on a positive trace to the Carroll Suite of springs, it is now believed that Confusion Creek is likely a tributary to the phreatic conduit which drains to Toronto Springs from the Thunder River sump in Carroll Cave. Dye injections conducted one month later focused on delineating a recharge area for the newly discovered Confusion Creek. Dye injections occurred in the central arm of Davis Hollow, further downstream in the northern and southern arm of Barnett Hollow and a re-trace was conducted from the Whirlpool Sink. Results of the traces for the fifth round confirmed the connection of the Whirlpool Sinkhole to Confusion Creek in Carroll Cave. A connection between the lower portion of the southern arm of Barnett Hollow to the main DL7stream was also confirmed (Fig. 10). The dye injected into Davis Hollow was not detected in-cave, as the injection location may have been in a gaining reach of the streamway. However the injected dye was detected in the Carroll Suite at Toronto Springs. A plausible explanation for this finding is that the dye remained in the surface stream channels and was transported to Mill Creek and then Wet Glaize Creek. An area just below the confluence to Mill and Wet Glaize Creeks, at the edge of the Montreal Fault Block, has been shown to lose flow along this reach (see Seepage Runs below). Thus, the dye injected in Davis Hollow is believed to have flowed to the Carroll Suite of springs via this losing reach of Wet Glaize Creek. Although somewhat speculative, this trace appears to confirm the hypothesis that Wet Glaize Creek is also a recharge source to Toronto Springs.

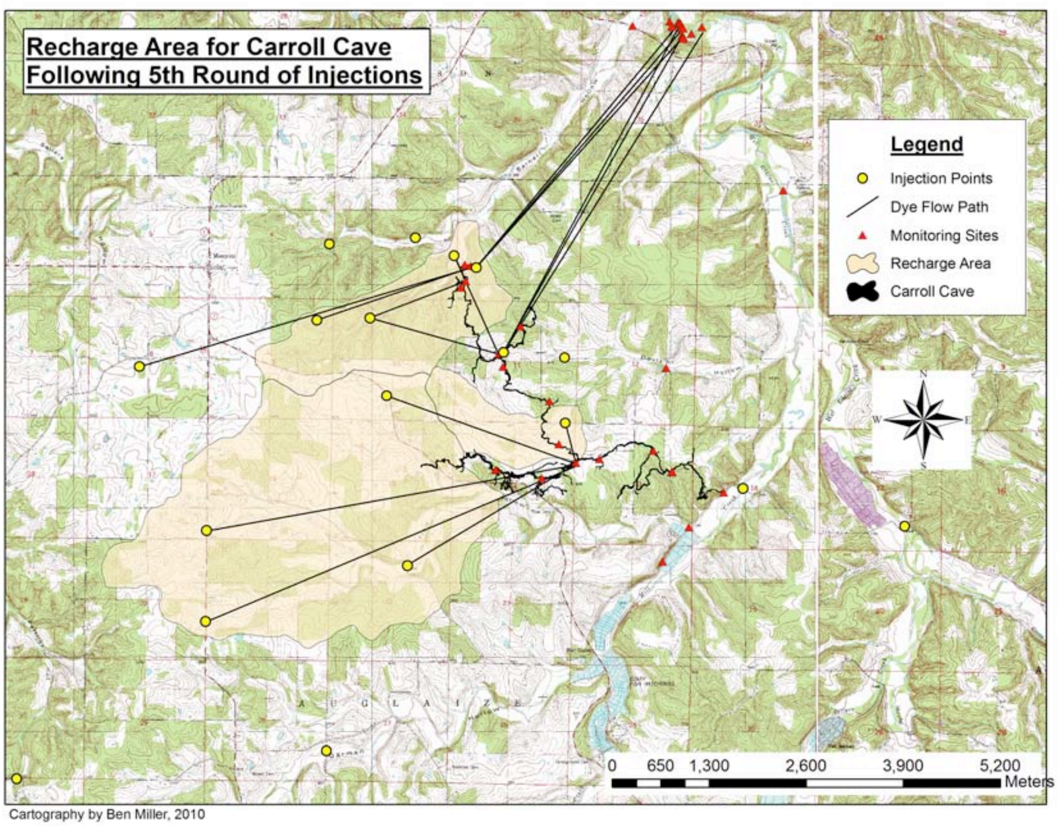


Figure 10: Recharge area map for Carroll Cave, after fifth round of injections.

The sixth round of injections involved two injections and was intended to definitively confirm the connection between Mill Creek, Wet Glaize Creek and Toronto Springs. Recall that the previous injections into Mill Creek and Wet Glaize Creek were deemed unusable due to inundation of the springs from a runoff event following the dye injection. Fluorescein dye was injected in Wet Glaize Creek at Seven Springs Road and sulphorhodamine B was injected into Mill Creek, also at Seven Springs Road. Packets changed three days later at Toronto Springs had positive detections of fluorescein, however the sulphorhodamine B injected into Mill Creek was never detected at any sites in Toronto Springs. The first set of charcoal packets, changed three after the injections, had fluorescein detections for sites TS1, TS2, TS4, TS5, TS6, TS7, TS10, and TS11. One week later springs TS12 and TS13 had detectable levels of fluorescein, but the springs which had fluoresced the previous week had returned to near background fluorescence levels. Spring TS3 and TS8 were the only two springs at Toronto Springs which showed no signs of a positive trace from Wet Glaize Creek. While the dye trace does not expand the recharge area of Carroll Cave, it does provide crucial evidence of the connection between the upper reaches of Wet Glaize Creek and the springs at Toronto Springs (Fig. 11).

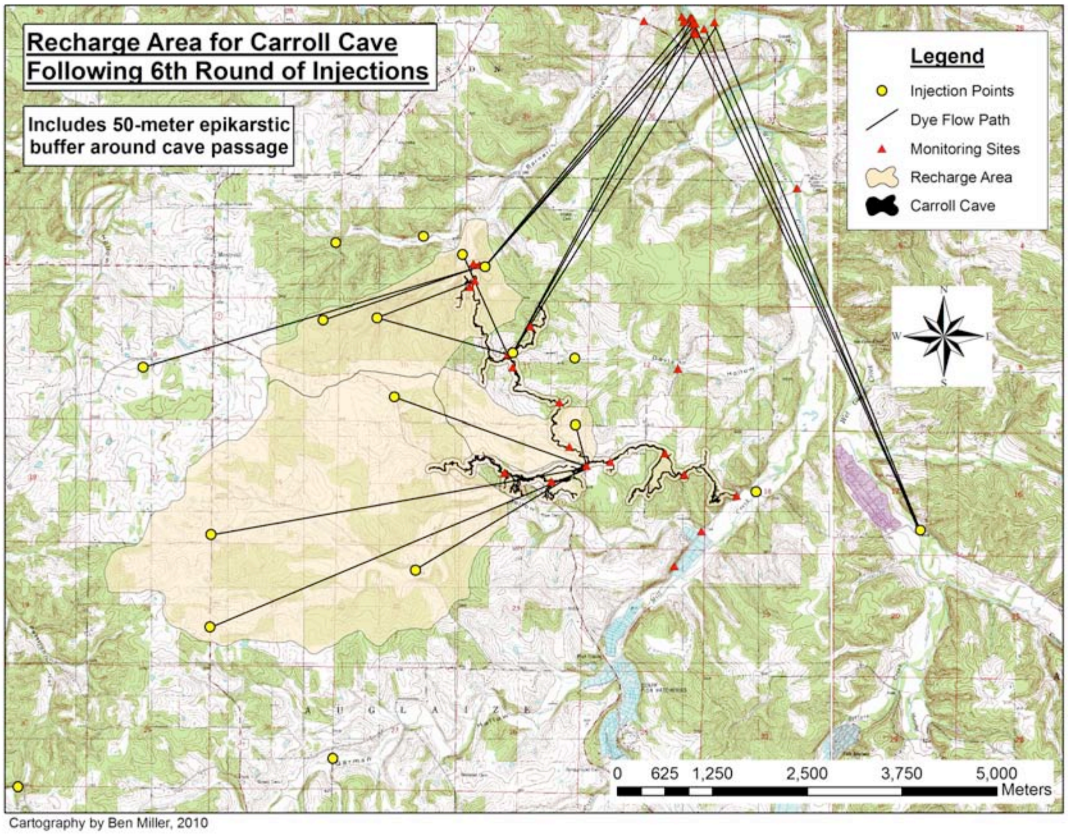


Figure 21: Dye tracing map for the Carroll Cave area, after sixth round of injections.

Table 3: Table of dye injections and positive traces.

Round #: Injection #	Date	Location Description	UTM-NAD 83 Easting/Northing	Elev. (m)	Dye Injected	Dye Amt.	Injection Method	Positively Traced To
1:1	10/2/2008	Carroll Cave - Thunder River just below DL7	E: 539751 N: 4201297	228.6	Fluorescein	1.8 kg (4 lbs)	Poured directly into flowing stream	Toronto Springs - Carroll Suite *
1:2	10/3/2008	Traw Hollow - north arm, south of Traw Hollow Rd. off Hwy BB	E: 535772 N: 4198913	310.9	Sulphorhodamine B	2.27 kg (5lbs)	Tanker Truck, 2000 gal.	Carroll Cave - Thunder River
1:3	10/3/2008	Traw Hollow - south arm, off Hwy BB	E: 535754 N: 4197887	316.9	Eosine	2.27 kg (5lbs)	Tanker Truck, 2000 gal.	Carroll Cave - Thunder River
2:1	4/19/2009	Traw Hollow - at Traw Hollow Rd.	E: 538459 N: 4198437	280.4	Rhodamine WT	1.36 kg (3 lbs)	Tanker Truck, 2000 gal.	Carroll Cave - Thunder River
2:2	4/19/2009	Side arm to Traw Hollow - off Hwy 7	E: 538185 N: 4200730	298.7	Fluorescein	0.91 kg (2 lbs)	Poured directly into flowing stream	Carroll Cave - Thunder River
2:3	4/19/2009	Barnett Hollow - north arm	E: 537407 N: 4202731	277.4	Tinopal	1.8 kg (4 lbs)	Poured directly into pool	Not detected at monitored sites
3:1	9/19/2009	Whirlpool Sinkhole - south arm of Barnett Hollow	E: 537245 N: 4201724	280.4	Fluorescein	1.36 kg (3 lbs)	Dry Set	Toronto Springs - Carroll Suite *
3:2	9/19/2009	Barnett Hollow - south arm at Bikkor Road	E: 537921 N: 4201770	280.4	Rhodamine WT	1.36 kg (3 lbs)	Tanker Truck, 2000 gal.	Carroll Cave - DL7 main stream
3:3	9/19/2009	Mill Creek - at Seven Springs Rd.	E: 542961 N: 4199473	260.6	Sulphorhodamine B	1.8 kg (4 lbs)	Poured directly into flowing stream	Detected at all Toronto Springs
3:4	9/19/2009	Wet Glaize Creek - at Seven Springs Road	E: 545091 N: 4198929	234.7	Eosine	2.04 kg (4.5 lbs)	Poured directly into flowing stream	Detected at all Toronto Springs
4:1	1/31/2010	Garman Hollow - at Brown Way Rd.	E: 537377 N: 4195953	283.5	Sulphorhodamine B	1.8 kg (4 lbs)	Poured into stream sediments	Not detected at monitored sites

Table 3: Table of dye injections and positive traces. (cont'd)

4:2	1/31/2010	Davis Hollow – at Mill Creek Rd.	E: 540585 N: 4200343	262.1	Eosine	2.27 kg (5lbs)	Poured directly into flowing stream	Carroll Cave – Thunder River
4:3	2/16/2010	Pettijohn Hollow – at High Point Rd.	E: 533229 N: 4195604	322.2	Rhodamine WT	2.27 kg (5lbs)	Dry Set	Not detected, poss. Haha Tonka Spring
4:4	2/16/2010	"Hippie Shack" Sinkhole – south of Montreal	E: 534892 N: 4201042	313.9	Fluorescein & Tinopal	2.27 kg (5 lbs) FL, 15 lbs OB	Poured directly into flowing stream	Carroll Cave – Confusion Creek
5:1	4/28/2010	Carroll Cave – Confusion Creek in DL7 Side Passage	E: 539335 N: 4202312	216.4	Tinopal	1.36 kg (3 lbs)	Poured directly into flowing stream	Toronto Springs – Carroll Suite *
5:2	5/31/2010	Davis Hollow – central branch	E: 540554 N: 4201225	253.0	Fluorescein	1.36 kg (3 lbs)	Poured directly into flowing stream	Davis Hollow, TS
5:3	5/31/2010	Whirlpool Sinkhole – south arm of Barnett Hollow	E: 537245 N: 4201724	280.4	Eosine	1.36 kg (3 lbs)	Dry Set	Carroll Cave – Confusion Creek
5:4	5/31/2010	Barnett Hollow – north arm near Barnett Hollow Cave	E: 538661 N: 4202834	259.1	Sulphorhodamine B	1.36 kg (3 lbs)	Dry Set	Not detected at monitored sites
5:5	5/31/2010	Barnett Hollow – south arm at end of Thiess Property	E: 539107 N: 4202600	256.0	Rodamine WT	1.8 kg (4 lbs)	Dry Set	Carroll Cave – DL7 main stream
6:1	10/26/2010	Wet Glaize Creek – at Seven Springs Road	E: 545091 N: 4198929	234.7	Fluorescein	1.36 kg (3 lbs)	Poured directly into flowing stream	TS1, TS2, TS4, TS5,TS6, TS7, TS10,TS11,TS12, TS13
6:2	10/26/2010	Mill Creek – at Seven Springs Road	E: 542961 N: 4199473	260.6	Rhodamine WT	1.36 kg (3 lbs)	Poured directly into flowing stream	Not detected at monitored sites

* Note: Carroll Suite of springs at Toronto Springs is TS1, TS4, TS5, TS6, TS9, TS10, TS11, TS12, & TS13. However after March 2010 TS9 was not able to be monitored

Seepage Runs

A series of three different seepage runs were conducted along portions of Wet Glaize Creek, major tributaries, and other sources contributing flow to Toronto Springs. The seepage runs were conducted in December 2009, September 2010, and October 2010 in order to observe different flow conditions at the sites. In all cases no significant precipitation events occurred immediately prior to or during the seepage run, which is crucial to capturing base flow conditions and losing reaches along the stream way. The results from the seepage runs and other discharge measurements are summarized in Tables 4-7, with the upper-most measurements listed at the top of the table, proceeding downstream as one moves down in the table. Seepage runs maps are presented in Figures 12-15.

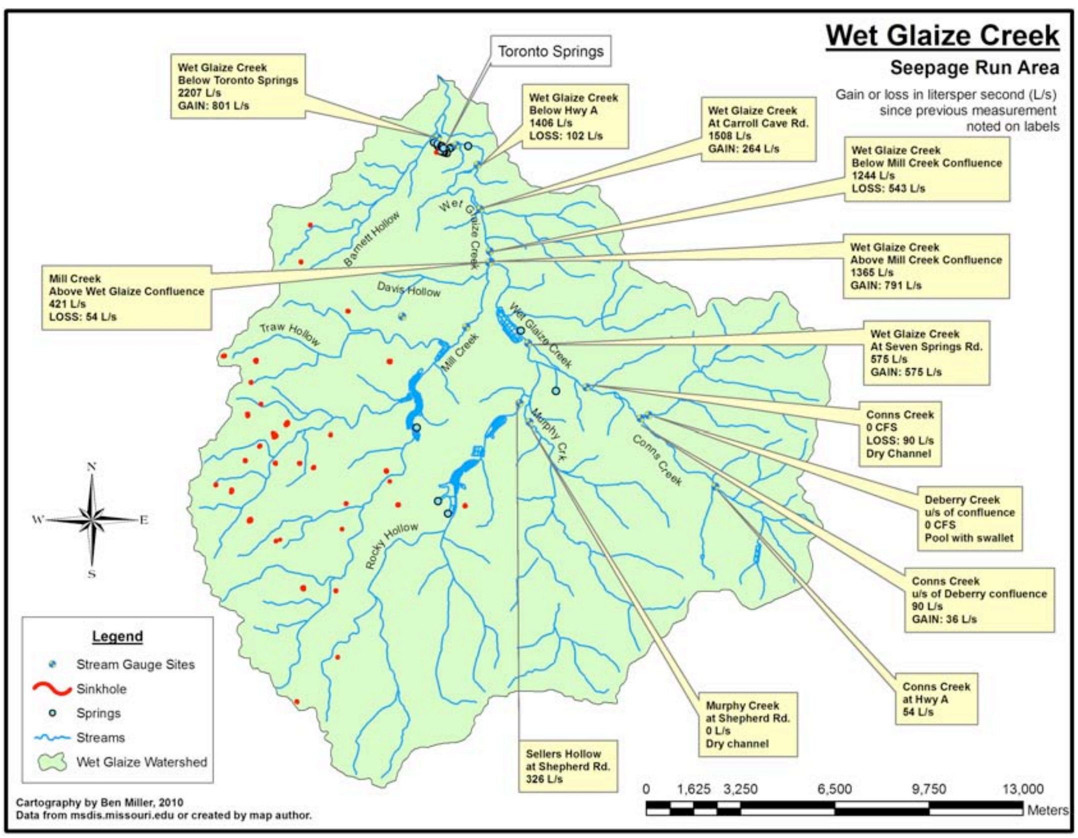


Figure 32: Wet Glaize watershed with December 2009 stream gauging locations & measurements.

The December 2010 seepage run examined the overall hydrologic conditions present within the Wet Glaize watershed and examined not only Wet Glaize Creek but each of the main tributaries to the stream. Measurement locations in the watershed included Conn's Creek, Deberry Creek, Garman Hollow, Murphy Creek, Sellers Hollow, and Mill Creek (see Fig. 12). Above Seven Springs Road Wet Glaize Creek is divided into three major streams; Conn's Creek, Murphy Creek, and Sellers Hollow; though the largest valley of the three streams is Conn's Creek and as such this stream was chosen as the focus of the upper portion of the seepage run. Upper Conns Creek below Deberry Creek loses entirely, losing approximately 91 L/s to the sub-surface flow system. This behavior has been noted by previous researchers and this portion of the stream has been successfully dye traced to Blue Hole Spring, a third magnitude spring approximately 0.5 km downstream of Seven Springs Road (Dean et al., 1969). The upper tributaries to Wet Glaize Creek, above Seven Springs Road, primarily consist of completely losing streams and during the seepage run Deberrry Creek and Murphy Creek were completely dry. A major losing portion of Wet Glaize Creek was identified directly below the confluence of Mill Creek and Wet Glaize Creek, where an estimated 541 L/s were lost within a 0.4 km stream reach (Fig. 13 and Table 4). A second losing reach was identified on Wet Glaize Creek between Carroll Cave Road and Highway A where 102 L/s were lost to seepage. In total 699 L/s were lost in Wet Glaize Creek between Seven Springs Road and Toronto Springs. A measurement below Toronto Springs found a gain of 801 L/s contributed to the flow of Wet Glaize. The difference of 102 L/s between the flow lost in Wet Glaize Creek above Toronto Springs and the flow gained below the springs is the contributions from streams within Carroll Cave. The flow in Thunder River has only been measured a handful of times, but the 102 L/s unaccounted for in the gain could easily be a reasonable estimate for Thunder River. Confusion Creek, within the DL7 side passage also has been dye traced to Toronto Springs however has never been gauged, due to the inaccessible

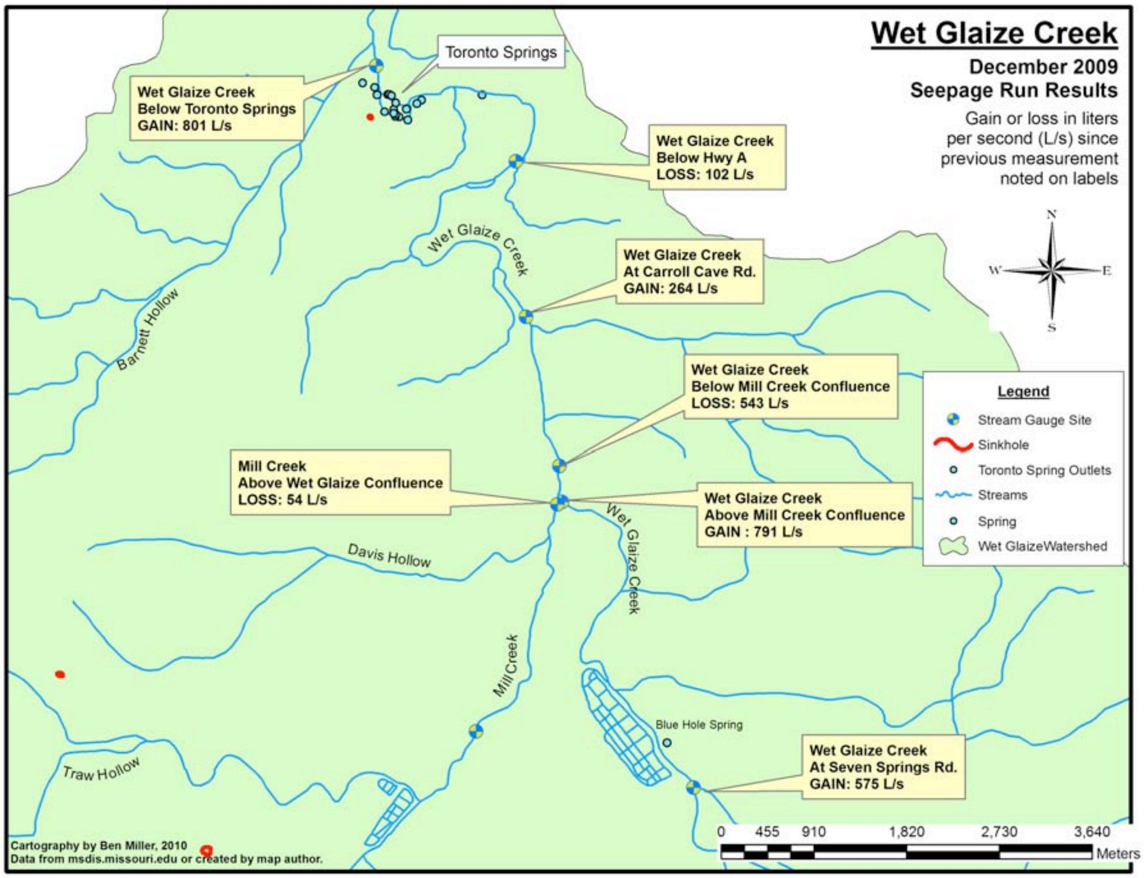


Figure 13: Seepage run map from December 2009, showing gain or loss of streamflow.

and extremely remote nature of the stream. Conducting additional seepage runs from Seven Springs Road down to Toronto Springs and including the cave streams would attempt to further document and explain these phenomena.

Table 4: December 2009 seepage run data.

Location	Flow (L/s)	Gain (L/s)	Loss (L/s)
Mill Creek @ Seven Spring Rd.	475.44	-	-
Mill Creek above confluence	421.35	-	54.09
Wet Glaize Creek @ 7 Springs Rd.	574.83	-	-
Wet Glaize Creek above confluence	1365.44	790.61	-
Wet Glaize Creek below confluence near Monitoring Site	1243.96	-	542.83
Wet Glaize Creek below Carroll Cave Rd.	1507.59	263.63	-
Wet Glaize Creek below Hwy A	1405.93	-	101.66
Wet Glaize Creek below Toronto Springs	2207.30	801.37	-
Net Loss			698.58

The second seepage run along Wet Glaize Creek occurred in mid-September, 2010.Weather conditions had been stable for several days previous and no precipitation was forecast for the day of the seepage run, so base flow conditions were expected in Wet Glaize Creek. The second seepage run began at Seven Springs Road and proceeded downstream to Toronto Springs. Previously measured locations upstream of Seven Springs Road were eliminated in order to conduct additional measurements along the losing reach near the confluence of Mill Creek and Wet Glaize Creek (Fig. 14). The measurements of Mill Creek and Wet Glaize Creek immediately upstream of the confluence had a combined flow of 566 L/s less than the previous seepage run had documented. However in the losing stretch below the confluence , where previously 538 L/s had been lost, only 255 L/s were lost to seepage in the streambed. The other documented losing reach between Carroll Cave Road and Highway A, showed a loss of 376 L/s, an increase in flow loss of nearly 283 L/s from the previous seepage run. The total loss for Wet Glaize Creek above Toronto Springs for the second seepage run was 645 L/s and the gain below Toronto Springs was 1150 L/s. Though the total stream loss was nearly the same in the second seepage run as compared to the first, however the locations of the primary stream flow loss changed. The primary losing reach of Wet Glaize Creek in the second seepage run was between Carroll Cave Road and Highway A. This site is located 5.5 km further downstream from the losing reach previously identified near the confluence of Mill Creek and Wet Glaize Creek.

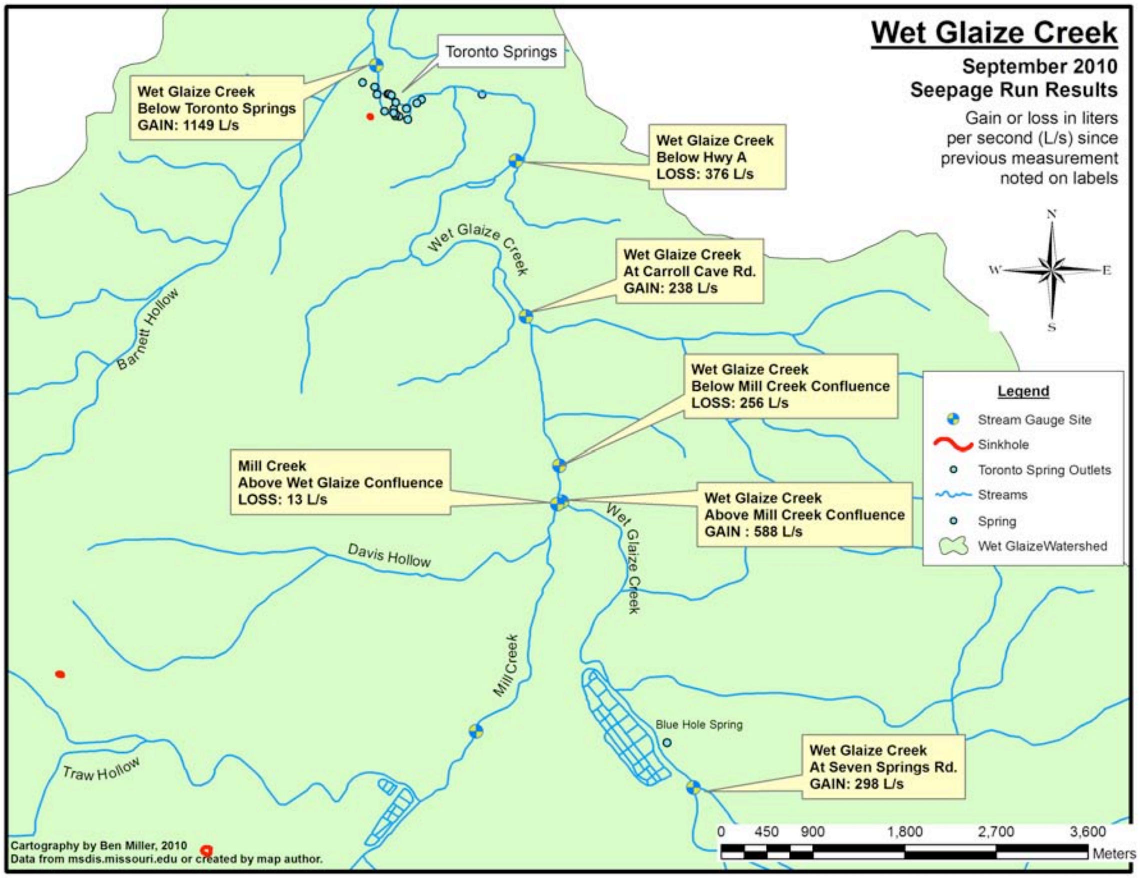


Figure 14: Seepage run map from September 2010, showing gain or loss of stream flow.

Table 5: September 2010 seepage run data.

