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Temporal Variations in Spring Water Chemistry and Comparison of Variable Paleozoic Aquifer Discharges in the Ridge and Valley Province of Northwestern Georgia

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TEMPORAL VARIATIONS IN SPRING WATER CHEMISTRY AND COMPARISON OF VARIABLE PALEOZOIC AQUIFER DISCHARGES IN THE RIDGE AND VALLEY PROVINCE OF NORTHWESTERN GEORGIA

by

OLIVER WOOD COSTELLO

Under the Direction of Dr. Seth Rose

ABSTRACT

Flow rates and solute concentrations from eight springs in the Ridge and Valley Province in northwestern Georgia were used to determine flow types and to measure each aquifer's ability to remove contamination for possible use by an encroaching urban and suburban population. This study determined and interpreted the fluctuations in chemistry of each of the sampled spring's water based upon temporal variations of precipitation in the area and variations in the chemistries measured at each weekly sampling event. This study showed that precipitation-induced springs were more likely to incur contamination from a pollutant which occurred in the drainage basin; while carbonate aquifer springs, which were not consistently influenced by precipitation, were not as likely to be contaminated when disturbances or pollutants occurred within the drainage basin.

INDEX WORDS: Spring water chemistry, Carbonate aquifer springs, Precipitation-induced springs, Ridge and Valley province

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1. INTRODUCTION

The Ridge and Valley Province of Georgia is located in the northwestern corner of the state of Georgia and bordered to the east by the Blue Ridge, to the south by the Piedmont and to the northwest by the Cumberland Plateau (Georgia Geologic Survey, 2003). This area is characterized by long narrow ridges separated by valleys which are composed of sedimentary rocks formed during the Paleozoic period (Butts and Gildersleeve, 1948). Limited studies have been conducted on the Paleozoic sedimentary aquifers of the Ridge and Valley Province of northwestern Georgia throughout the past. A study of the groundwater chemistry of the study area was first performed in the late 1960’s by the Geologic Survey of Georgia’s Department of Mines and Mining and Geology (Cressler, 1970). Later, in 1978, the United States Geological Survey (U.S.G.S.) began an aquifer analysis program called the Regional Aquifer System Analysis (RASA) to further study the potential collection of groundwater from large aquifer systems in the U.S. during drought periods (Hollyday and Smith, 1990). The Appalachian Valley-Piedmont phase of the U.S.G.S. RASA survey included eight states from Alabama to Pennsylvania; however, the Ridge and Valley province of northwestern Georgia was not as well studied as the more populated Ridge and Valley of the northeastern United States (Swain et al., 2004). The lack of knowledge of the Ridge and Valley area is attributed to the complex nature of the underlying geologic features, including thrust faults and complex erosional features (Rutledge and Mesko, 1996). Due to the presence of large unconfined aquifers this area has been classified as a region of high risk of groundwater contamination by the Georgia Department of Natural Resources (Aldaheff and others, 2003).

This study investigated the changes in spring water chemistry and interpreted the chemical changes to determine the flow path that ground water takes between the wet winter season and into the drier summer season. Generally the water that recharged these sedimentary rock aquifers is rain-induced infiltration versus recharge from streams or rivers. Ahearn et al. (2004) showed stream water chemistry fluctuation had an initial flushing period at the beginning of the rainy season and a diluting phase that followed in the late rainy to early dry period. Spring discharges that respond quickly after rain events, chemically and volumetrically, are more vulnerable to influences from the surface (Fetter, 2001). In the Ridge and Valley Province of northwestern Georgia, the most susceptible aquifers are conduit flow paths through carbonate aquifers. Since the conduit flow is more susceptible to influences from precipitation, they are at a greater risk from potential contamination (Garner and Mayer, 2004).

Carbonate aquifers can exhibit flow differences from open solution channels to the other extreme where the aquifer behaves as a diffuse homogeneous medium (Fetter, 2001). The aquifer systems of the Ridge and Valley Province can exhibit conduit flow based on the dissolution of the rock as well as the presence of deformation features (Garner and Mayer, 2004).

The flow through carbonate aquifers to a spring discharge point has been described as either conduit or diffuse flow (Shuster and White, 1971). Conduit flow is generally characterized by turbulent and variable flow through solution openings, while diffuse flow can be characterized by flow through small pores and fractures or the matrix of the rock (Harmon and others, 2006). The generally constant flow through the aquifer allows us to describe the flow rate using Darcy's Law (Fetter, 2001).

To determine flow type Pavlicek (1996) used specific conductance of spring flow over spring high and low flow periods. For dilute freshwater, the relationship between specific conductance and dissolved solids is commonly well defined for these waters and specific conductance can be used to extrapolate flow types for aquifers (Seaber, 1988). Large fluctuations in spring water chemistry would suggest that the water did not have time to equilibrate with the surrounding rock. If flow remained relatively constant, then the type of flow can be determined by the variations in specific conductance (Pavlicek, 1996). This constant flow would suggest more of a conduit flow spring than a diffuse flow spring. In a diffuse flow spring water has a much longer residence time, and results in for very little fluctuations in chemistry (Shuster and White, 1971). By understanding the flow type and fluctuations in geochemistry, each of the spring's aquifers were classified as either conduit or diffuse flow.

Analysis of the major ion concentrations recorded in the eight springs demonstrated the susceptibility of each aquifer to contamination by surface waters based upon the flow dynamics. Spring discharges that responded quickly to rain events, chemically and volumetrically, are more vulnerable to influences from the surface (Fetter, 2001). Flow is generally thought to occur in fractures or solution openings versus pore openings in the rocks (Rutledge et al., 1996). Spring waters that did not reach equilibrium with the surrounding water did not spend enough time in contact with the rock to allow for chemical reactions to occur (Kehew, 2001). In the Ridge and Valley Province of northwestern Georgia, the most susceptible aquifers contain conduit flow paths through carbonate aquifers. Since the conduit flow is more susceptible to influences from precipitation, they are at a greater risk from potential contamination (Garner and Mayer, 2004).

Carbonate minerals are thought to be the most abundant parent for most of the dissolved ions in fresh groundwater (Kehew, 2001). As meteoric water falls, it reacts with carbon dioxide in the atmosphere; it increases the hydrogen activity in water, thus lowering the pH by producing carbonic acid (Hem, 1985). Once the water percolates into the vadose zone it can begin to react with the surrounding rock. As the reactions occur, the unsaturated vadose zone allows for the continued reaction with carbon dioxide (Hem, 1985). Once the water enters the saturated zone it can either be in an open or closed system with respect to carbon dioxide (Kehew, 2001). A closed system limits the continued reaction to dissolve additional calcite. Field pH, alkalinity titrations, and ion analysis can be used to determine whether the spring water discharge is in equilibrium with calcite or dolomite.

This study additionally examined the major ion chemistry of each spring to determine its equilibrium state with respect to calcite. Carbonate aquifers are generally characterized by weathering reactions (Groves and Meiman, 2005). The evolution of flow paths through a karst aquifer has been interpreted using numerical modeling and simulations; however, variations in water pH, temperature, and pressure affect the rate of dissolution.

Through groundwater chemical analysis of springs in the Ridge and Valley Province in northwestern Georgia, the study examined the geochemical signatures of the selected springs to determine the potential source of the water by suggesting rock types and formation characteristics for each aquifer and the flow type for each. This study explains a possible flow type for groundwater discharging from springs by analyzing the water chemistry of the selected springs that have near constant flow and the amounts of precipitation that occur in the area. Investigating the groundwater discharged through springs can provide insight with respect to the path of the ground water. Such studies allow a unique insight to the path of the groundwater and its potential for use as a drinking water source for neighboring communities. Additionally, this modeling can be further utilized to predict contaminants in other aquifer systems.

2. STUDY AREA

Geology and Hydrogeology of the Ridge and Valley Province

The Ridge and Valley Province of northwestern Georgia stretches from Alabama in the south in Canada to the north. The Ridge and Valley Province is located in the northwestern corner of Georgia and is composed of marine and terrestrial sedimentary rocks formed during the Paleozoic period and partially deformed during the Appalachian orogeny (Butts and Gildersleeve, 1948). This area is physiographic ally characterized by long narrow ridges separated by valleys. In Georgia, the Ridge and Valley Province is bordered to the east by the Blue Ridge, to the south by the Piedmont and the northwest by the Cumberland Plateau (Aldaheff and others, 2003).

Geologic structures in the Ridge and Valley Province are typically folding and thrust faulting. A general Georgia Ridge and Valley Province groundwater study was performed in 1971 by Charles Cressler and the Ridge and Valley Province was studied by Miller (1990); however, much of this area's hydrogeology has not been studied in Georgia. The sedimentary rocks are generally carbonate, sandstone or shale; of these carbonate rocks are the better aquifers (Miller, 1990). Maupin, M.A. and Barber (2000) estimated the total volume of water pumped out of the Ridge and Valley Province in North Georgia for public use is 226 million gallons/day. The province is made up of 80 percent carbonate rocks and 20 percent sandstone or unconsolidated sediment (Maupin and Barber, 2000). Generally the USGS Ground Water Atlas rates and names the aquifers based upon specific formation names and the area (Miller, 1990). The geology of the spring sites in their respective counties and have been mapped by the Georgia Geologic Survey below modified from Aldaheff and others (2003) (Figure 1).

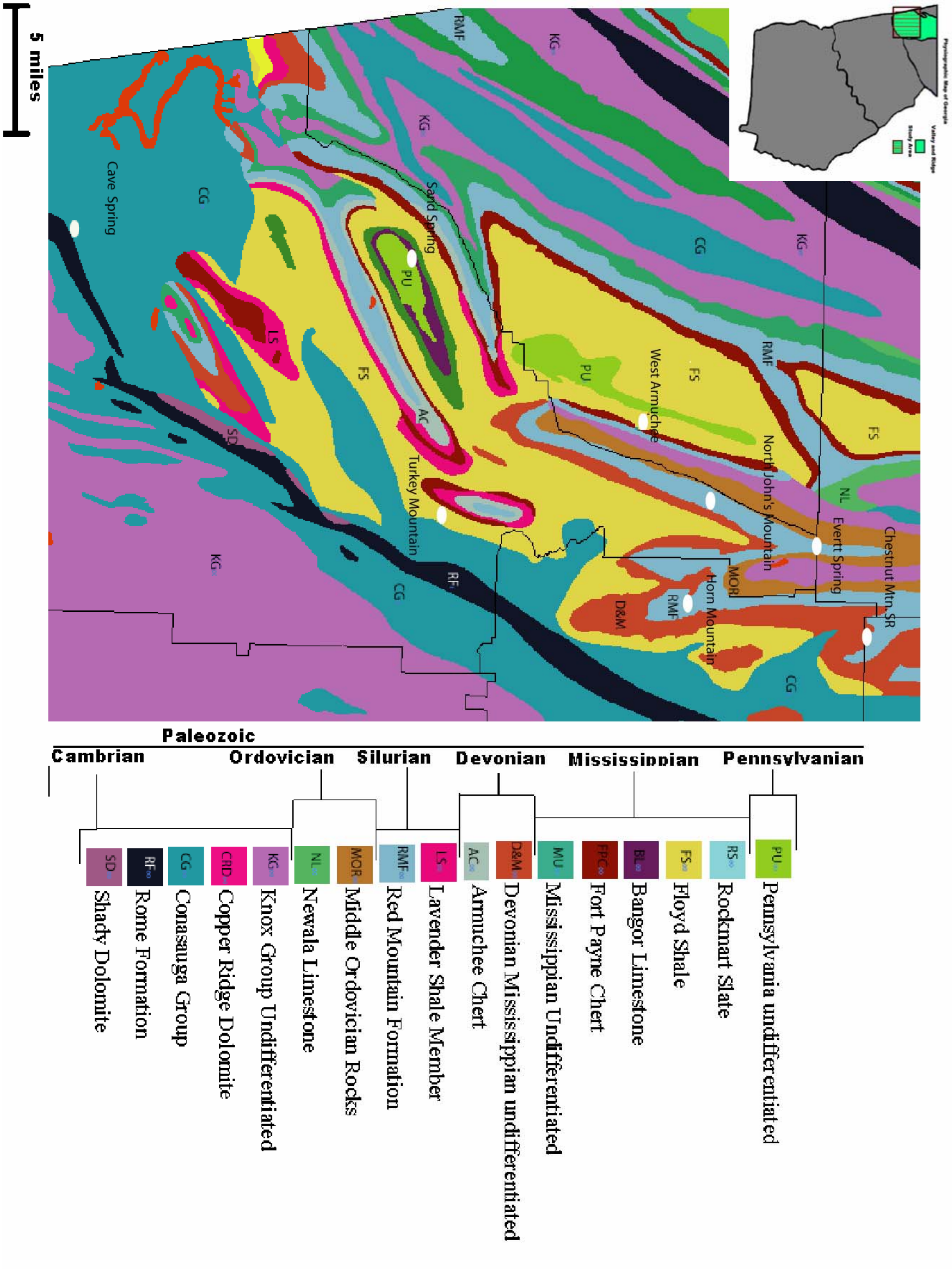

Figure 1: Location of Spring Sites and Geological Formations Aldaheff et al (2003).

To understand the geologic attitude of the area, measurements were collected to produce the cross-section. The geologic data collected cuts approximately along the cross-section line. The bedding orientation data were collected, plotted on Stereo Win 1.2, and oriented according to the apparent dip. The structural data are presented in a stereo net which plots the poles of the geologic data collected (Figure 2).

All of the formations that occur in the study area were deposited in the Paleozoic Era. During the Cambrian Period the Shady Dolomite, Rome Formation, Conasauga Group, Copper Ridge Dolomite, and the Knox Group Undifferentiated were deposited. The Ordovician formations include the Rockmart Slate, Newala Limestone, and Middle Ordovician Group. The Silurian formations include the Red Mountain and Lavender Shale Member. The formations from the Devonian and Mississippian periods include the Armuchee Chert, Devonian/Mississippian Undifferentiated, Mississippian Undifferentiated, Fort Payne Chert, Bangor Limestone, and Floyd Shale. The Pennsylvanian Period formations are mapped as Pennsylvanian Undifferentiated.

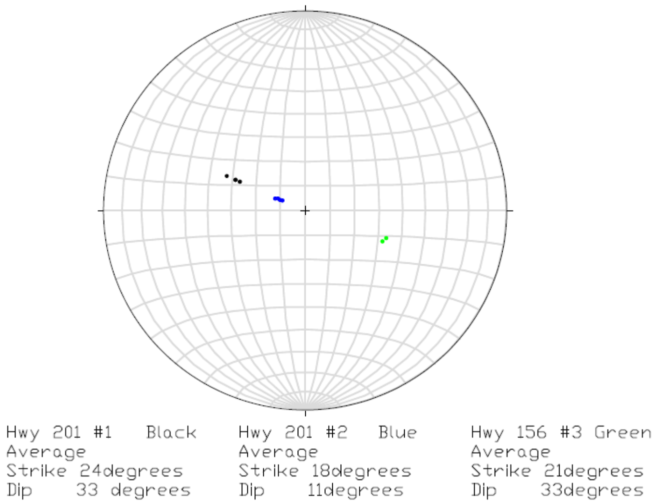

Figure 2: Plot of the Geologic Data.

Figure 2 shows the plot of the poles of the geologic data collected at each of the three structural sites. The data has been corrected to show the apparent dip with respect to the cross-section.

Geologic mapping was required to interpret the spring flow. Geologic attitudes (strike and dip of the bedding), for rock formations in the study area, were collected over the months of March and April 2007. This information was collected to help produce a geologic cross-section to better understand the three dimensional aspects of the aquifer systems. The eastern portion of the following cross-section (Figure 4) was modified from Cressler (1971) and the Digital Environmental Atlas of Georgia (Aldaheff and others, 2003). The western portion of the cross-section was produced from the Digital Environmental Atlas of Georgia and the field work from the spring of 2007 (Figures 3 and 4). The general geology of the Ridge and Valley Province is shown as rolling valleys and hills. The region is composed of sedimentary rocks and despite folding and thrust faulting has experienced little to no metamorphism.

These three sites were located once the cross-section line was drawn. Site #1 is located along Highway 201 where a section of the Conasauga formation is exposed. Site #2 is located farther to the north along Highway 201, to the east of where the thrust fault should have been exposed. Since no visible surface exposure of the two western thrust faults was visible within the study area, the attitude of the faults was interpreted to be the same as the thrust faults to the east of the study area. The most eastern fault was mapped by Cressler (1971) and has a known attitude. Site #3 is located on Highway 156 to the northwest of the city of Villanow.