Location	Flow (L/s)	Gain (L/s)	Loss (L/s)
Mill Creek @ 7 Springs Rd.	356.30	-	-
Mill Creek above confluence	342.98	-	13.32
Wet Glaize Creek @ 7 Springs Rd.	298.45	-	-
Wet Glaize Creek above confluence	886.22	587.78	-
Wet Glaize Creek below confluence	973.08	-	256.12
Wet Glaize Creek nearest to Monitoring Site	1296.02	322.94	-
Wet Glaize Creek below Carroll Cave Rd.	1534.21	238.19	-
Wet Glaize Creek below Hwy A	1158.44	-	375.77
Wet Glaize Creek below Toronto Springs	2307.13	1148.69	-
Net Loss			645.21

A third seepage run was conducted along Wet Glaize Creek between Seven Springs Road and below Toronto Springs in October 2010 following a two-week time interval with no precipitation, one of the longest periods of no rain during the study. Since conditions were near optimal base flow, the third seepage run sought to further refine the seepage behavior and examine the variations in the location of primary losing reaches observed in the previous two seepage runs. As in the second seepage run, the third round of measurement locations would focus on the stream reach from Seven Springs Road to below Toronto Springs, with additional measurements just above Toronto Springs, at selected springs, and in Thunder River within Carroll Cave. The flow in Wet Glaize above the confluence with Mill Creek was the lowest study with a flow of 357 L/s. Loss in the losing reach below the confluence was minimal and nearly within the accuracy of the wading rod setup, with a loss of only 6 L/s. An additional 37 L/s were lost between Carroll Cave Road and Highway A, though a total of only 52 L/s were lost in Wet Glaize Creek above Toronto Springs. A previously

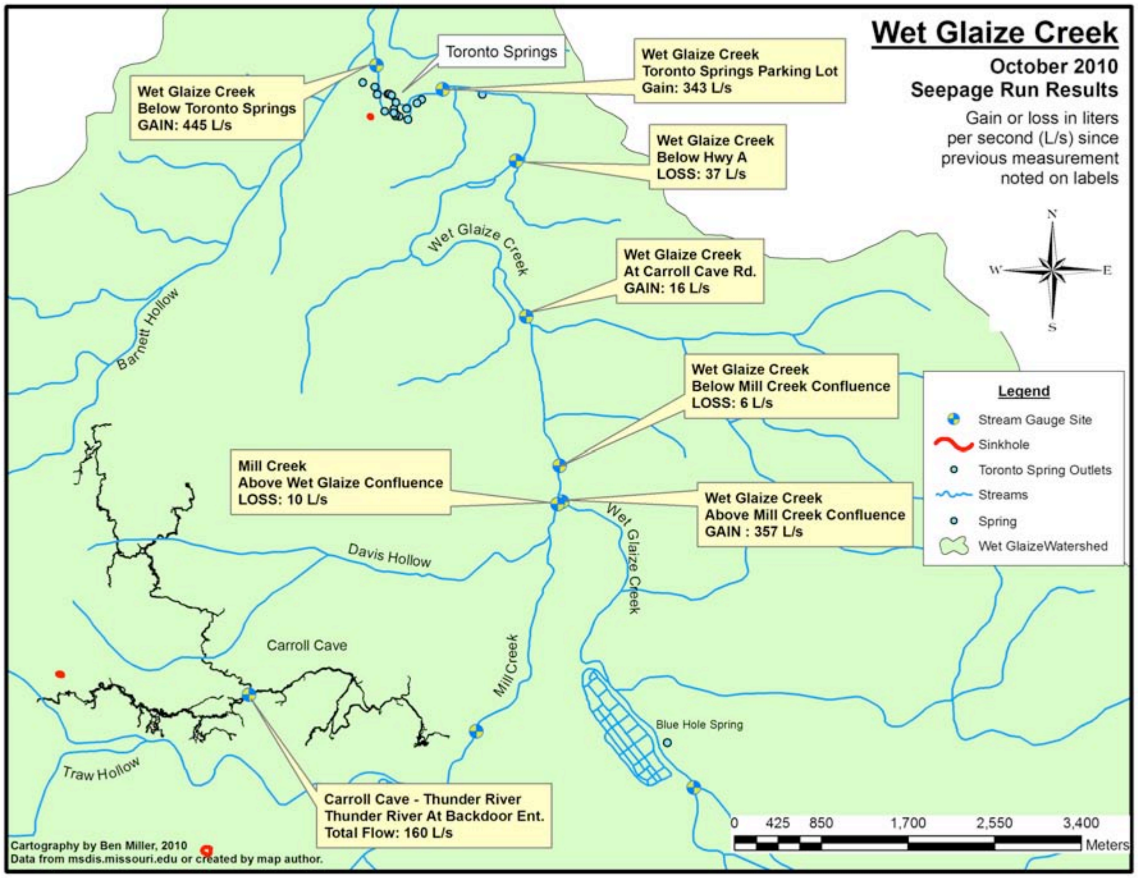


Figure 15: Seepage run map from October 2010, showing gain or loss of stream flow.

undocumented gaining reach was found between Highway A and directly above Toronto Springs, where 343 L/s were gained, likely through springs located in the streambed as no visible outlets have been documented. Thunder River within Carroll Cave was gauged at 159 L/s (Table 7), however if one considers the flow from side passages downstream of the gauging site then the contribution from Carroll Cave to Toronto Springs could be as much as 250-300 L/s. The gain from Toronto Springs was measured at 445 L/s, much greater than the total loss in Wet Glaize Creek above the springs.

Table 6: October 2010 seepage run data.

Location	Flow (L/s)	Gain (L/s)	Loss (L/s)
Mill Creek @ 7 Springs Rd.	231.35	-	-
Mill Creek above confluence	221.44	-	9.91
Wet Glaize Creek @ 7 Springs Rd.	-	-	-
Wet Glaize Creek above confluence	357.36	-	-
Wet Glaize Creek below confluence	573.13	-	5.66
Wet Glaize Creek nearest to Monitoring Site	598.34	25.20	-
Wet Glaize Creek below Carroll Cave Rd.	614.76	16.42	-
Wet Glaize Creek below Hwy A	577.95	-	36.81
Wet Glaize Creek immediately above T.S.	921.43	343.48	
Wet Glaize Creek below Toronto Springs	1366.00	444.57	-
Net Loss			645.21

Table 7: Various spring and cave stream measurements.

Location	Flow (L/s)
TS1 Spring	22.65
Toronto Springs -south side at TS7 site	117.80
TS13 - 9/31/2010	85.52
TS13 - 10/7/2010	81.84
Thunder River - 10/7/2010	159.71

Geochemistry and Statistical Analysis

Datalogger Data

A total of 25 datalogger datasets were collected during the sampling period from April 2009 through September 2010. With each of the 25 datasets a corresponding dataset exists for the reference station at site TS7. Each of the time-series graphs for each spring and each sampling period are in Appendix A. The end members, Carroll Cave and Wet Glaize Creek, along with 11 spring sites, were monitored via dataloggers at least twice throughout the duration of the sampling period. The data retrieved from the sampling period were processed via the steps outlined in methodology and base flow conditions were identified in the data, extracted, and used for the statistical analysis. Base flow datasets chosen for each sampling period are outlined in Table 8.

The selected data were analyzed for normality and the majority of the data was found to be non-normalized data. In addition log transforms did not result in normally distributed data. Thus, as per the flow chart outlined in Figure 5, non-parametric statistical methods of U-Tests and H-Tests were used to analyze seasonal and site differences in the water chemistry parameters measured by the YSI dataloggers.

Mann-Whitney tests (U-tests) were employed to determine any seasonal differences by site. The geochemistry of karst waters is affected by the dissolutional processes occurring in a hydrologic system, and often these processes are greatly affected by seasonal influences on temperature, CO_2 concentration, and precipitation. Because of these seasonal variations it was necessary to determine whether statistically significant differences were present between warm and cool season data for a site. Seasonal differences between cool and warm season data were determined for the eight sites which

Table 8: Base flow periods for datalogger sampling regimes, including dates chosen for analysis. Orange cells indicate warm season sampling periods and blue cells indicate cool season periods.

Site	Start Date/Time	End Date/Time	Total Days	3 day intervals	Interval Chosen	Dates Selected
TS1	4/22/2009 7:31	4/28/2009 7:31	6.00	4.00	2	4/23/2009 7:31 - 4/26/2009 7:31
TS2	5/4/2009 16:46	5/8/2009 5:46	3.54	1.54	1	5/4/2009 16:46 - 5/7/2009 16:46
TS4	5/23/2009 7:31	6/9/2009 17:16	17.41	15.41	11	6/3/2009 7:31 - 6/6/2009 7:31
TS5	7/7/2009 11:46	7/11/2009 15:46	4.17	2.17	2	7/8/2009 11:46 - 7/11/2009 11:46
TS6	7/17/2009 23:01	8/10/2009 4:31	23.23	21.23	19	8/5/2009 23:01 - 8/8/2009 23:01
TS8	10/16/2009 20:01	10/23/2009 0:01	6.17	4.17	2	10/18/2009 20:01 - 10/21/2009 20:01
TS10	11/7/2009 15:16	11/11/2009 3:31	3.51	1.51	1	11/7/2009 15:16 - 11/10/2009 15:16
TS11	11/21/2009 19:00	11/30/2009 19:00	9.00	7.00	2	11/23/2009 19:00 - 11/26/2009 19:00
TS12	12/21/2009 22:45	12/24/2009 22:45	3.00	1.00	1	12/21/2009 22:45 - 12/24/2009 22:45
TS13	1/14/2010 9:46	1/22/2010 19:45	8.42	6.42	4	1/18/2010 9:15 - 1/21/2010 9:15
WG1	3/11/2010 7:45	3/21/2010 23:45	10.67	8.67	5	3/16/2010 7:45 - 3/19/2010 7:45
CC1	3/3/2010 13:45	3/9/2010 0:30	5.45	3.45	1	3/3/2010 13:45 - 3/6/2010 13:45
TS1	1/14/2010 9:46	1/22/2010 19:45	8.42	6.42	4	1/18/2010 9:15 - 1/21/2010 9:15
TS2	4/15/2010 9:15	4/20/2010 0:30	4.64	2.64	2	4/16/2010 9:15:00 - 4/19/2010 9:15
TS4	4/15/2010 9:15	4/20/2010 0:30	4.64	2.64	2	4/16/2010 9:15:00 - 4/19/2010 9:15
TS5-2	6/18/2010 22:16	6/23/2010 4:45	4.27	2.27	2	6/19/2010 22:16 - 6/22/2010 22:16
TS6-2	5/6/2010 0:16	5/12/2010 0:16	6.00	4.00	3	5/9/2010 0:16 - 5/12/2010 0:16
TS8-2	7/16/2010 22:16	7/21/2010 5:30	4.30	2.30	1	7/16/2010 22:16 - 7/19/2010 22:16
TS10-2	5/6/2010 0:16	5/12/2010 0:16	6.00	4.00	3	5/9/2010 0:16 - 5/12/2010 0:16
TS11-2	6/18/2010 22:16	6/23/2010 4:45	4.27	2.27	2	6/19/2010 22:16 - 6/22/2010 22:16
TS12-2	7/16/2010 22:16	7/21/2010 5:30	4.30	2.30	1	7/16/2010 22:16 - 7/19/2010 22:16
TS13-2	8/15/2010 19:46	8/20/2010 13:31	4.74	2.74	2	8/16/2010 19:46 - 8/19/2010 19:46
WG1-2	9/20/2010 1:15	9/28/2010 14:30	8.55	6.55	3	9/23/2010 01:15 - 9/26/2010 01:15
CC1-2	9/8/2010 11:31	9/15/2010 13:46	7.09	5.09	4	9/11/2010 11:31 - 9/14/2010 11:31

had sampling periods in both seasons. Three sites had no cool season data and thus the U-tests were used to determine whether significant differences existed between two warm season datasets. The U-tests for the parameters of temperature, pH, and SpC for all of the sites in every case yielded significant seasonal differences with P-values less than 0.05. Because of the significant seasonal differences for sites, cool and warm weather data were separated and analyzed separately. One exception was made in splitting the seasonal datasets with regards specifically to site TS2. The data for the site exhibited unseasonably cool season characteristics for any of the springs even though the sampling period was technically in the warm season. Because of the uncharacteristically low temperatures for the TS2 datalogger measurements it was ultimately decided to include the TS2 data in the cool season data analysis.

Tables displaying the H-test results are found in Tables 11-13. Letter designations, found within the tables and above column s in the accompanying graphs, are used to show which sites are statistically significantly different from one another. Sites which have different letters are statistically significantly different from one another.

H-tests for temperature were calculated for both cool and warm season datasets and critical differences calculated for each season. Warm season temperature produced six different groupings of the eleven sites, with a maximum of three sites in one groups, and cool season temperature had four groupings of nine sites, with a maximum of four sites in one group (Table 9, Fig. 16). In the warm season, spring TS8 and Carroll Cave (CC1) had the lowest mean rank, indicating that the sites had on average the lowest temperature in the warm season. Wet Glaize Creek had the highest mean rank for temperature in the warm season. In the cool season dataset, Wet Glaize Creek had the lowest overall temperature and was grouped along with spring TS2 (Fig. 17). Carroll Cave and three springs within the "Carroll Suite"; TS12, TS1 and TS13; had the highest mean ranks and were grouped together showing a similarity with respect to cool season temperature.

Table 9: H-test results for temperature, sites with the same letter designations are not significantly different from one another.

Warm Season Temperature	Site	Mean Rank	Letter Desig.	Cool Season Temperature	Site	Mean Rank	Letter Desig.
	TS8	755	A		WG1	194	A
	CC1	786	A		TS2	384	A
	TS12	879	A		TS8	895	B
	TS11	1223	B		TS10	933	B
	TS13	1277	B		TS11	1655	C
	TS5	1327	B		TS12	1846	C, D
	TS1	1650	C		CC1	1856	D
	TS4	1928	D		TS1	1929	D
	TS10	2280	E		TS13	2014	D
	TS6	2346	E	Critical Difference : 199.7			
	WG1	3035	F				
Critical Difference : 253.3							

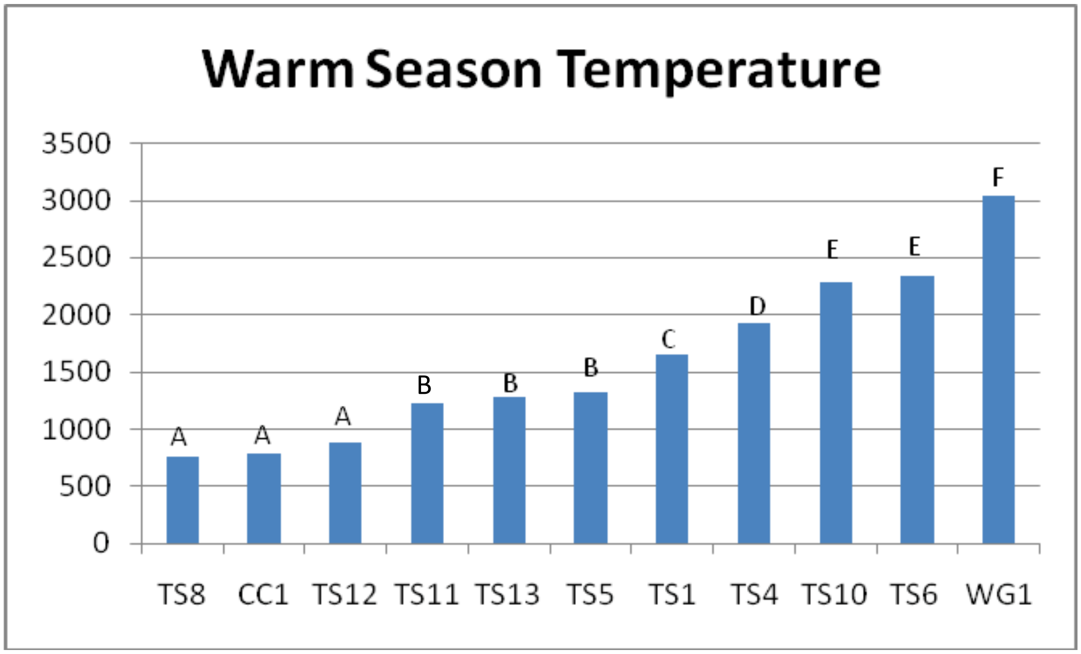


Figure 16: H-test results for warm season temperature, letter designations used to illustrate groupings from Table 9.

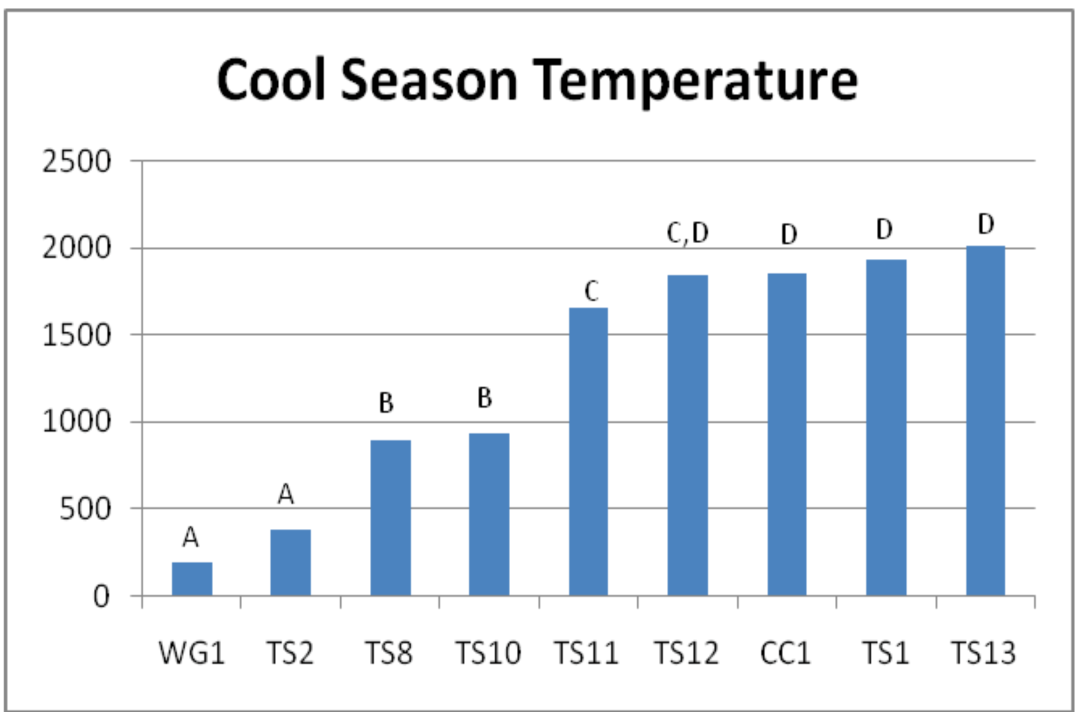


Figure 47: H-test results for cool season temperature, letter designations used to illustrate groupings from Table 9.

H-test analyses of warm and cool season pH showed significant differences among sites (Table 10, Figs. 18-19). Significant differences in mean rank for the warm season resulted in seven groups within 11 sites. Cool season pH mean ranks produced seven groupings of nine sites, with a maximum of two sites in one group showing that sites were significantly different with respect to pH in cool seasons (Table 12). In both the warm and cool seasons spring TS12 had the lowest mean rank for pH and Wet Glaize Creek (WG1) had the highest mean rank. For both the warm and cool season datasets, spring TS12 had the lowest mean rank and thus the most acidic measurements of the monitored springs and Wet Glaize Creek had the most basic measurements with regards to pH. Carroll Cave (CC1) paired with spring TS8 in the warm season mean ranks and in the cool season dataset Carroll Cave was paired with spring TS10.

Table 10: H-test results for pH, sites with the same letter designations are not significantly different from one another.

Warm Season pH	Site	Mean Rank	Letter Desig.	Cool Season pH	Site	Mean Rank	Letter Desig.
	TS12	202	A		TS12	195	A
	TS13	696	B		TS1	601	B
	TS10	916	B,C		TS11	765	B,C
	TS5	957	C		TS13	830	C
	TS6	1396	D		CC1	1380	D
	TS11	1583	D,E		TS10	1502	D
	TS8	1819	E		TS8	1872	E
	CC1	1829	E		TS2	2108	F
	TS4	2407	F		WG1	2452	G
	TS1	2645	F	Critical Difference : 199.7			
	WG1	3035	G				
Critical Difference : 253.3							

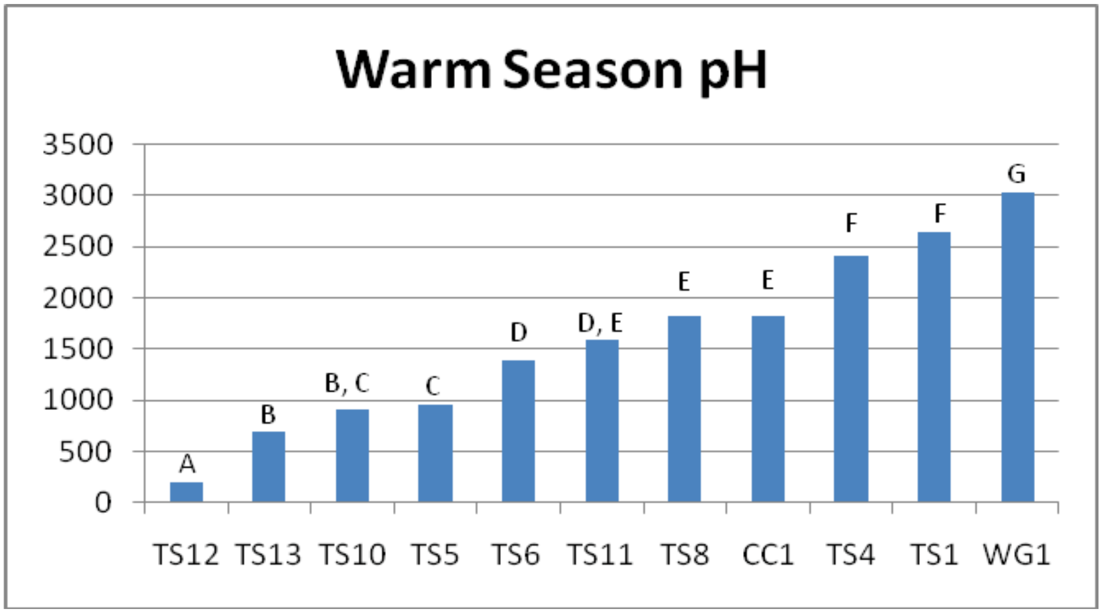


Figure 58: H-test results for warm season pH, letter designations used to illustrate groupings from Table 10.

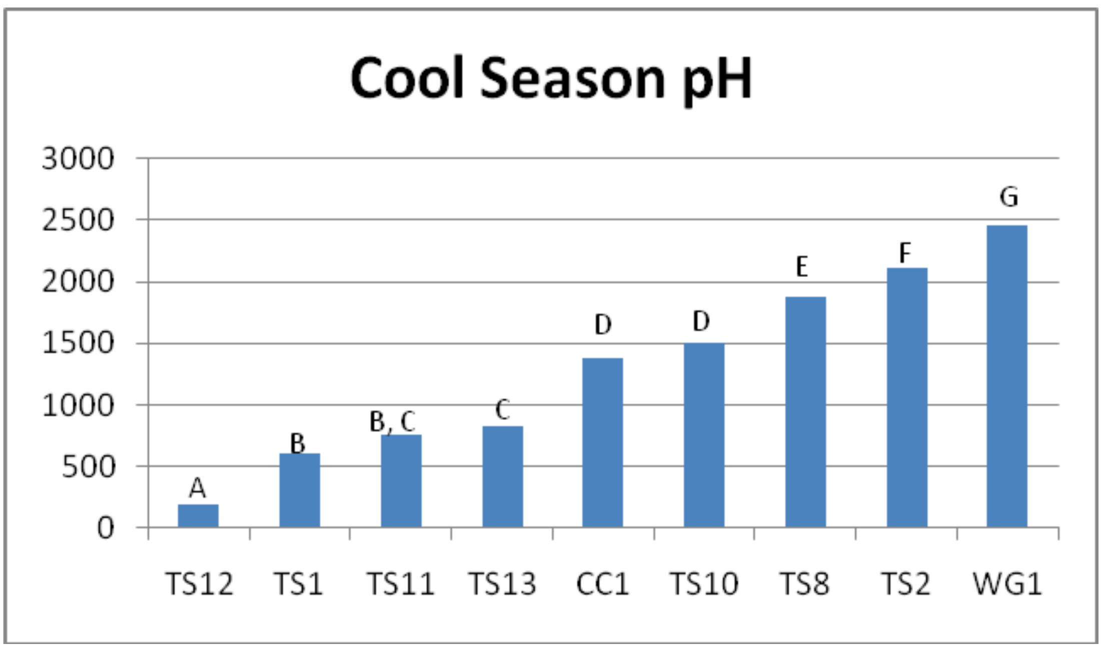


Figure 19: H-test results for cool season pH, letter designations used to illustrate groupings from Table 10.

H-test results showed significant differences among site in SpC in both warm and cool seasons (Table 11, Figs. 21-22). The mean ranks separation for warm season SpC produced seven grouping of the eleven sites, with a maximum of three sites in one groups, and cool season SpC had six groupings of nine sites, with a maximum of two sites in one group showing that more sites were significantly different from one another in cool seasons (Table 10). Wet Glaize Creek had the lowest mean rank for SpC in the warm season and the highest mean rank for SpC in the cool season. In warm seasons spring TS8 had the highest mean rank SpC, which was also found to be true with regards to the *in situ* measurements collected during ion sample collection (Appendix II). Carroll Cave had the next highest mean rank for SpC in the warm seasons. During the cool seasons site TS13 had the lowest mean rank for SpC. Carroll Cave was paired with spring TS10 in the cool season dataset, the cave had also been grouped previsously with TS10 in the cool season pH mean ranks.

Table 11: H-test results for Specific Conductivity, sites with the same letter designations are not significantly different from one another.

Warm Season Specific Conductivity	Site	Mean Rank	Letter Desig.	Cool Season Specific Conductivity	Site	Mean Rank	Letter Desig.
	WG1	249	A		TS13	313	A
	TS1	677	B		TS1	367	A
	TS10	810	B		TS11	736	B
	TS5	888	B		TS10	1054	C
	TS11	1338	C		CC1	1193	C
	TS12	1826	D		TS2	1653	D
	TS4	1850	D		TS12	1810	D
	TS13	1973	D,E		TS8	2122	E
	TS6	2199	E		WG1	2457	F
	CC1	2663	F	Critical Difference : 199.7			
	TS8	3013	G				
Critical Difference : 253.3							

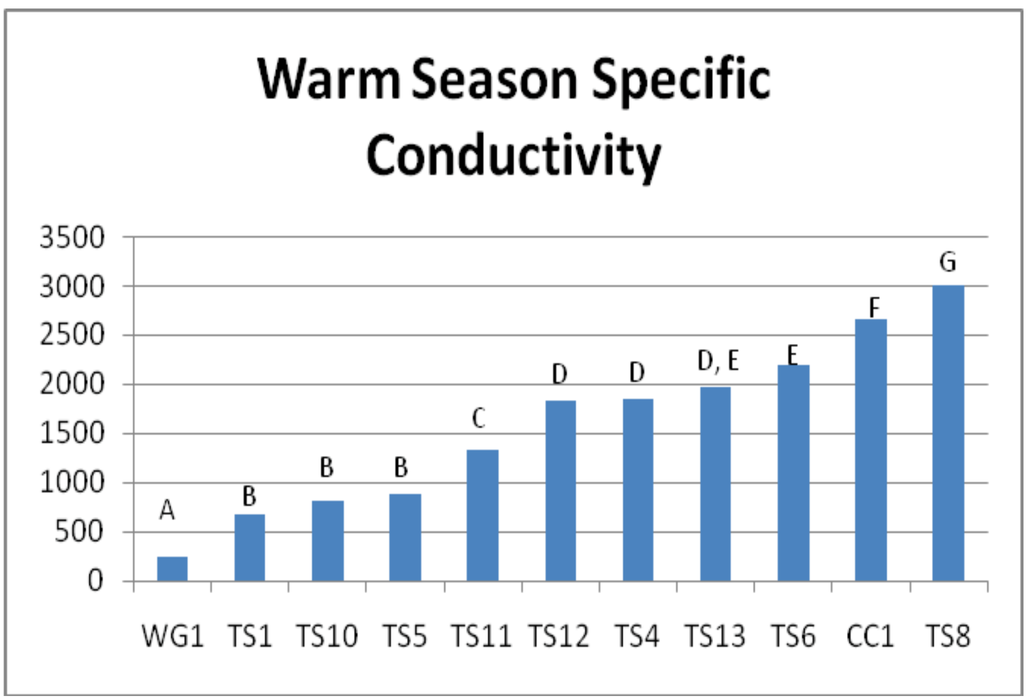


Figure 20: H-test results for warm season Specific Conductivity, letter designations used to illustrate groupings from Table 11.

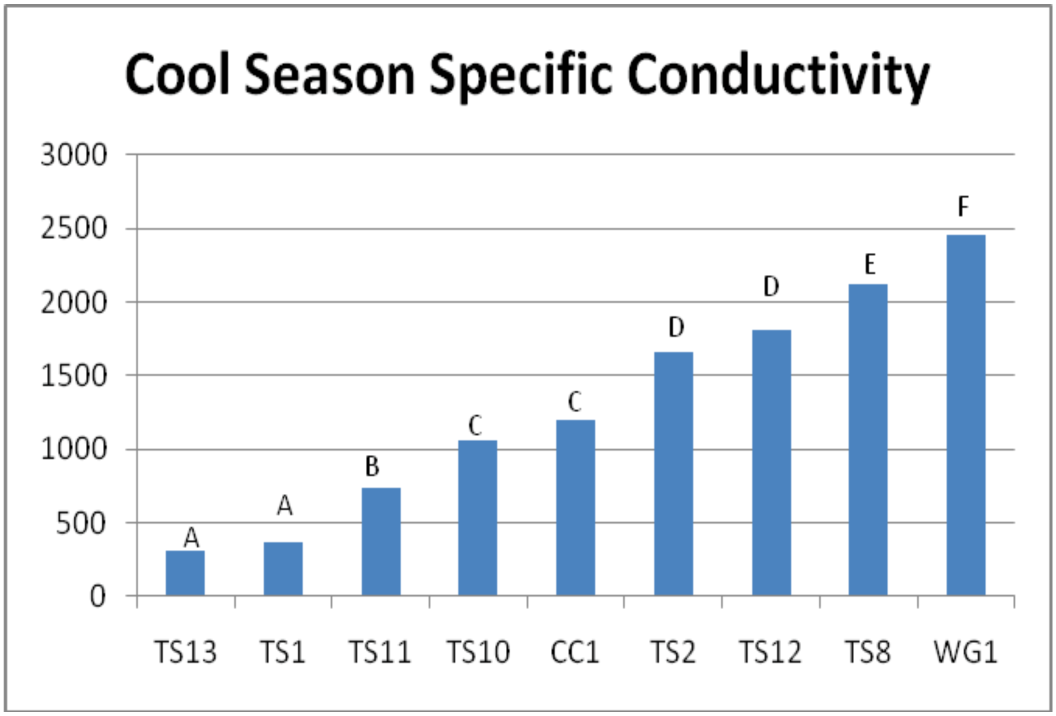


Figure 61: H-test results for cool season Specific Conductivity, letter designations used to illustrate groupings from Table 11.

Two End Member Mixing Model

The creation of a two-end member involved the use of a simple equation to calculate the ratio of an individual spring to an end member with the highest value of a specific parameter (Equation 1). This analysis was conducted for all the major cations, bicarbonate, in situ measurements taken during sample collection, and calculated values of saturation indices for dolomite and the partial pressure of CO_2. In each case the proportions of the end members contributions were calculated. After this analysis it became clear that not all parameters measured or calculated could be used in the creation of the mixing model as Carroll Cave and Wet Glaize Creek appeared to not be the primary end members. In order to create an accurate representation of the end members the parameters in which there were three or less outliers were selected for discussion and in the creation of the overall mixing model. The parameters in which Carroll Cave and Wet Glaize represent the two primary end members are calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), and specific conductivity (µs/cm) (Figs. 22-26, Tables 11-14). The values of SpC were measured in situ during the collection of ion samples and thus represent measurements for all monitored sites plus end members at nearly the same time and hydrologic conditions. The four geochemical parameters mixing models are then averaged and used to calculate an overall representation of a two end member mixing model for the 11 monitored springs at Toronto Springs (Fig. 27, Table 15).

Each of the geochemical parameters used to create the overall mixing model have outliers which can help to describe the complex hydrologic functioning which is occurring at Toronto Springs. Outliers occurred in some of the mixing models and were identified where proportions of flow from end members were over 100% or were a negative value. This was an indication that a site had either a greater value than the highest end member or a lower value than the lowest end member. Spring TS8 was one example of an anomoly, where the site was outside of end member ranges for all mixing models. Typically the value on TS8 were greater than Caroll Cave (CC1) and thus ended up with over 100% proportion from Carroll Cave. Spring TS12 was another site which appeared as an outlier for both the bicarbonate and specific conductivity mixing models, sharing the same behavior as TS8 in that the site was shown greater than Carroll Cave. The only other outlier shown in the mixing models which was not greater than Carroll Cave was spring TS2, which is believed to be influenced greater by Wet Glaize Creek. In the bicarbonate mixing model TS2 was shown to be an outlier with an average bicarbonate value lower than that of Wet Glaize Creek.

By displaying the tabular data for each mixing model spatially other patterns and groupings become apparent which may provide further insight into the connections between springs. In the calcium mixing model springs TS1, TS4, TS5, TS6, TS7, TS10 and TS11 all had very similar proportions of flow from the end members, with a span of seven percent between the lowest and highest sites (Fig. 22, Table 11). The magnesium mixing model also had groupings of similar sites; TS4, TS5, TS7, TS10 and TS11 all had very similar proportions of magnesium and were within a span of only three percent variance (Fig. 23, Table 12). Bicarbonate proportions were very similar for five site including; TS1, TS4, TS5, TS7, and TS11; all of which had proportions within a span of five percent (Fig. 24, Table 13). Specfic conductivity had two primary groupings of sites with sites TS1, TS4, andTS13 occuring within a four percent span and sites TS10 and TS11 occuring within a one percent span (Fig. 25, Table 14). The overall mixing model which combines the four previous mixing model into one model describing end member proportions to springs has a grouping of four sites; TS1, TS4, TS10, and TS11; which all occur within a span of six percent (Fig. 26, Table 15). The grouping of sites from the mixing model analysis helps to illustrate the complex interactions and mixing occuring between recharge sources at Toronto Springs.

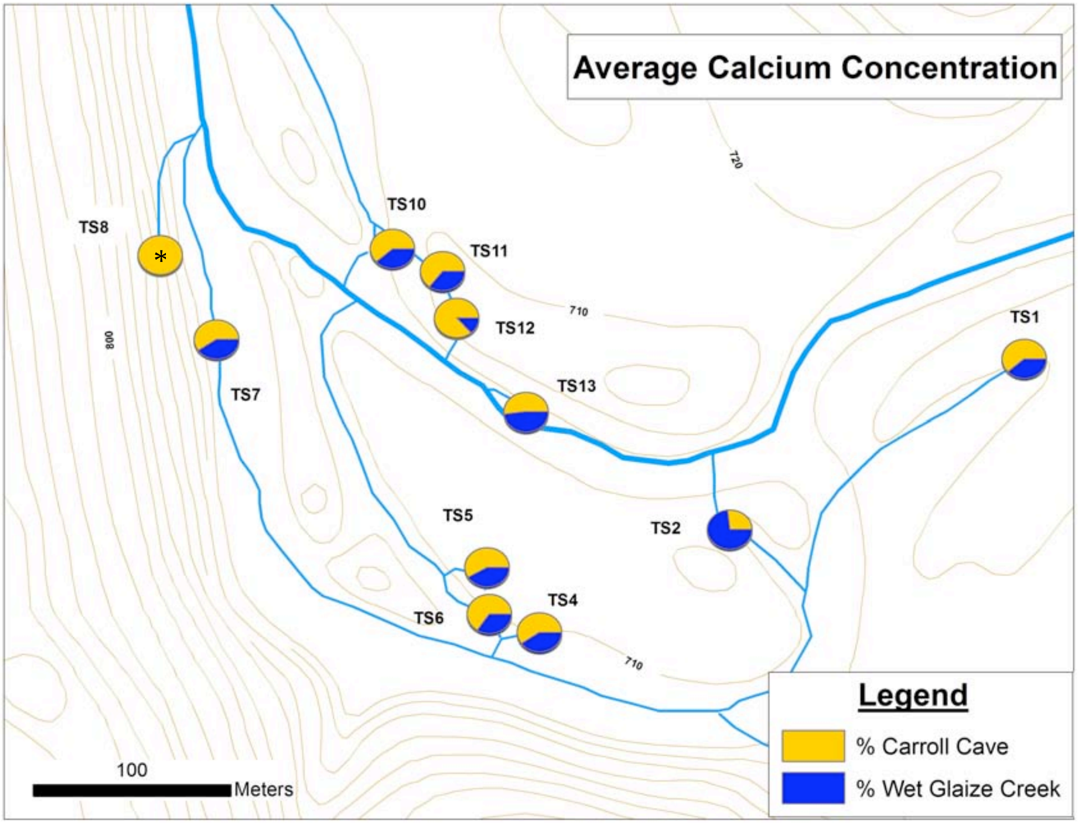


Figure 72: Two-end member mixing model for Toronto Springs using average calcium ion concentration, springs which were outliers are noted with an asterisk*.

Table 12: End member proportions for calcium ion concentration.

Site	% Carroll Cave	% Wet Glaize Creek
WG1	0%	100%
TS1	61%	39%
TS2	27%	73%
TS4	59%	41%
TS5	58%	42%
TS6	65%	35%
TS7	59%	41%
TS8	107%	-7%
TS10	61%	39%
TS11	64%	36%
TS12	87%	13%
TS13	52%	48%
CC1	100%	0%

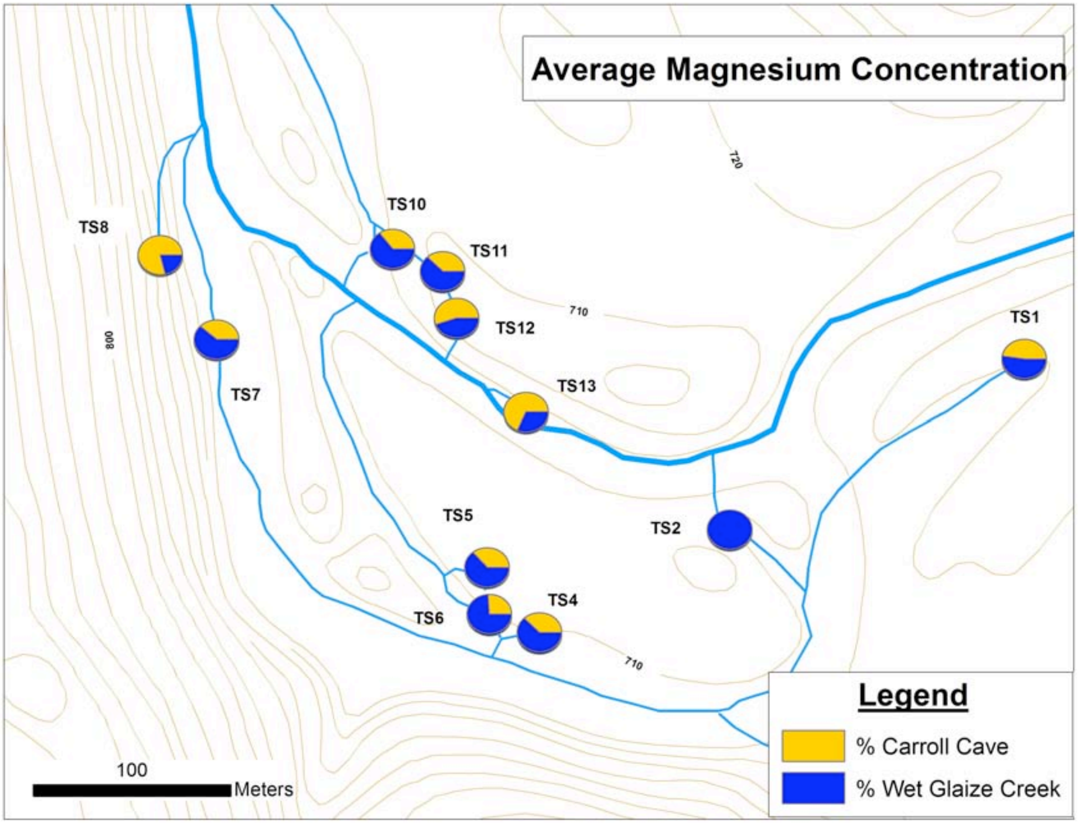


Figure 83: Two-end member mixing model for Toronto Springs using average magnesium ion concentration, springs which were outliers are noted with an asterisk*.

Table 13: End member proportions for magnesium ion concentration.

Site	% Carroll Cave	% Wet Glaize Creek
WG1	0%	100%
TS1	48%	52%
TS2	0%	100%
TS4	38%	62%
TS5	37%	63%
TS6	26%	74%
TS7	39%	61%
TS8	79%	21%
TS10	36%	64%
TS11	38%	62%
TS12	55%	45%
TS13	68%	32%
CC1	100%	0%

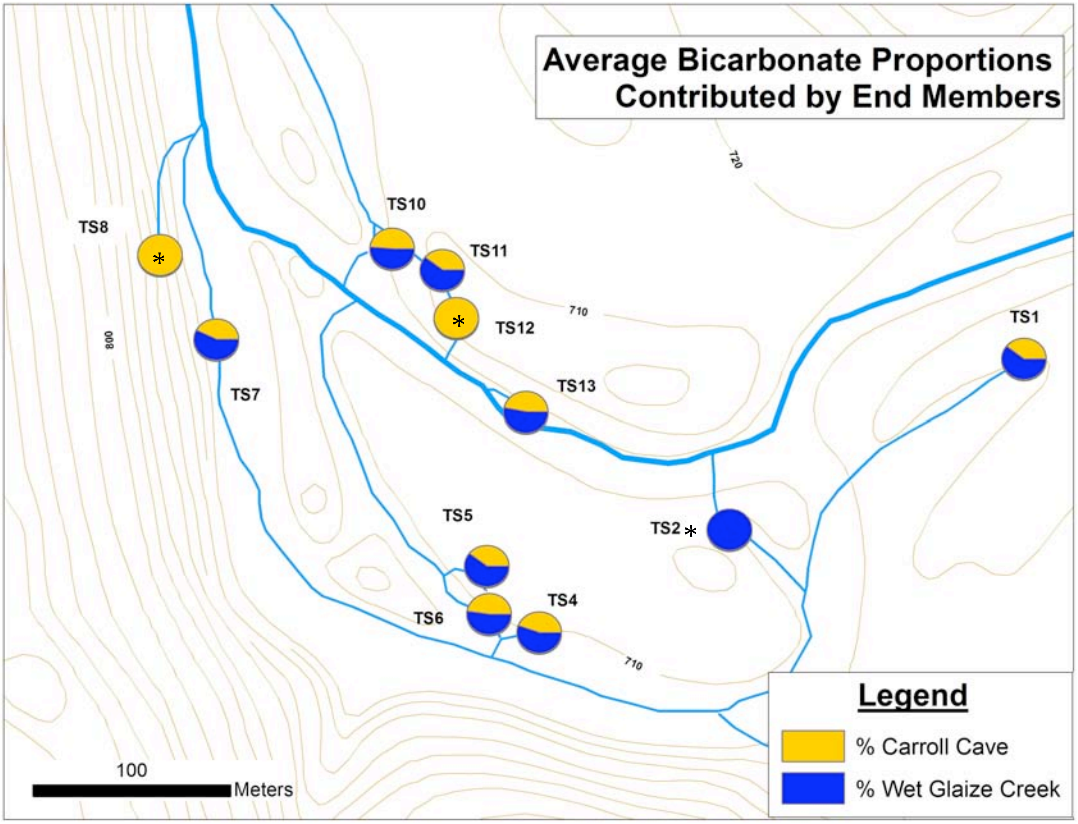


Figure 94: Two-end member mixing model for Toronto Springs using average bicarbonate ion concentration, springs which were outliers are noted with an asterisk*.

Table 14: End member proportions for bicarbonate ion concentration.

Site	% Carroll Cave	% Wet Glaize Creek
WG1	0%	100%
TS1	40%	60%
TS2	-18%	118%
TS4	45%	55%
TS5	40%	60%
TS6	48%	52%
TS7	43%	57%
TS8	157%	-57%
TS10	49%	51%
TS11	40%	60%
TS12	110%	-10%
TS13	47%	53%
CC1	100%	0%

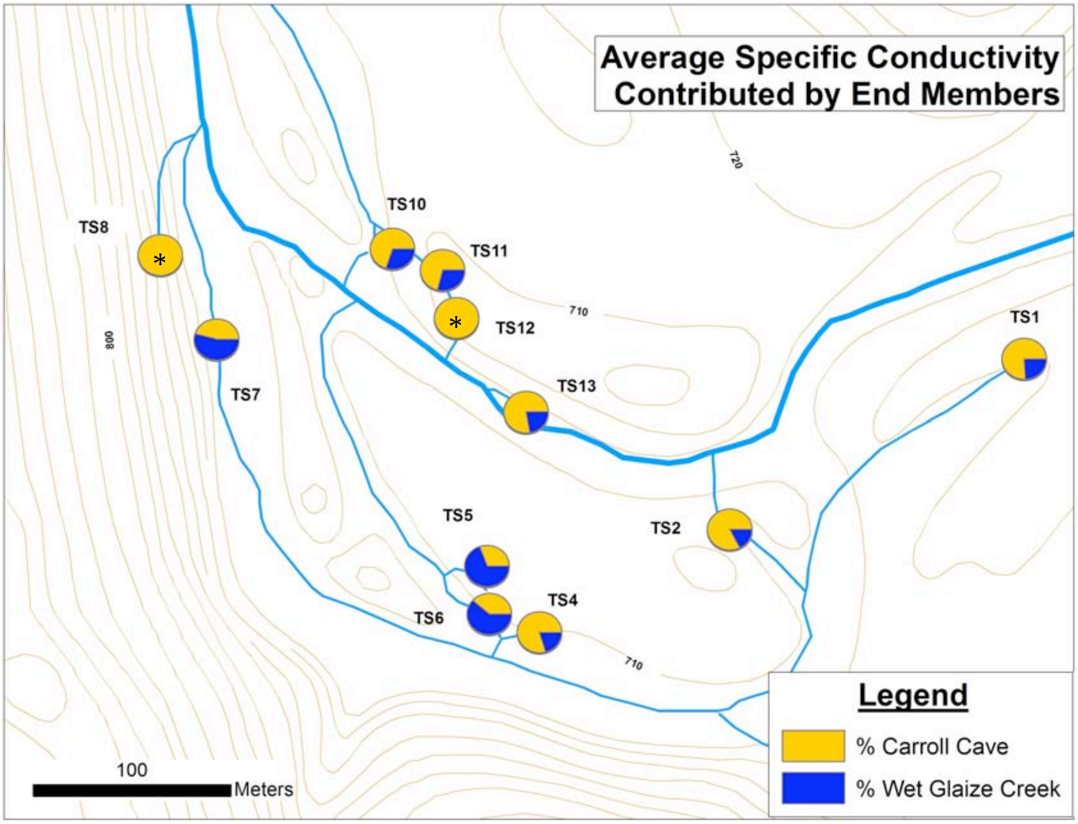


Figure 105: Two-end member mixing model for Toronto Springs using average Specific Conductivity, springs which were outliers are noted with an asterisk*.

Table 15: End member proportions for Specific Conductivity.

Site	% Carroll Cave	% Wet Glaize Creek
WG1	0%	100%
TS1	76%	24%
TS2	17%	83%
TS4	80%	20%
TS5	31%	69%
TS6	39%	61%
TS7	46%	54%
TS8	174%	-74%
TS10	70%	30%
TS11	71%	29%
TS12	133%	-33%
TS13	78%	22%
CC1	100%	0%

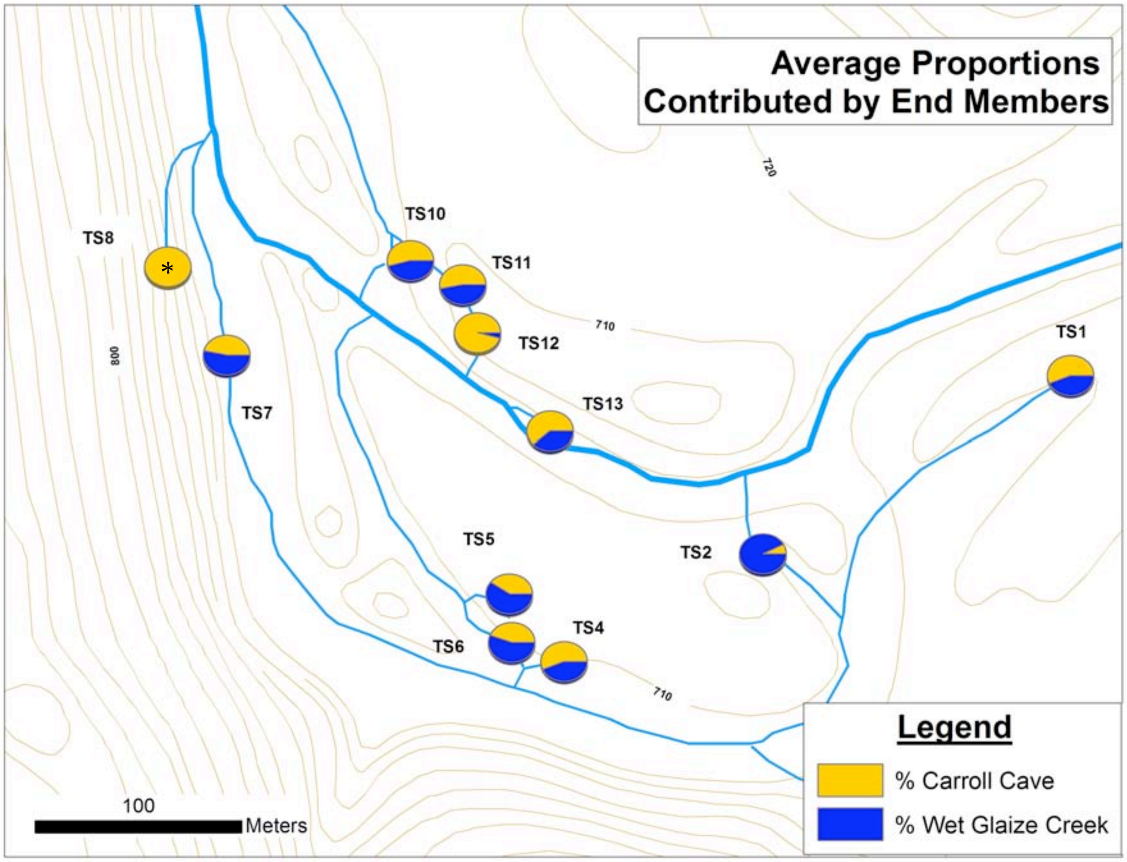


Figure 116: Two-end member mixing model for Toronto Springs using average proportions contributed by end members, springs which were outliers are noted with an asterisk*.

Table 16: Average end member proportions for all monitored sites.

Site	%Carroll Cave	%Wet Glaize Creek
WG1	0%	100%
TS1	56%	44%
TS2	7%	93%
TS4	56%	44%
TS5	41%	59%
TS6	45%	88%
TS7	47%	53%
TS8	129%	-29%
TS10	54%	46%
TS11	53%	47%
TS12	96%	4%
TS13	61%	39%
CC1	100%	0%

Chapter 4: Discussion

Following the six rounds of dye injections a recharge area of 18.53 km^2 has been delineated for Thunder River and Confusion Creek in Carroll Cave (Fig. 11). No hydrologic connection was established with Carroll River, and thus, it is believed that Carroll River primarily receives recharge from diffuse epikarstic aquifers above and adjacent to the cave passage. For this reason an epikarst buffer of 50 m around the cave passage was created for the Carroll River arm to account for the area that likely contributes flow to this cave stream. In terms of the sub-basins within the delineated recharge area, Traw Hollow is the largest with 12.9 km^2 accounting for 71% of the recharge area (Table 18). The other sub-basins in the recharge area include Barnett Hollow, the second largest at 3.6 km2, and the southern arm of Davis Hollow with an area of 1.5 km2, the combined total of these two sub-basins account for approximately 28% of the recharge area. Losing streams were the primary means of recharge to

Table 17: Recharge area sub-basins in the Carroll Cave Recharge Area.

Recharge Area Sub-Basins & Features	Area (km^2)	% of Total Recharge Area
Traw Hollow	13.17	71.1%
Barnett Hollow	3.63	19.6%
Davis Hollow	1.51	8.1%
Whirpool Sink & Hippie Shack Sink	0.23	1.2%
Total	18.53	

Carroll Cave, accounting for 98% of the overall recharge area. Sinkholes accounted <2% of the recharge area, showing that discrete recharge via sinkholes was a minor component for this karst aquifer. The findings of the dye tracing work clearly demonstrated that losing stream hydrology dominates the recharge of the aquifer and this mode of recharge (i.e. flood water recharge) is also consistent with the highly dendritic nature of the Carroll Cave system. Further, this cave pattern is indicative of branchwork caves formed in bedded rock (Palmer and Palmer, 2009). The hydrologic connections between Carroll Cave and Toronto Springs are now well documented and a recharge area for Carroll Cave has been delineated. However, some additional work remains to be done in terms of identifying individual first order drainages and specific sinkholes along the western boundary of the recharge area which may contribute flow to the Carroll system.

With the delineated recharge area land use within the recharge area and the sub-basins of the recharge area can be examined (Table 19). Land use within the

Table 18: Land use types in the Carroll Cave Recharge Area.

Land Use Type	Area (km^2)	% of Total Recharge Area
Grassland	10.41	56.20%
Deciduous Forest	6.96	37.54%
Deciduous Woody - Herbaceous	0.79	4.28%
Cropland	0.09	0.51%
Evergreen Forest	0.07	0.39%
Barren Sparsely Vegetated	0.06	0.34%
Impervious Surface	0.06	0.30%
Open Water	0.04	0.22%
Low Intensity Urban	0.03	0.14%
Herbaceous Dominated Wetland	0.01	0.08%

Carroll Cave recharge area is dominated by grasslands and deciduous forests, which account for 93.8% of the total area (Fig. 28). Typical threats to groundwater quality, such as impervious surfaces, cropland, and sparsely vegetated areas, are fortunately at a minimum, with only 1.4% of the recharge area consisting of these threats. While urban development of the recharge area has been minimal, other less obvious threats to water quality do exist within the recharge area. For example, sinkhole and streamside dumps are common in this area and the lack of sewer infrastructure implies that any homes or businesses within the recharge area utilize on-site sewer treatment. In addition, much of the grassland in the recharge areas is used as pasture for grazing cattle. The on-site sewers and cattle-grazing operation could be sources of nutrients and fecal bacteria to the cave streams (Boyer and Pasquarell 1999, Kelly et al. 2009, Owen and Pavlowsky, 2010). However, it appears that the threats to water quality in the Carroll Cave recharge area were much less than other karst recharge areas of the Ozarks (Lerch et al., 2005; Lerch, 2009).

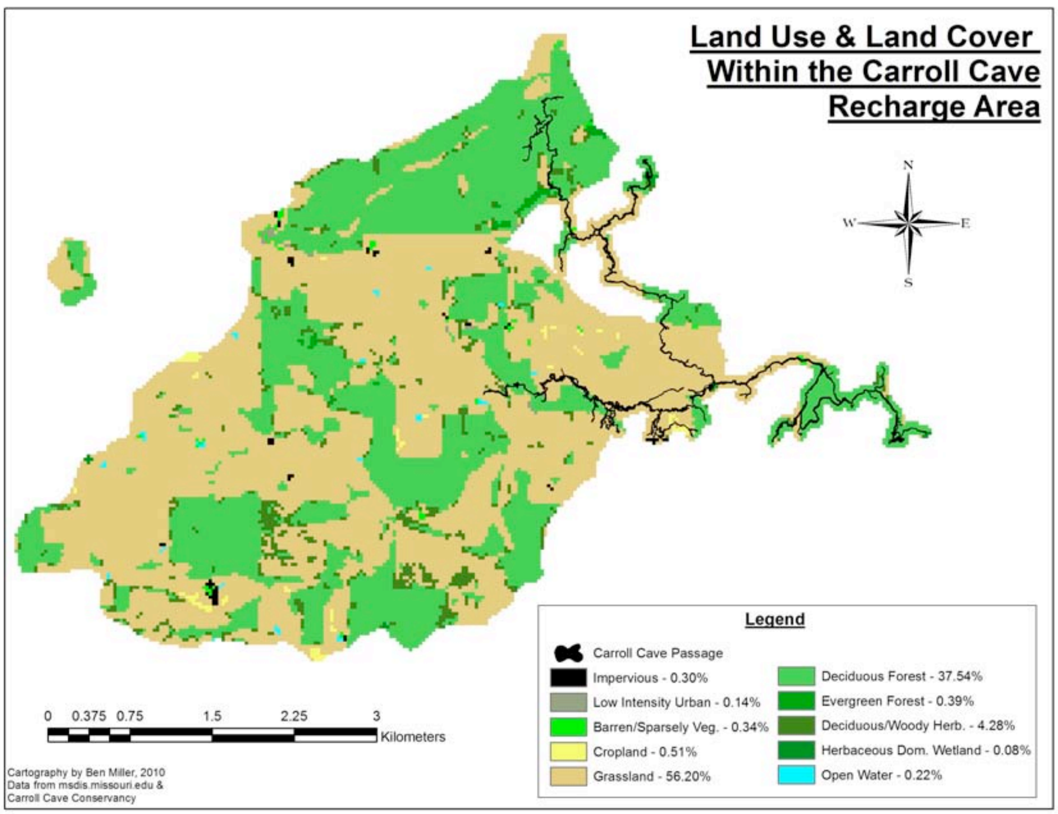


Figure 127: Land use map of the Carroll Cave Recharge Area.

The other important factor that was confirmed via the dye tracing is a definite hydrologic connection between Wet Glaize Creek and the springs at Toronto Springs. Dye injected into Wet Glaize Creek at Seven Springs Road reappeared within three days at eight sites at Toronto Springs, and appeared at two more springs within the next week. The only springs that did not show a connection to Wet Glaize Creek were springs TS3 and TS8. Spring TS8 has not been shown to be part of the mixing zone of Carroll Cave and Wet Glaize through dye tracing and is believed to have an independent recharge area separate from that of the other springs at Toronto.

The results from the three seepage runs uncovered some unusual characteristics about the hydrologic behavior of Wet Glaize Creek above Toronto Springs. Seepage run data indicated two primary losing reaches along Wet Glaize Creek, a 0.4 km stretch directly below the confluence with Mill Creek and a 3.6 km stretch between Carroll Cave Road and Highway A. However loss within these losing reaches appears to vary inversely with flow in Wet Glaize Creek. When flow in Wet Glaize Creek is higher the primary losing reach is the 0.4 km reach directly below the Mill Creek confluence. As flow in Wet Glaize begins to decrease from lack of precipitation, the lower losing reach becomes the dominant losing reach. Under base flow conditions, the loss of stream flow to seepage is minimal in Wet Glaize Creek, below Seven Springs Road, and Carroll Cave likely becomes the primary end member contributing flow to Toronto Springs.