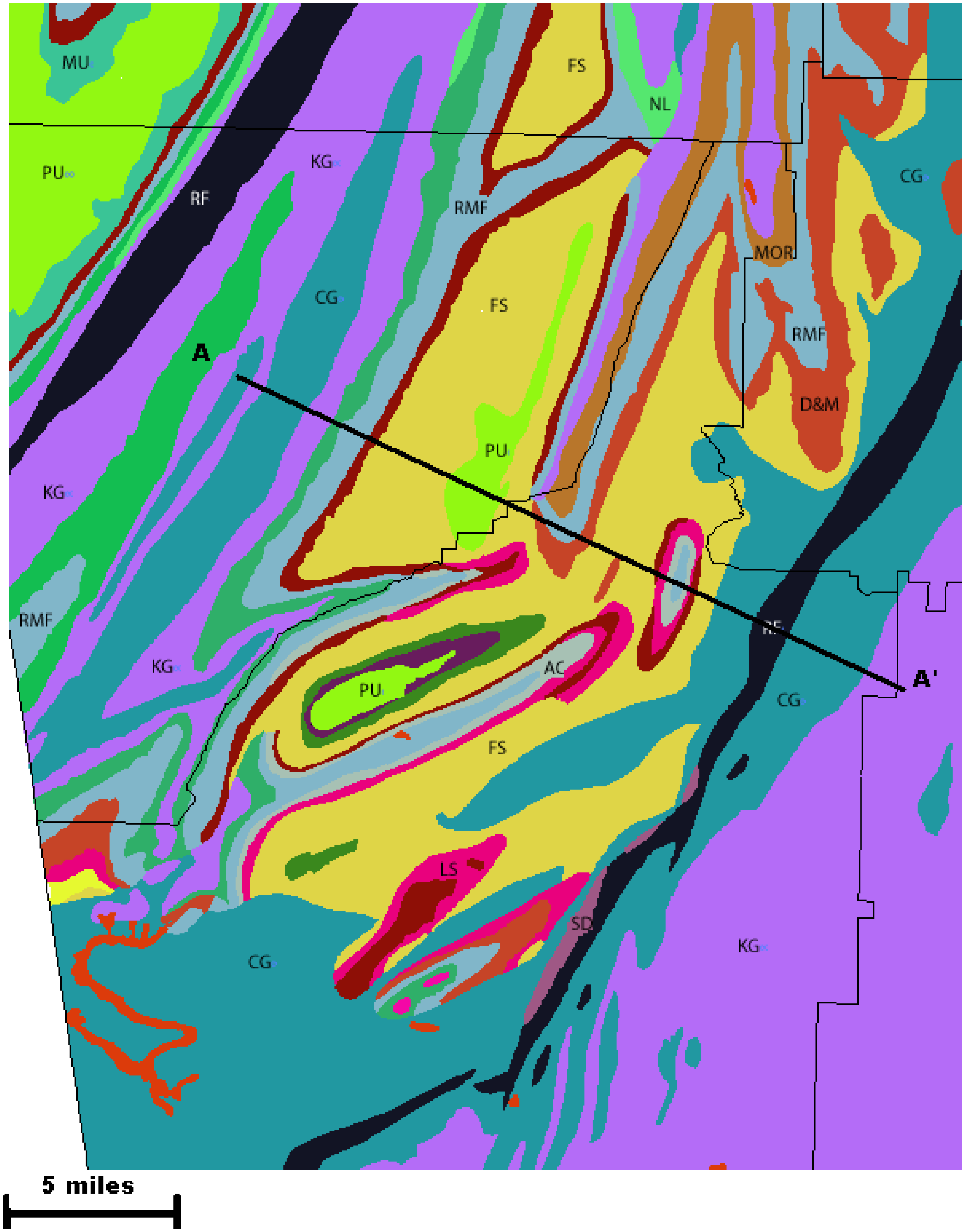

Figure 3: Cross-Section Line Location from Aldaheff et al (2003).

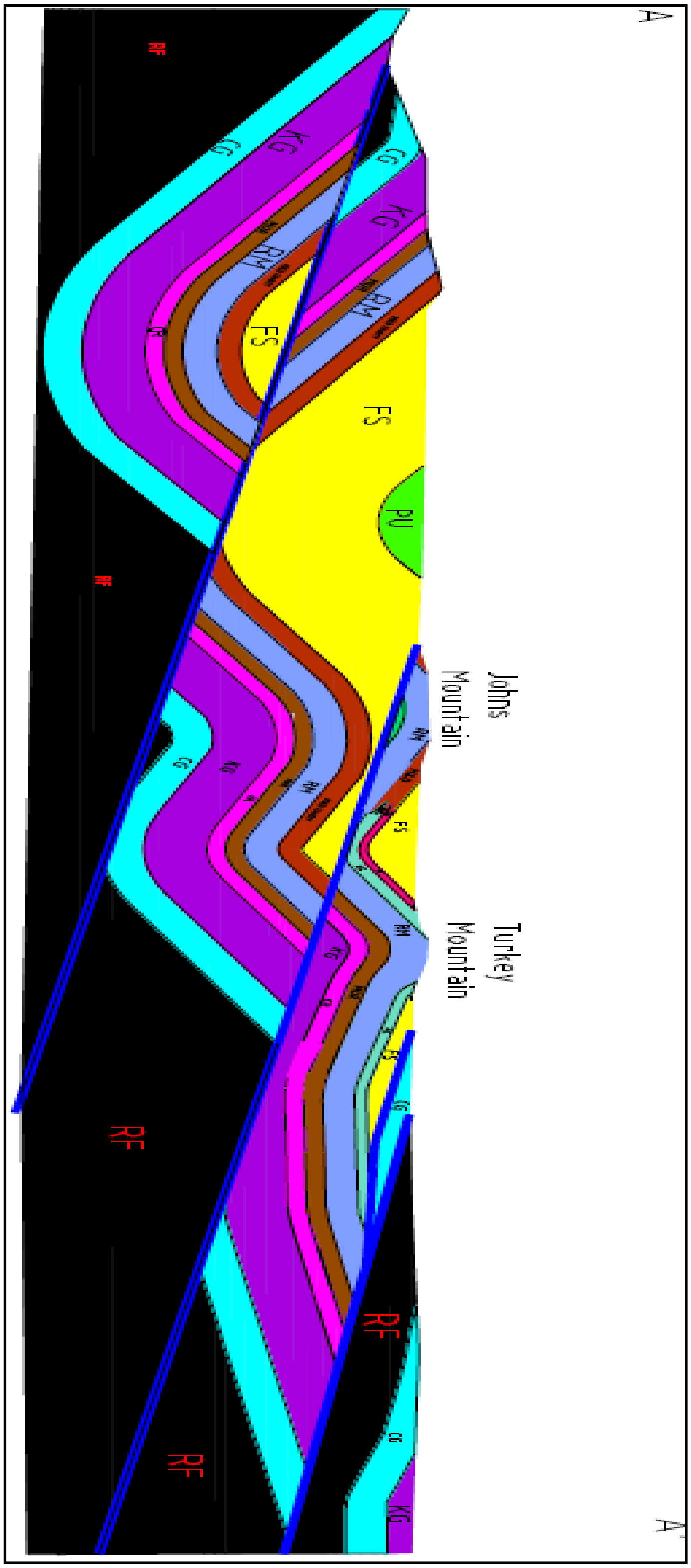

Figure 4: Geologic Cross-Section Modified from Cressler (1971) and Aldaheff et al (2003).

A series of eight springs was chosen in the Ridge and Valley Province in the northwestern corner of Georgia. Table 1 lists the eight sampling sites along with their abbreviated codes, and their county location within.

Table 1: List of Spring Sites and County Locations

Spring Sites	Georgia County	Codes
Cave Spring	Floyd	CS
Sand Spring	Floyd	SS
North John's Mountain	Walker	NJM
Horn Mountain	Gordon	JM
Chestnut Mountain Shooting Range	Gordon	CMSR
Everett Springs	Floyd	ES
West Armuchee	Walker	WA
Turkey Mountain	Floyd	TM

Each of these eight springs was chosen based upon several factors. First, a N45°E line bisecting the Valley and Ridge province which followed the trend of the ridges in this corner of Georgia was drawn on a topographic map of North Georgia.

The towns that fell along the line having high topographic relief characteristics were scouted as potential spring sampling sites. Ease of access and non-private property issues were considered during the selection process. Once the sites were located and determined acceptable for sampling, each site was marked with a hand held GPS receiver. The locations were converted from UTM using the United States Corp of

Engineer’s program, CORPSICON into Georgia State Plane region 16 format so that each spring could be easily identified on the Georgia Geologic Atlas.

Flow volumes were not used as a factor in determining if the spring was suitable, since recharge and chemical variations over the study period were the characteristics being analyzed during this study. Flow volumes could also be indicative of aquifer types, since precipitation-induced springs are more likely to have higher fluctuations in discharge amounts while carbonate aquifers generally have a more diffuse recharge and flow. Spring properties such as potential basin geology and high and low flow discharges were not used in the selection process to keep a varied selection of springs.

Finally, after several months of scouting though the region, eight springs were chosen. The springs were located on topographic and geologic maps to produce the cross-section (Figure 4). Each spring is described individually in the following section.

Spring Study Sites

Cave Spring-Location #1 (CS)

The city of Cave Spring, Georgia is a small, spring-dependent community located approximately twenty miles southwest of Rome, Georgia in Floyd County. Water emerges from the aquifer in a cave system in the center of town. The city collects all of its municipal drinking water from the cave before the water leaves the cave entrance. The city allows water to pass through the cave entrance to be collected by local residents and to be used for a natural water community swimming pool for the summer. The city maintains the site as a local park and historic site, which can be accessed at nearly all times. The chemistry at Cave Spring was extensively studied by Garner and Mayer (2004) to determine a geochemical baseline for future comparisons. During the year, the spring provides a fairly constant discharge, approximately two million gallons per day (MGD) as discussed by Garner and Mayer (2004). There are two rock quarries and large cattle and agricultural sites in the vicinity of the springs that are sites of potential contamination of the aquifer system. In the Garner and Mayer (2004) study, no contamination from the surrounding agricultural or industrial sites was identified. The discharge occurs from the Conasauga formation and is believed to be recharged additionally by the Knox formation residual soils.

Sand Spring-Location #2 (SS)

The spring is located on the southern part of the Rocky Mountain syncline on the northern side of Lavender Mountain just outside of Rome, Georgia in Floyd County. This spring is located in the Georgia Department of Natural Resources Wildlife Resources Division Berry College Wildlife Management Area (BCWMA).The area however, is maintained by Berry College. Since the spring is located inside the area, which is protected from environmental impact, there is very little development within five to ten miles of the site. There are two small private residences that are located within ten miles of the spring site and one home has a small cattle farm. In Cressler's (1971) mapping of this spring area, he sampled a larger spring approximately four miles west of the site. The discharge channel of the spring was filled with fine clays and loose chert rubble material.

The GGS Digital Environmental Atlas of Georgia (2003) shows the Fort Payne and Armuchee Chert formations in contact at the approximate location of the SS site.

North John's Mountain-Location #3 (NJM)

This spring is located on the western side of John's Mountain in the John's Mountain Wildlife Management Area (JMWMA) in the area of Villanow, Georgia in Gordon County. This area of the park is mainly used by fishermen accessing the trout stream at the parking area. All of the trails that lead into this area of the park were closed due in the late 1990's to heavy land use. Roads still exist over the mountain yet they are not accessible by motorized vehicles due to large constructed berms of soil and trees. The spring emerges over one mile from the nearest open or usable trail and is only accessible by bushwhacking along the creek. The spring exhibited a consistent flow throughout the study period with little to no visible decline in wet or dry periods. With the exception of occasional hunters the site was virtually not used due to the steep sided cliffs on either side of the valley or the steep gradient with which the stream flowed down hill from the mountain side. The discharge at this site occurred in a sandstone rubble. Aldaheff and others (2003) showed the Red Mountain formation is stratagraphically above the Floyd Shale at this site.

Horn Mountain-Location #4 (HM)

This spring is located on the southern most extent of the John's Mountain Wildlife Management Area (JMWMA) in Gordon County. This management area is used in the fall and winter for turkey and deer hunting and all of the surrounding JMWMA was easily accessible due to the low topographic relief above the spring head. Flow at the location here varied more than at the other sites throughout the wet and dry seasons. During the spring sampling events, only Wildlife Resource Division rangers were encountered. In addition, no development above the spring discharge was observed. There is a residence with a small farm approximately five miles down hill from the spring's location. The discharge emerges from a heavy clay soil. Aldaheff and others (2003) shows the spring site in the Silurian Red Mountain formation.

Chestnut Mountain Shooting Range-Location #5 (CMSR)

This spring is located in the northern most extent of the John's Mountain Wildlife Management Area (JMWMA). This area is located five miles east of the town of Villanow, Georgia in Gordon County and is currently used as a shooting range as well as for hunting. Very little use of the area outside of the shooting range was observed. The spring is approximately one mile off of a side dirt road within a steep sided valley. Depending on the time and amount of the last rain fall the location of the spring tended to change within fifty feet of its original location. Again the spring discharged into a sandstone rubble filled channel, that was designated a part of the Red Mountain formation, by the Aldaheff and others (2003).

Everett Springs-Location #6 (ES)

This spring is located along Everett Springs Road North of Highway 156 in Everett Springs, Georgia in Floyd County. This small church community appears to have developed around the springs in the late 1800's. The spring site is located along the easement of the road on property maintained by the community church. The spring appears to no longer be in use due to the low flow and the observation that the water contained an orange-red colored algae. Flow occurred through a man made well structure and measurement of less than a liter a minute was found when collecting samples. Though Cressler (1971) mapped this spring, he did not sample it after determining that the flow rate was too low. Cressler (1971) shows the middle Ordovician rocks outcropping on top of the Floyd Shale Formation at the spring site.

West Armuchee-Location #7 (WA)

This spring is located in the John's Mountain Wildlife Management Area (JMWMA) in the East Armuchee Valley and discharges into Armuchee Creek, North of the town of Subligua, Georgia in northeastern Chattooga County. This is the southwest corner of the wildlife management area, located on the western side of John's Mountain. The wildlife management area is composed of residential estates and small farms. This park is heavily used for equestrian activities. The spring is located about three-fourths of a mile from the nearest trail. The spring emerges from a limestone outcropping approximately twenty feet in elevation over the river. The flow at this spring is very low and during extremely dry periods flow was limited to a trickle. Numerous sinkholes were observed in the area where the ground surface was saturated which suggested heavy discharge. The flow was very low and diffuse. The area is currently being used as a horse park, however the site was previously an old home site with numerous rock walls and a dug well. Cressler (1971) showed the spring discharge occurs at the contact of the Conasauga Formation on top with the Knox Group below.

Turkey Mountain-Location #8 (TM)

This spring is located approximately ten miles from the city of Rome, Georgia on private property to the North of Highway 140. The land owner collects water for a small vineyard and orchard area. The unused portion is diverted at the discharge point in the rock and not affected by potential contamination to a public access collection point and parking lot. This area is fairly developed compared to the other springs in the studied area. A large industrial carpet facility located approximately three miles south and numerous residential facilities surround the site. Furthermore, Turkey Mountain is the site of several chert mining operations in the early 1900's. Since the spring discharged through a polychlorinated vinyl pipe the discharge rate was easily measured at a consistent eight to ten gallons per minute. Aldaheff and others (2003) map Turkey Mountain as composed of four formations: the Fort Payne Chert, the Armuchee Chert, the Red Mountain formation, and the Lavender Shale member.

3. SAMPLING AND ANALYTICAL METHODS

The eight springs were selected based upon the geology at the discharge site and surrounding recharge basin, topography of the surrounding landscape, accessibility of the discharge point, and flow rate. A total of 136 spring water samples were collected from January, 2005 through June, 2005 for this investigation.

Field Sample Collection

Each of these springs were tested and sampled weekly for a period of six months to monitor the potential for fluctuations in the chemical make up of the discharging water. This period was selected to ensure that the wetter weather would provide additional volume and ease of measurement. Single samples from each site were collected weekly and stored in one half liter, acid cleaned polyethylene containers. Bottles were thoroughly rinsed with sample water from the springs before final sample collection.

Temperature/pH/Conductance Measurements

Specific conductance was measured in the field with an YSI 85 specific conductance meter. Initial field measurements of water temperature and pH were collected using a hand-held Accumet AP 84 Temperature/pH meters. These measurements were collected for an additional variable to compare the springs. To ensure quality measurements, both meters were calibrated by measuring known standards before each weekly field-sampling event by using pH=4.00 and pH=7.00 buffers.

Precipitation

The precipitation rates were based upon the data collected from the University of Georgia (UGA) Agricultural commissions Northwest Research and Education Center weather station in Floyd County. This UGA station was chosen since it most closely approximates the central study area when compared to the potential stations located in the extremities of the region. The Northwest Research and Education Center reports the weather for the region as well as daily precipitation and evapotranspiration volumes. Daily totals were collected and then graphed to show the fluctuations over the study period (Figure 11).

Evapotranspiration

Evapotranspiration (ET) includes the transpiration of plants and the evaporation of water from land surfaces (Fetter, 2001). For this study ET was collected from the UGA agriculture website and determined the potential ET, which is the measure of the ET that would occur from a standard agricultural crop (University of Georgia, 2007). The ET was calculated by UGA using a formula based upon the temperature and precipitation rates. This is a potential rate since actual measurement is very difficult to calculate.

Environmental Data

Information on regional precipitation was recorded from the University of Georgia Department of Agriculture website (http://www.griffin.uga.edu) which compiled information from a weather station on the northern side of Rome, Georgia. Additionally, stream base flow data was recorded from the USGS website (http://ga.water.usgs.gov/) to examine potential links between regional base flow and changes in the flow of the sample spring systems.

Saturation Index

Saturation Index (SI) is a number calculated to measure the tendency of natural water to dissolve or precipitate a mineral (Ball and Nordstrom, 1991). The SI is calculated using the following formula:

$$\mathbf{SI = \log_{10} \frac{Ion\ Activity\ Product}{K\ (mineral)}}$$

Where ion activity product (iap) is the activity of the ions that compose the mineral:

$$\mathbf{Iap = (Ca)\ (CO3)}$$

Where ( ) = the activity for each ion. K is solubility product of the mineral being measured, in the case of this study calcite:

$$\mathbf{K\ (calcite) = (Ca)\ (CO3)}$$

From the equation above if iap = K (log 1 = 0), the water is in equilibrium with the mineral and a positive number means that the water is supersaturated with a mineral and the mineral will precipitate. A negative saturation index suggests that the water is under-saturated and will dissolve a mineral. The calculation is based upon the pH (acidity-alkalinity), the Eh (redox potential), the ion concentration, and the temperature.