Several possible hypotheses explain the losing reaches below the Mill Creek confluence and the dependence of the seepage on the flow conditions in Wet Glaize Creek. One hypothesis is that stream flow is lost along structural features, which cross Wet Glaize Creek in the immediate vicinity of the confluence (Fig.29). The confluence with Wet Glaize Creek crosses one edge of the Montreal Fault Block which may be pirating the flow from Wet Glaize Creek during higher flow regimes. The fracture or conduit may be slightly perched and likely filled with alluvium at the upstream end as no obvious open features exist alongside Wet Glaize Creek in the vicinity of the Mill Creek confluence. Another possible condition may be a water-filled conduit or fracture located in or below the streambed. When Wet Glaize Creek has a higher flow, a greater head

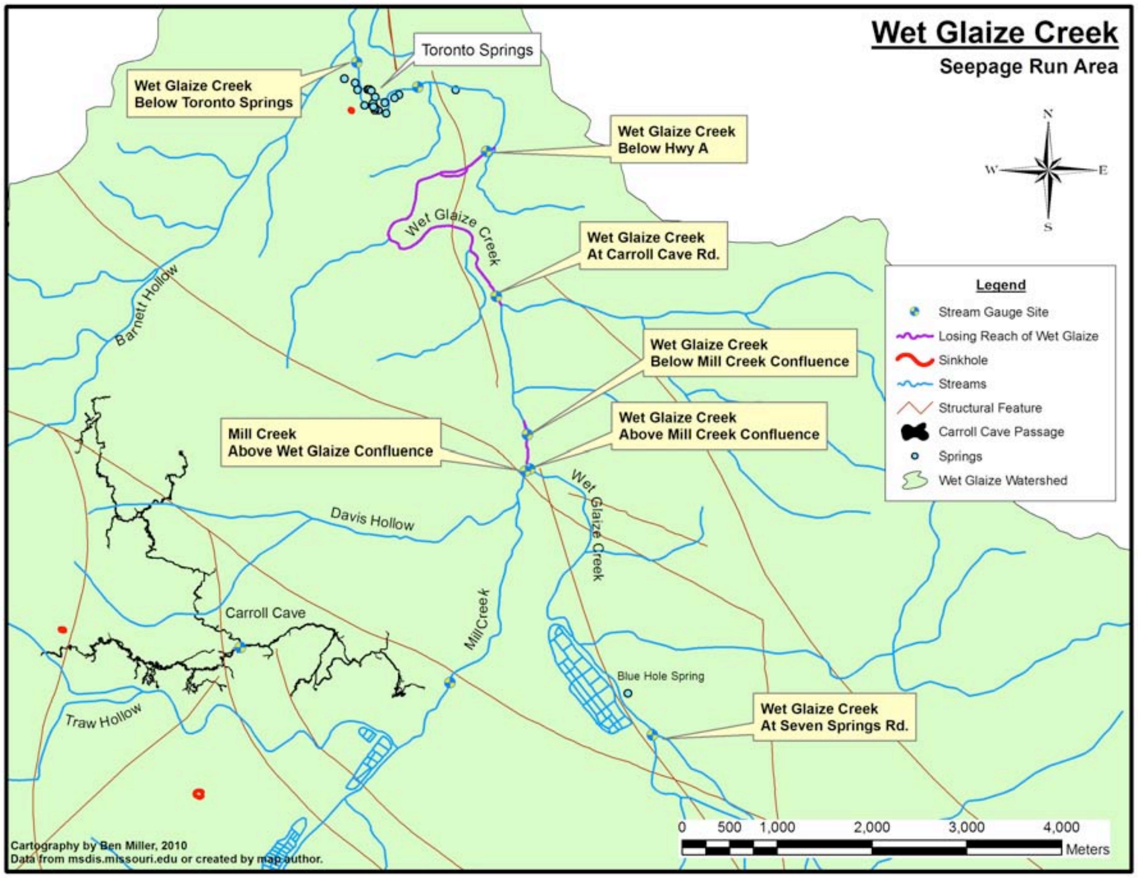


Figure 138: Seepage run area of Wet Glaize Creek, showing structural features.

pressure on the fracture opening could force more of the stream flow into the fracture. Finally, the sediment size and sorting along the losing reaches may play a role in the amount of flow lost during different flow regimes. If finer sediments line the streambed or are below the coarser larger cobble-sized sediments, these fine sediments might create a barrier to stream flow loss in low flow periods due to the small amount of pore space between the sediment grains. In higher flow periods the stream might rise high enough to be flowing through or in contact with larger coarser sediments which would have large pore spaces between sediment grains and thus would be more susceptible to the transmission of water. If the sediments are well-sorted vertically in the Wet Glaize Creek alluvial area, this may have created a setting in which the loss of flow along Wet Glaize Creek varied inversely with stream discharge.

The lower losing reach of Wet Glaze Creek between Carroll Cave Road and Highway A may also be controlled by structural features or the flow loss may occur by a meander cutoff. A fault crosses Wet Glaize Creek at least five times in the 3.6 kilometer-long reach of stream below Carroll Cave Road (Fig. 29). It is very possible that flow could lose along any one of the locations where the fault intersects the stream channel or perhaps along the fault at several locations. Flow may also be losing along the meander just upstream of Highway A. Toronto Springs is located on the backside of the ridge to the north of this meander, the loss of flow may be a result of a cutoff spring setting where flow cuts through the meander and resurges at Toronto Spring. Seepage runs along the lower portion of the Wet Glaize Creek watershed have documented a loss of stream flow under a range of varying flow conditions. In addition, the amount and location of lost flow is strongly related to the amount of flow in the Wet Glaize Creek channel. This varying loss is likely due to the multiple interactions of the stream channel with structural features, sediment sorting and porosity, the hydraulic head in the sub-surface conduit and possible cutoff spring behavior.

The groupings of sites using the H-test ranking of means and means separation tests has shown some relationships which confirm findings of the dye tracing and the ion analysis. Warm season temperature groupings include a low mean rank grouping of sites

TS8, Carroll Cave (CC1), and spring TS12 (Fig. 15). Spring TS12 is known to be hydrologically connected to Carroll Cave, via dye tracing, and spring TS 8 is a spring which discharges from a known cave located in the same bedrock as Carroll Cave. Thus, the three sites are not statistically significantly different from one another. The temperature relationship between Carroll Cave and TS12 is maintained even in the cool season data analysis where the springs are grouped together along with TS1 and TS13 (Fig. 16). Other springs in the "Carroll Suite" are also found to be similar with respect to temperature. Both in the warm season and cool season various springs from the "Carroll Suite" group together, which may indicate a similar mixture of recharge sources for those springs in the hydrologic conditions that were present during the sampling period. As outlined previously the "Carroll Suite" represents springs that have been positively dye traced from Carroll Cave (see Dye Tracing in Results and Discussion). Wet Glaize Creek (WG1) and spring TS2 are not statistically significantly different with respect to temperature in the cool season dataset, which supports the mixing model results that spring TS2 is largely recharged by Wet Glaize Creek.

Warm and cool season pH datasets have similar relationships to that of temperature, however the sites are not grouped in the same grouping as in temperature. Carroll Cave (CC1) and spring TS8 are grouped together in the warm season dataset along with spring TS11, a spring that is part of the "Carroll Suite" of springs. Spring TS11 is also grouped with spring TS6, another part of the "Carroll Suite". Although Wet Glaize Creek and spring TS2 had statistically different mean ranks for cool season pH, these sites did have the highest mean ranks among the springs. Carroll Cave is grouped with spring TS10, a spring that has been successfully traced from the cave. In much of the time series data pH would respond similarly to specific conductivity following precipitation events. Because the pH datasets for the springs have a narrower span in the range of pH values, it is believed that pH in the study area is largely controlled by a combination of dolomite dissolution and precipitation events.

H-test results for specific conductivity show some similarities to that of the pH datasets but also show unique signatures. In the warm season dataset Wet Glaize Creek (WG1) had the lowest mean rank for SpC and in the cool season had the highest mean rank for SpC. The monitoring site for Wet Glaize Creek is located approximately two kilometers downstream of Blue Hole Spring, which had been previously dye traced from the upper reaches of Conn's Creek (Dean, 1969). The low mean rank for SpC at Wet Glaize Creek in the warm season is likely due to the frequency of precipitation events which would create lower SpC values overall. In the cool season dataset, in which Wet Glaize Creek had the highest mean rank, the high rank is believed to be the opposite effect where little to no precipitation created longer residence time. Thus the water discharging from Blue Hole Spring would have had more contact time with the local bedrock and therefore a higher SpC. Many of the springs within the "Carroll Suite" were grouped together in three main groups, such that the only spring which is not grouped with another "Carroll Suite" spring is TS11 in the warm season data. Carroll Cave and spring TS8 are neighbors in the mean ranks in the warm season, though the sites are separated by several sites in the cool season dataset. Carroll Cave is paired with spring TS10 again as it was in the cool pH H-tests, indicating the two sites are not statistically significantly different for two of the three H-tests in the cool season. Some of the "Carroll Suite" springs are grouped together with TS13 and TS1 grouped together as the lowest mean ranks. Interestingly TS2 and TS12 are grouped together even though the springs receive recharge from different sources, TS2 has never had a positive trace from Carroll Cave, though this may indicate that there is some minor groundwater influence on the geochemistry of spring TS2, which would cause the grouping with TS12.

The H-test results did provide discrimination among the springs in their geochemical and physical properties. The fact that some sites pair together for more than one parameter in a season, e.g. spring TS10 and Carroll Cave (CC1), indicates the two sites have very similar geochemistry in a given season. Not all sites group together from test to test and from season to season, which is likely indicative of the influence on seasonal changes in precipitation, temperature, and hydrologic conditions. It is also important to note that in many of the H-test sets springs from the “Carroll Suite” often group together and the groups of the springs may overlap with other groupings of “Carroll Suite” springs. The ratio’ed H-test data did not share the same groupings as in the mixing model (see below) and thus may not adequately account for the variations, temporally and hydrologically, in the spring system. However the H-tests were successful in establishing that the springs do have unique individual geochemical properties. This behavior shows that while the springs have unique geochemistry, they are similar, which may be due to the proportions of flow received by each spring from the end members, Carroll Cave and Wet Glaize Creek.

The two-end member mixing models used to describe the mixing setting occurring at Toronto Springs have shown additional similarities, with respect to end member proportions, which exist between the springs. By examining the spatial distribution of these sites, and their similar proportions, insights about the fracture or conduit network that supplies water to the spring outlets can be illuminated. The groupings of these sites and the fact that certain sites are often grouped together illustrates that some springs, while separated geographically from one another, may be receiving their flow from similar conduits or fractures. For each of the mixing models, springs TS1, TS4, TS10, and TS11 had proportions that were within a close range of one another, typically within 1-5% of each other. This may indicate that those four springs are supplied by the same conduit or fracture and as such are receiving near equal proportions of the end member recharge. Spring TS2, which has been thought to be largely recharge by flow from Wet Glaize Creek, shows that the majority of the flow to the spring is from Wet Glaize for four out of the six mixing models and in fact indicates that the water is identical with respect to bicarbonate. The fact that the spring does not show near 100% of the recharge from Wet Glaize on all parameters may be due to other minor groundwater sources contributing flow to the spring, since Carroll Cave has never been successfully dye traced to spring TS2. The other spring that was consistently an outlier of the system is spring TS8 (Grotte Hole Cave). Spring TS8 was typically closest to the Carroll Cave end member but had consistently higher values for calcium, magnesium, bicarbonate and specific conductivity. This may be due to the fact that both spring TS8 and Carroll Cave are cave streams which are in the same bedrock and thus would be expected to have similar geochemical signatures. While some outliers exist in each of the mixing models it is believed that the models accurately describes the mixing zone setting occurring at ten of springs at Toronto Springs which are receiving recharge from Carroll Cave and Wet Glaize Creek.

Based on the mixing model analysis for Toronto Springs, the end members of Carroll Cave and Wet Glaize Creek can be used to represent the larger contributions from surface flow and groundwater flow systems as exemplified by the results from springs TS2 and TS8. The results of the ion concentrations and the mixing model for TS8 showed that its geochemical properties were very similar to that of Carroll Cave, yet results of the dye tracing showed it was not hydrologically connected to the cave. TS8 represents a separate karst aquifer formed in the same bedrock, resulting in its similarity to Carroll Cave. Spring TS2 was another site that was not traced to Carroll Cave, yet it showed an apparent recharge contribution from the cave. This apparent contribution is believed to be groundwater recharge from other local sources with similar chemical properties to the cave. Thus, these two springs illustrated that Carroll Cave can be used as a proxy for groundwater flow within this system. Additionally, Wet Glaize Creek was not traced to TS8, yet it showed an apparent contribution of surface water when Mg^{2+} data were used for the mixing model. Thus, Wet Glaize Creek can be used as a proxy for the surface stream flow systems found within the system. Statistical analyses (H-tests) have indicated that the eleven monitored springs have geochemically unique properties. Groups of springs, which are geographically separated from one another and in some cases on opposite sides of Wet Glaize Creek, were shown to have similar proportions of flow contributed by groundwater and surface water. This behavior is indicative of distinct conduits which are supplying springs or groups of springs. Thus, Toronto Springs represents a unique distributary spring system where water from groundwater flow systems mixes with water from surface stream flow systems to discharge via distinct conduits within the flood plain of Wet Glaize Creek.

Chapter 5: Conclusions

A recharge area of 18.5 km2 has been delineated for Carroll Cave through a series of over 20 dye injections. Thunder River and Confusion Creek in Carroll Cave are connected to eight of the 13 springs at Toronto Springs, resurging from springs on the north and south sides of Wet Glaize Creek. The largest of the streams in Carroll Cave is recharged via the losing stream drainages of Traw Hollow and Davis Hollow. Confusion Creek and the DL7 side passage stream are recharged via the south arm of Barnett Hollow, with at least two large sinkholes been positively traced from the Whirlpool Sinkhole and the "Hippie Shack" sinkhole south of Montreal. The upper portion of Wet Glaize Creek near Seven Springs Road has been positively traced to ten of the springs at Toronto Springs. Land use within the Carroll Cave recharge area is dominated by 94% grassland and deciduous forest, and the largest sub-basin supplying recharge to Carroll Cave is Traw Hollow.

Seepage runs along Wet Glaize Creek and Mill Creek have identified two major losing reaches of the stream way between Seven Springs Road and Toronto Springs. One primary losing reach is located directly below the confluence of Mill Creek with Wet Glaize Creek, where losses as great as 543 L/s have been documented. The second primary reach is between Carroll Cave Road and Highway A, where losses of 375 L/s have been documented. Each losing reach is in close proximity to local faults, including one edge of the Montreal Fault Block, which crosses Wet Glaize Creek just below confluence with Mill Creek. Stream flow losses are concentrated around the structural features however flow loss in Wet Glaize Creek has a direct relationship to the stream flow of Wet Glaize. A higher percentage of flow is lost to seepage in higher flow regimes and at very low flows there is almost no loss of stream flow to seepage. This behavior may be caused by several different factors; including alluvium filled fractures, head pressure on stream bed opening, or sediment porosity variations. This provides evidence that the springs at Toronto Springs may be dominated by Wet Glaize Creek in higher flow regimes and dominated by flow from Carroll Cave during lower or base flow regimes.

Base flow data gathered via dataloggers has yielded three-day datasets for eleven springs at Toronto Springs and the end members of Carroll Cave and Wet Glaize Creek. Springs which are a part of the "Carroll Suite" of springs typically grouped together, though the ranking order of the springs may vary from season to season and by parameter. Carroll Cave often shared similarities with spring TS8, which is not part of the "Carroll Suite", and with spring TS10, which is hydrologically connected to the cave. Wet Glaize Creek often was grouped with or closely neighbored by spring TS2, a site that is believed to be largely recharged only by Wet Glaize Creek. The H-test analysis has shown that while the springs retain geochemically unique signatures they do group together and share geochemical properties with other springs in the system or with end members.

Mixing model analysis of calcium, magnesium, bicarbonate, and specific conductivity has yielded an overall mixing model for the springs at Toronto Springs. The mixing model analysis has illuminated groups of springs which consistently have very similar water chemistry, notably the springs of TS1, TS4, TS10 and TS11 which vary by less than five percent in the mixing models. The mixing model may also help to understand the complex geometry of the system, springs which have proportions very close to that of other springs may be receiving flow from the same conduit or fractures. The mixing models have also highlighted nuances in some springs which were thought to receive recharge from only one end member, as in the case of TS2 which shows some influence from groundwater when the primary source for the spring was proposed to be Wet Glaize Creek. Spring TS8 was an outlier in all of the mixing models, except temperature, typically having values greater than Carroll Cave with no influence from Wet Glaize Creek. The similarities between TS8 and Carroll Cave showed that the geochemistry of groundwater systems in Gasconade Dolomite were very similar and this supports the use of Carroll as an indicator of the groundwater recharge for a given spring.

A multi-proxy approach to examining the mixing zone setting present at Toronto Springs involved the use of dye tracing, seepage runs, and geochemistry to quantitatively describe the contribution of recharge sources to the springs. Flow from Thunder River and Confusion Creek in Carroll Cave and flow from Wet Glaize Creek are the primary recharge sources or end members, which contribute flow to ten of the springs at Toronto Springs. Two springs not connected to Carroll Cave, TS2 and TS8, provided additional support for the development of a generalized mixing model to estimate the recharge sources to 10 of the springs at Toronto Springs. Based on end member mixing analysis, the end members can be used as proxies for the flow systems of the study area, with Carroll Cave as a proxy for groundwater flow and Wet Glaize Creek as a proxy for surface stream flow. The springs at Toronto Springs were shown to have distinct geochemical properties; however, groups of springs in geographically different areas of the mixing zone receive similar proportions of flow from groundwater and surface flow systems, including springs on opposite sides of Wet Glaize Creek. This behavior along with dye tracing results supports the hypothesis that distinct conduits are supplying flow to springs or groups of springs. This represents a new model for distributary spring systems in that the water discharging from the eleven springs at Toronto Springs is not geochemically homogenous – i.e., a single recharge source resurging through the alluvium. The geochemical properties of the individual springs are a result of the contributions of flow from groundwater and surface stream flow systems. These results strongly support the existence of a sub-surface conduit network that supplies the springs. A preliminary conceptual model of the hydrogeologic setting of this conduit structure has been developed based on these results (Fig. 29). Toronto Springs represents a unique multiple outlet alluvial spring system where groundwater flow mixes with surface flow to resurge, via distinct conduits, from as many as ten different spring outlets along the north and south sides of Wet Glaize Creek. These findings have provided a new geophysical model for the hydrology of distributary spring systems.

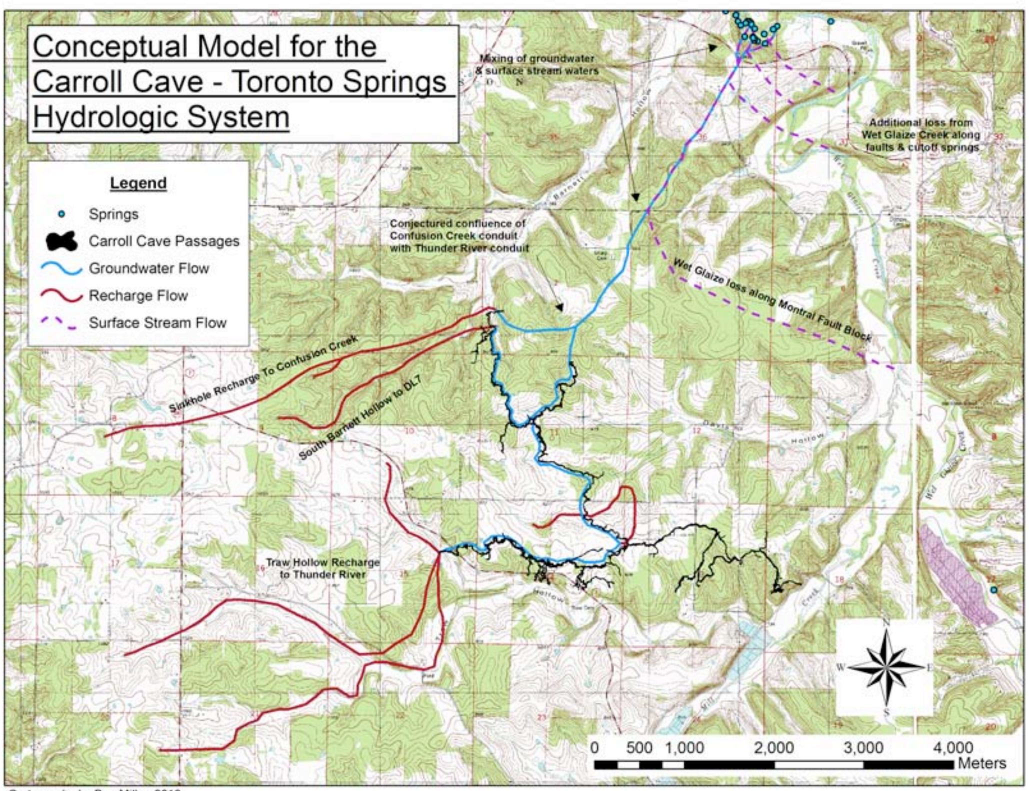


Figure 29: Conceptual model showing flow contributed by groundwater and surface stream flow systems to springs at Toronto Springs.

Bibliography

Anyonge, W., and Roman, C., New Body Mass Estimates for *Canis Dirus*, the Extinct Pleistocene Dire Wolf. Journal of Vertebrate Paleontology, Vol. 26, No. 1, p 209-212.

Beckman, H.C. and Hinchey, N.S., 1944, The large springs of Missouri. Missouri Geological Survey and Water Resources, XXIX (2): 63.

Boyer, D.G., and Pasquarell, G.C., 1999, Agricultural land use impacts on bacterial water quality in a karst groundwater aquifer. Journal of the American Water Resouces Association 35(2):291–300.

Chan, Y., and Walmsley, R.P., 1997, Learning and understanding the Kruskel-Wallis One-Way Analysis-of Variance-by-Ranks Test for differences among three or more independent groups. Physical Therapy, 77:12, p 1755-1761.

Christman, M.C., and Culver, D.C., 2001, The relationship between cave biodiversity and available habitat. Journal of Biogeography, 28, p 367-380.

Dean, T.J., Williams, J.H., Lutzen, E.E.,and Vineyard, J.D., 1969, Geologic report on the Bennett Spring project, Laclede and Dallas Counties, Missouri: Missouri Geological Survey and Water Resources (now Missouri Division of Geology and LandSurvey), unpublished manuscript, p 15.

Drake J.J., and Harmon, R.S., 1973, Hydrochemical Environments of Carbonate Terrains. Water Resources Research, 9:4, p 949-957.

Eaton, A.D., Clesceri, L.S., and A.E. Greenburg, (eds.), 2005, Standarad Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC.

Elliott, W.R., 2007, Zoogeography and biodiversity of Missouri caves and karst. Journal of Cave and Karst Studies, 69:1, p 135-162.

Field, M.S., 1988, *The vulnerability of karst aquifers to chemical contamination*: EPA, 600/D-89/008, p 13

Field, M., R. Wilhelm, J. Quinlan, and T. J. Aley, 1995, An assessment of the potential adverse properties of fluorescent tracer dyes used for groundwater tracing. Environmental Monitoring Assessment., 38, p 75–96.

Florea, L.J., and Vacher, H.L., 2006, Springflow Hydrographs: Eogenetic versus Telogenetic Karst. Groundwater, 44:3, p 352-361.

Ford, D., and Williams, P., 2007, *Karst Hydrology and Geomorphology*. Wiley and Sons, West Sussex, England, p 562.

Gholami, V., Azodi, M., and Taghvaye Salimi, E., 2008, Modeling of karst and alluvial springs discharge in the central Alborz highlands and on the Caspian southern coasts. Caspian Journal of Environmental Science, 6:1, p 41-45.

Golscheider, N., Meiman, J., Pronk, M., and Smart, C., 2008, Tracer tests in karst hydrogeology and speleology. International Journal of Speleology, 37:1, p 27-40.

Greenburg, A.E., A.D. Eaton, and L.S. Clesceri. 1992a. Part 3000, Metals. Methods 3500-K D. and 3500-Na D., pp. 3-80 and 3-93. *In* Standard Methods for the Examination of Water and Wastewater. 18th Edition. American Public Health Association, Washington, DC.

Greenburg, A.E., A.D. Eaton, and L.S. Clesceri. 1992b. Part 3000, Metals. Methods 3500-Ca B. and 3500-Mg B. pp. 3-57 and 3-73. *In* Standard Methods for the Examination of Water and Wastewater. 18th Edition. American Public Health Association, Washington, DC.

Harvey, E.J., Skelton, J., and Miller, D.E., 1983, Hydrology of Carbonate Terrane-Niangua, Osage Fork, and Grandglaize Basins, Missouri: Mo. Dept. of Natural Resources, Div. of Geology and Land Survey, WR 35, p 136.

Hawksley, O., 1965, Short-faced bear (*Arctodus*) fossils from Ozark caves. Bulletin of the National Speleological Society, Vol. 27, p 77-92.

Hawksley, O., 1981, Quaternary vertebrates from Carroll Cave, Camden County, Missouri. Missouri Speleology, Vol. 21, p 199-213.

Helwig, J.A., 1965, Geology of Carroll Cave, Camden County, Missouri. Bulletin of the National Speleological Society, 27:11, p 11-26.

Hess, J.H., and White, W.B., 1993, Groundwater geochemistry of the carbonate karst aquifer, south-central Kentucky, U.S.A.. Applied Geochemistry, Vol. 8, p 189-204.

Jones, W.K., 1984, Dye tracer tests in karst areas. The NSS Bulletin, Vol. 46, p 3-9.

Jones,W.K., H.H. Hobbs, C.M.Wicks, R.R. Currie, L.D. Hose, R.C. Kerbo, J.R. Goodbar, and J. Trout, eds. 2003. *Recommendations and Guidelines for Managing Caves on Protected Lands*. Special Publication no. 8. Charlestown,W.V.: Karst Waters Institute, 95.

Kelly, W.R., Panno, S.V., Hackley, K.C., Martinsek, A.T., Krapac, I.G., Weibel, C.P,, Storment, E.C., 2009, Bacteria contamination of groundwater in a mixed land-use karst region. Water Qual ExpoHealth 1:69–78

Kruskal, W.H., and Wallis, W.A., 1952, Use of Ranks in One-Criterion Variance Analysis. Journal of American Statistical Association, 47:260, p 583-621.

Lerch, R.N., Wicks, C.M., and Moss, P.L. 2005. Hydrologic characterization of two karst recharge areas in Boone County, Missouri. Journal of Cave and Karst Studies. 67:158-173.

Lerch, R.N. 2009. Contaminant transport in two central Missouri karst recharge areas, Proceedings of the 15th International Congress of Speleology, Kerrville, TX

Meiman, J., 1993, The effects of recharge basin land-use practices on water quality at Mammoth Cave National Park. In: D. L. Foster (Editor), *National Cave Management Proceedings, Bowling Green, Kentucky, October 23-26, 1991*. American Cave Conservation Assocation, p 33-47.

Middendorf, M., 1984, Bedrock Geology of the Montreal Quadrangle, Missouri: Geologic Map, Missouri Division of Geology and Land Survey, Rolla, MO.

Missouri Department of Conservation, 2010, *Missouri Species and Communities of Conservation Concern*. Jefferson City, MO: Missouri Department of Conservation, 2010. Print.

Musgrove, M., and Banner, J.L., 1993, Regional ground-water mixing and the origin of saline fluids: Midcontinent, United States. Science, Vol. 259, p 1877-1881.

Owen, M.R., and Pavlowsky, R.T., 2010 "Base Flow Hydrology and Water Quality of an Ozarks Spring and Associated Recharge Area, Southern Missouri, USA." *Environmental Earth Sciences* 61.8, p 1-15. Online.

Padgett, D.J., 2001, Noteworthy Collections and Spread of Exotic Aquatics in Missouri. Castanea, Vol. 66, No. 3, p 303-306.

Palmer, A.N. 1995. Geochemical models for the origin of macro-scopic solution porosity in carbonate rocks, In *Unconformities in carbonate strata: their recognition and the significance of associated porosity*, eds. Budd, D., P. Harris, and A. Saller, 77-101. : American Association of Petroleum Geologists, Memoir 63

Palmer, A.N. 2007. *Cave geology*. Dayton, OH, Cave Books.

Palmer, A. N., and Palmer, M.V., 2009, *Caves and Karst of the USA: a Guide to the Significant Cave and Karst Areas of the United States of America*. Huntsville, Ala.: National Speleological Society.

Panno, S.V., Krapac, I.G., Weibel, C.P., and Bade, J.D., 1996, Groundwater contamination in karst terrain of southwestern Illinois. Illinois State Geological Survey Environmental Geology Series 151. Champaign, Illinois.

Panno, S. V., Hackley, K.C., Hwang, H.H. and Kelly W.R., 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. Chemical Geology 179, p 113-128.

Quinlan, J.F., and Rowe, D.R., 1977, Hydrology and Water Quality in the Central Kentucky Karst: Phase I. National Technical Information Service. Research Report 101, January 1977.

Quinlan, J.F., 1990, Special problems of ground-water monitoring in karst terranes. In: Nielson, D.M., and Johnson, A.L., (eds), Ground water and vadose zone monitoring. American society for testing and materials., STP 1053, Philadelphia, PN, p 275-304.

Quinlan, J.F., and Ray, J.A., 1996, Normalized base-flow discharge of groundwater basins: a useful parameter for estimating recharge area of springs and for recognizing drainage anomalies in karst terranes. International Journal of Rock Mechanics and Mining Sciences and Geomechanics Abstracts, Vol. 33, No. 2.

Ryan, M., and Meiman, J., 1996, An Examination of Short Term Variations in Water Quality at a Karst Spring in Kentucky. Groundwater. 34:1, p 23-30.

Scanlon, B.R., and Thrailkill, J., 1987, Chemical Similarities Among Physically Distinct Spring Types in a Karst Terrain. Journal of Hydrology. 89:3/4, p 259-279.

Shuster, E.T., and White, W.B. 1971, Seasonal Fluctuations in the Chemistry of Limestone Springs: A Possible Means Characterizing Carbonate Aquifers. Journal of Hydrology. 14:2, p 93-128.

Skelton, J., 1976, Missouri Stream and Springflow Characteristics: Low-Flow Frequency and Flow Duration: Mo. Dept. of Natural Resources, Geological Survey, WR 32, p 76.

Smart, P. L., 1984, A review of the toxicity of twelve fluorescent dyes used for water tracing, NSS Bulletin., 46, p 21–33.

Smith, H., Wood, P.J., and Gunn, J., 2003, The influence of habitat structure and flow permanence on invertebrate communities in karst spring systems. Hydrobiologia, Vol. 510, p 55-66.

Troester, J.W., and White, W.B., 1986, Geochemical Investigations of Three Tropical Karst Drainage Basins in Puerto Rico. Groundwater. 24:4, p 475-482.

Valdiya, K.S., and Bartarya, S.K., 1991, Hydrogeological studies of springs in the catchment of the Gaula River, Kumaun Lesser Himalaya, India. Mountain Research and Development, 11:3, p 239-258.

Vandike, J.E., 1982, The Effects of the November 1981 Liquid-Fertilizer Pipeline Creak on Groundwater in Phelps County, Missouri: Mo. Dept. of Natural Resources, Div. of Geology and Land Survey, WR 75, p 26.

Vandike, J.E., 1996, The Hydrology of Maramec Spring. Missouri Department of Natural Resources, Division of Geology and Land Survey, Water Resources Report Number 55, p 104.

Vesper, D.J., Loop, C.M., and White, W.B., 2000, Contaminant Transport in Karst Aquifers, Theoretical and Applied Karstology, 13: p 63-73.

Vineyard, J. D., and Feder, G.L., 1974, Springs of Missouri: Mo. Geological Survey and Water Resources, WR 29,212 p., 94 figs., 26 tbls. Revised edition (1982).

Wilson, C.G. et al., 2008, Quantifying relative contributions from sediment sources in Conservation Effects Assessment Projects watersheds. Journal of Soil and Water Conservation. 63:6, p 523-532.

Appendix A:
Time Series Graphs of Datalogger Data for Individual Springs Compared to the Reference Site

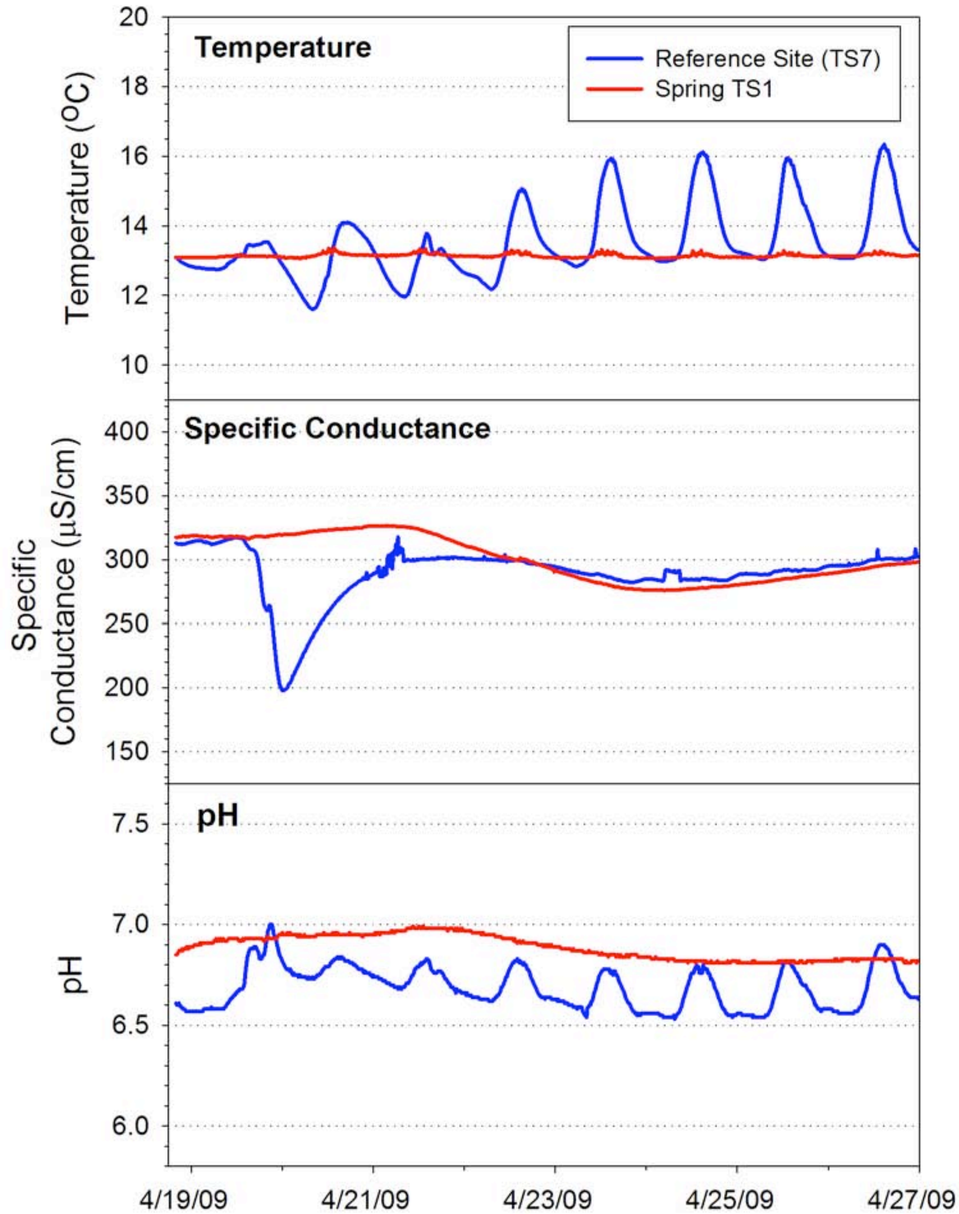


Figure A-1: Warm season time series data for Spring TS1 compared to reference site TS7.

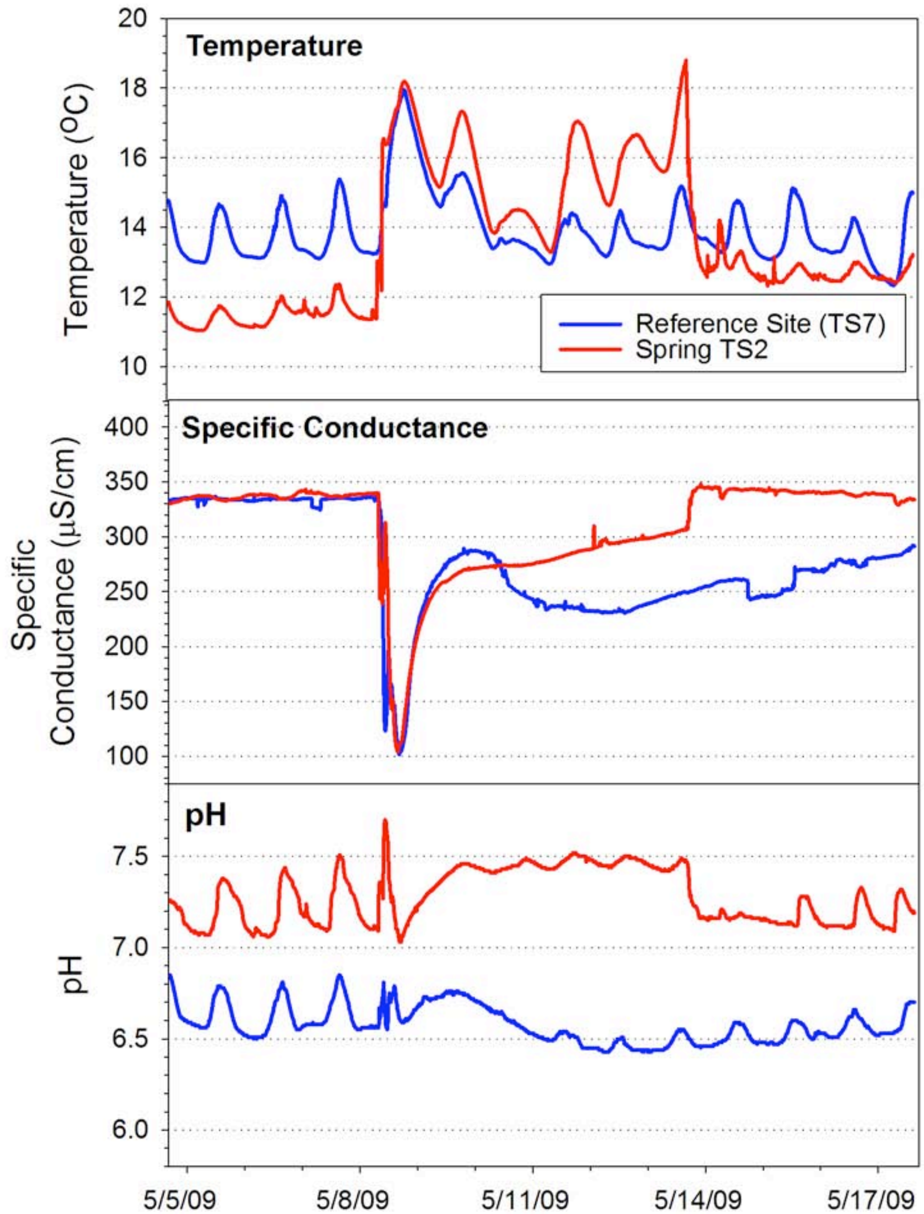


Figure A-2: Warm season time series data for Spring TS2 compared to reference site TS7

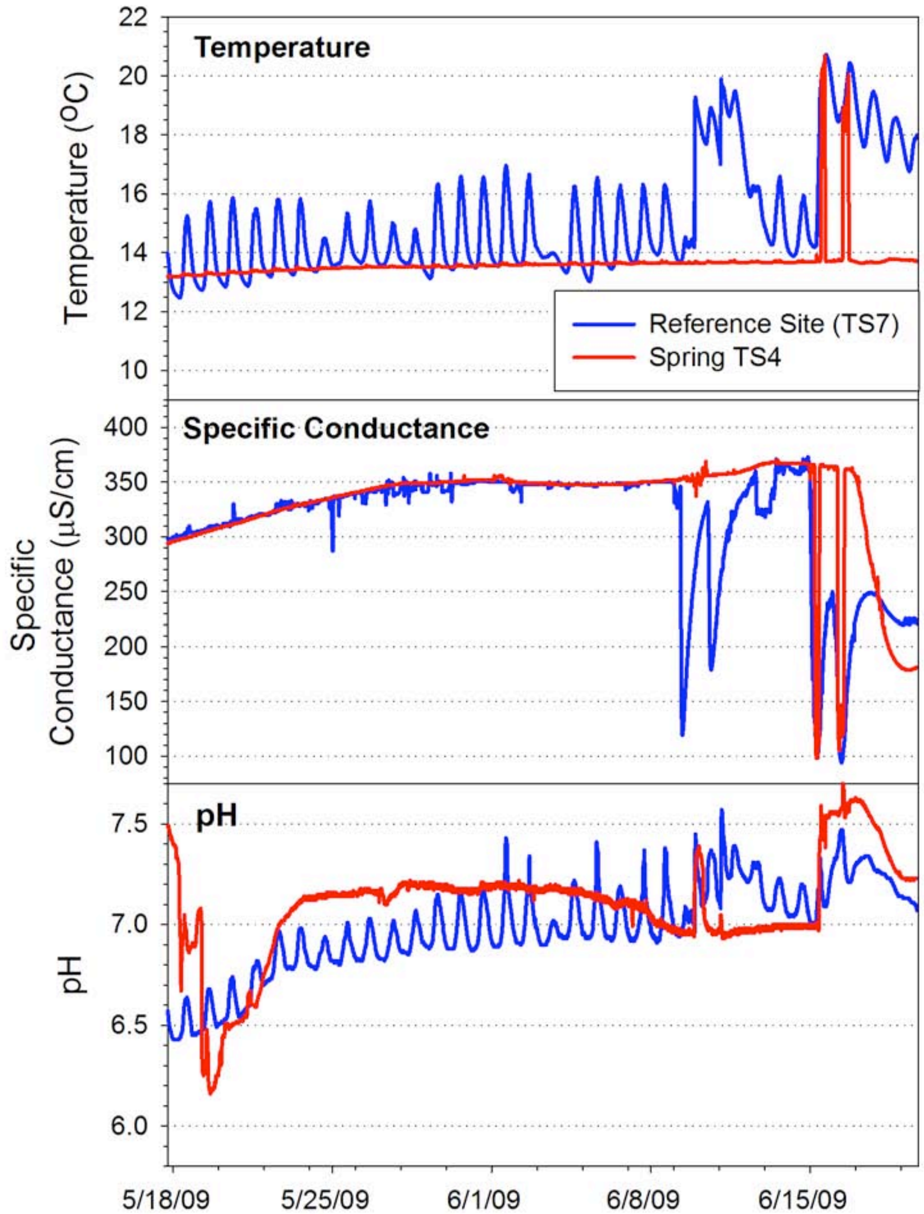


Figure A-314: Warm season time series data for Spring TS4 compared to reference site TS7.

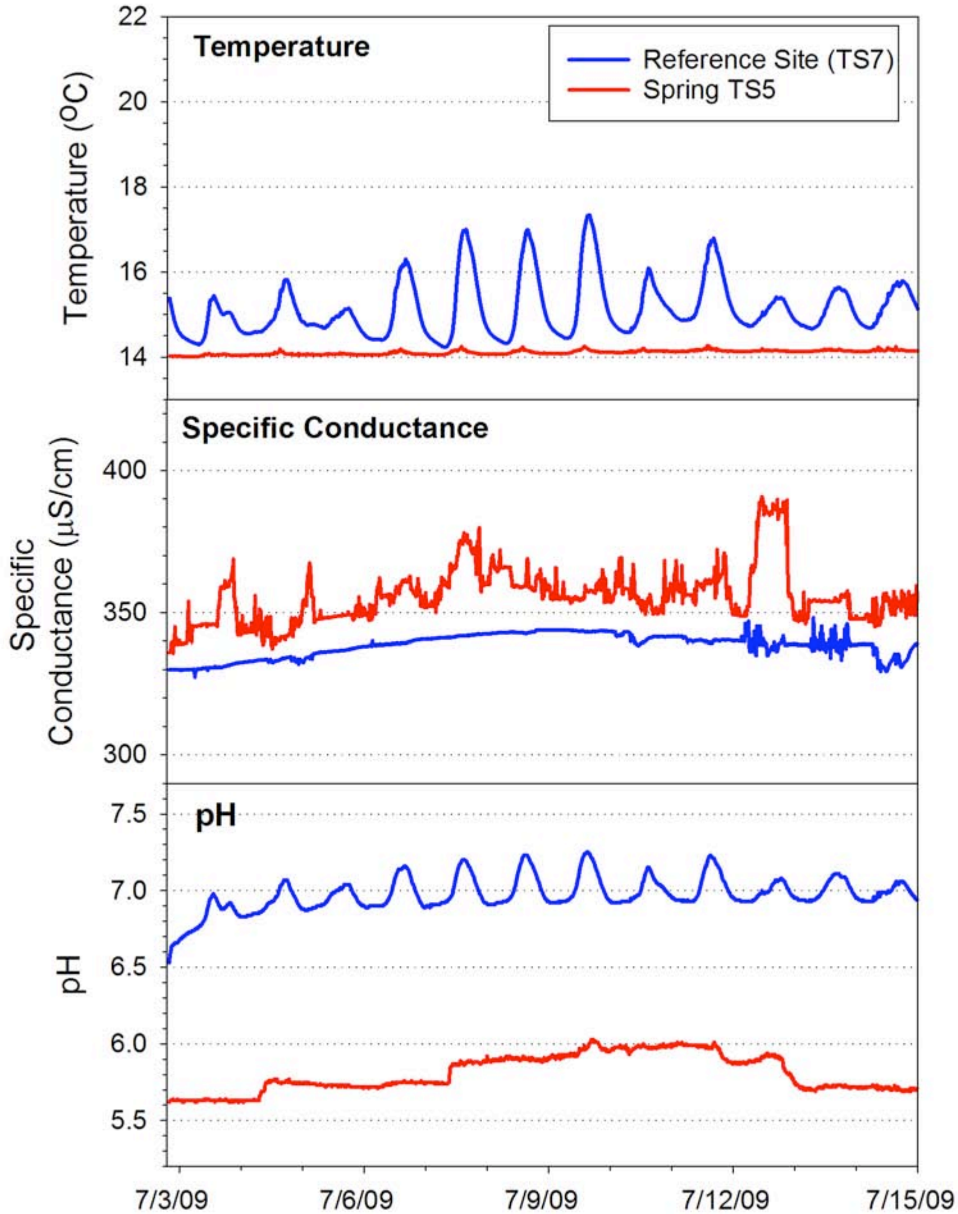


Figure A-4: Warm season time series data for Spring TS5 compared to reference site TS7.

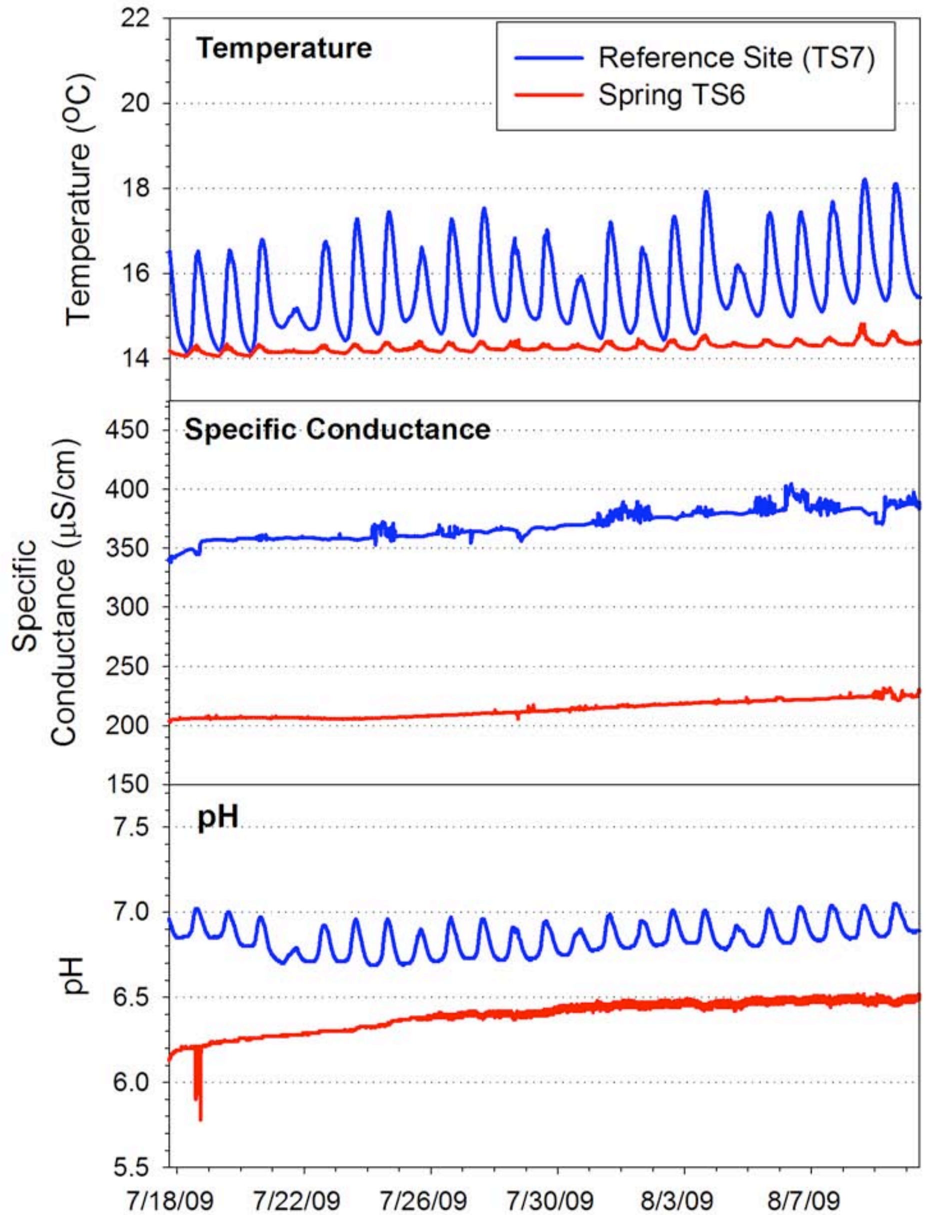


Figure A-5: Warm season time series data for Spring TS6 compared to reference site TS7.

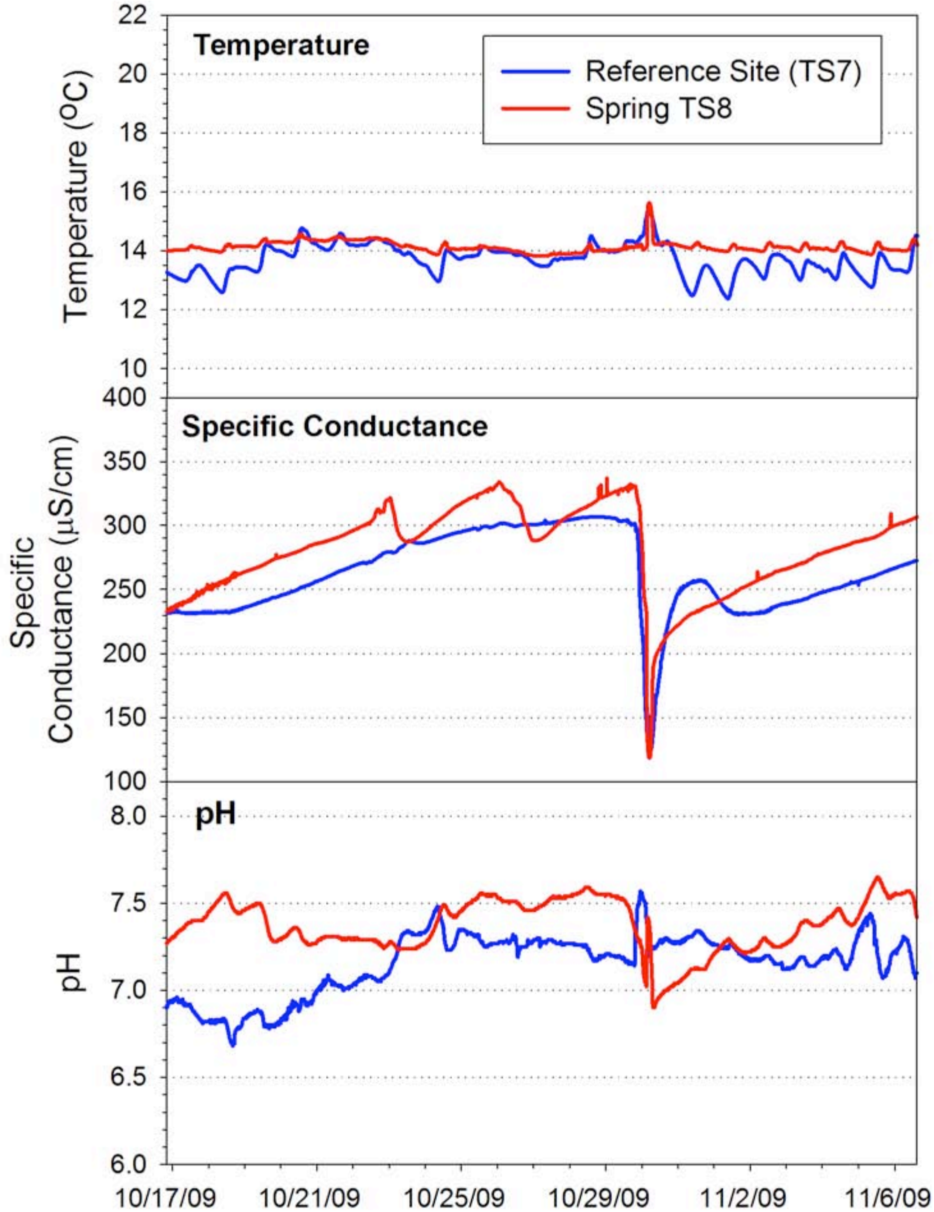


Figure A-6: Cool season time series data for Spring TS8 compared to reference site TS7.

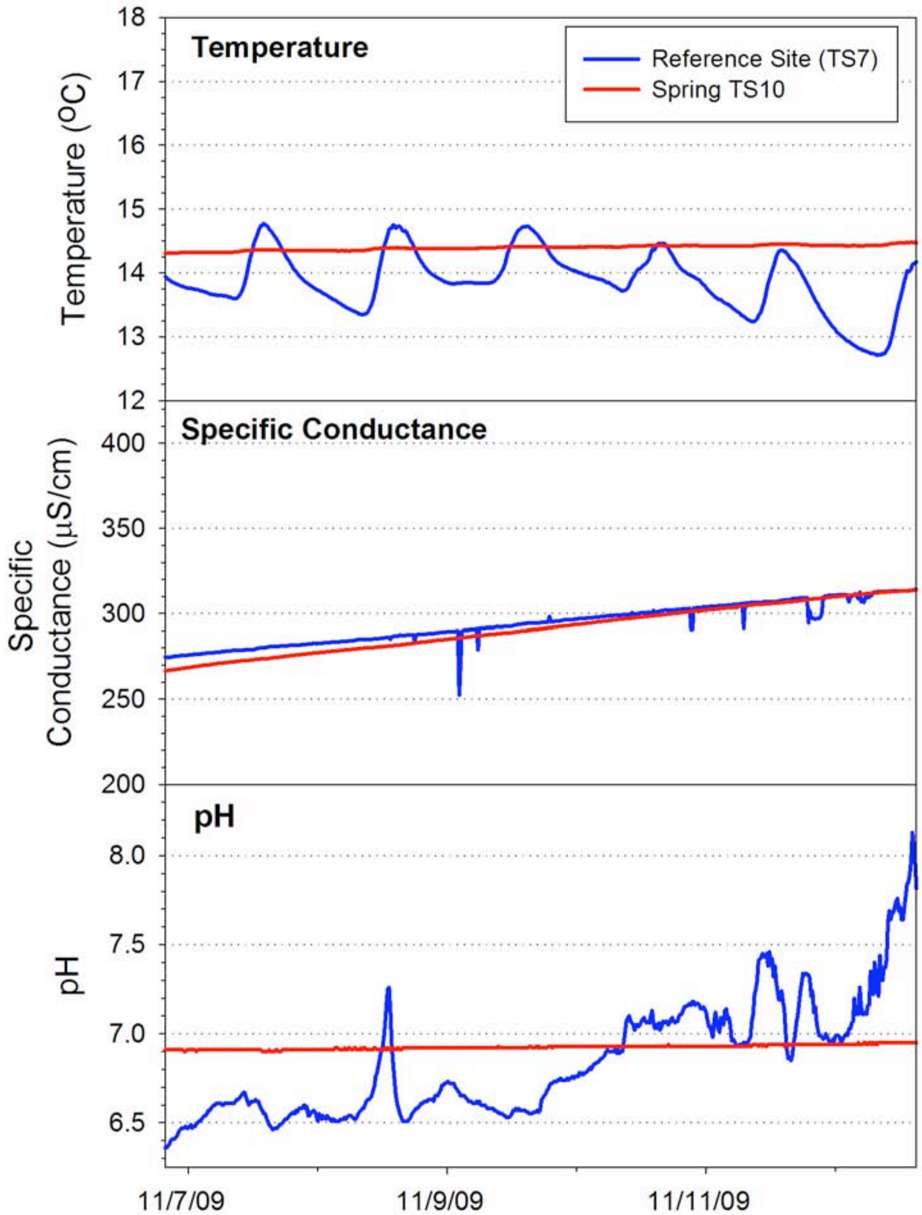


Figure A-7: Cool season time series data for Spring TS10 compared to reference site TS7.

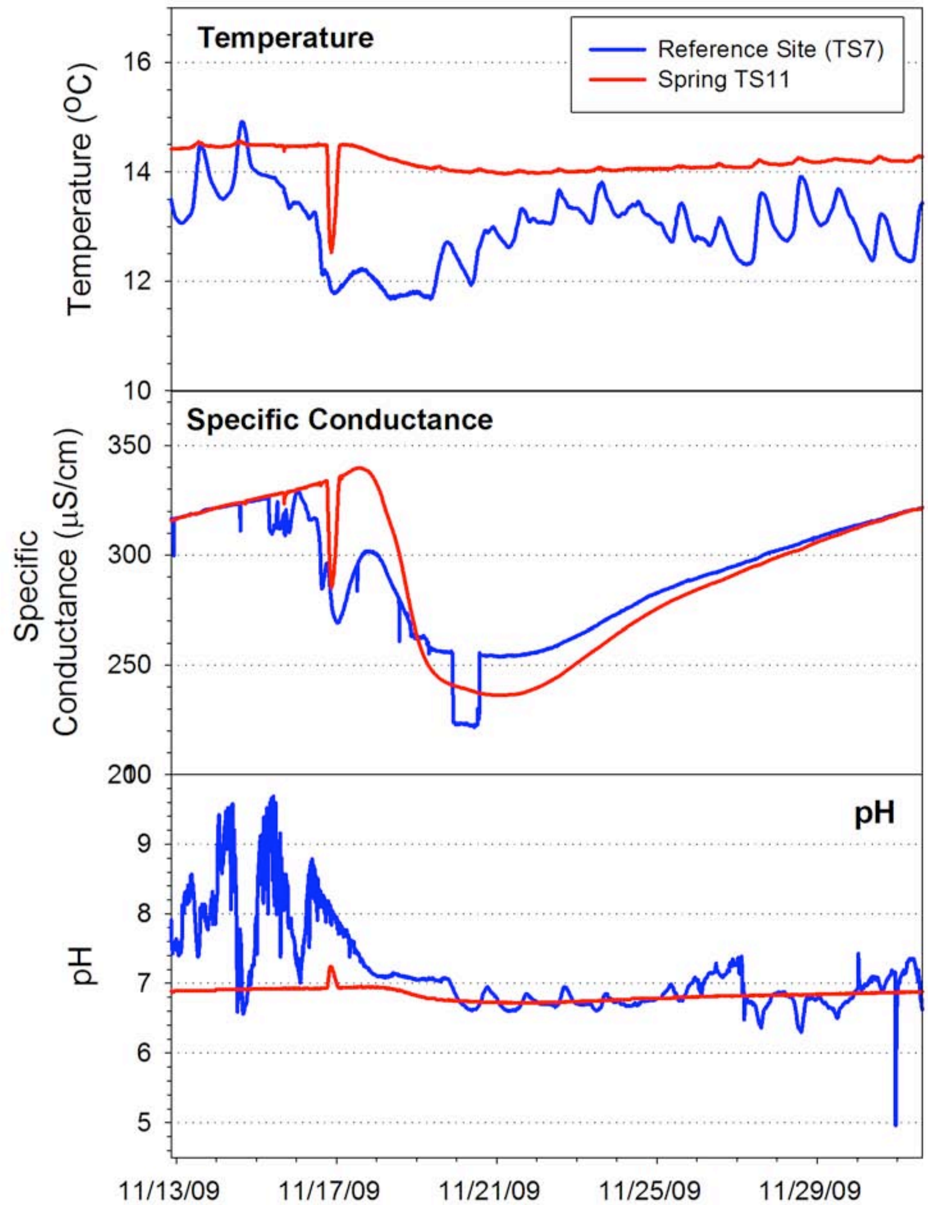


Figure A-8: Time series data for Spring TS11 compared to reference site TS7.