WATEQ is a chemical speciation code for natural waters. It uses field measurements of temperature, pH, Eh, dissolved oxygen and alkalinity, and the chemical analysis of a water sample as input and calculates the distribution of aqueous species, ion activities, and mineral saturation indices that indicate the tendency of a water to dissolve or precipitate a set of minerals. WATEQ was first developed by Truesdell and Jones in 1974 as one of the first geochemical equilibrium models to be widely used. WATEQ is a speciation code; it calculates the distribution of elements among aqueous species (Ball and Nordstrom, 1991). The usual reason for doing the calculation is to obtain saturation indices for minerals and partial pressures of gases, which whether minerals (and gases) should dissolve or precipitate in the solution. The program needs a complete major element chemical analysis (Ca^{+2}, Mg^{+2}, Na^{+1}, K^{+1}, SO_4^{-2}, Cl^{-1}, HCO_3^{-1}, alkalinity, and field pH) to make the calculation (Ball and Nordstrom, 1991).

Ion Analysis

The geochemical characterization of spring discharges is a common technique used to understand the hydrogeology of springs and groundwater flow systems (Hem, 1985). Spring discharge sampling was selected as a less intrusive and more cost effective method of obtaining a sample to examine the aquifer's chemical analysis than well installation above each discharge point. Additionally spring discharge sampling allowed for the collection of water that is possibly representative of a large drainage area (Knoppman, 1991).

Each sample was divided and tested for alkalinity within 24 hours of initial collection for alkalinity and ion analysis. Alkalinity titrations used 0.2N sulfuric acid and an Orion 720A pH meter to determine the breakpoint and reported as mg/l bicarbonate. The precision of the titrations was greater than 5%.

The remaining sample was filtered using a 0.45µ membrane and placed into two separate polyethylene bottles. The two bottles were individually labeled for cation and anion analyses. The bottle marked cation was treated with strong nitric acid to keep ions in solution, while the anion sample was not treated.

Individual cations which were analyzed included calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^{+1}), and potassium (K^{+1}) and individual anions which were analyzed included sulfate (SO_4^{-2}), bicarbonate (HCO_3^{-1}), and chloride (Cl^{-1}). These ions were chosen since they constitute the major ions in groundwater (Hem, 1985). Samples were analyzed using the Lachat IC5000 ion chromatograph for anion analysis and the Perkin Elmer Atomic Absorption Spectrophotometer 3110 for cation analysis.

The Perkin Elmer Atomic Absorption Spectrophotometer 3110 was used to measure the concentration of the cations. Samples of known cation concentrations were analyzed for calibration purposes before any sample was run for the day. These samples were plotted absorption versus concentration. Additionally, throughout the analysis the standards were run for quality control.

The AA spectrophotometer uses the visible or ultraviolet light that is absorbed by the measured atoms to measure the ionic concentration in the sample. To produce a gas phase of the sample, a pump pushes the sample continuously into an oxy-acetylene flame. Since each element becomes excited by a particular wave length of light an ion specific lamp is used for each element.

Samples were run on all cations at the same time. To ensure that the machine was functioning properly and determine the appropriate peak times for each cation, standards of known concentration were analyzed to produce a regression line for each cation (Figures 6-9).

The chloride and sulfate anions were tested using the chromatograph, while bicarbonate was measured through titration. The sodium, calcium, magnesium, and potassium cations were tested using the spectrophotometer. The following graphs show the calibration curves run for each ion (Figures 5-10) run in this study.

The Lachat IC5000 Ion Chromatograph was used to analyze the anions. The bicarbonate/carbonate eluent method was used: rapid anion method. The sample is filtered to 0.45ųm and then through a 0.20ųm syringe membrane. The sample is injected into a stream of eluent carbonate/ bicarbonate for anions, then drawn out over a charged column. The ions are separated by strength of the charge. The weakest charged ions move the further along the column than stronger charged ions. Smaller charged ions are the first to appear at the end of the column and analyzed by a electrical conductivity detector.

Samples were run on all anions at the same time. To ensure that the machine was functioning properly and determine the appropriate peak times for each anion, standards of known concentration were analyzed to produce a regression line for each anion (Figures 10-11).

The standard samples for the ions were run every ten samples through out all testing to ensure that the machines did not fluctuate in accuracy and precision. The values that resulted from the duplicate testing were used to calculate the percent error for each element. Percent error was calculated as follows:

$$\text{Percent (\%) error} = \frac{[\text{accepted value - measured value}]}{[\text{accepted value}]} \text{ X } 100$$

The amount of precision determines that a group of sample results are repeatable and have a common reference point. To ensure that measurements were accurate and precise, known standards were run every tenth sample throughout the testing phase of this thesis. For all of the ion analysis, every sample was run three times. The mean and standard deviation were calculated for each. A standard deviation was calculated for each of the replicated cation tests.

$$\sigma = \sqrt{\ } ((\sum (\text{total}-(\text{mean}))/ (n-1))$$

σ = Standard deviation

total = all results combined

mean = average of the results

n = number of results

The standard deviation was then used to calculate the relative standard deviation for each cation. All testing had a relative standard deviation of 5% or less.