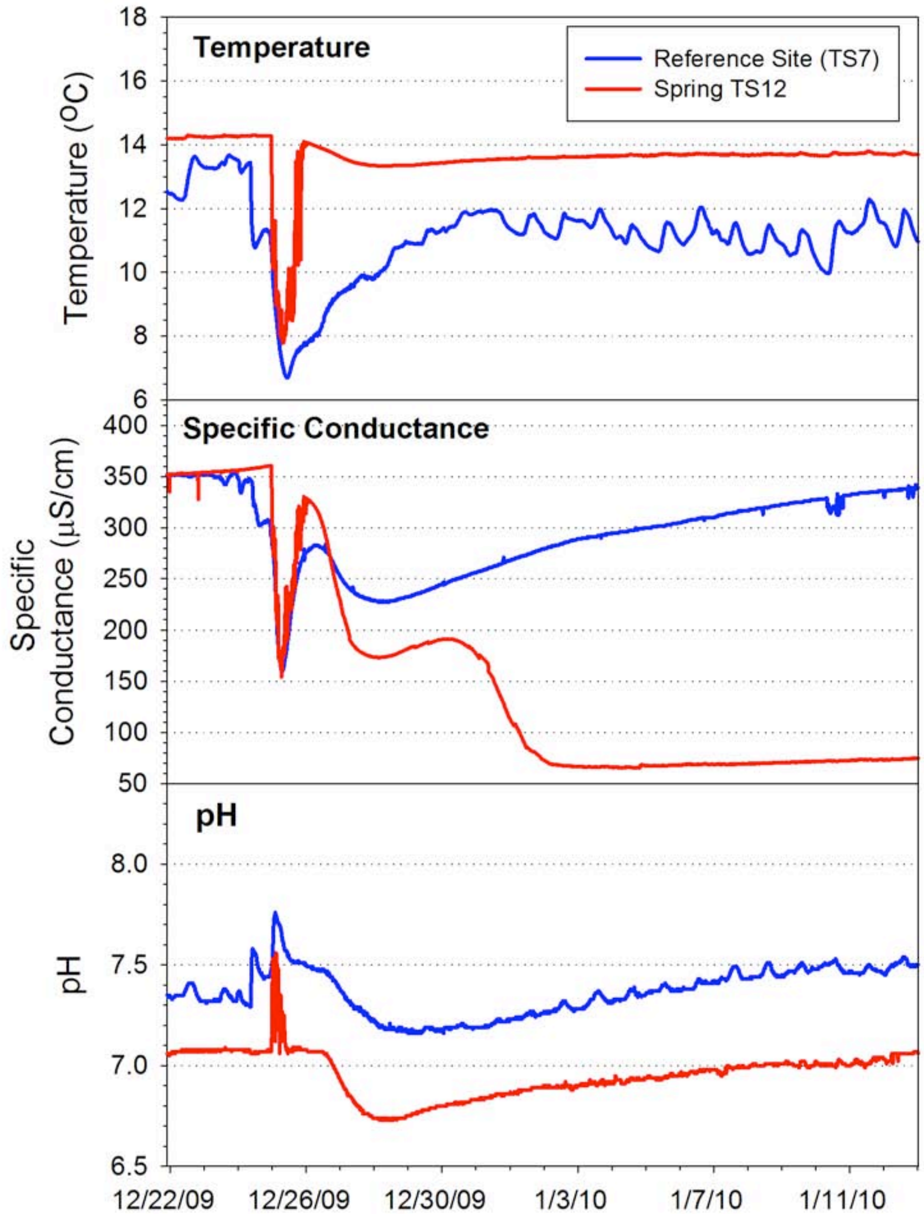


Figure A-9: Cool season time series data for Spring TS12 compared to reference site TS7.

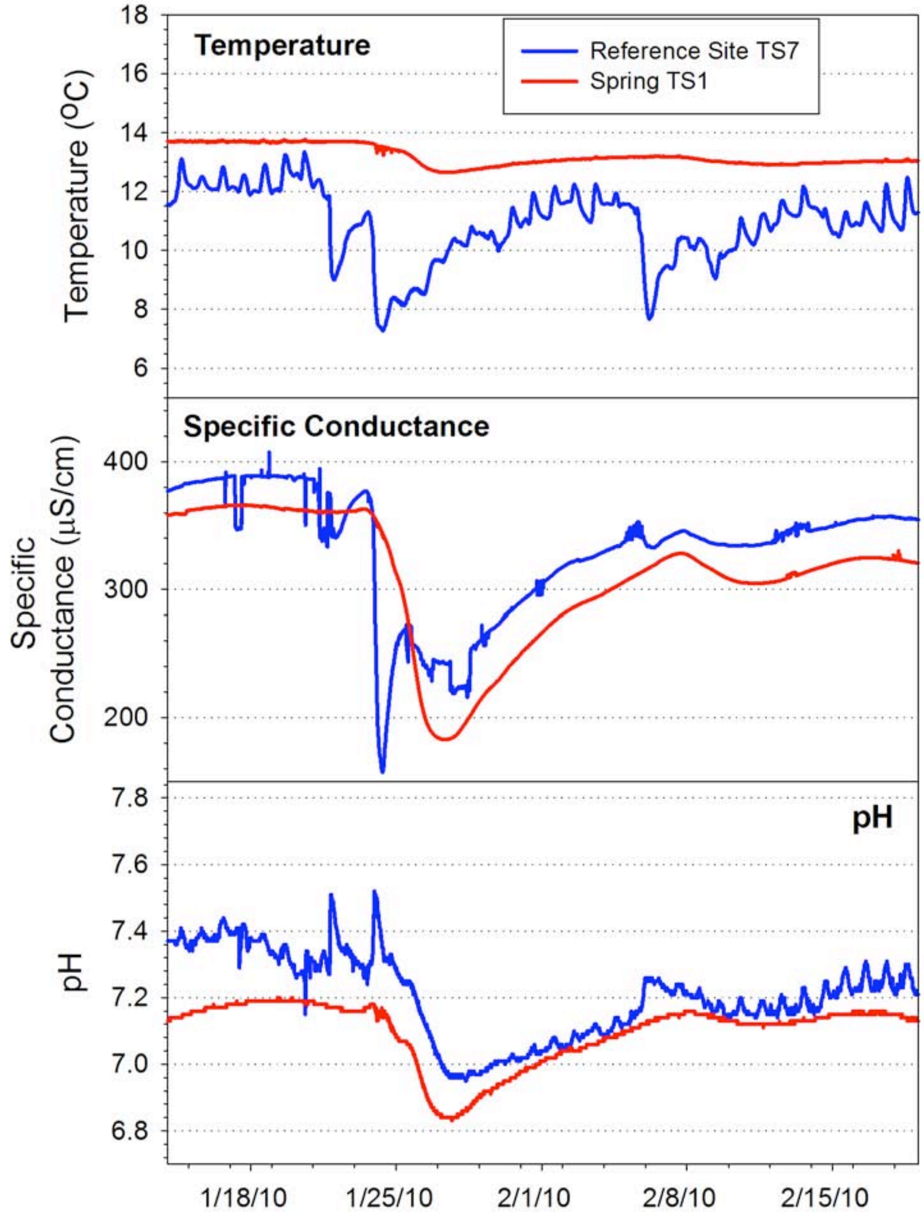


Figure A-10: Cool season time series data for Spring TS1 compared to reference site TS7.

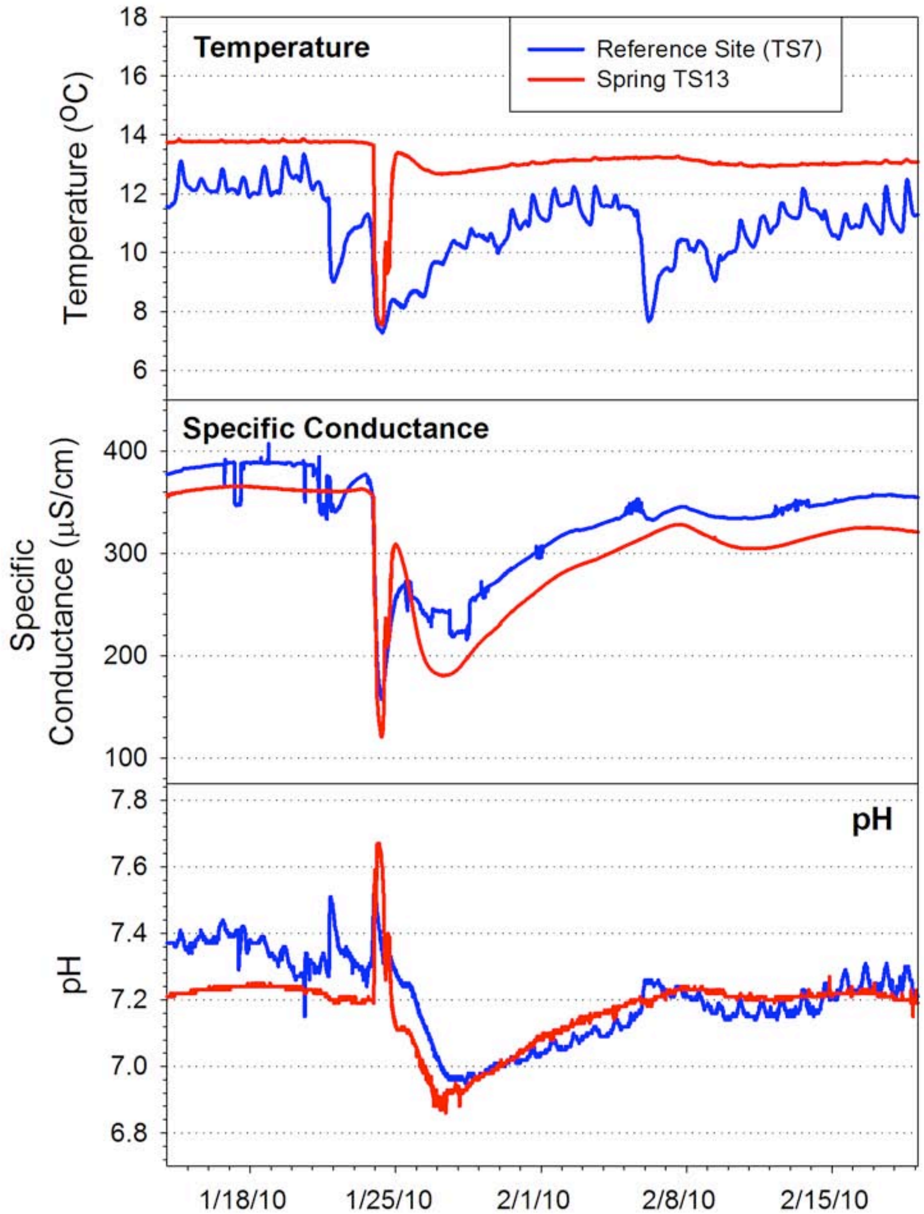


Figure A-11: Cool season time series data for Spring TS13 compared to reference site TS7.

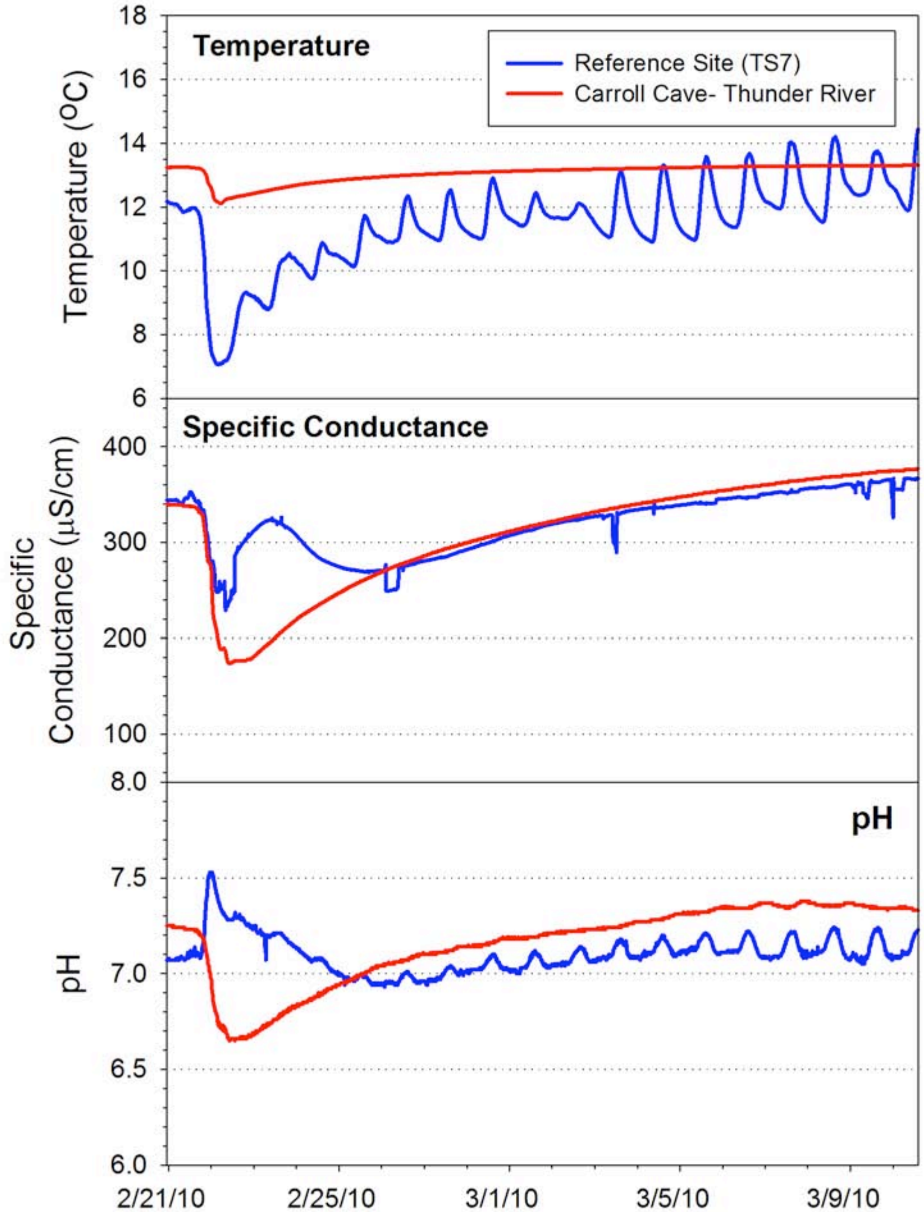


Figure A-12: Cool season time series data for Thunder River in Carroll Cave (CC1) compared to reference site TS7.

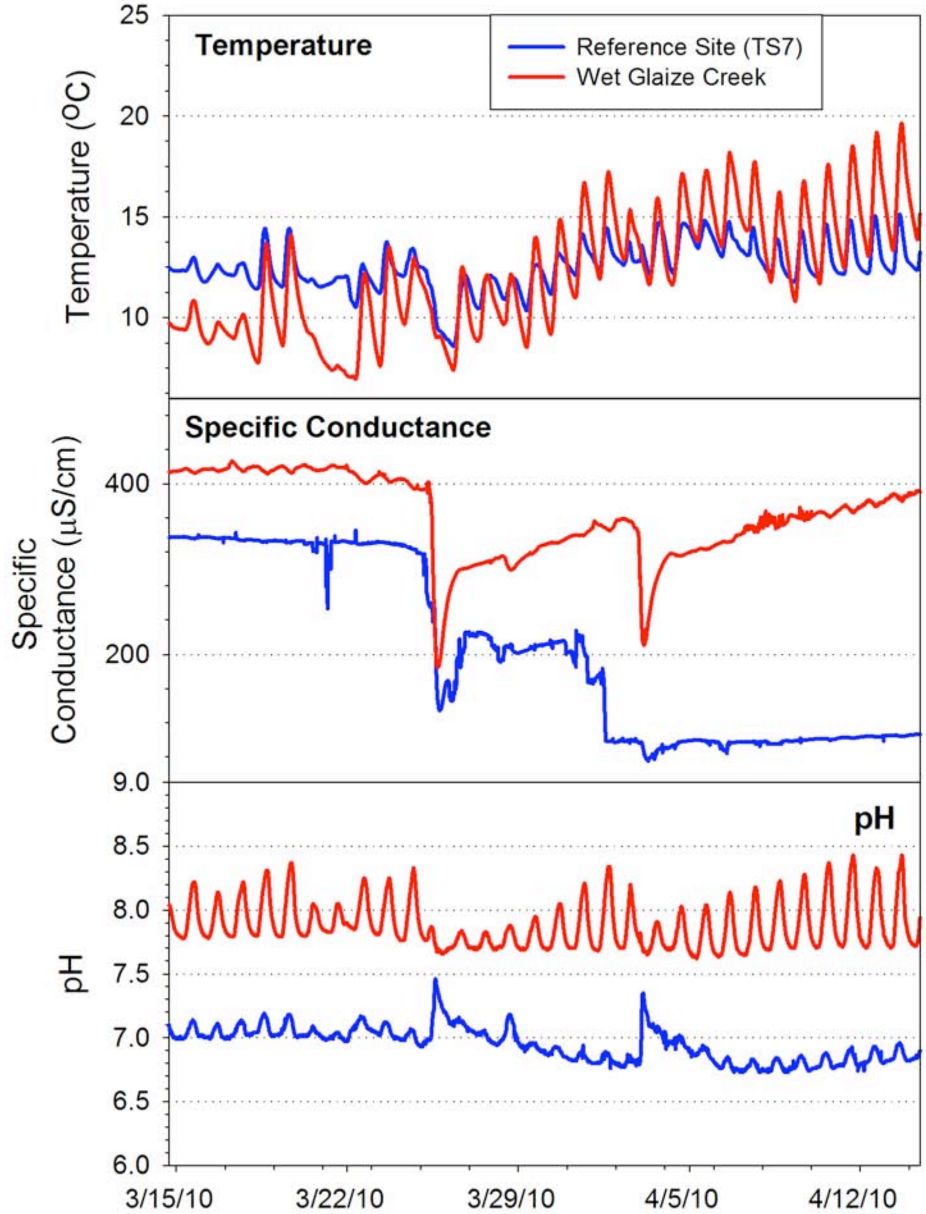


Figure A-13: Cool season time series data for Wet Glaize Creek (WG1) compared to reference site TS7.

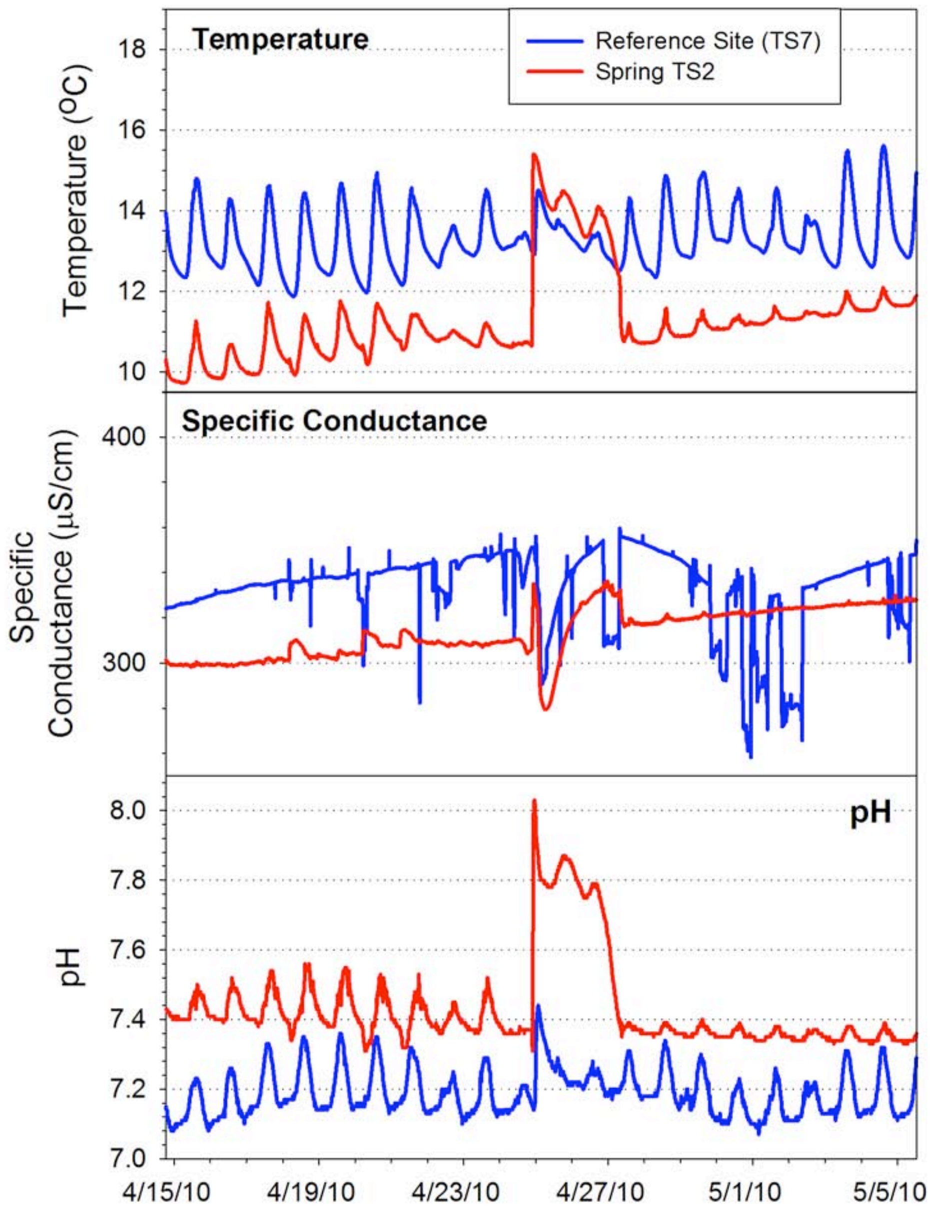


Figure A-14: Warm season time series data, set 2, for Spring TS2 compared to reference site TS7.

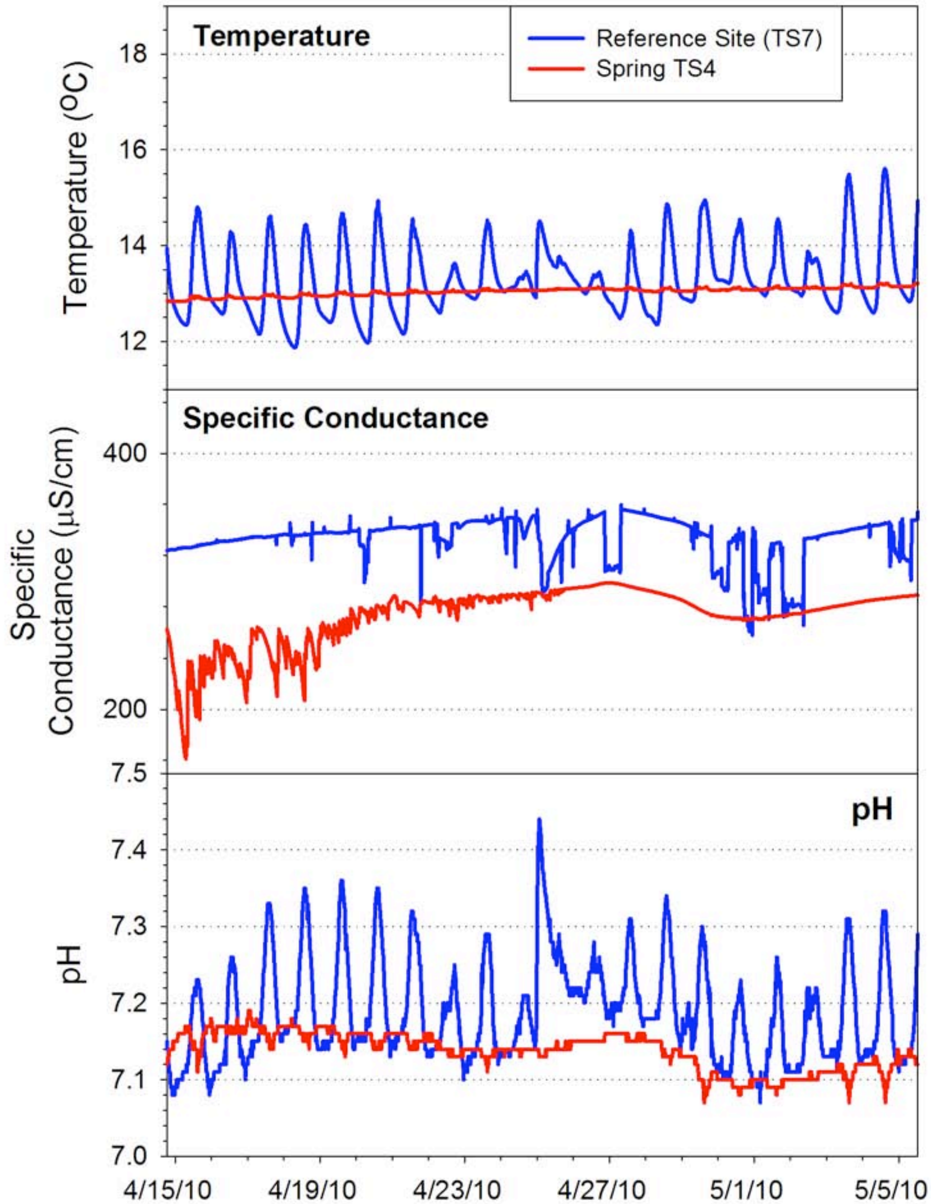


Figure A-15: Warm season time series data, set 2, for Spring TS4 compared to reference site TS7.

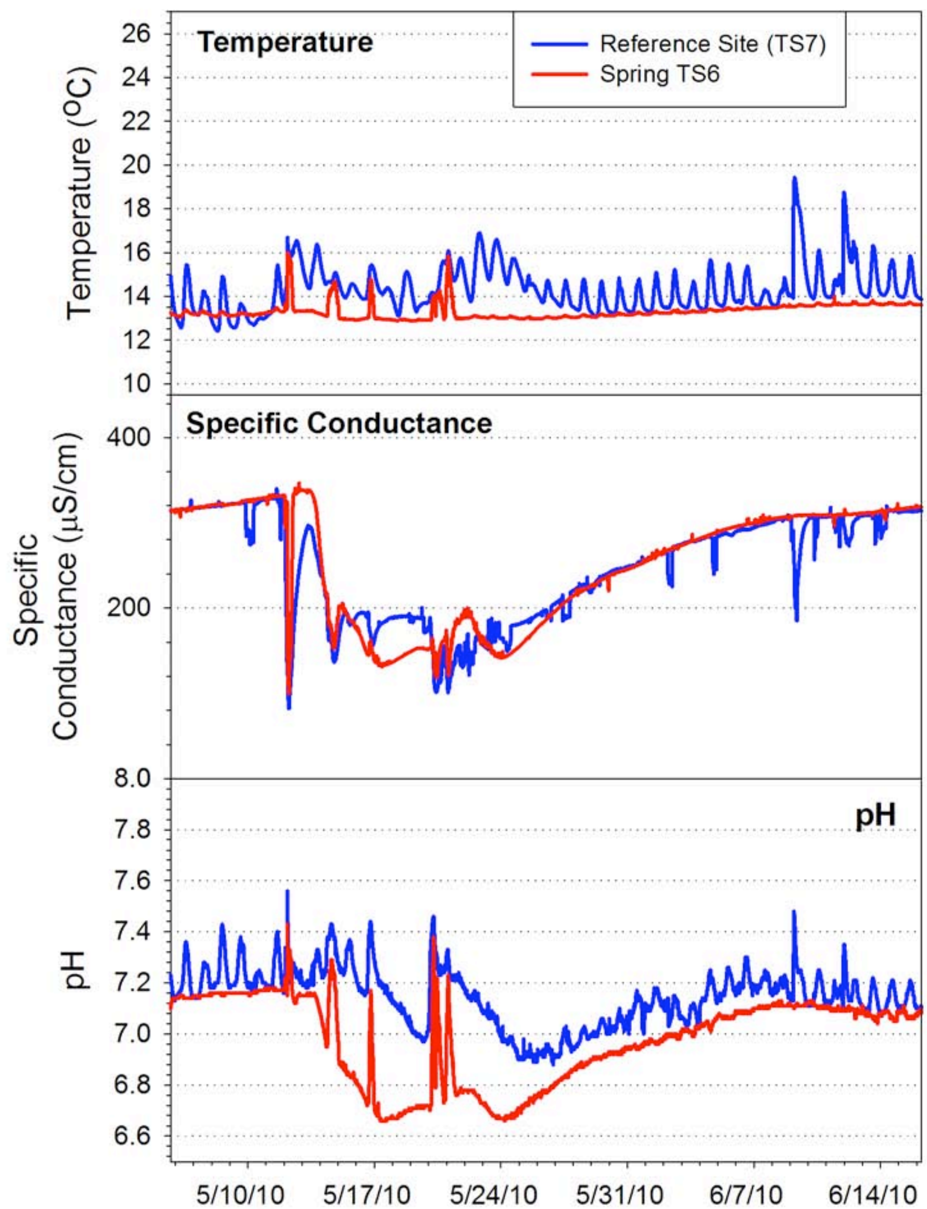


Figure A-16: Warm season time series data, set 2, for Spring TS6 compared to reference site TS7.

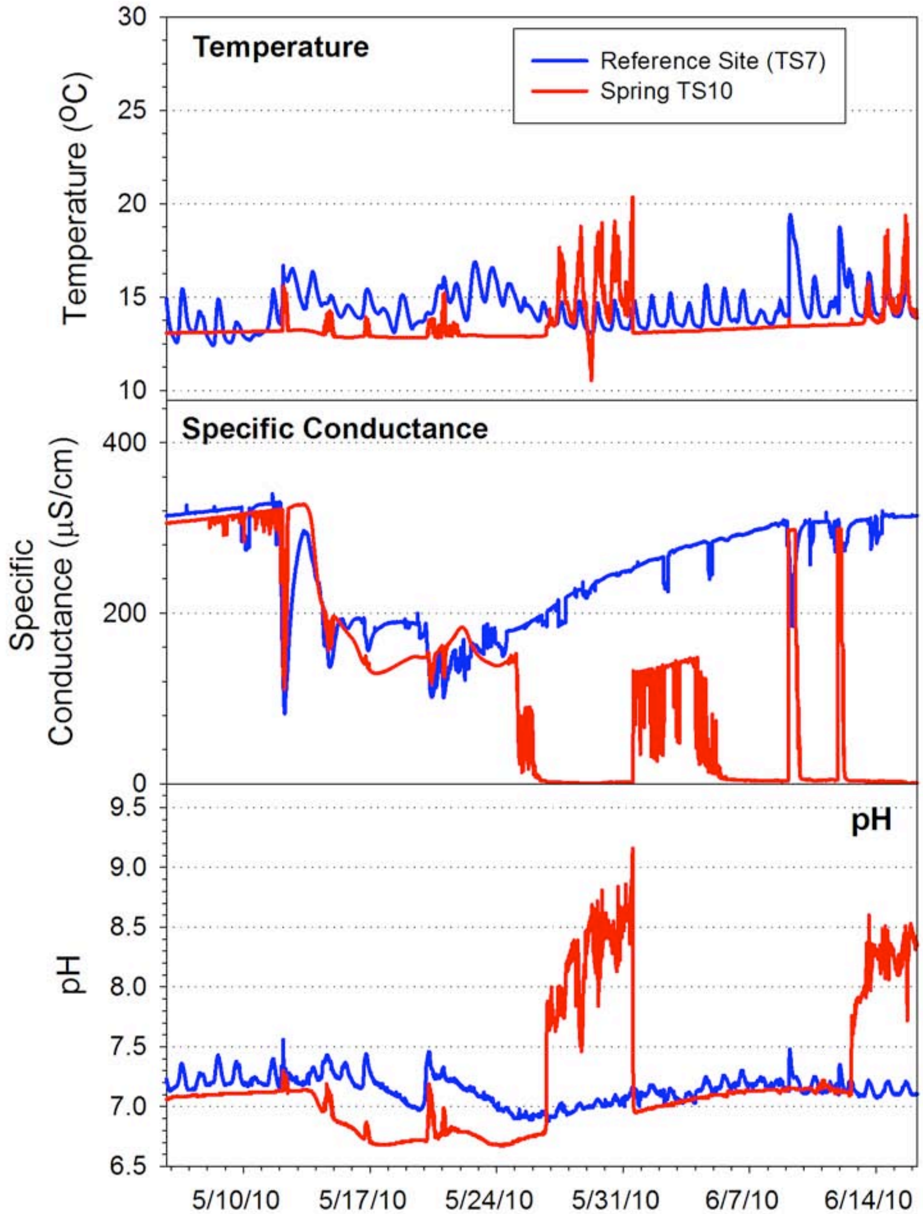


Figure A-17: Warm season time series data for Spring TS10 compared to reference site TS7.

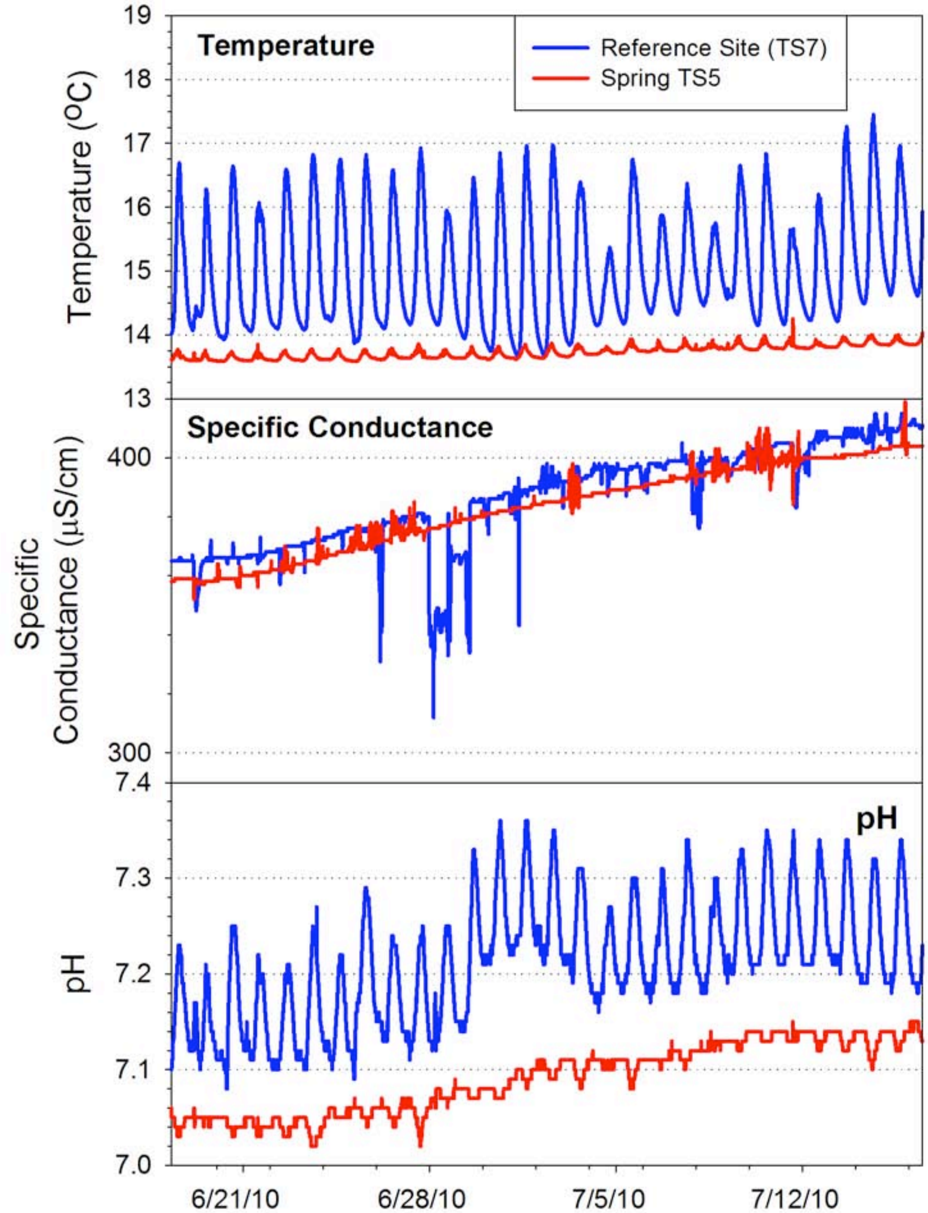


Figure A-18: Warm season time series data, set 2, for Spring TS5 compared to reference site TS7.

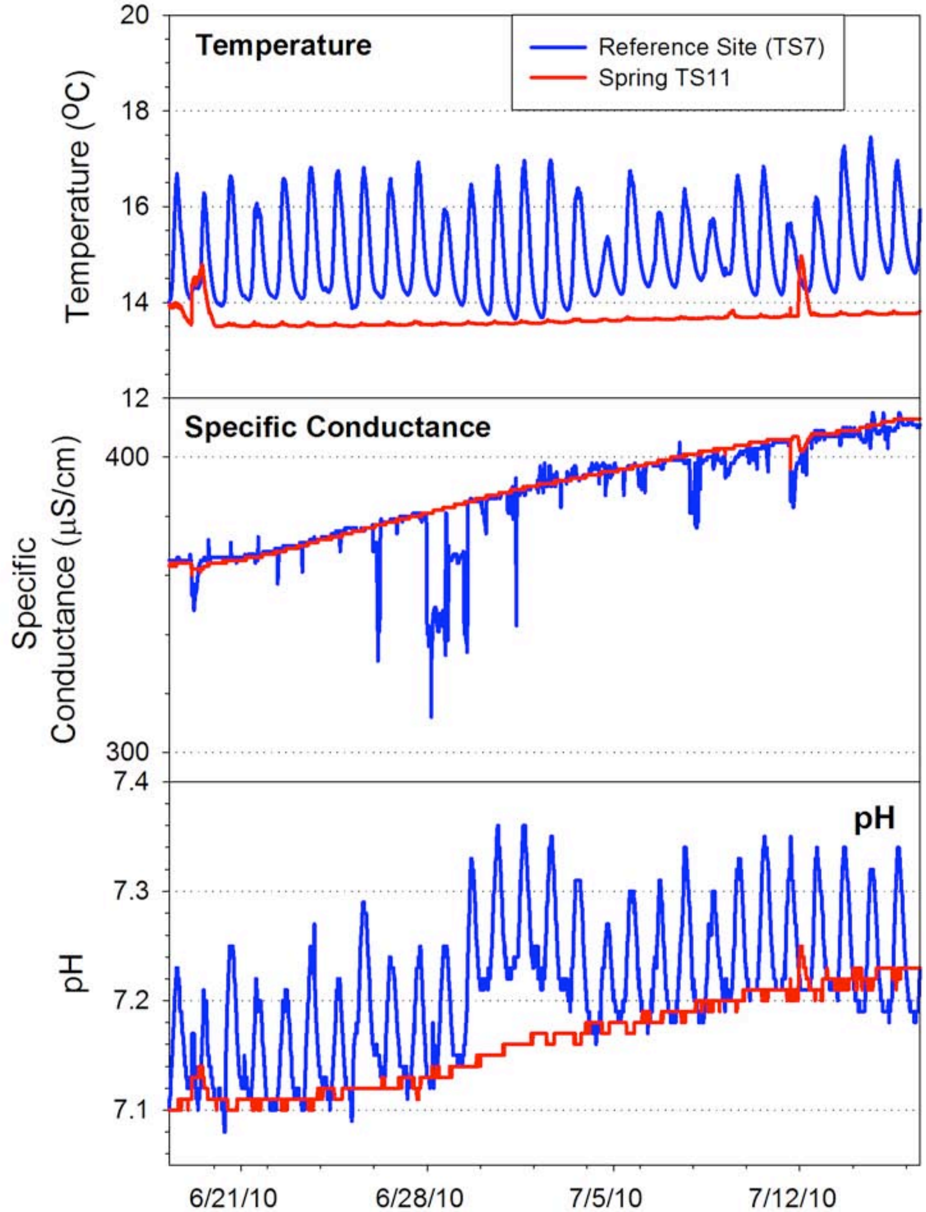


Figure A-19: Warm season time series data for Spring TS11 compared to reference site TS7.

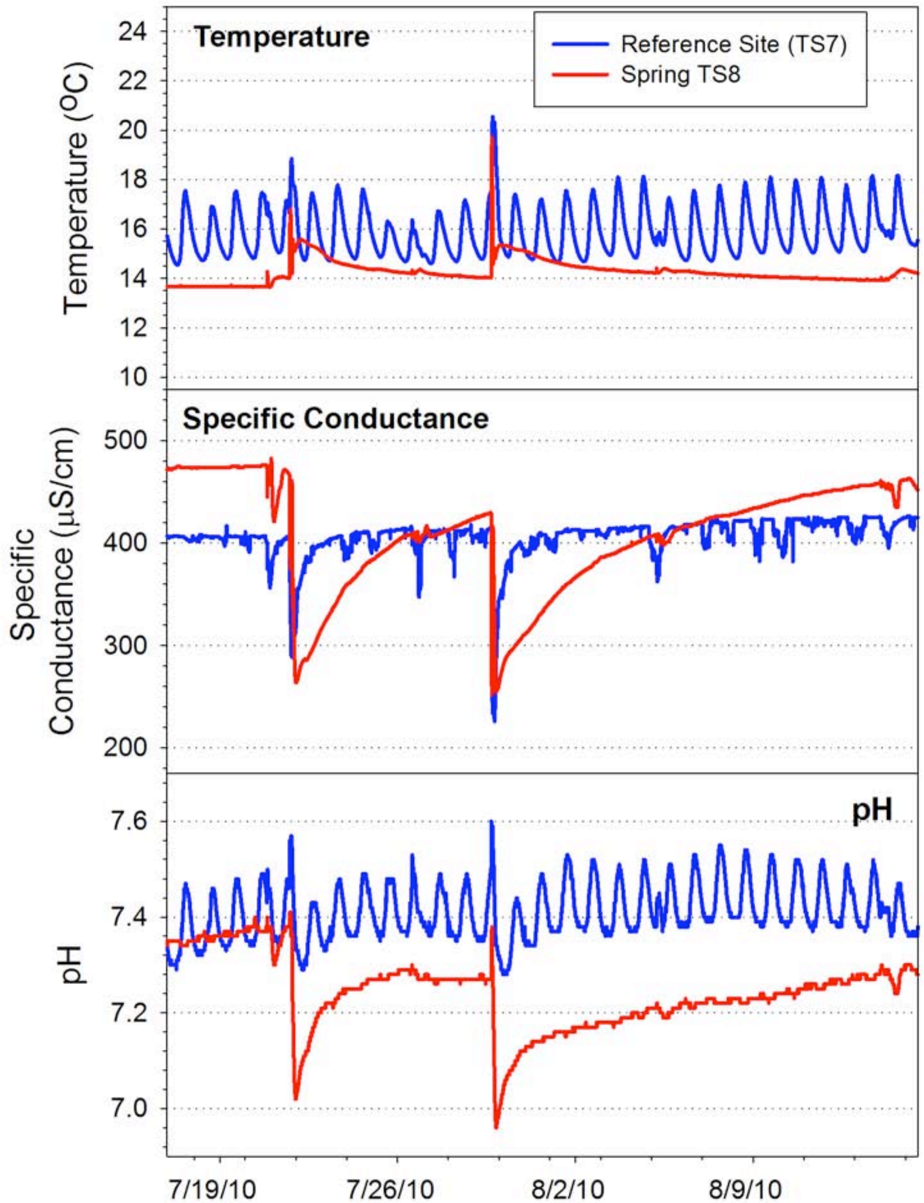


Figure A-20: Warm season time series data for Spring TS8 compared to reference site TS7.

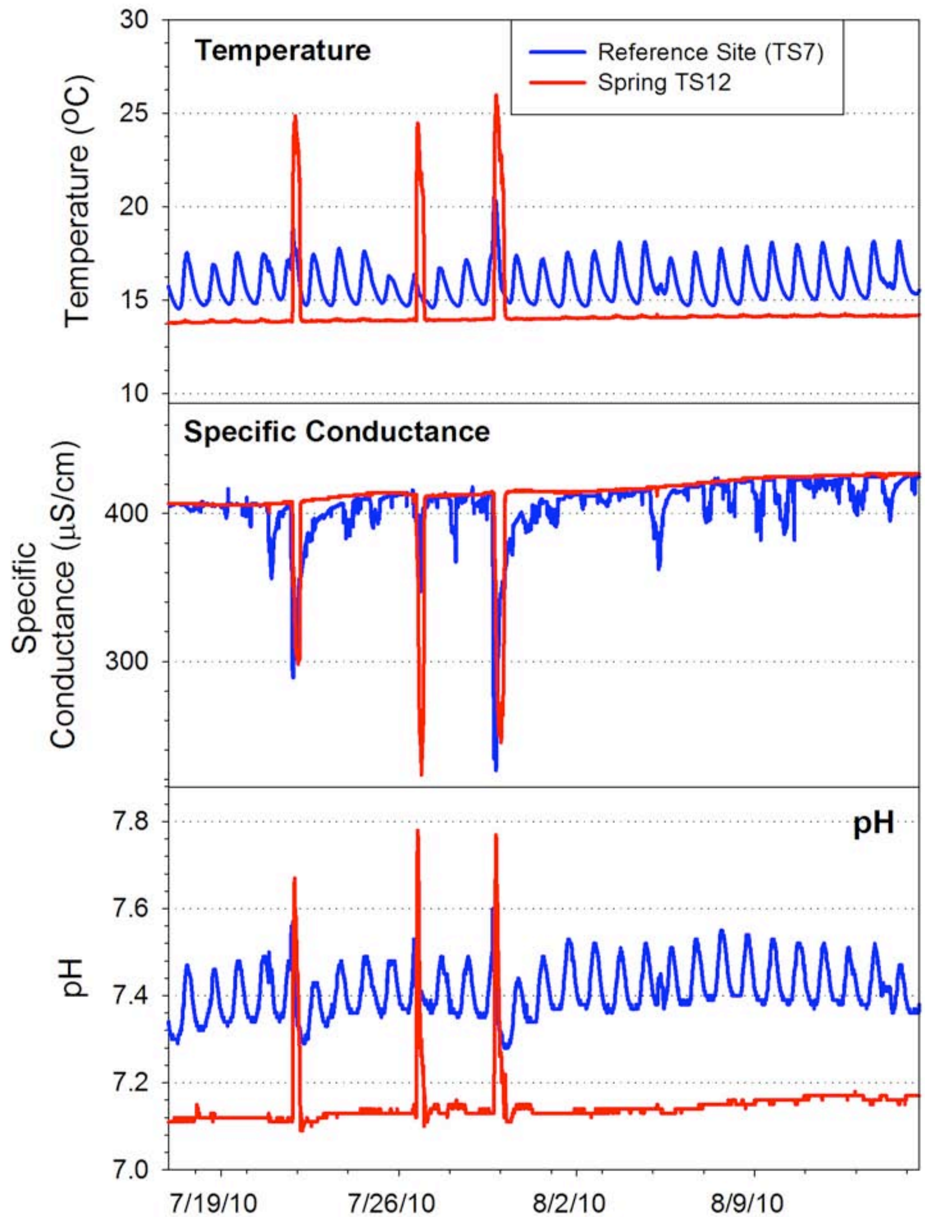


Figure A-21: Warm season time series data for Spring TS12 compared to reference site TS7.

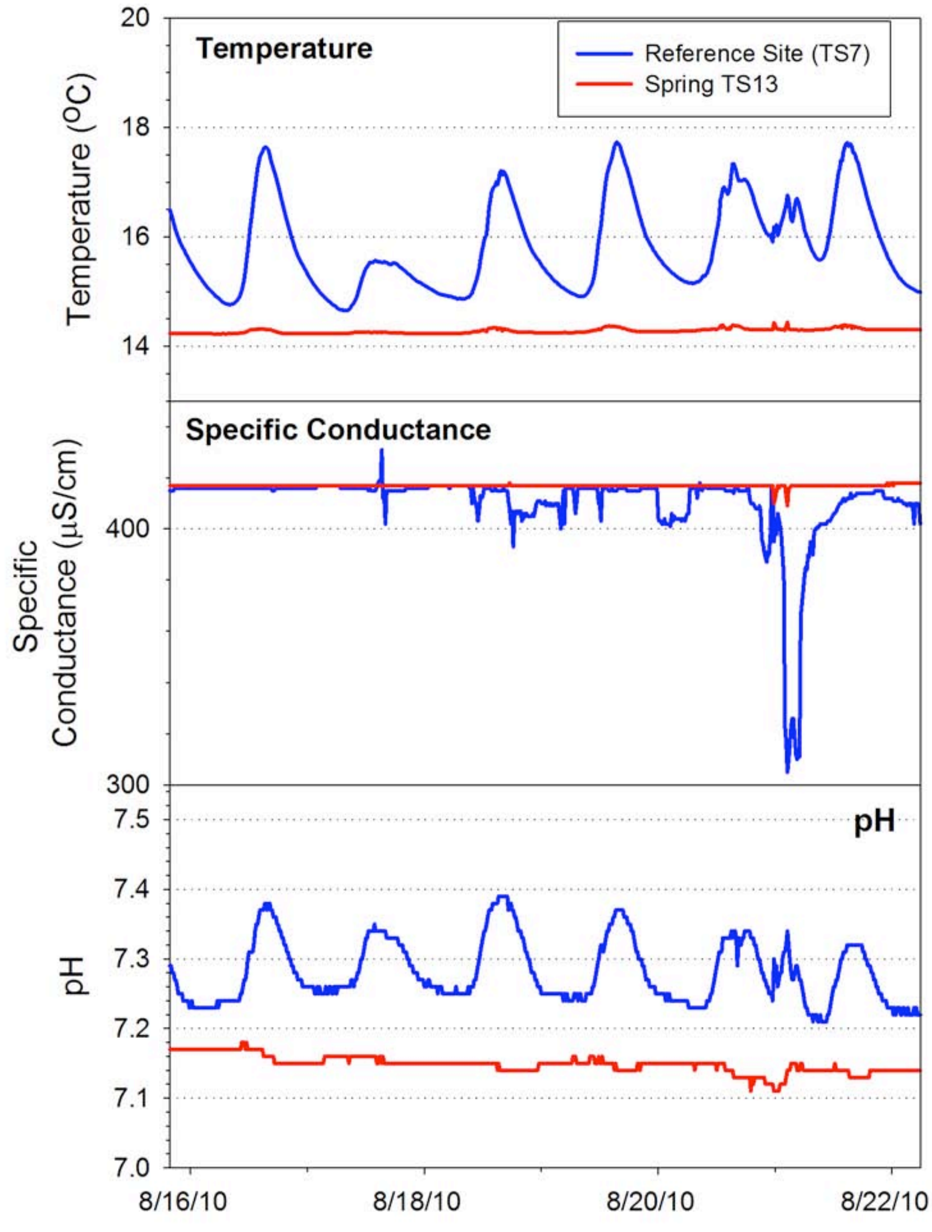


Figure A-22: Warm season time series data for Spring TS13 compared to reference site TS7.

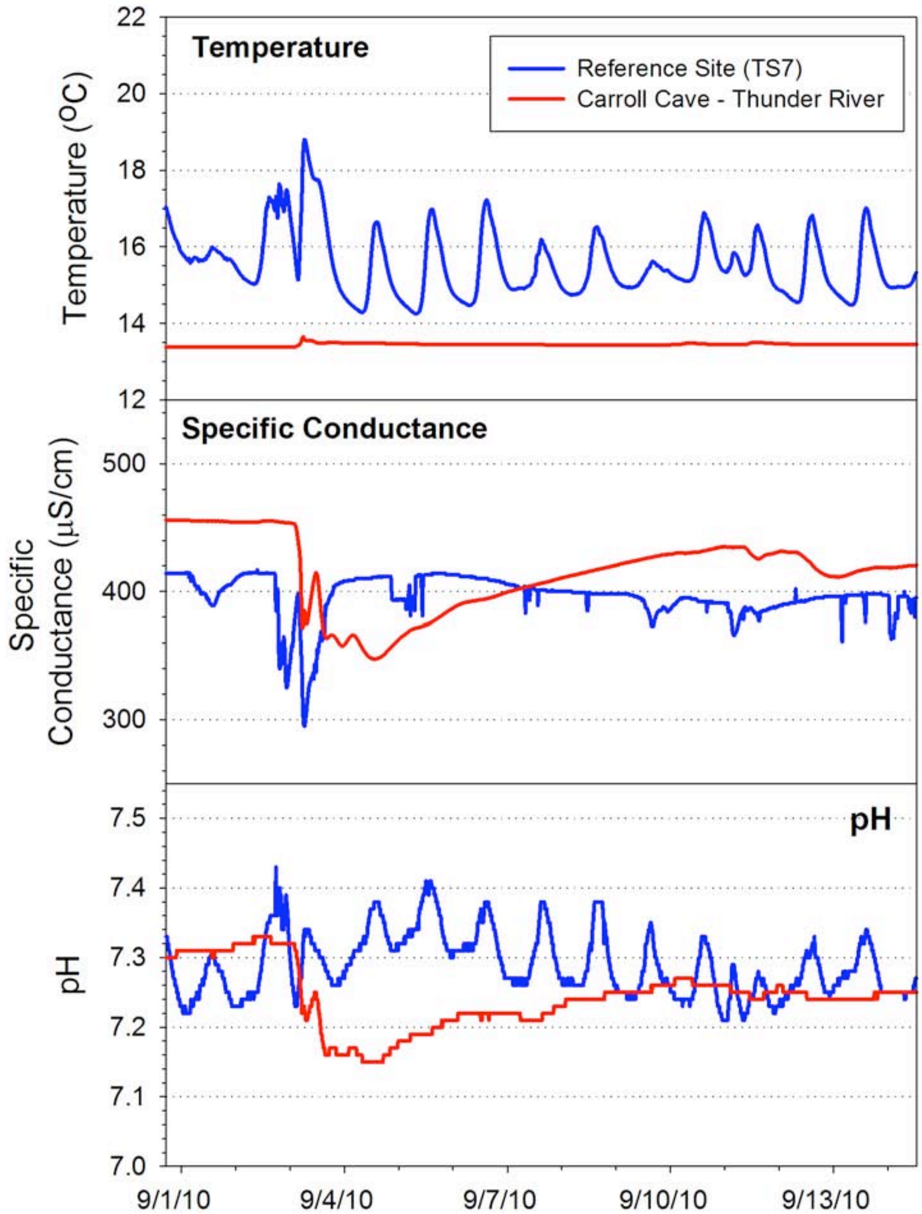


Figure A-23: Warm season time series data for Thunder River in Carroll Cave (CC1) compared to reference site TS7

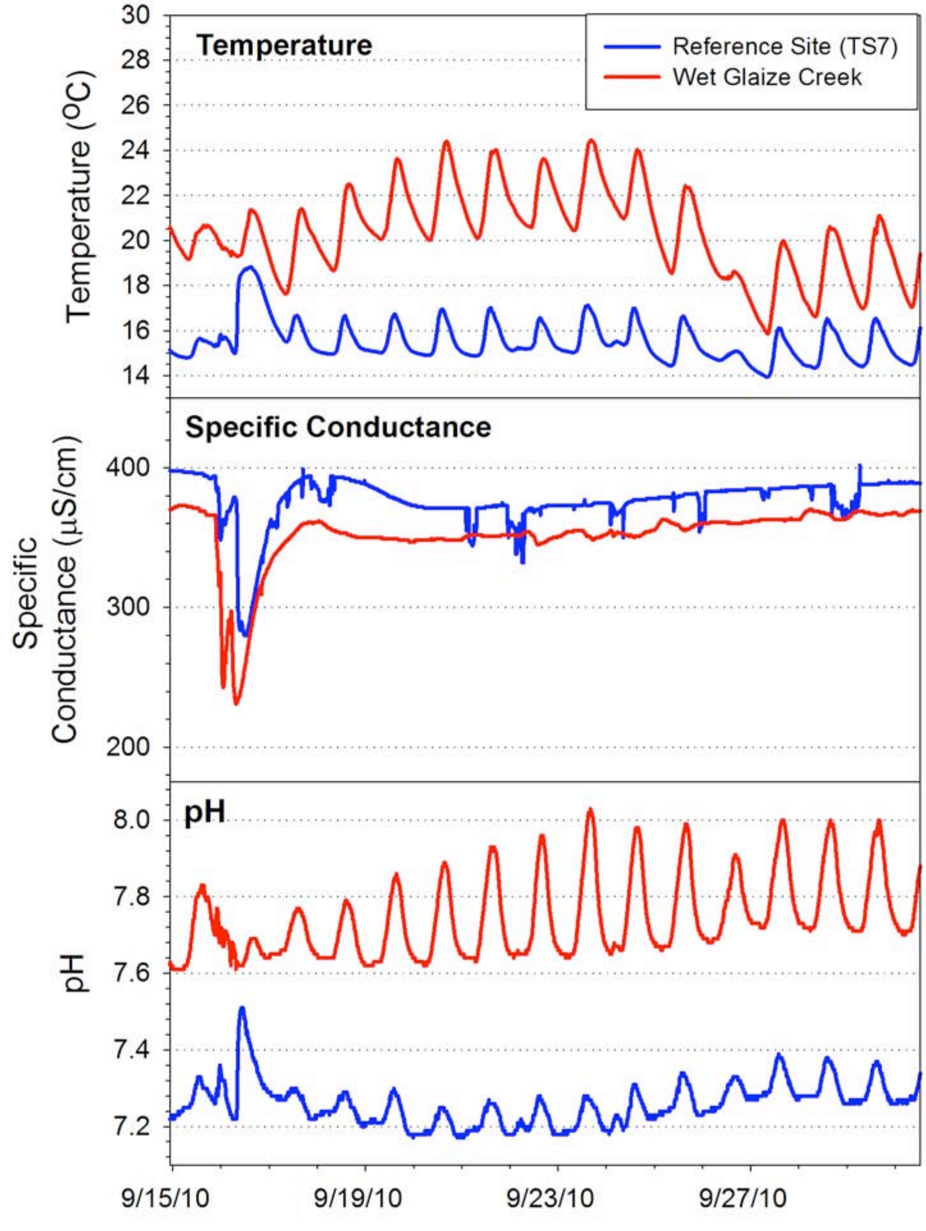


Figure A-24: Warm season time series data for Wet Glaize Creek (WG1) compared to reference site TS7.