$$\sigma\ (\text{rel}) = (\sigma / \text{mean})\ X\ 100$$

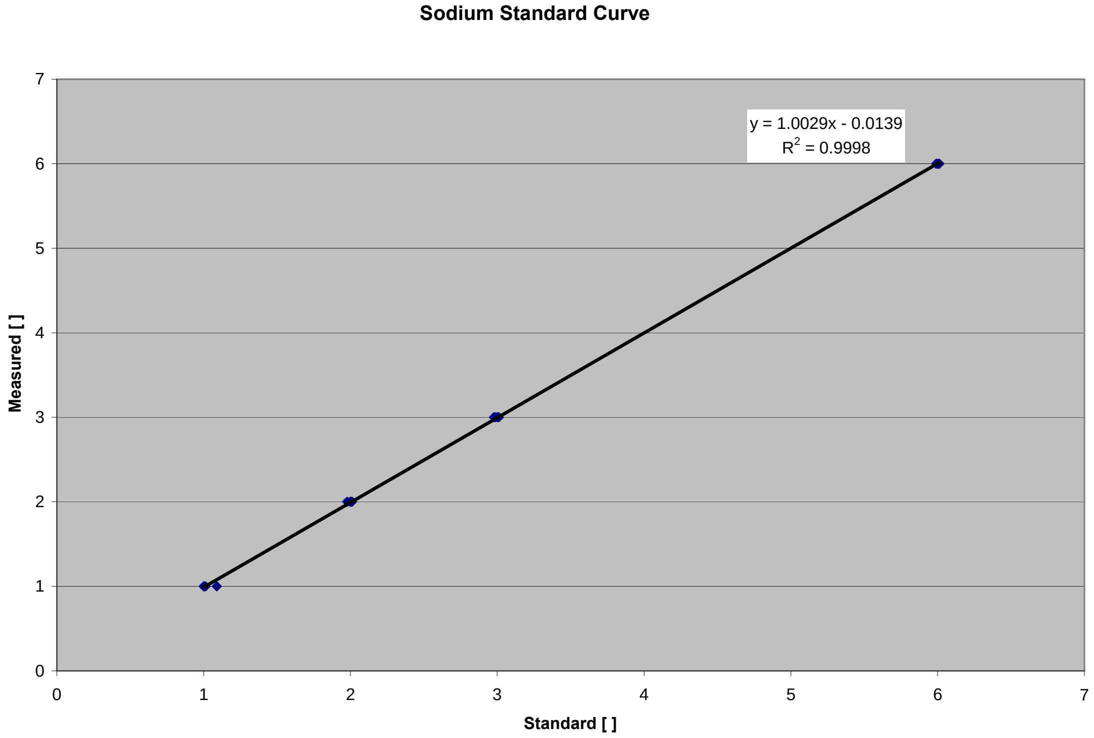

Figure 5: Sodium Standard Curve

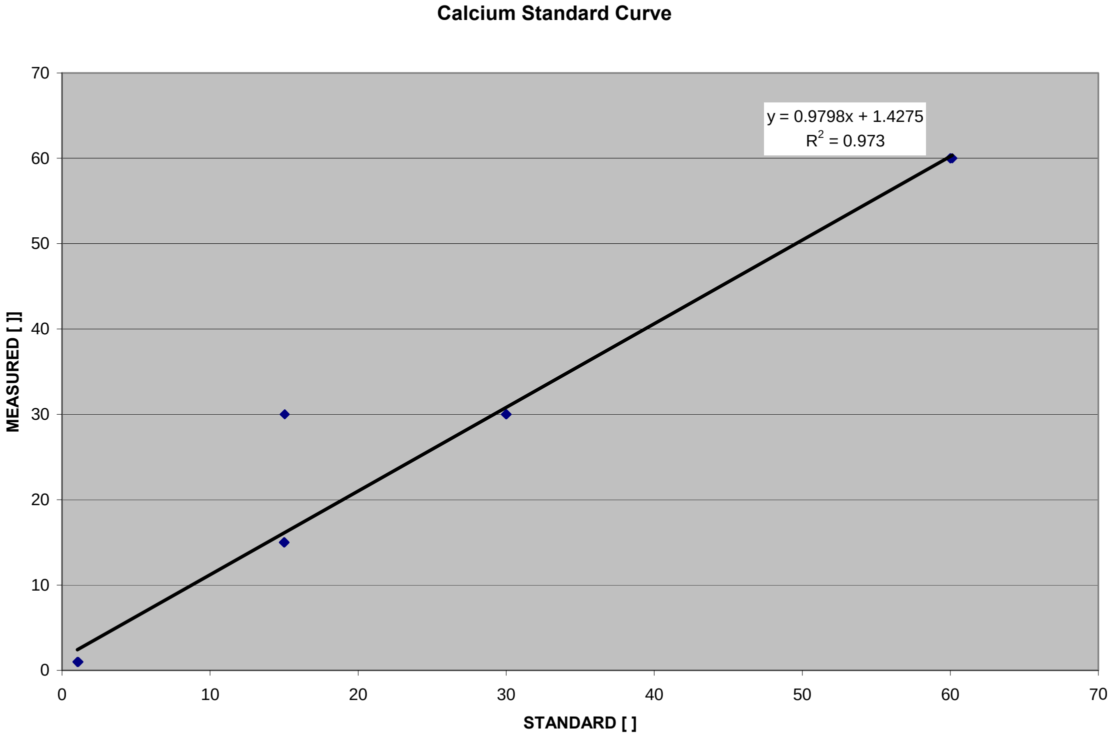

Figure 6: Calcium Standard Curve

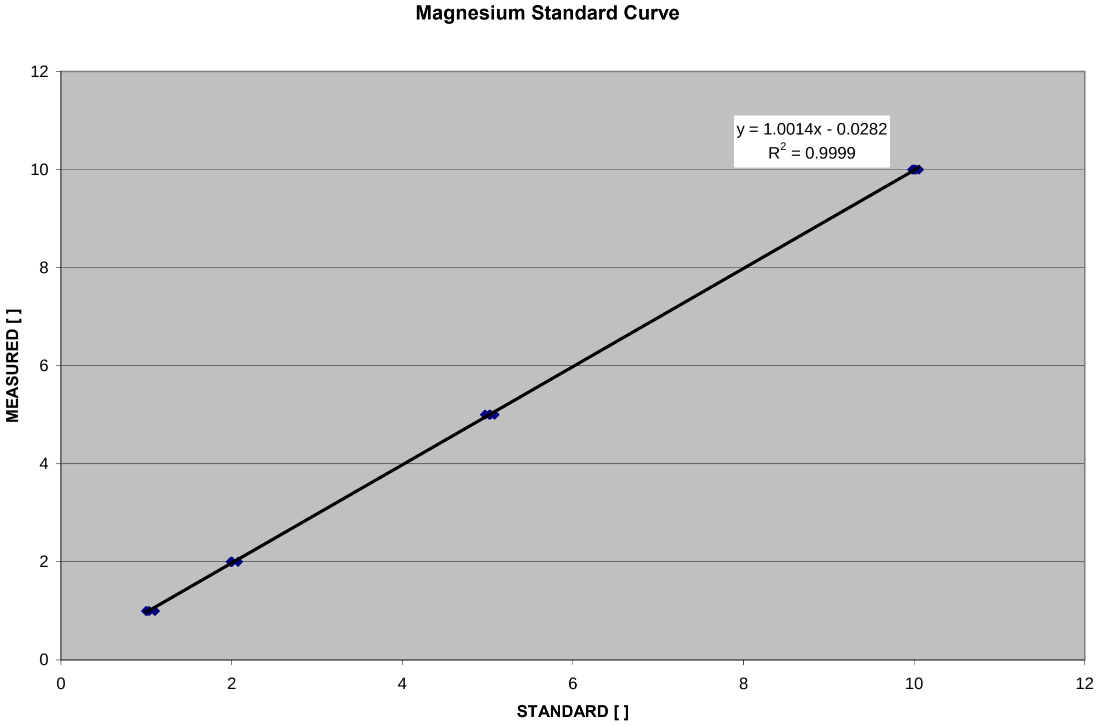

Figure 7: Magnesium Standard Curve

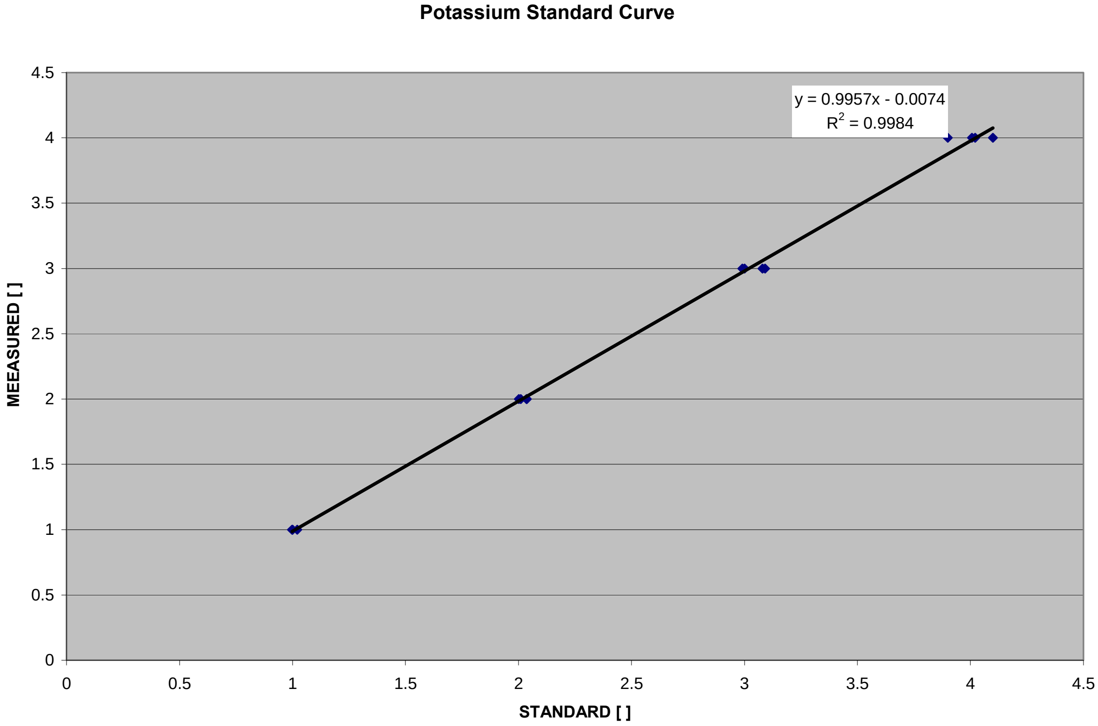

Figure 8: Potassium Standard Curve

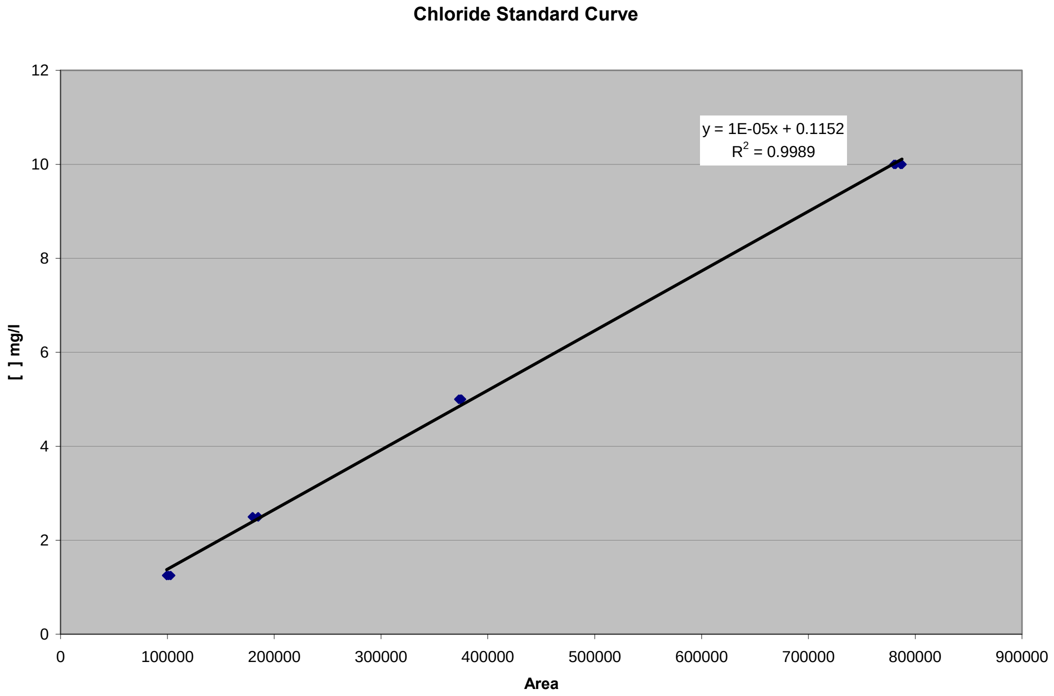

Figure 9: Chloride Standard Curve

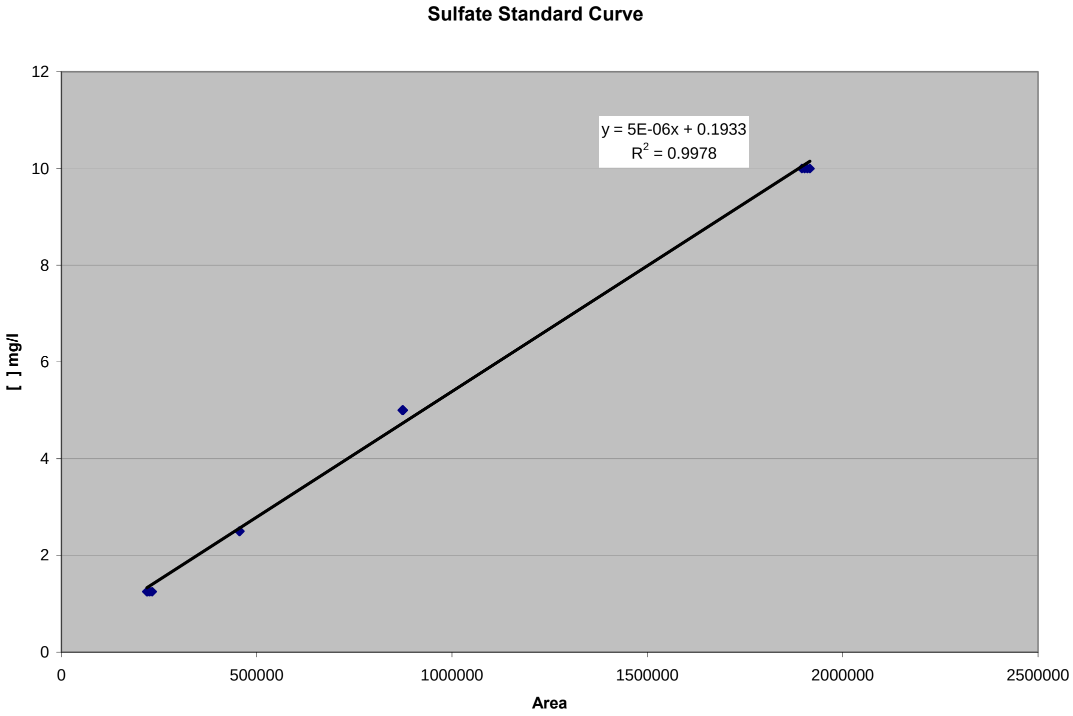

Figure 10: Sulfate Standard Curve

4. RESULTS

Precipitation and Evapotranspiration Results

Each of the spring major ion concentration graphs were compared to the rainfall rates for the region over the study period. The precipitation rates were based upon the data collected from the University of Georgia (UGA) Agricultural commissions Northwest Research and Education Center weather station in Floyd County. There are four weather stations maintained by UGA. The Northwest Research and Education Center reports the weather for the region as well as daily precipitation and evapotranspiration volumes. Daily totals were collected and filed to account for the numbers and then graphed to show the fluctuations over the study period. A trend line was added to the graph showing an average overall volume instead of individual rain events. Rainwater amounts in the state of Georgia have been monitored since 1978 by the National Atmospheric Deposition Program (NADP). Their studies at their Pike County facility have shown average rain water conductivity levels of 15 ųS and a maximum conductivity of 24.7 ųS since 1978. This high was used to separate the springs that are directly influenced by precipitation, by comparing the conductivity to the twenty-nine year high.

In Figure 12, the blue line represents precipitation and the red trend line shows the average precipitation in each day in Rome, Georgia collected by the UGA Agriculture Commission. It shows the frequency of rain events decreasing after the midpoint of the study period; however, large rain events still occur periodically. During the mid point of the study period, April 1, 2005, the average ET overtakes the average precipitation (Figure 13).Figure 13, the purple line shows the ET estimated by Georgia Automated

Environmental Monitoring Network on the individual sampling dates for the region and the blue line shows the rainfall events for the study period. The agriculture department at UGA uses the Penman equation to calculate ET. The Penman equation uses temperature, wind speed, relative humidity and solar radiation to estimated ET (Georgia Automated Environmental Monitoring Network 2008).

In Figure 14, to facilitate the observation of the decline in the sample area's rain totals averaged weekly precipitation over the course of the study period is charted here. This chart is used to compare the precipitation fluctuations with the changes in chemistry at each spring site.

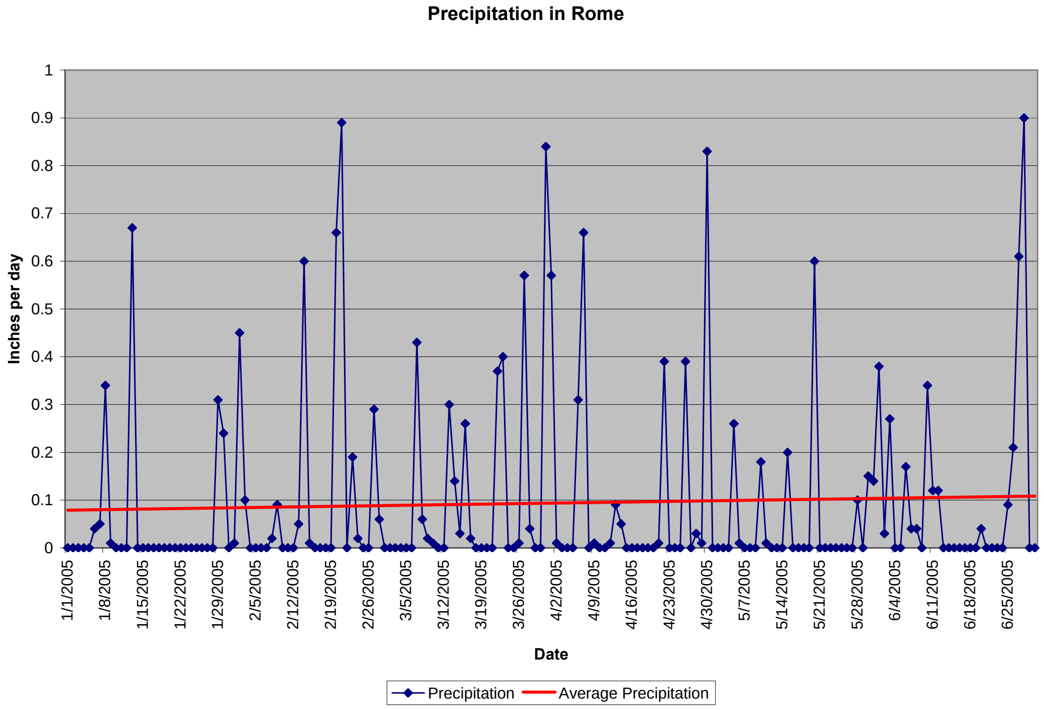

Figure 11: Precipitation in Rome, Georgia

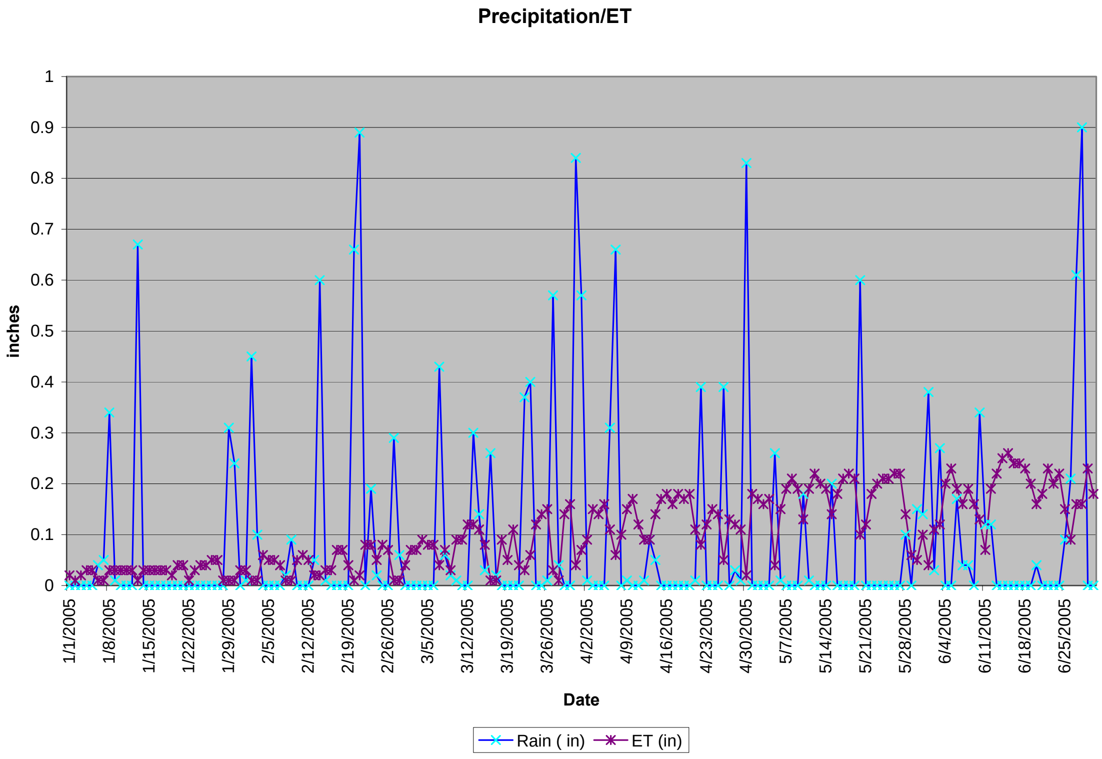

Figure 12: ET in Rome, Georgia

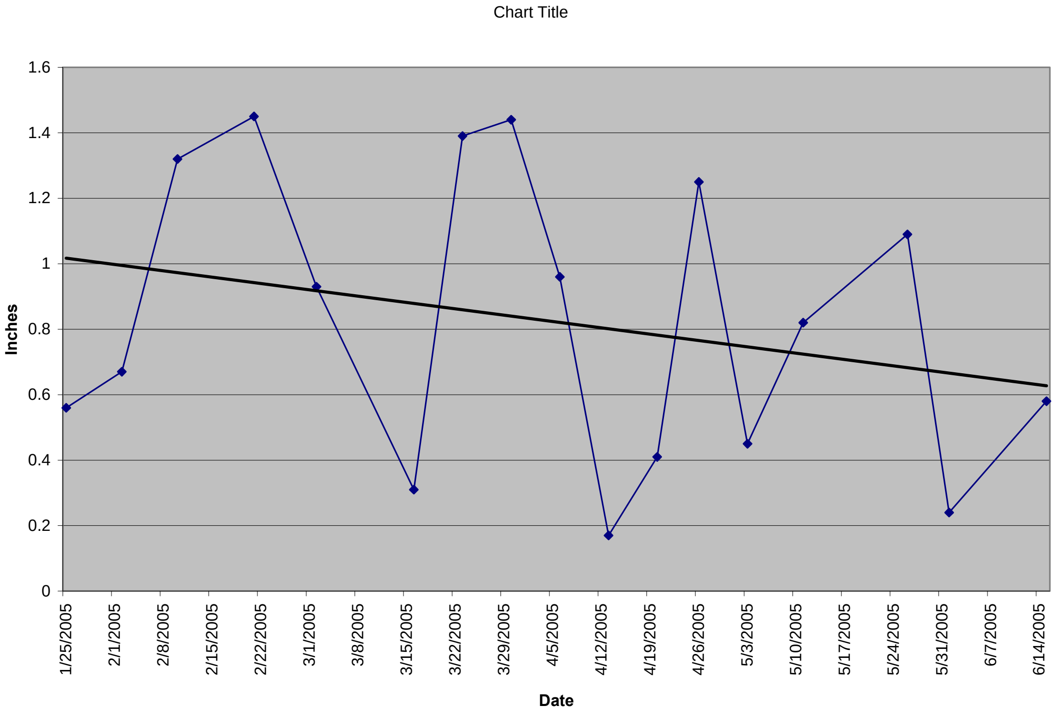

Figure 13: Weekly Rain Totals in Rome, Georgia

Temperature/pH/Conductance of Springs

Each spring's field data was examined to determine any variations in their conductivity, pH, and temperature readings. Changes in conductivity can demonstrate the flow patterns that occur in the carbonate aquifer. Conductivity varied greatly from spring to spring as well as single spring sites over the entire season. See appendix A for a graphical representation of all field data.

Major Ion Chemistry of Springs

Once all the results of the laboratory and field collection were collected, the information was plotted graphically (Appendix A and Appendix B). Tables 2-10 show the average values for each parameter tested and the variation in the spring flow characteristics.

Table 2: Cave Spring Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
CS	Conductivity	189.9	17	22.4	165.7	220.1
	pH	7.2	17	0.2	6.7	7.6
	Temp	14.5	17	0.5	13.8	15.8
	Break pt.	4.9	17	0.3	5.1	6.3
	HCO3	128.9	17	7.2	124.4	152.5
	Cl	1.6	4	0.1	1.5	1.7
	SO4	0.9	4	0.0	0.9	0.9
	Mg	10.7	4	0.3	10.3	11.0
	Ca	20.6	4	1.1	19.0	21.4
	K	0.4	4	0.1	0.3	0.5
	Na	0.6	4	0.1	0.5	0.7
	% error	3.9	4	1.2	2.4	5.1
	anion	2.1	4	0.0	2.1	2.2
	cations	1.9	4	0.0	1.9	2.0
	TDS	161.2	4	2.2	159.6	164.4
	lg iap/KT(calcite)	0.8	4	0.1	0.6	0.9

Table 3: Sand Spring Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
SS	Conductivity	136.8	17	36.2	78.1	211.1
	pH	6.5	17	0.3	5.9	7.0
	Temp	12.4	17	0.6	11.3	13.7
	Break pt.	3.0	17	0.8	2.1	5.4
	HCO3	77.3	17	24.0	50.0	136.7
	Cl	1.8	6	0.2	1.6	2.0
	SO4	2.1	6	0.2	1.8	2.3
	Mg	2.1	6	0.6	1.3	2.7
	Ca	27.0	6	8.4	21.5	43.5
	K	0.7	6	0.1	0.6	0.8
	Na	1.0	6	0.2	0.8	1.2
	% error	3.9	6	3.1	0.8	9.5
	anion	1.4	6	0.4	1.2	2.3
	cations	1.6	6	0.5	1.3	2.4
	TDS	116.5	6	35.6	97.6	188.5
	lg iap/KT(calcite)	-1.3	6	1.1	-1.9	1.0

Table 4: North John's Mountain Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
NJM	Conductivity	13.8	17	3.3	10.0	22.1
	pH	5.5	17	0.7	3.7	6.5
	Temp	12.7	17	1.0	11.0	14.3
	Break pt.	0.0	17	0.0	0.0	0.0
	HCO3	0.0	17	0.0	0.0	0.0
	Cl	1.5	2	0.1	1.4	1.6
	SO4	1.2	2	0.0	1.2	1.3
	Mg	0.4	2	0.0	0.4	0.4
	Ca	0.6	2	0.0	0.6	0.6
	K	0.5	2	0.0	0.5	0.5
	Na	0.6	2	0.0	0.6	0.6
	% error	2.7	2	0.3	2.5	2.9
	anion	0.1	2	0.0	0.1	0.1
	cations	0.1	2	0.0	0.1	0.1
	TDS	4.9	2	0.1	4.8	5.0
	lg iap/KT(calcite)	-5.1	2	0.0	-5.2	-5.1

Table 5: John's Mountain Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
JM	Conductivity	14.2	17	2.4	11.3	19.3
	pH	4.6	17	0.4	4.2	5.5
	Temp	11.4	17	0.8	10.2	13.1
	Break pt.	0.0	17	0.0	0.0	0.0
	HCO3	0.0	17	0.0	0.0	0.0
	Cl	1.5	3	0.1	1.4	1.5
	SO4	0.9	3	0.4	0.6	1.3
	Mg	0.2	3	0.1	0.2	0.3
	Ca	0.3	3	0.2	0.2	0.5
	K	0.4	3	0.2	0.3	0.7
	Na	0.5	3	0.0	0.5	0.5
	% error	0.7	3	0.8	0.1	1.5
	anion	0.1	3	0.0	0.1	0.1
	cations	0.1	3	0.0	0.1	0.1
	TDS	3.9	3	0.6	3.4	4.6
	lg iap/KT(calcite)	-5.6	3	0.2	-5.8	-5.5

Table 6: Chestnut Mountain Shooting Range Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
CMSR	Conductivity	29.3	17	7.8	22.1	52.0
	pH	4.8	17	0.3	5.0	5.8
	Temp	10.6	17	1.4	10.5	14.8
	Break pt.	0.0	17	0.0	0.0	0.0
	HCO3	0.0	17	0.0	0.0	0.0
	Cl	3.2	2	0.4	1.7	2.5
	SO4	4.1	2	1.5	1.0	3.9
	Mg	1.4	2	0.8	0.2	1.8
	Ca	1.0	2	0.6	0.5	1.4
	K	0.8	2	0.6	0.4	1.2
	Na	1.6	2	0.3	0.8	1.4
	% error	4.2	2	3.7	1.6	6.8
	anion	0.1	2	0.0	0.1	0.1
	cations	0.1	2	0.1	0.1	0.2
	TDS	7.6	2	3.5	5.1	10.1
	lg iap/KT(calcite)	-4.8	2	0.7	-5.3	-4.4

Table 7: Everett Springs Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
ES	Conductivity	379.1	17	28.8	316.1	413.0
	pH	6.9	17	0.2	6.5	7.2
	Temp	15.1	17	1.1	13.6	18.8
	Break pt.	9.6	17	2.4	7.9	17.5
	HCO3	217.3	17	13.7	192.8	256.2
	Cl	5.4	5	0.5	4.5	5.7
	SO4	2.6	5	0.2	2.2	2.8
	Mg	7.6	5	0.3	7.1	7.9
	Ca	55.3	5	0.5	54.6	55.8
	K	0.6	5	0.1	0.5	0.8
	Na	5.5	5	0.2	5.2	5.7
	% error	2.2	5	1.0	0.6	3.3
	anion	3.8	5	0.1	3.7	3.9
	cations	3.6	5	0.0	3.6	3.7
	TDS	297.4	5	6.4	290.4	304.9
	lg iap/KT(calcite)	0.5	5	0.2	0.3	0.7

Table 8: West John's Mountain Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
WJM	Conductivity	183.5	17	42.8	119.5	287.7
	pH	6.6	17	0.3	5.8	7.0
	Temp	10.9	17	1.5	9.1	13.5
	Break pt.	4.6	17	0.6	3.6	5.7
	HCO3	114.2	17	12.8	94.4	139.1
	Cl	1.7	5	0.3	1.2	2.0
	SO4	1.6	5	0.3	1.2	2.0
	Mg	3.0	5	0.3	2.6	3.2
	Ca	37.7	5	4.1	32.3	43.1
	K	0.5	5	0.1	0.4	0.6
	Na	0.7	5	0.1	0.6	0.8
	% error	4.6	5	3.6	0.2	7.5
	anion	1.9	5	0.1	1.9	2.0
	cations	2.2	5	0.2	1.9	2.5
	TDS	159.0	5	7.0	152.8	169.9
	lg iap/KT(calcite)	-1.2	5	0.1	-1.4	-1.0

Table 9: Turkey Mountain Major Ion Data

Spring name	Parameters	Average value	# of samples taken	Standard Deviation	low value	high value
TM	Conductivity	83.3	17	23.8	45.0	128.0
	pH	6.2	17	0.2	5.9	6.5
	Temp	12.6	17	0.4	12.1	13.5
	Break pt.	1.7	17	0.7	0.3	2.3
	HCO3	41.9	17	16.8	6.1	56.1
	Cl	2.2	5	0.2	1.9	2.4
	SO4	3.0	5	0.1	2.9	3.2
	Mg	3.0	5	0.9	1.5	3.5
	Ca	9.5	5	3.0	4.3	11.6
	K	0.6	5	0.0	0.5	0.6
	Na	1.4	5	0.4	0.8	1.7
	% error	3.2	5	1.4	1.6	4.3
	anion	0.9	5	0.3	0.3	1.0
	cations	0.8	5	0.2	0.4	1.0
	TDS	64.4	5	22.7	24.1	77.7
	lg iap/KT(calcite)	-2.9	5	0.6	-3.9	-2.4

WATEQ is designed to analyze a set of water chemistry and determine the saturation indices for that data set. The variations in the chemistries detected at each of the spring sites were plotted graphically to produce trends in the chemical variations. See Appendix B from all individual spring laboratory testing results.

Based upon preliminary field testing the springs were separated into carbonate aquifer and precipitation-induced springs. Once ion analysis was completed the ion analytical data was keyed into the WATEQ modeling program. Since bicarbonate represented the major anion in each of the springs, the average conductivity for each spring was used to determine the spring classification. Carbonate aquifer springs were those higher conductivity springs and were approaching equilibrium with calcite. Table 10 shows the spring divided into their respective groups and their average conductivity.

The line for spring saturation was based upon the computer model analysis that determined the possible material that the discharging water was in equilibrium with calcite. In Table 10 below, carbonate aquifer and precipitation-induced springs are divided by sampling locations.

Table 10: Conductivity Averages of Sample Sites in ųS

Carbonate Aquifer Springs	Conductivity (µS)	Precipitation-induced Springs	Conductivity (µS)
Cave Spring	191.8	North John's Mountain	5.5
Sand Spring	136.8	Horn Mountain	14.2
Everett Springs	379.1	Chestnut Mountain Shooting Range	29.3
West Armuchee Spring	183.5		
Turkey Mountain Spring	83.3		

Once analysis was completed, a preliminary line separating the carbonate aquifer and precipitation-induced springs based upon the levels of conductivity was drawn from field testing (Table 2). The precipitation-induced spring generally tended to have low conductivities and was not near equilibrium with calcite. The carbonate aquifer springs were grouped to include all of the sites that did not have a conductivity that dropped below 45 ųS over the course of the study period. There was one exception, Chestnut Mountain Shooting Range, which varied greatly from the low 20’s ųS to the high 50’s ųS. For the purpose of this study the Chestnut Mountain Shooting Range was included into the precipitation-induced spring's group. Carbonate aquifer springs were separated again based upon the fluctuating conductivity. The fluctuating conductivity levels with the changes in rainfall volume were used to determine the flow type; diffuse or conduit. The following figures compare trends between rainfall and conductivity over the sampling period of the study.

In Figure 15, Cave Spring does not experience quick or significant fluctuations in conductivity as a result of precipitation events. As the weekly precipitation volumes increase and decrease there is no change that coincides with a change in conductivity. There is a decreasing trend that occurs both in the conductivity and the rain volume over the course of the study period.

The Figure 16 shows that both the conductivity and the rain volumes had very large fluctuations over the study period. While none of the peaks for the two factors exactly lined, there appears to be an offset of peaks. This offset could be the result of a delay in rain water reaching the spring.

In Figure 17, field sampling showed that the conductivity generally remained under 15 ųS, with the exception of one sample of 22 ųS, which is still below the maximum conductivity for rain water measured by the NADP for Georgia.

The Figure 18 of Horn Mountain was classified with within the precipitation-induced springs. The conductance observed during the study period was too low too accurately comparing chemical fluctuations to the fluctuations of the weekly rain volume. The spring water's chemical composition was below the measurable accuracy and precision of the lab equipment used.

The Figure 19 shows for each of the sampling events do appear to have a significant relationship with the precipitation. The water tested below the spring site on the mountain had conductivity above 70 ųS, while during the regular study period the spring had level of conductivity, slightly higher than that measured in Georgia's rainwater. The gap that occurs at the end of the graph results from the spring drying up.

The Figure 20 shows that there is little correlation between the peaks of the precipitation line and the peaks on the conductivity line. There was a drop in average conductivity that occurred in a similar rate to the average drop in rain volume. This graph shows that the high conductivity of the spring does not represent the bicarbonate ion solely. The Ca^{+2} ions were considerably higher than in any other spring. The average Ca^{+2} cation were 55 mg/L. These properties suggest that the water that discharges through this spring passes through a limestone aquifer. The only carbonate material is an Upper and Middle Ordovician undivided formation, including the Murfreesboro, Ridley, Moccasin, and Bays formation found stratagraphically below the Red Mountain formation on John's Mountain. Since there is little to no change in chemistry and constant flow rate, this aquifer exhibits a diffuse flow network. The filtration received by the water passing through the rock matrix would allow for the reduction in the amount of treatment needed at this discharge point.

The graph shows that the bicarbonate does relate with the conductivity, since the calcium ion is very high the fluctuations for the conductivity are more exaggerated. To determine flow type the conductivity is compared to the weekly rain events in the following graph.

The Figure 21 shows that both the conductivity and the rain volumes had very large fluctuations over the study period. The peaks for each of the factors appear to have some relationship, since with each peak in rainfall there is an increase in conductivity. Over the course of the study period the average rain volume dropped while the average conductivity did not decrease significantly.

The Figure 22 shows that both the conductivity and the rain volumes had very large fluctuations over the study period. Unlike the other carbonate aquifer springs, large fluctuations occurred at nearly every sampling event. The fluctuations do not appear to have a significant relationship with the precipitation.