Appendix B.
Ion Analysis Data

February 21, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	NO_2^{-} (mg/L)	Br^{-} (mg/L)	NO_3^{-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	2/21/10	7.80	-	286.0	30.4	22.0	1.20	3.80	192	n.a.	4.76	n.a.	n.a.	1.61	n.a.	6.6
TS1	2/21/10	7.29	-	308.0	34.3	31.2	1.10	3.50	197	0.01	4.16	n.a.	n.a.	3.09	0.08	5.07
TS2	2/21/10	7.84	-	288.0	31.2	23.4	1.20	3.90	194	0.01	4.65	n.a.	n.a.	1.48	n.a.	6.55
TS4	2/21/10	7.05	-	307.0	35.6	25.0	1.00	3.50	203	0.01	4.02	n.a.	n.a.	2.94	n.a.	5.16
TS5	2/21/10	7.04	-	307.0	33.2	23.8	1.10	3.50	202	n.a.	4.14	n.a.	n.a.	3	n.a.	5.16
TS6	2/21/10	7.03	-	307.0	35.8	25.8	1.10	3.70	201	0.02	4.14	n.a.	n.a.	3.07	0.08	5.07
TS7	2/21/10	7.21	-	303.0	33.3	24.0	1.10	4.80	196	0.02	6.85	n.a.	n.a.	2.5	n.a.	5.19
TS8	2/21/10	7.60	-	315.0	31.7	23.3	1.80	6.90	191	n.a.	10.79	n.a.	n.a.	3.69	0.14	5.79
TS10	2/21/10	7.10	-	291.0	34.1	24.4	1.20	3.50	200	0.02	4.13	n.a.	n.a.	2.97	n.a.	5.09
TS11	2/21/10	7.04	-	293.0	34.0	23.8	1.00	3.70	198	n.a.	4.16	n.a.	n.a.	3.09	0.06	5.11
TS12	2/21/10	7.05	-	292.0	33.4	23.8	1.10	3.90	199	0.03	3.85	n.a.	n.a.	2.61	n.a.	5.13
TS13	2/21/10	7.12	-	308.0	34.0	24.2	1.20	3.80	201	n.a.	4.09	n.a.	n.a.	2.99	n.a.	5.13
CC1	2/21/10	7.40	-	295.0	33.4	22.7	1.50	4.50	187	0.02	7.44	n.a.	n.a.	5.12	0.12	4.8

March 11, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	NO_2^{-} (mg/L)	Br^{-} (mg/L)	NO_3^{-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	3/11/10	8.10	-	298.0	32.9	29.7	1.20	4.50	213							
TS1	3/11/10	7.23	-	370.0	35.5	29.6	1.00	4.10	232							
TS2	3/11/10	7.18	-	328.0	30.7	26.5	1.10	4.10	206							
TS4	3/11/10	7.13	-	369.0	36.0	30.3	1.00	3.60	225							
TS5	3/11/10	7.15	-	367.0	35.1	29.5	1.00	3.70	229							
TS6	3/11/10	7.24	-	365.0	36.1	20.9	0.90	3.60	226							
TS7	3/11/10	7.26	-	367.0	35.9	30.3	1.00	4.00	228							
TS8	3/11/10	7.35	-	411.0	40.8	26.0	0.90	3.90	251	n.a	5.39	n.a	n.a	3.47	n.a	6.46
TS10	3/11/10	7.04	-	352.0	36.2	30.5	1.00	3.90	223							
TS11	3/11/10	7.04	-	368.0	36.5	31.0	1.00	4.30	225							
TS12	3/11/10	7.15	-	370.0	37.3	31.5	1.00	4.10	229							
TS13	3/11/10	7.12	-	370.0	36.1	30.2	1.00	3.90	230							
CC1	3/11/10	7.32	-	377.0	40.4	33.9	1.00	4.10	257							

March 28, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	3/28/10	7.77	12.1	249.0	29.2	18.8	1.50	5.10	171							
TS1	3/28/10	6.76	12.5	231.0	26.5	16.2	1.20	4.80	150							
TS2	3/28/10	7.79	11.9	257.0	29.8	19.3	1.50	5.40	162							
TS4	3/28/10	7.02	12.5	230.0	26.2	15.5	1.10	4.10	147							
TS5	3/28/10	6.94	12.5	230.0	28.3	17.3	1.30	4.80	153							
TS6	3/28/10	7.01	12.5	231.0	28.6	17.0	1.30	4.70	149							
TS7	3/28/10	7.43	12.0	251.0	29.3	18.4	1.40	5.40	159	0.02	4.19	n.a	n.a	2.42	n.a	6.62
TS8	3/28/10	7.31	11.0	254.0	30.6	18.9	1.20	4.20	172							
TS10	3/28/10	6.97	12.5	230.5	28.1	16.8	1.40	4.10	152							
TS11	3/28/10	6.99	12.5	231.3	27.9	16.5	1.20	4.30	154							
TS12	3/28/10	-	-	-	-	-	-	-	-							
TS13	3/28/10	7.00	12.5	231.1	28.3	17.2	1.30	3.90	147							
CC1	3/28/10	6.80	12.8	246.8	30.2	18.0	1.40	4.40	152							

April 14, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	4/14/10	7.64	16.0	343.0	35.7	23.8	1.30	3.95	220							
TS1	4/14/10	6.38	13.0	343.9	37.3	23.5	1.10	3.74	218							
TS2	4/14/10	7.22	11.3	318.9	34.9	22.4	1.50	3.78	199							
TS4	4/14/10	6.90	12.9	344.5	36.9	23.9	1.00	3.60	223							
TS5	4/14/10	7.11	13.0	347.1	39.4	25.6	1.00	3.61	223							
TS6	4/14/10	7.17	13.1	329.3	38	24.6	1.10	3.66	218							
TS7	4/14/10	7.02	15.3	294.2	38.0	24.4	1.00	3.77	221							
TS8	4/14/10	7.12	12.5	371.2	39.8	26.3	1.00	3.36	237							
TS10	4/14/10	6.81	12.9	341.1	36.4	23.2	1.10	3.69	223							
TS11	4/14/10	6.82	12.9	337.5	37.5	24.4	1.20	3.68	218							
TS12	4/14/10	6.92	12.9	334.8	37.4	24.0	-	3.60	223							
TS13	4/14/10	6.90	12.9	335.5	37.0	23.6	-	3.47	217	0.01	6.63	n.a	n.a	5.4	n.a	4.9
CC1	4/14/10	7.08	13.3	381.4	44.5	28.2	-	3.99	242	0.01	6.79	n.a.	n.a.	5.9	n.a.	4.97

April 26, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	NO_2^{-} (mg/L)	Br^{-} (mg/L)	NO_3^{-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	4/26/10	7.04	13.6	336.0	34.3	21.3	1.29	3.26	231							
TS1	4/26/10	7.03	13.1	367.3	38.5	22.6	1.07	3.05	244							
TS2	4/26/10	7.69	13.5	335.5	33.8	20.8	1.36	3.53	221							
TS4	4/26/10	7.11	13.1	368.4	37.9	22.4	1.06	3.01	247							
TS5	4/26/10	7.30	13.4	377.8	38.7	22.9	1.13	3.03	240							
TS6	4/26/10	7.10	13.1	365.1	39.6	23.3	1.16	3.19	242							
TS7	4/26/10	7.43	13.4	361.2	38.1	22.7	1.11	3.17	246							
TS8	4/26/10	7.40	12.5	381.9	40.6	24.4	1.22	3.15	259							
TS10	4/26/10	7.15	13.2	368.3	40.5	23.8	1.07	2.77	248							
TS11	4/26/10	7.13	13.1	364.3	39.6	23.1	1.06	2.74	247							
TS12	4/26/10	7.13	13.1	368.7	39.4	23.1	1.10	2.64	251	0.01	4.18	n.a.	n.a.	3.82	n.a.	5.55
TS13	4/26/10	7.14	13.1	368.6	40.8	40.8	1.09	2.72	242							
CC1	4/25/10	7.04	13.3	334.0	35.7	35.7	1.38	3.01	215							

May 31, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	5/31/10	7.98	19.6	287.1	28.2	21.5	1.91	3.81	206							
TS1	5/31/10	6.91	13.2	273.9	28.2	21.5	1.92	3.70	185							
TS2	5/31/10	7.11	14.3	284.2	26.8	21.0	1.73	3.59	169							
TS4	5/31/10	6.85	13.2	280.6	27.0	21.1	1.82	3.86	187							
TS5	5/31/10	6.85	13.2	280.8	27.3	21.2	1.71	3.31	188							
TS6	5/31/10	6.72	13.3	281.0	28.0	21.4	1.80	3.39	191	0.04	3.34	n.a.	n.a.	2.62	n.a.	4.57
TS7	5/31/10	7.08	14.3	285.3	27.2	21.2	1.68	3.43	190							
TS8	5/31/10	6.94	13.3	330.4	32.7	23.4	1.73	3.14	220							
TS10	5/31/10	6.82	13.2	282.2	28.0	21.2	1.78	3.35	187							
TS11	5/31/10	6.79	13.2	278.2	27.7	21.1	1.71	3.27	188							
TS12	5/31/10	-	-	-	-	-	-	-	-							
TS13	5/31/10	6.84	13.3	282.4	27.8	21.3	1.84	3.13	195							
CC1	5/31/10	6.64	13.2	318.1	30.3	22.2	1.87	3.50	211							

June 17, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	6/17/10	7.48	25.4	351.1	32.6	19.4	1.71	3.04	224							
TS1	6/17/10	6.19	13.6	381.3	35.4	21.5	1.46	3.09	240							
TS2	6/17/10	6.51	15.9	331.6	30.1	17.7	1.68	2.99	215							
TS4	6/17/10	6.36	13.8	383.8	36.2	21.6	1.33	2.82	245							
TS5	6/17/10	7.16	13.7	337.3	37.2	22.8	1.38	3.08	248							
TS6	6/17/10	7.00	13.7	376.2	36.5	22.0	1.41	3.12	250							
TS7	6/17/10	7.17	16.0	299.6	36.1	21.3	1.46	3.05	236							
TS8	6/17/10	6.89	14.1	413.8	46.5	28.1	1.55	3.01	310							
TS10	6/17/10	6.71	13.6	384.2	37.5	22.1	1.47	2.99	243							
TS11	6/17/10	7.31	14.8	380.6	36.5	21.5	1.45	3.01	240	0.04	4.42	n.a.	n.a.	5.07	0.1	5.08
TS12	6/17/10	7.14	14.7	377.2	35.9	21.5	1.51	3.10	241							
TS13	6/17/10	6.15	13.6	383.9	26.7	21.4	1.42	2.86	242							
CC1	6/17/10	-	-	-	41.5	24.3	1.53	3.24	271							

June 26, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	6/26/10	7.70	24.5	358.2	37.8	26.1	2.56	3.82	246							
TS1	6/26/10	7.08	13.6	371.7	37.9	25.3	1.77	3.20	257	0.02	4.31	n.a.	n.a.	4.75	0.11	5.23
TS2	6/26/10	7.23	16.7	320.9	32.4	21.5	2.21	3.38	222							
TS4	6/26/10	7.05	13.7	371.2	40.1	26.7	1.74	3.46	257							
TS5	6/26/10	7.01	13.6	371.7	40.1	26.8	1.79	3.54	246							
TS6	6/26/10	7.01	13.7	371.2	39.4	26.0	1.77	3.66	260							
TS7	6/26/10	7.20	16.0	371.5	38.6	25.6	1.72	3.47	253							
TS8	6/26/10	7.13	13.8	459.9	50.2	33.4	1.76	3.52	310							
TS10	6/26/10	6.96	13.6	372.5	40.5	26.5	1.81	3.25	249							
TS11	6/26/10	6.96	13.6	372.5	38.7	25.8	1.82	3.17	256							
TS12	6/26/10	6.99	13.9	373.2	40.2	26.4	1.87	3.30	265							
TS13	6/26/10	7.08	13.7	372.8	39.5	26.0	1.89	3.25	253							
CC1	6/26/10	6.95	13.4	334.1	45.7	30.5	2.06	3.82	287							

July 5, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	NO_2^{-} (mg/L)	Br^{-} (mg/L)	NO_3^{-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	7/5/10	7.80	26.4	353.1	33.8	21.7	2.04	3.29	240							
TS1	7/5/10	6.89	13.7	389.4	38.4	22.4	1.77	2.95	273							
TS2	7/5/10	7.09	17.8	361.0	35.0	20.2	2.12	3.23	248							
TS4	7/5/10	6.95	13.8	389.0	38.4	22.3	1.74	3.16	270							
TS5	7/5/10	6.95	13.8	387.6	38.6	22.6	1.74	3.04	266							
TS6	7/5/10	6.98	13.8	388.2	38.5	22.6	1.86	3.01	272							
TS7	7/5/10	7.21	16.1	382.7	39.1	22.5	1.76	2.91	268							
TS8	7/5/10	7.16	13.7	464.7	46.3	27.5	1.53	2.92	325	0.02	4.94	n.a.	n.a.	5.35	n.a.	6.05
TS10	7/5/10	6.99	13.7	381.1	39.0	22.5	1.81	2.94	277							
TS11	7/5/10	7.01	13.7	388.0	38.6	22.2	1.79	2.98	271							
TS12	7/5/10	7.12	13.7	390.2	38.2	21.9	1.80	2.99	279							
TS13	7/5/10	7.01	13.7	388.0	37.9	21.7	1.79	2.95	273							
CC1	7/5/10	7.06	13.4	348.1	44.2	25.3	1.84	3.49	301							

August 15, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	8/15/10	7.54	26.6	386.2	29.3	14.7	1.69	2.11	252							
TS1	8/15/10	7.17	14.3	442.3	48.6	26.9	1.08	2.16	284							
TS2	8/15/10	7.27	16.1	440.7	46.3	25.8	1.15	2.12	285							
TS4	8/15/10	7.13	14.3	441.9	47.2	26.7	1.03	2.14	285							
TS5	8/15/10	7.06	14.2	372.5	45.5	25.6	0.97	2.08	282							
TS6	8/15/10	7.08	14.3	341.9	46.4	26.3	0.97	2.12	295							
TS7	8/15/10	7.31	16.5	445.0	46.2	26.1	1.05	2.16	290							
TS8	8/15/10	7.11	14.2	447.6	47.5	27.3	1.36	2.11	298							
TS10	8/15/10	7.09	14.3	442.5	43.4	24.7	1.01	1.99	292	0.06	4.5	n.a.	n.a.	1.87	n.a.	5.05
TS11	8/15/10	7.09	14.3	442.7	47.2	26.9	1.02	2.23	279							
TS12	8/15/10	7.11	14.4	443.4	45.8	26.0	0.95	2.10	291							
TS13	8/15/10	7.18	14.3	442.7	46.2	26.3	0.95	2.12	295							
CC1	8/15/10	7.21	13.5	480.6	48.4	27.4	0.95	2.52	302							

August 31, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	8/31/10	7.21	25.9	410.0	30.6	15.8	1.51	2.21	250							
TS1	8/31/10	6.96	14.3	448.0	37.6	16.5	1.54	2.14	276							
TS2	8/31/10	7.58	21.9	446.0	38.4	16.7	1.98	2.27	273							
TS4	8/31/10	6.79	14.5	448.0	39.3	17.2	1.31	1.85	282	0.09	4.5	n.a.	n.a.	3.18	n.a.	5.07
TS5	8/31/10	7.35	14.7	371.0	38.2	16.7	1.31	1.84	279							
TS6	8/31/10	7.42	14.4	417.0	38.1	16.7	1.35	1.85	275							
TS7	8/31/10	7.04	17.1	448.0	39.6	17.4	1.40	1.96	277							
TS8	8/31/10	6.91	14.6	499.0	41.5	18.2	1.26	1.85	306							
TS10	8/31/10	6.54	14.5	448.0	38.2	16.7	1.32	1.82	286							
TS11	8/31/10	7.39	14.5	450.0	39.0	16.9	1.25	1.88	281							
TS12	8/31/10	7.38	14.5	450.0	39.3	17.1	1.31	1.89	271							
TS13	8/31/10	7.10	14.5	450.0	38.9	16.9	1.36	1.93	279							
CC1	8/31/10	7.52	13.5	495.0	42.4	18.2	1.32	2.24	297							

September 14, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	NO_2^{-} (mg/L)	Br^{-} (mg/L)	NO_3^{-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	9/14/10	7.70	21.6	396.0	34.3	21.8	2.42	3.29	243							
TS1	9/14/10	7.01	14.7	428.0	42.4	24.4	2.08	2.51	264							
TS2	9/14/10	7.78	20.6	399.0	40.8	23.3	2.15	2.57	265							
TS4	9/14/10	7.04	14.5	432.0	41.2	23.7	2.11	2.76	260							
TS5	9/14/10	7.85	14.6	423.0	37.7	21.0	2.59	2.91	242							
TS6	9/14/10	7.67	14.6	420.0	40.6	23.0	2.17	2.58	261							
TS7	9/14/10	7.64	15.6	414.0	39.9	23.1	2.08	2.87	275							
TS8	9/14/10	7.29	14.7	404.0	38.0	21.5	2.35	2.51	243							
TS10	9/14/10	7.27	14.5	428.0	40.9	23.4	1.98	2.63	262							
TS11	9/14/10	7.47	14.6	427.0	40.7	23.1	2.04	2.68	265	0.09	4.17	n.a.	n.a.	3.28	n.a.	4.93
TS12	9/14/10	7.98	14.6	430.0	42.8	24.3	2.22	2.71	267							
TS13	9/14/10	6.72	14.6	428.0	40.4	22.9	2.03	2.65	268							
CC1	9/14/10	7.36	13.5	457.0	42.6	24.0	2.32	3.21	277							

September 21, 2010

Sample ID	Date	pH	Temp. C	SPC (µs/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	NO_2^{-} (mg/L)	Br^{-} (mg/L)	NO_3^{-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
WG1	9/21/10	7.76	23.8	367.0	28.6	13.9	1.82	3.92	237	0.07	5.25	n.a.	n.a.	1.64	n.a.	5.51
TS1	9/21/10	6.81	14.5	387.0	36.7	14.8	1.58	3.49	257	0.09	4.11	n.a.	n.a.	3.29	n.a.	4.89
TS2	9/21/10	6.97	21.7	384.0	33.8	13.9	1.99	4.15	254	0.1	4.99	n.a.	n.a.	1.51	n.a.	5.4
TS4	9/21/10	6.90	14.6	3914.0	34.0	14.6	1.61	3.53	239	0.09	4.08	n.a.	n.a.	3.26	n.a.	4.89
TS5	9/21/10	6.83	14.7	379.0	35.1	14.6	1.55	3.34	249	0.09	4.05	n.a.	n.a.	3.28	n.a.	4.9
TS6	9/21/10	6.85	14.5	393.0	36.4	14.9	1.56	3.70	252	0.09	4.05	n.a.	n.a.	3.28	n.a.	4.9
TS7	9/21/10	7.14	17.2	391.0	34.6	14.7	1.53	3.73	242							
TS8	9/21/10	6.85	14.6	402.0	36.8	15.0	1.83	5.41	253							
TS10	9/21/10	6.97	14.6	393.0	34.8	14.4	1.43	3.54	246							
TS11	9/21/10	6.92	14.8	386.0	36.4	14.9	1.66	3.76	248							
TS12	9/21/10	6.91	14.6	387.0	36.0	14.7	1.39	3.50	254							
TS13	9/21/10	6.92	14.6	387.0	34.9	14.8	1.50	3.69	241	0.09	4.13	n.a.	n.a.	3.44	n.a.	4.89
CC1	9/21/10	6.95	13.6	403.0	36.9	15.1	1.51	4.17	257							

Appendix C.

Tables of derived values of saturation indices for dolomite and pCO_2/Atmospheric CO_2

Saturation Index for Dolomite

Site	2/21/10	3/11/10	3/28/10	4/14/10	4/26/10	5/31/10	6/17/10	6/26/10	7/5/10	8/15/10	8/31/10	9/14/10	9/21/10
WG1	-0.25	0.59	-0.48	-0.36	-1.58	0.13	-1.53	-0.10	-0.03	-0.72	-1.34	-0.21	-0.36
TS1	-1.07	-1.06	-2.70	-2.88	-1.48	-2.09	-3.97	-1.31	-1.68	-0.92	-1.66	-1.39	-2.07
TS2	-0.13	-1.35	-0.47	-1.31	-0.33	-1.80	-3.56	-1.25	-1.44	-0.76	-0.42	0.11	-1.82
TS4	-1.59	-1.27	-2.22	-1.81	-1.32	-2.23	-3.60	-1.32	-1.57	-1.01	-1.95	-1.37	-1.98
TS5	-1.66	-1.23	-2.28	-1.34	-0.95	-2.22	-1.96	-1.44	-1.57	-1.19	-0.86	0.11	-2.08
TS6	-1.63	-1.18	-2.16	-1.27	-1.33	-2.46	-2.30	-1.41	-1.50	-1.10	-0.73	-0.12	-2.01
TS7	-1.35	-1.00	-1.23	-1.56	-0.68	-1.75	-2.02	-1.07	-1.05	-0.66	-1.46	-0.15	-1.49
TS8	-0.62	-0.75	-1.37	-1.26	-0.65	-1.80	-2.15	-0.84	-0.85	-1.01	-1.60	-0.99	-2.00
TS10	-1.53	-1.45	-2.23	-2.01	-1.19	-2.27	-2.89	-1.53	-1.46	-1.14	-2.46	-0.91	-1.82
TS11	-1.67	-1.44	-2.19	-1.98	-1.26	-2.34	-1.72	-1.53	-1.45	-1.11	-0.76	-0.51	-1.88
TS12	-1.65	-1.18	-	-1.77	-1.25	-	-2.06	-1.42	-1.21	-1.06	-0.80	0.56	-1.89
TS13	-1.49	-1.27	-2.19	-1.85	-1.03	-2.20	-4.16	-1.29	-1.46	-0.90	-1.35	-2.01	-1.92
CC1	-1.03	-0.69	-2.52	-1.25	-1.43	-2.49	-	-1.33	-1.16	-0.79	-0.39	-0.66	-1.78

pCO_2/Atmospheric CO_2

Site	2/2/10	3/10/10	3/28/10	4/14/10	4/26/10	5/31/10	6/17/10	6/26/10	7/5/10	8/15/10	8/31/10	9/14/10	9/21/10
WG1	6.757	3.739	6.407	11.605	47.061	5.256	20.081	12.847	10.336	19.920	41.097	12.020	10.587
TS1	22.298	30.144	58.023	201.181	50.415	50.807	349.832	47.474	78.347	42.869	67.498	57.843	89.011
TS2	6.219	30.166	5.783	26.066	10.076	29.750	155.420	30.461	47.641	35.041	17.888	10.732	67.583
TS4	40.028	36.800	31.276	62.053	42.455	58.995	241.933	50.929	67.586	47.191	102.273	53.025	67.372
TS5	40.816	35.785	39.041	38.246	26.731	59.303	38.720	53.410	66.585	54.853	27.942	7.654	82.575
TS6	41.483	28.829	32.371	32.643	42.532	81.239	56.448	56.516	63.525	54.805	23.350	12.495	79.600
TS7	26.769	27.641	13.009	48.091	20.310	35.787	37.183	36.631	37.999	32.688	58.524	14.295	40.671
TS8	10.630	24.687	18.338	39.433	22.607	56.210	89.848	50.742	49.671	51.553	84.295	27.942	80.020
TS10	35.180	44.867	36.217	76.380	38.866	63.194	106.849	60.653	63.118	53.106	184.546	31.464	59.022
TS11	40.004	45.261	35.046	72.915	40.510	68.084	26.908	62.392	59.005	50.664	25.599	20.106	66.938
TS12	39.298	35.725	-	59.248	41.110	-	39.971	60.433	47.148	50.544	25.263	6.260	69.970
TS13	33.766	38.484	32.689	-	38.460	62.984	387.872	46.824	59.462	43.536	49.558	114.344	64.878
CC1	16.506	27.016	53.682	44.434	43.338	107.630	-	70.986	57.919	41.110	19.801	26.694	63.741

Appendix D:
H-Test Mean Values and Critical Difference Tables

Note: Bright yellow highlighted cells indicate sites which are not statistically significantly different

pH - Warm Season

Critical Difference = 253.3

	Mean Rank	TS12	TS13	TS10	TS5	TS6	TS11	TS8	CC1	TS4	TS1	WG1
TS12	202.704	0										
TS13	696.249	493.545	0									
TS10	916.161	713.4567	219.9118	0								
TS5	957.754	755.0502	261.5052	41.59343	0							
TS6	1396.393	1193.689	700.1436	480.2318	438.6384	0						
TS11	1583.400	1380.696	887.1505	667.2388	625.6453	187.0069	0					
TS8	1819.830	1617.126	1123.581	903.6696	862.0761	423.4377	236.4308	0				
CC1	1829.170	1626.465	1132.92	913.0087	871.4152	432.7768	245.7699	9.3391	0			
TS4	2407.990	2205.285	1711.74	1491.829	1450.235	1011.597	824.59	588.1592	578.8201	0		
TS1	2645.349	2442.645	1949.1	1729.189	1687.595	1248.957	1061.95	825.519	816.1799	237.3599	0	
WG1	3035.000	2832.296	2338.751	2118.839	2077.246	1638.607	1451.6	1215.17	1205.83	627.0104	389.6505	0

pH- Cool Season

Critical Difference = 199.7

	Mean Rank	TS12	TS1	TS11	TS13	CC1	TS10	TS8	TS2	WG1
TS12	195.5709343	0								
TS1	601.2560554	405.7	0							
TS11	765.1418685	569.6	163.8858	0						
TS13	830.6712803	635.1	229.4152	65.52941	0					
CC1	1380	1184.4	778.7439	614.8581	549.3287	0				
TS10	1502.415225	1306.8	901.1592	737.2734	671.7439	122.4152	0			
TS8	1872.186851	1676.6	1270.931	1107.045	1041.516	492.1869	369.7716	0		
TS2	2108.984429	1913.4	1507.728	1343.843	1278.313	728.9844	606.5692	236.7976	0	
WG1	2452.773356	2257.2	1851.517	1687.631	1622.102	1072.773	950.3581	580.5865	343.7889	0

Temperature - Warm Season

Critical Difference = 253.3

	Mean Rank	TS8	CC1	TS12	TS11	TS13	TS5	TS1	TS4	TS10	TS6	WG1
TS8	755.8979239	0										
CC1	786.0086505	30.11073	0									
TS12	879.4134948	123.5156	93.40484	0								
TS11	1223.3391	467.4412	437.3304	343.9256	0							
TS13	1277.095156	521.1972	491.0865	397.6817	53.75606	0						
TS5	1327.624567	571.7266	541.6159	448.2111	104.2855	50.52941	0					
TS1	1650.435986	894.5381	864.4273	771.0225	427.0969	373.3408	322.8114	0				
TS4	1928.091696	1172.194	1142.083	1048.678	704.7526	650.9965	600.4671	277.6557	0			
TS10	2280.690311	1524.792	1494.682	1401.277	1057.351	1003.595	953.0657	630.2543	352.5986	0		
TS6	2346.403114	1590.505	1560.394	1466.99	1123.064	1069.308	1018.779	695.9671	418.3114	65.7128	0	
WG1	3035	2279.102	2248.991	2155.587	1811.661	1757.905	1707.375	1384.564	1106.908	754.3097	688.5969	0

Temperature - Cool Season

Critical Difference = 199.7

	Mean Rank	WG1	TS2	TS8	TS10	TS11	TS12	CC1	TS1	TS13
WG1	194.266436	0								
TS2	384.733564	190.4671	0							
TS8	895.432526	701.1661	510.699	0						
TS10	933.0207612	738.7543	548.2872	37.58824	0					
TS11	1655.096886	1460.83	1270.363	759.6644	722.0761	0				
TS12	1846.648789	1652.382	1461.915	951.2163	913.628	191.5519	0			
CC1	1856	1661.734	1471.266	960.5675	922.9792	200.9031	9.351211	0		
TS1	1929.131488	1734.865	1544.398	1033.699	996.1107	274.0346	82.4827	73.13149	0	
TS13	2014.66955	1820.403	1629.936	1119.237	1081.649	359.5727	168.0208	158.6696	85.53806	0

Specific Conductivity - Warm Season

Critical Difference = 253.3

	Mean Rank	WG1	TS1	TS10	TS5	TS11	TS12	TS4	TS13	TS6	CC1	TS8
WG1	249.3460208	0										
TS1	677.1591696	427.8131	0									
TS10	810.3460208	561	133.1869	0								
TS5	888.3650519	639.019	211.2059	78.01903	0							
TS11	1338.025952	1088.68	660.8668	527.6799	449.6609	0						
TS12	1826.49308	1577.147	1149.334	1016.147	938.128	488.4671	0					
TS4	1850.693772	1601.348	1173.535	1040.348	962.3287	512.6678	24.20069	0				
TS13	1973.217993	1723.872	1296.059	1162.872	1084.853	635.192	146.7249	122.5242	0			
TS6	2199.359862	1950.014	1522.201	1389.014	1310.995	861.3339	372.8668	348.6661	226.1419	0		
CC1	2663.968858	2414.623	1986.81	1853.623	1775.604	1325.943	837.4758	813.2751	690.7509	464.609	0	
TS8	3013.024221	2763.678	2335.865	2202.678	2124.659	1674.998	1186.531	1162.33	1039.806	813.6644	349.0554	0

Specific Conductivity - Warm Season

Critical Difference = 253.3

	Mean Rank	TS13	TS1	TS11	TS10	CC1	TS2	TS12	TS8	WG1
TS13	313.9930796	0								
TS1	367.1522491	53.15916955	0							
TS11	736.0069204	422.0138408	368.8546713	0						
TS10	1054.678201	740.6851211	687.5259516	318.6712803	0					
CC1	1193	879.0069204	825.8477509	456.9930796	138.321799	0				
TS2	1653.301038	1339.307958	1286.148789	917.2941176	598.622837	460.301038	0			
TS12	1810.979239	1496.986159	1443.82699	1074.972318	756.301038	617.979239	157.678201	0		
TS8	2122.889273	1808.896194	1755.737024	1386.882353	1068.21107	929.889273	469.588235	311.910035	0	
WG1	2457	2143.00692	2089.847751	1720.99308	1402.3218	1264	803.698962	646.020761	334.110727	0