CAVE SPRING FIELD DATA RESULTS

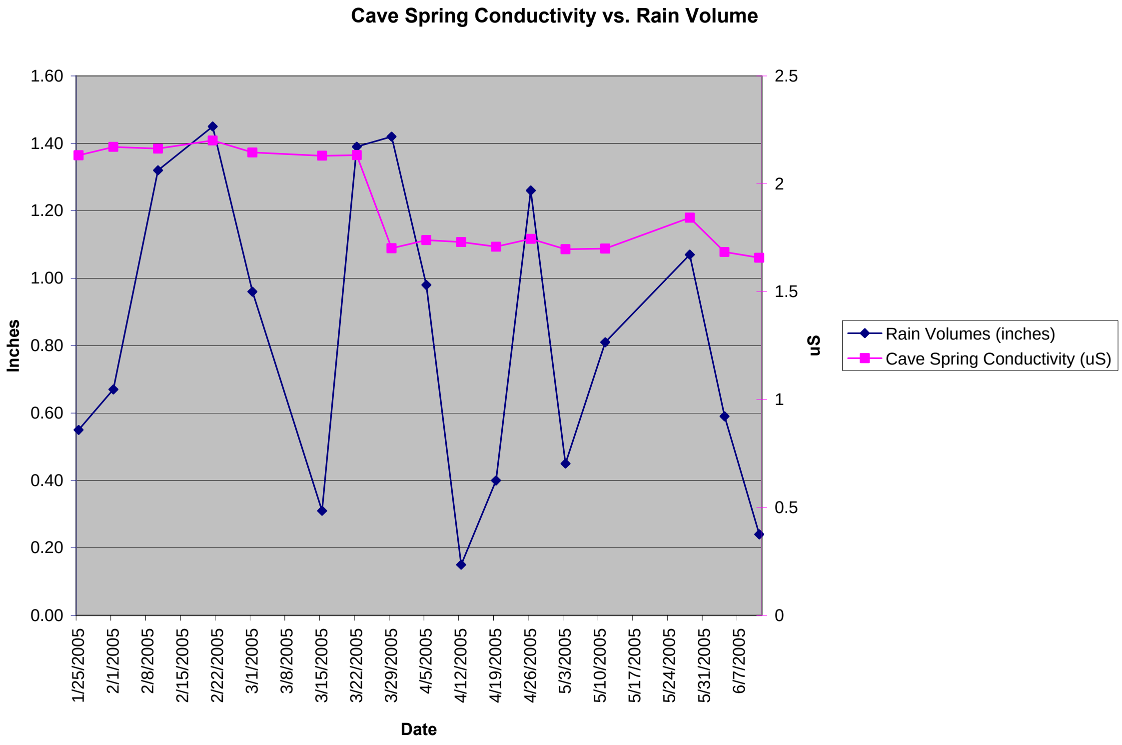

Figure 14: Cave Spring Conductivity vs. Rain Volume

SAND SPRING FIELD DATA RESULTS

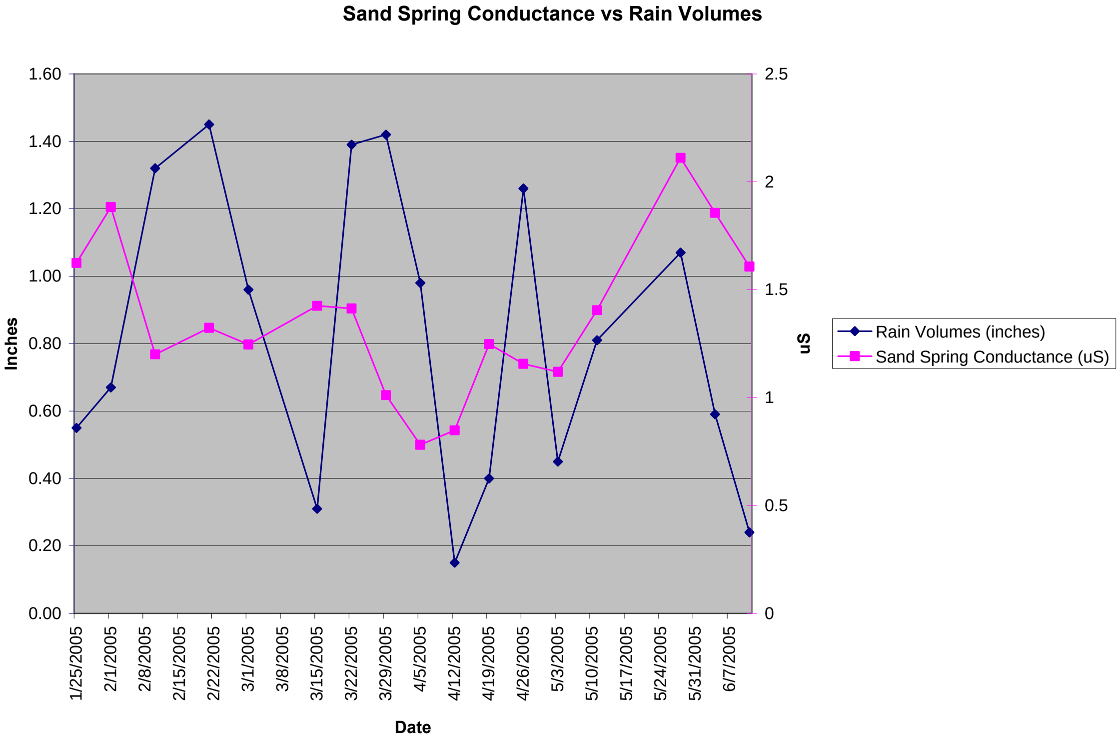

Figure 15: Sand Spring Conductance vs. Rain Volume

NORTH JOHN’S MOUNTAIN FIELD DATA RESULTS

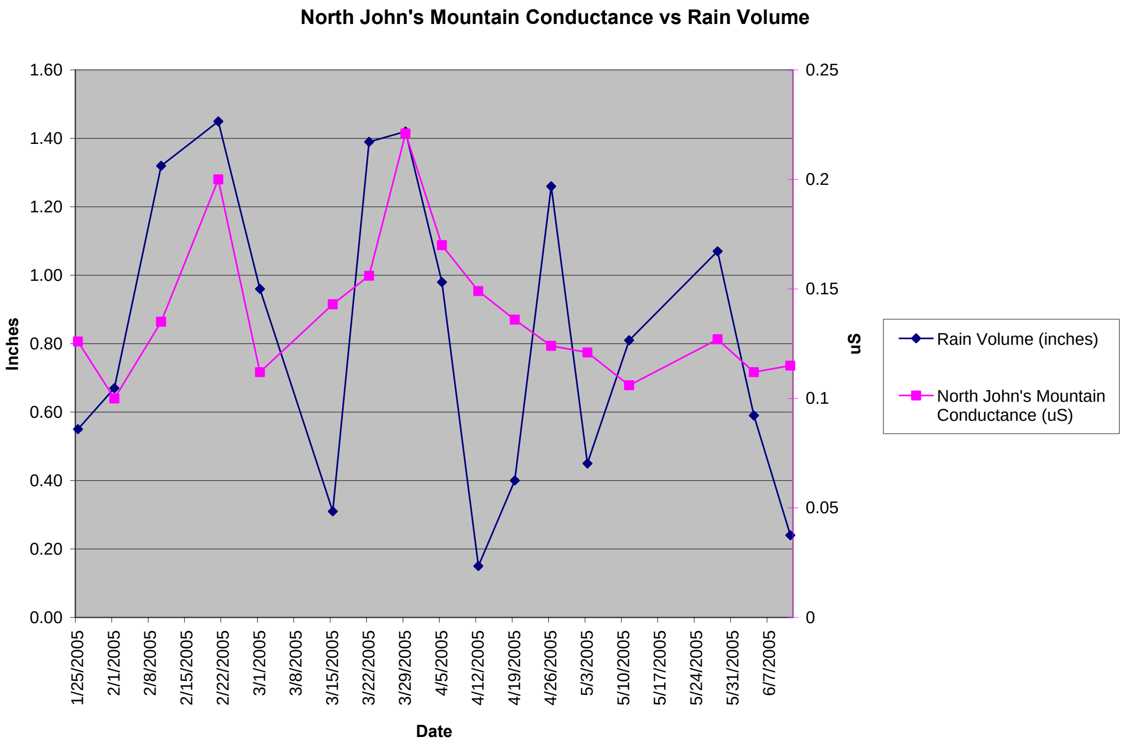

Figure 16: North John’s Mountain Conductance vs. Rain Volume

HORN MOUNTAIN FIELD DATA RESULTS

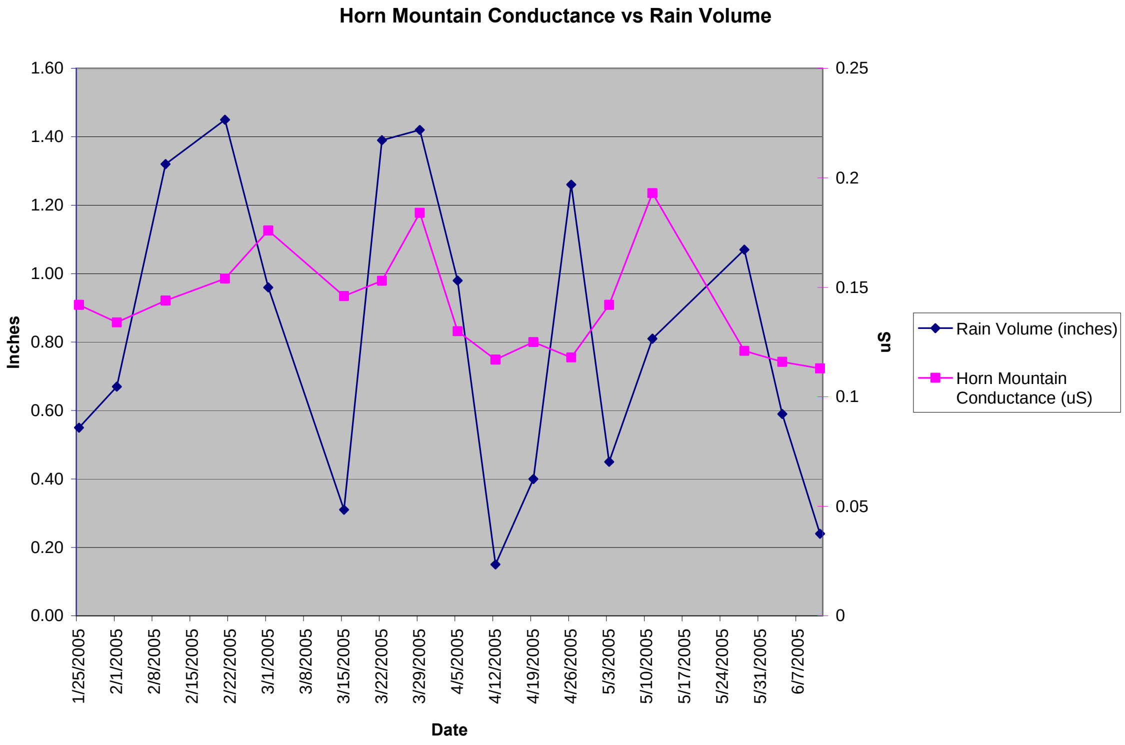

Figure 17: Horn Mountain Conductance vs. Rain Volume

CHESTNUT MOUNTAIN SHOOTING RANGE FIELD DATA RESULTS

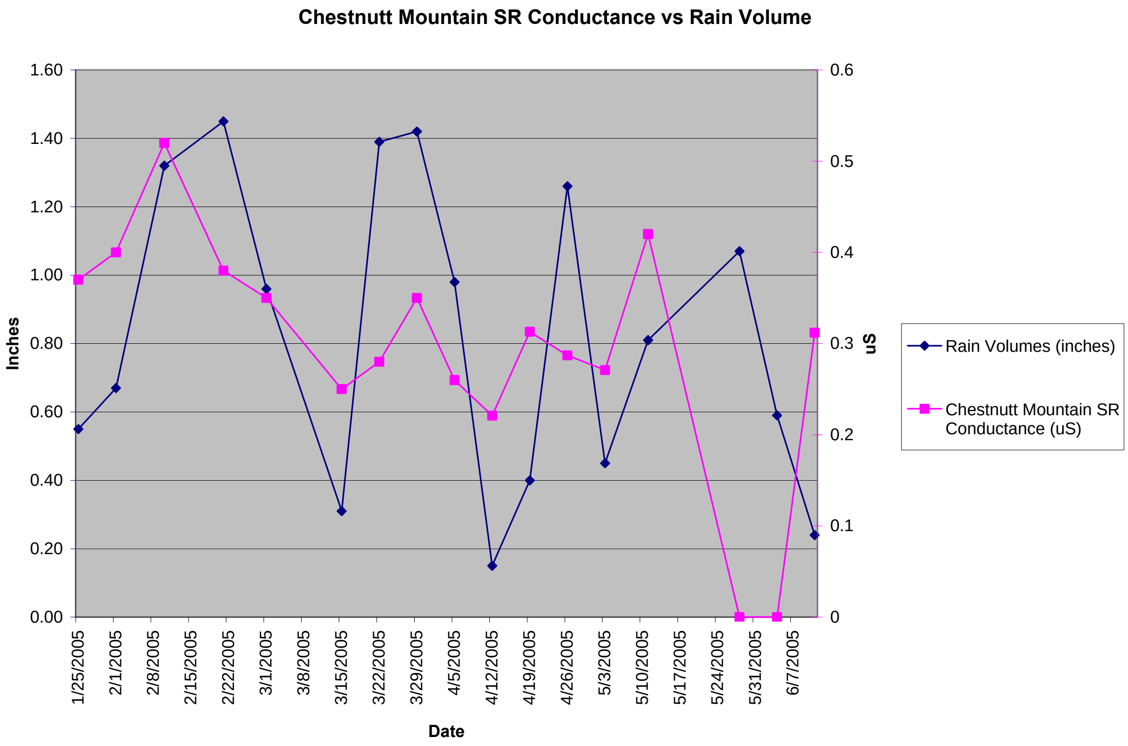

Figure 18: Chestnut Mountain Shooting Range Conductance vs. Rain Volume

EVERETT SPRINGS FIELD DATA RESULTS

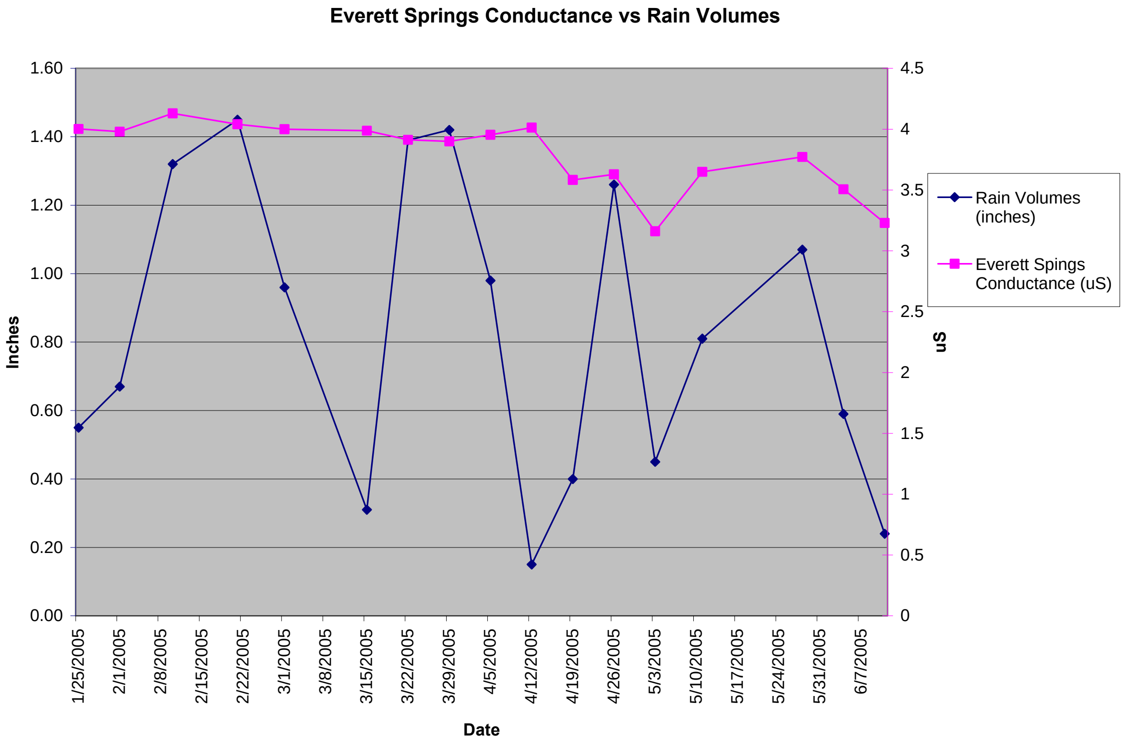

Figure 19: Everett Springs Conductance vs. Rain Volume

WEST ARMUCHEE FIELD DATA RESULTS

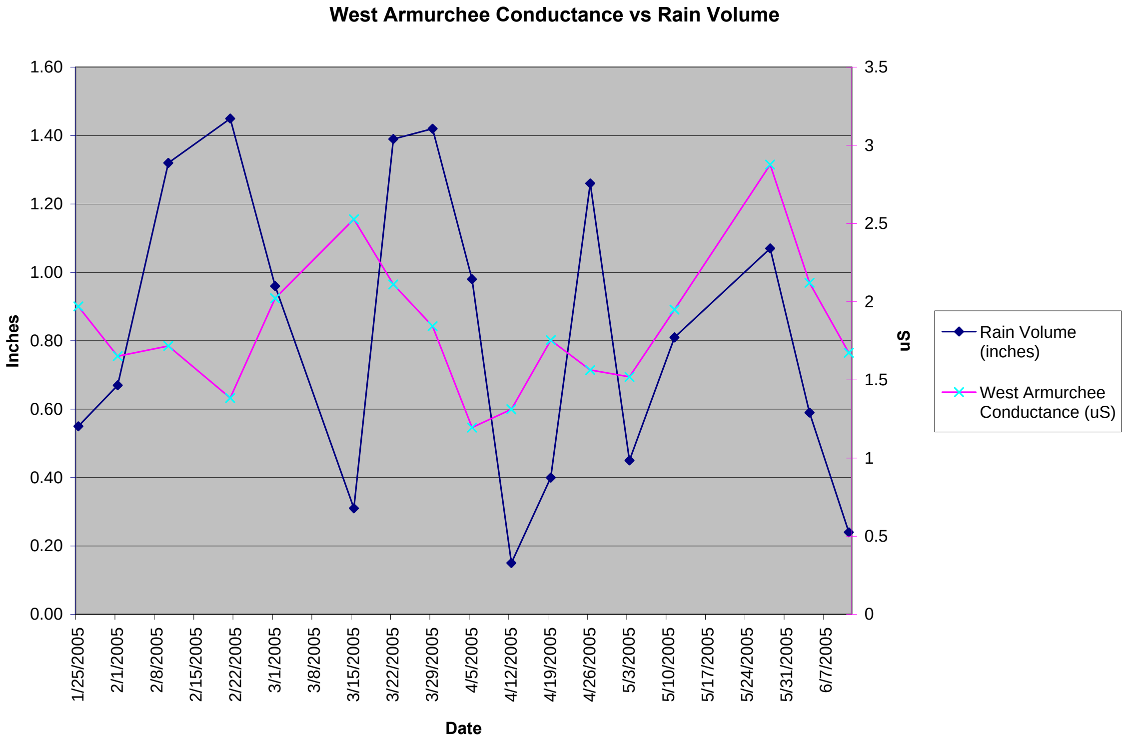

Figure 20: West Armuchee Conductance vs. Rain Volume

TURKEY MOUNTAIN FIELD DATA RESULTS

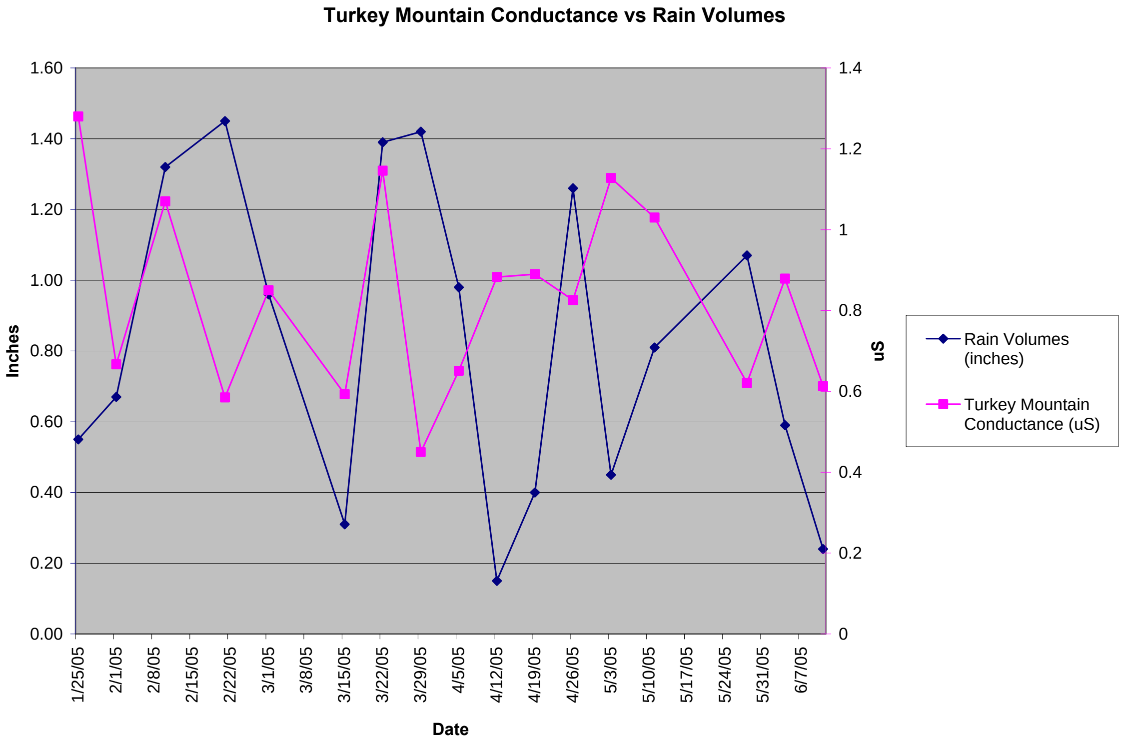

Figure 21: Turkey Mountain Conductance vs. Rain Volume

5. DISCUSSION

The carbonate aquifer spring group included the springs with high conductivity (Cave Spring, Sand Spring, West Armuchee, and Everett Springs), which are referred to as the suspect carbonate aquifers, versus the precipitation-induced spring group with low conductivity (North John's Mountain, Horn Mountain, and Chestnut Mountain Shooting Range), now referred to as the suspect precipitation-induced springs. There was a large distinction between the conductivity of the two classifications. Precipitation-induced springs resulted as the spring discharge that approximates the chemistry of rain water. Rainwater has generally low conductivity and low pH (Kehew, 2001). For this study the springs which demonstrated an average conductivity level below 25 ɥS were included in the precipitation-induced spring category. Chestnut Mountain was included in the precipitation-induced springs since its average was close to that of rain water. Additionally, Chestnut Mountain Shooting Range's average conductivity was far below the nearest carbonate aquifer spring average.

The study period coincided with the winter wet season and the beginning of a summer dry season. The tail end of this study period coincided with a much wetter than normal summer season in the southeastern region. This was the 2005 summer when several large hurricanes hit the Gulf Coast of the United States.

The fluctuations of field measured conductivity levels for each of the carbonate aquifer springs were compared to the fluctuations that occurred in the weekly rain volumes during the sampling period. The changes in conductivity were used to compare variances that occurred due to influence from precipitation events. With the exception of

Chestnut Mountain Shooting Range all precipitation induced springs did not have enough conductivity to show an effect from the precipitation events. The following graphs are used to compare the fluctuations in the conductivity and weekly rain volumes. To compare these values, the Y-axis values were removed and each line was imported on the same graph.

Carbonate Aquifer Springs

Carbonate aquifers were broken down into conduit and diffuse flow networks. Conduit flow generally occurs through highly soluble material and is controlled by well developed surface drainage systems, while diffuse flow occurs in less soluble rocks such as shaley limestone or dolomite or in less developed drainage systems (White, 1969). Conduit flow is generally characterized by turbulent and varying flow through solution openings, while diffuse flow can be characterized by flow through small pores and fractures.

Cave Spring-Location #1 (CS)

Cave Spring was grouped into the carbonate aquifer springs group due to its high conductivity results from the field testing and the high bicarbonate levels from the laboratory analysis. Ionic analysis showed that the predominant anion was bicarbonate and minor chloride and sulfate ions. While calcium was the predominate cation, the magnesium levels were higher suggesting that there was some interaction with dolomitic material. The average WATEQ analysis determined the aquifer type to be a slightly supersaturated with respect to calcite.

The large peak of the bicarbonate in the early section of the study period is masked in the conductivity due to the high volume of rain that was occurring at this time (Figure 14). Unlike the other springs in this study, Cave Spring has been studied by Garner and Mayer, 2004. Its aquifer was described as discharging from the decomposing Knox Group residuum at the point where contact with the Conasauga Formation occurs. Overall this spring fluctuates very little over the course of the study period, with only small out lying variations. The conductivity drops and remains low through the remaining drier months of the study period. This drop in conductivity is similar to the dilution drop seen in stream discharges measured by Aheam et al., 2004.

Even though the spring discharges through a small cave network, this study demonstrated that the consistent flow and chemical make up determine that the spring's flow network was more diffuse than conduit as is supported by the laboratory analysis that was performed. This analysis agrees with the determination made by Garner and Mayer (2004). The diffuse nature of the aquifer net work showed the reason why water has been collected by the local people for so long. The aquifer allowed for the partial filtration of the water before discharging onto the surface. The diffuse flow helped the aquifer to prevent contamination spread to the discharge point.

Sand Spring-Location #2 (SS)

Sand Spring was classified as a carbonate aquifer spring due to its high conductivity levels. WATEQ analysis shows that the spring was supersaturated with respect to calcite at the first sample; however the remaining samples were undersaturated slightly with respect to calcite. Though the flow rates didn't appear to vary greatly with time, either the increase in volume of flow caused the dilution of the ions or additional water sources began infiltrating the aquifer. Figure 15 shows the apparent effect of precipitation on the spring’s chemical makeup.

The spring was discharging below a thick clay cliff containing Chert nodules. The discharge channel was filled with fine clays and loose chert rubble material. This geologic determination agrees with the Aldaheff and others (2003), which shows the Fort Payne and Armuchee Chert formations in contact at approximately the spring site. Approximately one-hundred yards below the spring there is an exposure of moderately to heavily weathered shaley material within the stream bed. Aldaheff and others (2003) shows this as the Floyd Shale formation. There are several discharges along the same formational contact near the base of the mountain, such as the larger spring that Cressler (1971). The top of Lavender Mountain is capped with Red Mountain formation sandstone, which holds a small reservoir that serves Berry College.

Everett Springs-Location #6 (ES)

Everett Springs was also a carbonate aquifer spring located in the basin between Horn Mountain and John’s Mountain. Since the spring ran very slowly, flow rate was measurable by collecting the entire overflow, which was calculated as approximately 24 g/hr or just under 600g/day based upon collection of study samples. This rate of flow did not change measurably through out the study period. Everett Springs had the highest conductivity of all of the study springs, averaging 380 ųS over the coarse of the study period. With the exception of a few small fluctuations the pH and temperature of the spring did not change over the period.

Additionally, as shown in Figure 19, the chemistries did not have much fluctuation for the same period. The valley where the spring was located contained numerous springs that all appeared to occur at the same elevation relative to each other. WATEQ analysis shows that the discharge was slightly supersaturated with respect to calcite over the course of the entire study period.

Since the flow did not change and the chemistries remained constant through the study period, this spring appeared to result from a diffuse recharge and flow network originating in the Red Mountain formation sandstone cap rocks of John’s Mountain, flowing through a Middle Ordovician Limestone that underlies it and discharging through the Floyd shale. One-quarter of a mile to the east is Rocky Creek, a slow moving stream. More discharge probably occurs with in the stream; however there was no visible evidence.

West Armuchee-Location #7 (WA)

West Armuchee spring was included in the carbonate aquifers due to the high conductivity samples collected over the course of the study period. Ionic analysis showed that the predominant anion was bicarbonate and included minor chloride and sulfate ions. While calcium was the predominate cation, the magnesium levels were higher suggesting that there was some interaction with dolomitic material. The average WATEQ analysis determined the aquifer type to be a slightly supersaturated with respect to calcite. In Figure 20 the conductivity does not directly relate to the rainfall volumes.

West Armuchee discharges from the Bangor limestone that is exposed under the Red Mountain formation at the contact of a thrust fault along the western side of John’s

Mountain. The spring discharges through numerous points along the side of the valley above Armuchee Creek. The major spring ions were calcium and bicarbonate. This location is categorized as a carbonate aquifer spring. Flow in this spring varied considerably throughout the study period, however there was a consistent wetland area that never dried out.

Turkey Mountain-Location #8 (TM)

Turkey Mountain spring is located along the south eastern end of Turkey Mountain. This spring appeared to have a constant flow over the course of the study period and slightly variable. According to the chemical data and flow this spring appears to be a result of a carbonate aquifer. WATEQ analysis shows that the spring in undersaturated with respect to calcite.

This site is the location that was used as a chert quarry in the early to mid 1900’s. There are four formations that make up Turkey Mountain according to Cressler (1971); the Fort Payne Chert, the Armuchee Chert, the Red Mountain formation, and the Lavender Shale member. None of these formations contains a potential carbonate aquifer. The Rome fault has been mapped to the east of Turkey Mountain; however, the Rome fault is broken up by numerous minor thrust faults. Also the Oostanaula River runs to the east of Turkey Mountain, approximately 120 feet down in elevation from the spring, which would keep groundwater flow coming from the west. In a 1946 Geologic Map of Northwest Georgia, Charles Butts mapped an undulation in the Rome fault at Turkey Mountain. This undulation shows a section of Conasauga formation that was placed on the east side of the mountain. The Conasauga is a shaley limestone, which helps to explain the presence of the calcium and bicarbonate ions. .

Since the conductivity falls nearly in line with the rain events (Figure 21) a new source is being accessed (Kehew, 2001), which would show that the Conasauga was only included in the aquifer after a rain event. Also, the rapid rise and fall in conductivity suggests that there is a form of conduit flow to the aquifer system that is added in rain events. These rain events created contact between rock and water in the recharge basin that has a carbonate portion allowing for decreased dissolution as the water traveled through the system. Since the aquifer was known to mainly cherty in nature, which is not reactive in natural rainwater, it is difficult to estimate the amount of time the water spends in the groundwater network or what kind of flow path was taken. The increased flow due to rainfall events show that the water did flow through conduit systems. The conduit systems would not allow for the passing groundwater to be filtered, showing that the contaminate potential to reach the discharge point was very likely.

Precipitation-induced Springs

The precipitation-induced springs were classified as such because they had chemistries that were similar in nature to rain water. The discharges of these springs had very low conductivities and slightly acidic pH’s similar to that found in the rainwater tests done by NADP’s website. Since the discharges occurred from aquifers that appeared to be composed of non-reactive material, the time the water spends underground is unknown.

North John’s Mountain-Location #3 (NJM)

North John’s Mountain is a low conductivity spring and is classified as a precipitation-induced spring. The spring did have spikes of conductivity during drier weather; however, the variations were below the level of error for the YSI Specific conductance sampling device. The pH and temperature for the site did not fluctuate very much, and remained very similar to rain water. As with all of the precipitation-induced springs WATEQ analysis showed that the discharge is very undersaturated with respect to calcite

The area is located in a steep valley composed of sandstone rubble and fill resulting from the weathering of the Silurian sandstone of the Red Mountain formation. All along the creek leading up to the spring, there were large sandstone boulders and cobble size rocks that bordered the stream and the varieties encountered were common for the study area. Above the discharge point North John's Mountain appeared to be capped by coarse sandstone, while the exposed material below varied from a very dark shaley material to a competent cherty rock. The Aldaheff and others showed the Red Mountain formation stratagraphically above the Floyd Shale at this site.

The spring's chemical data and relative geologic setting illustrated that the valley above this discharge point was filled with Alluvium material, collected from the weathering of the sandstone cap rock material. The large cobbles and fill material did not regulate the discharge at the spring, which caused the flow rate to fluctuate over the study period. Non-regulated flow occurred due to the conduit flow of the aquifer. Since the conduit flow network did not allow for any filtration and very little chemical reaction between the water and the rock, the resulting stream discharge has the potential to carry contaminates.

Horn Mountain-Location #4 (HM)

This site was a low conductivity spring that did not experience an extreme change in observable flow rates or field measurements over the study period. The titrations in the lab showed that there was an immeasurable amount of bicarbonate in the samples from this spring. The conductivity measured at this spring was well below the acceptable error for the YSI sampling device and below the measured maximum conductivity for rainwater in the state of Georgia. WATEQ analysis shows that the discharge is undersaturated with calcite and due to the higher sulfate anions was undersaturated with gypsum as well.

At the discharge point there is little in the way of lithic material. There is a thick clay-like soil layer in most areas and a very light pink regolith around the spring is present. Down hill from the discharge point there is sandstone material with a larger chert layer exposed at the base of the mountain. Based upon the comparison of the spring's location and the outcropping of rocks that were surrounding it, comparing these factors to the Georgia Digital Atlas, the spring discharge from originates in the Red Mountain formation. On the digital atlas the Red Mountain formation overlies a cherty Devonian-Mississippian undivided formation. The regolith provides a consistently large supply of water for the spring discharge which explains why the springs flow rate did not appear to fluctuate. This diffuse flow network slowed the water down allowing for a consistent rate of discharges at the spring mouth.

Since the flow did not vary visibly over the course of the study period even when periods of no rain occurred, it appears that the water remained in the groundwater network for a longer period of time. This extended time plus the diffuse nature of the spring showed that this discharge point is a viable option for water collection, since the water would be filtered before discharging.

Chestnut Mountain Shooting Range-Location #5 (CMSR)

The Chestnut Mountain Shooting Range location did not continuously run for the duration of the sampling season. During the month of June the spring dried up and no water was visible for approximately a half mile down hill. The water here was tested but not sampled due to the potential for contamination from additional aquifers that might, during normal conditions be hidden under the flow of the sample spring. Again the spring discharged into a sandstone rubble filled channel, that was designated a part of the Red Mountain formation, by Aldaheff and others.

Due to the variations in conductivity, this indicated there was a potential for mixing of precipitation-induced and carbonate aquifers to dilute the chemistries down stream. The bicarbonate ion did not vary greatly for this spring. WATEQ analysis shows that the spring in undersaturated with respect to calcite.

This spring's discharge was classified into the alluvial fill material with a conduit flow network system that allowed for quick draining of the groundwater system. The conduit nature of this groundwater flow path would allow potential contaminates to reach the discharge point with only small if any, filtration. Therefore, if water was needed, further treatment would be necessary.

6. CONCLUSION

With the increasing growth throughout the Southeast, especially within the state of Georgia, there is a need to determine additional resources for the supply of water. The relatively undisturbed corner of northwest Georgia could supply additional fresh water to the metropolitan areas but very little is known about this area and its ample groundwater supplies. Each of the eight spring discharges was examined to determine chemistry and flow type. These measurements were analyzed to understand the potential for contamination in this region.

This study compared the chemical fluctuations of eight springs in the Ridge and Valley Province of Northwestern Georgia. Based upon the chemical data and precipitation rates for the area of the study, the sites were separated into carbonate aquifer and precipitation- induced springs. The dissolved ions discharging from a spring allow insight into the path taken by the water. Measuring the discharge of each carbonate aquifer over a time frame allows the observer to determine the likely hood in which contaminates will be filtered out before the discharge point. Discharges that contain higher levels of ionic material traveled along slower, longer, or more diffuse paths. Cave spring, Everett spring, and West Armuchee spring samples show increased ionic content resulting from extended water rock contact. Sand spring shows the potential for contamination due to the lower saturation indices and conductivity levels at the discharge point. The precipitation-induced spring type was not separated in to flow types since the chemical results were below the percent error for each of the analytical devices.

Understanding the properties of the selected springs and using this knowledge to interpret other aquifer systems within the Ridge and Valley province will allow for the proper utilization of this groundwater as the development in the northern metropolitan Atlanta area increases.

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APPENDIX A: SPRING FIELD DATA

CAVE SPRING DATA

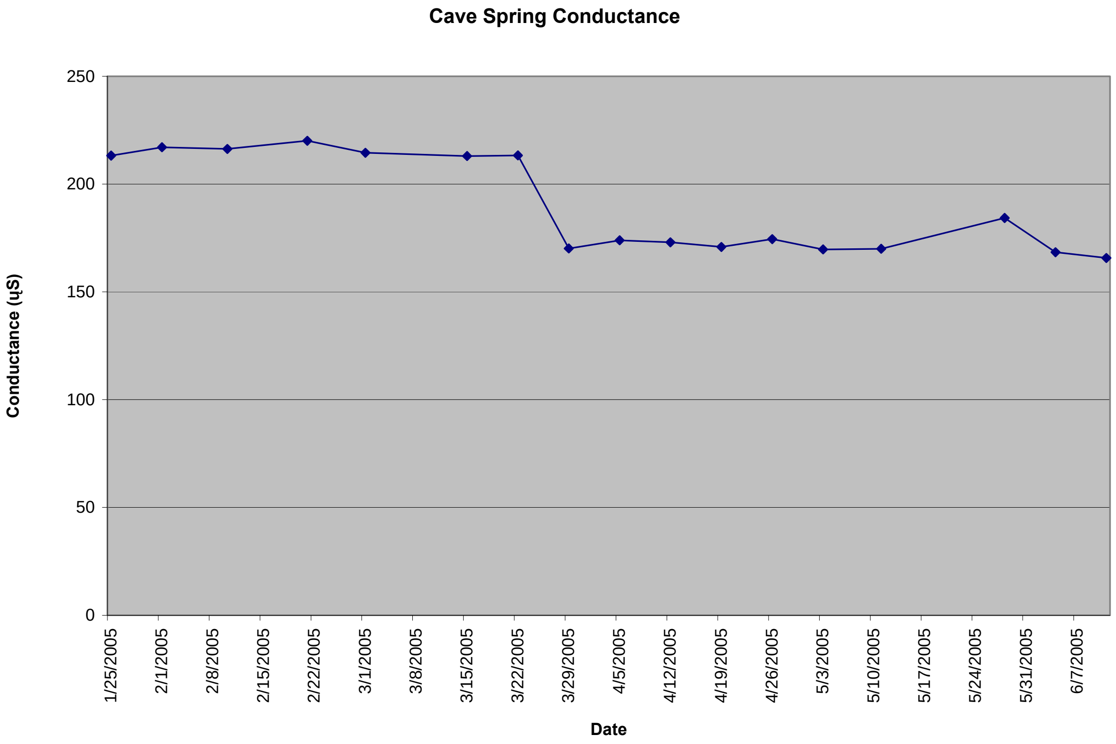

Figure 22: Cave Spring Conductance vs. Time

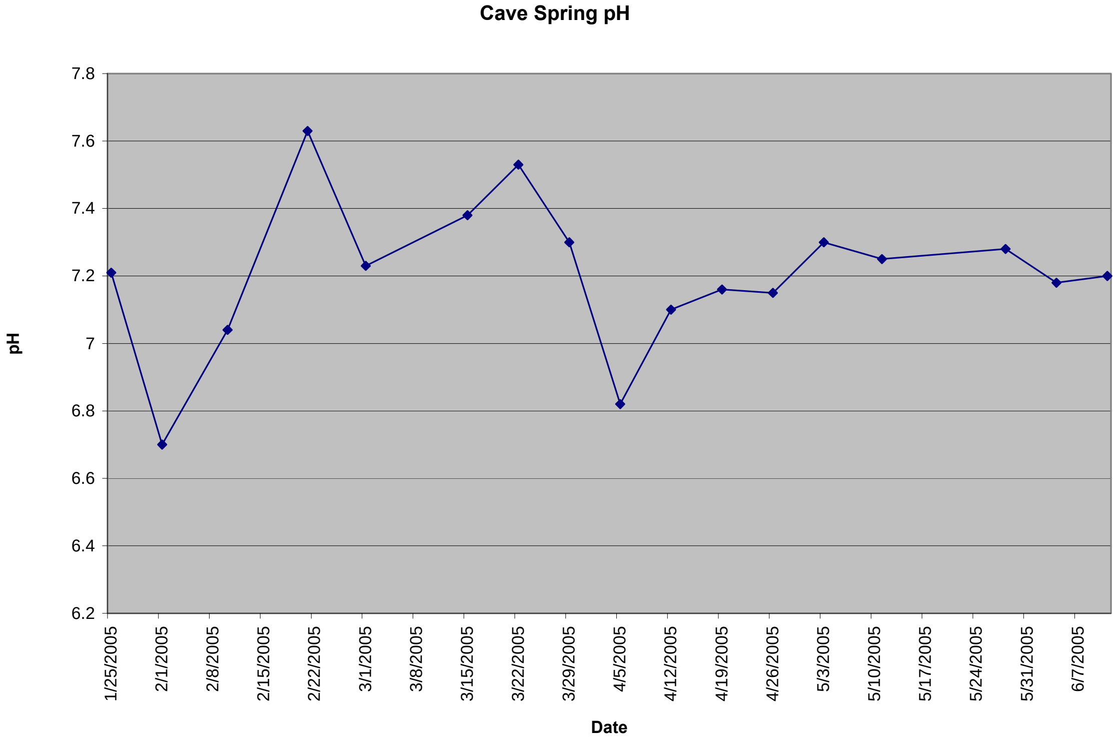

Figure 23: Cave Spring pH vs. Time

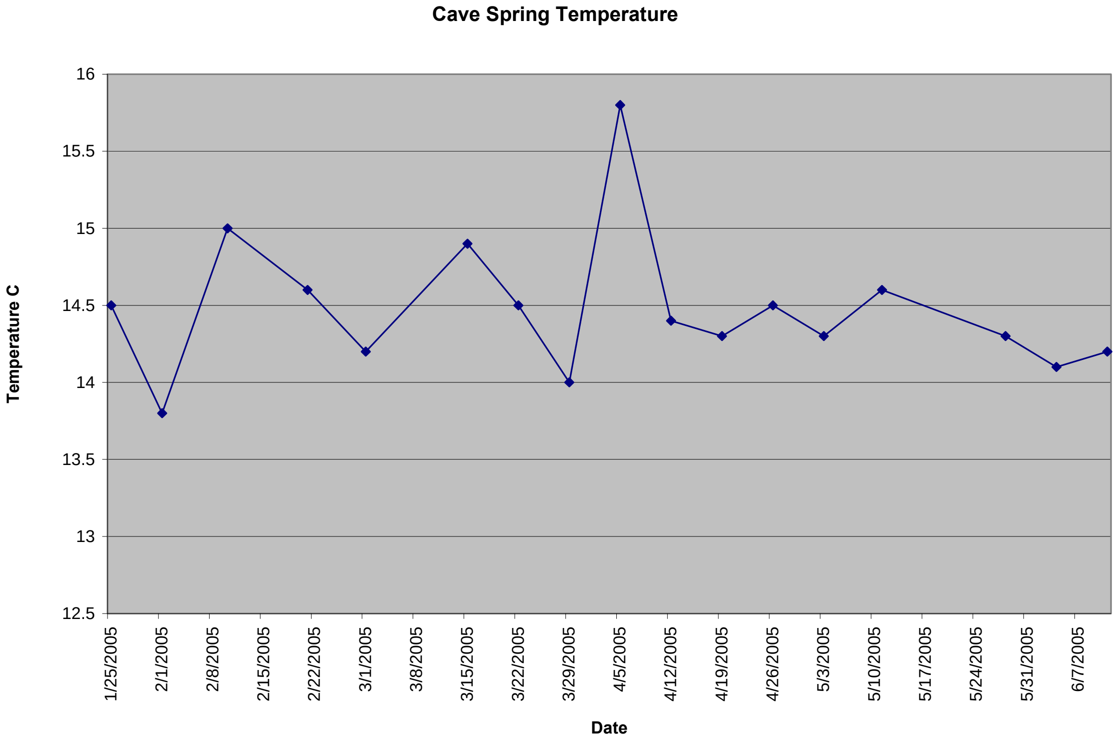

Figure 24: Cave Spring Temperature vs. Time

SAND SPRING DATA RESULTS

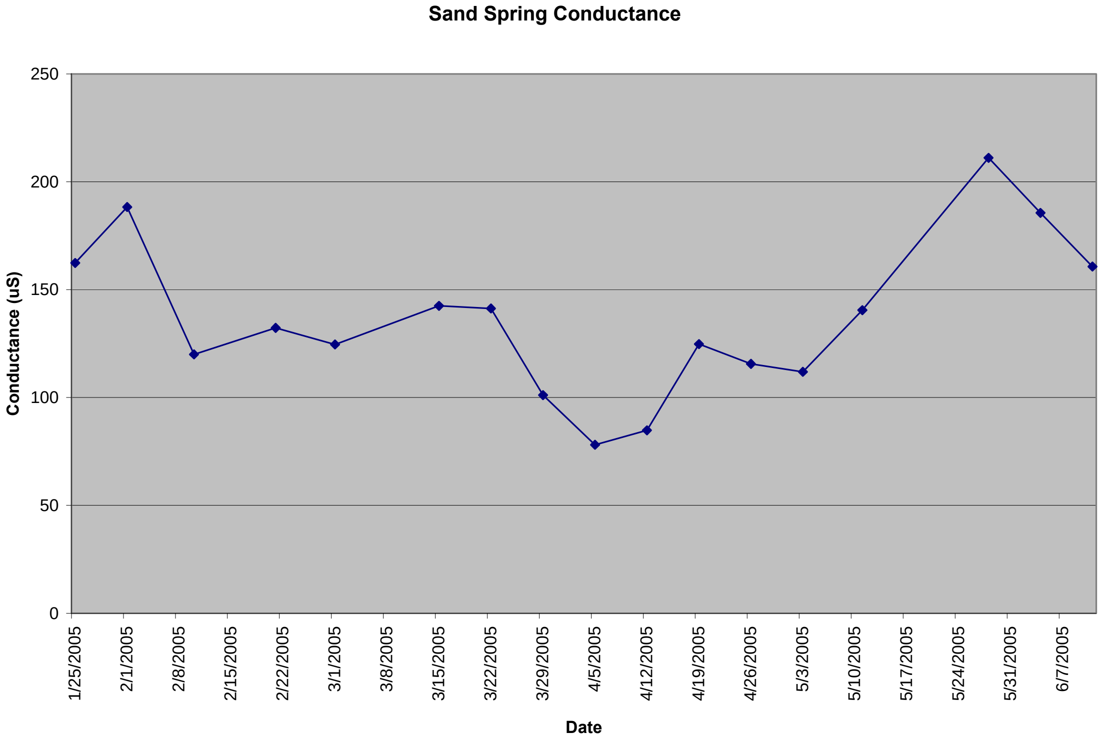

Figure 25: Sand Spring Conductance vs. Time

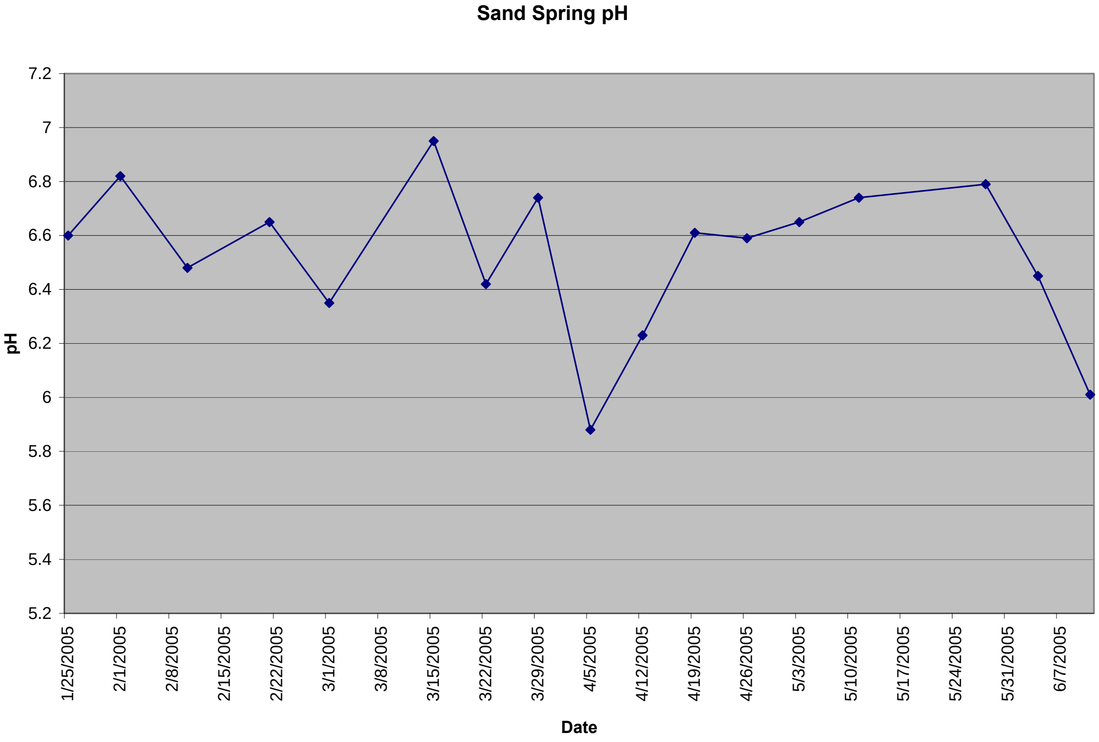

Figure 26: Sand Spring pH vs. Time

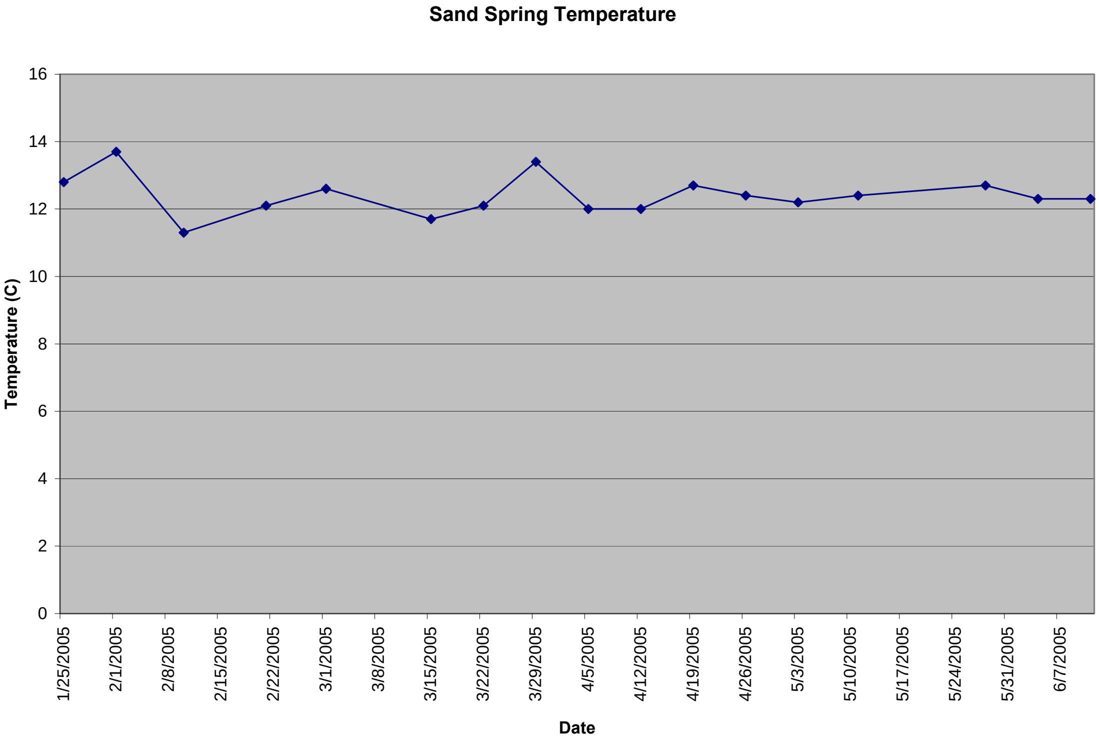

Figure 27: Sand Spring Temperature vs. Time

NORTH JOHN’S MOUNTAIN FIELD DATA

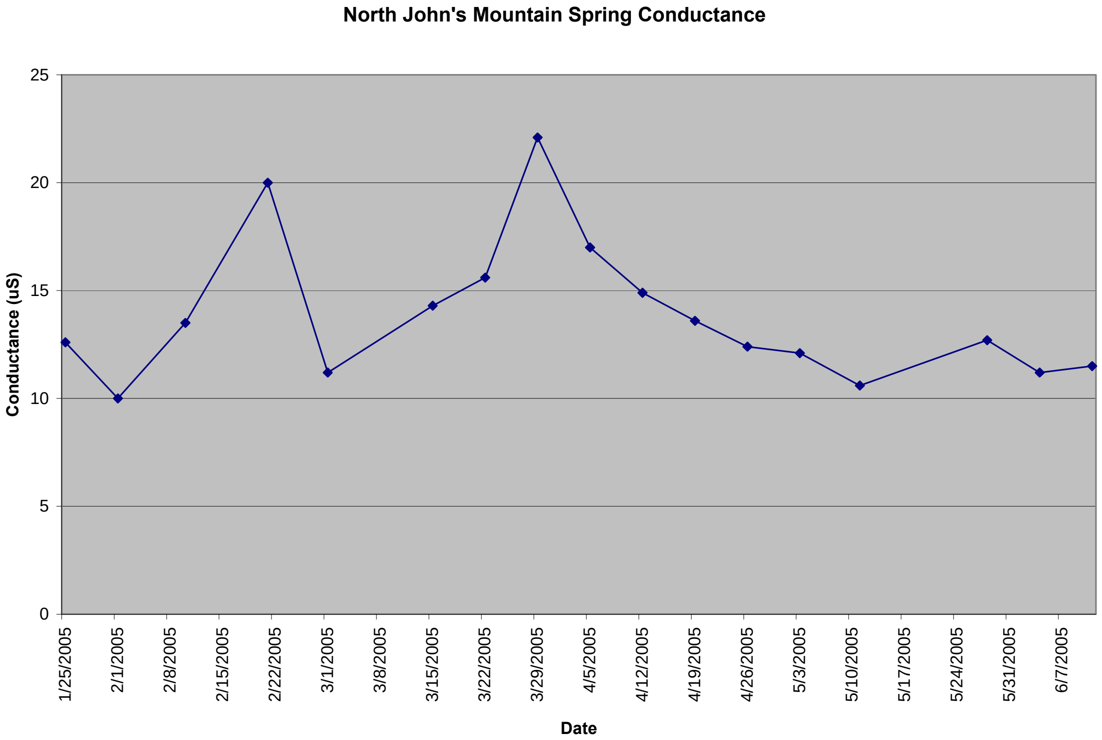

Figure 28: North John's Mountain Conductance vs. Time

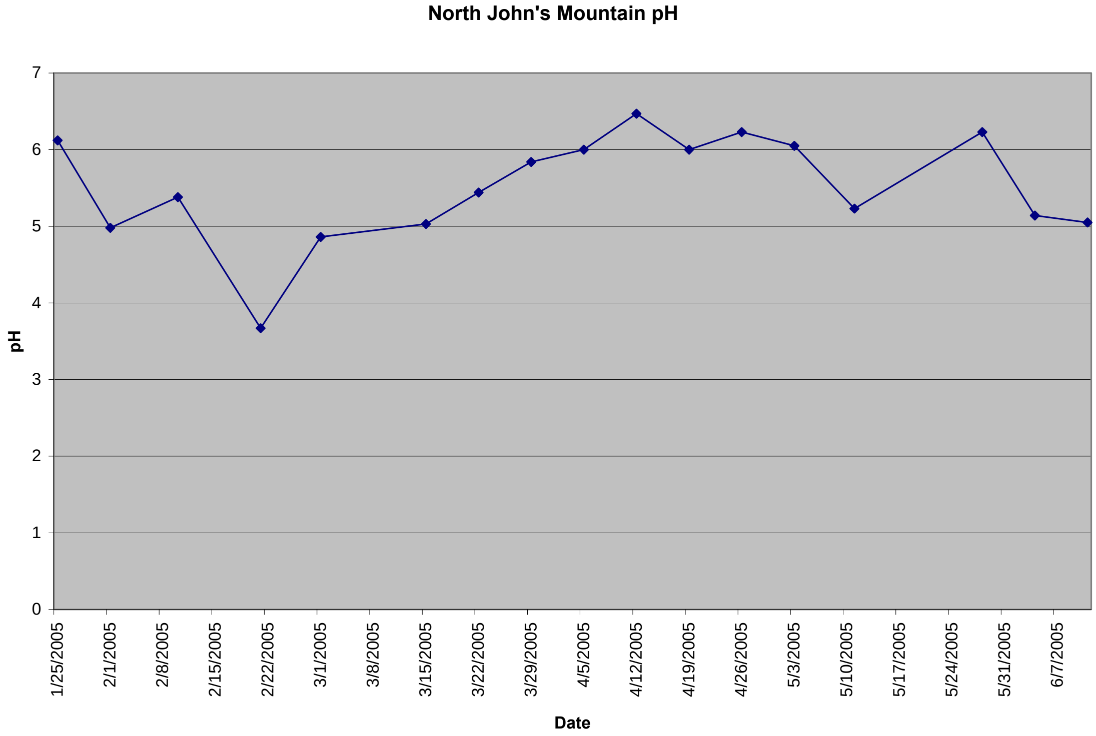

Figure 29: North John's Mountain pH vs. Time

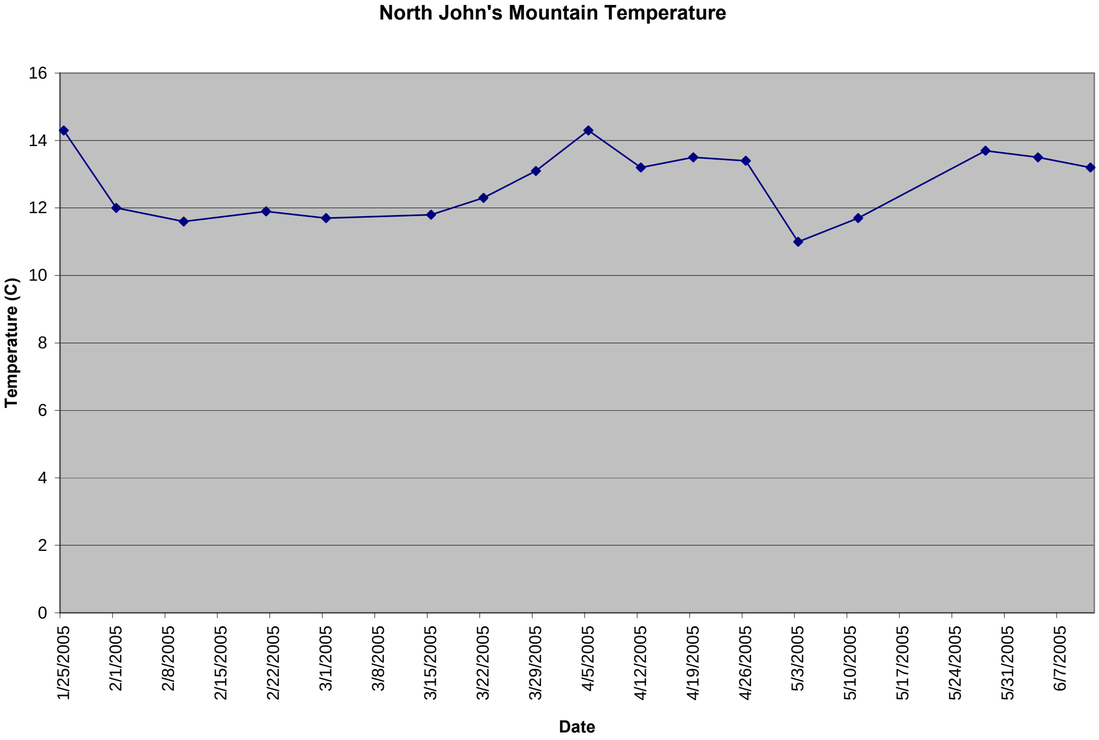

Figure 30: North John's Mountain Temperature vs. Time

HORN MOUNTAIN FIELD DATA RESULTS

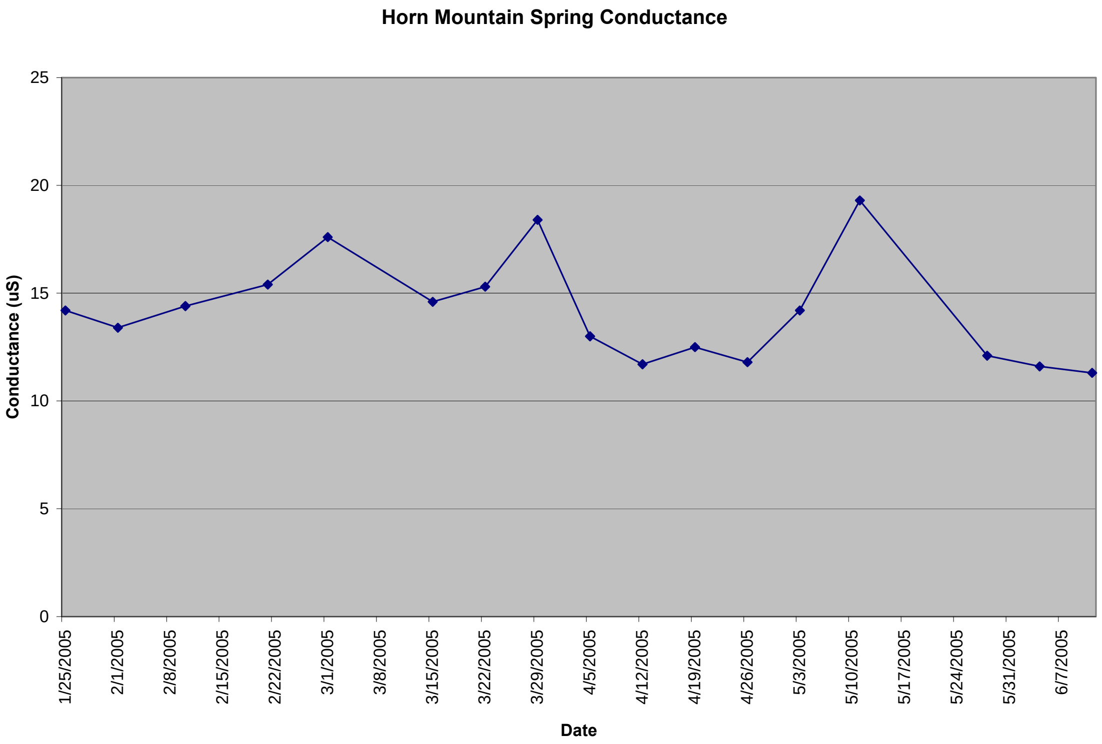

Figure 31: Horn Mountain Spring Conductance vs. Time

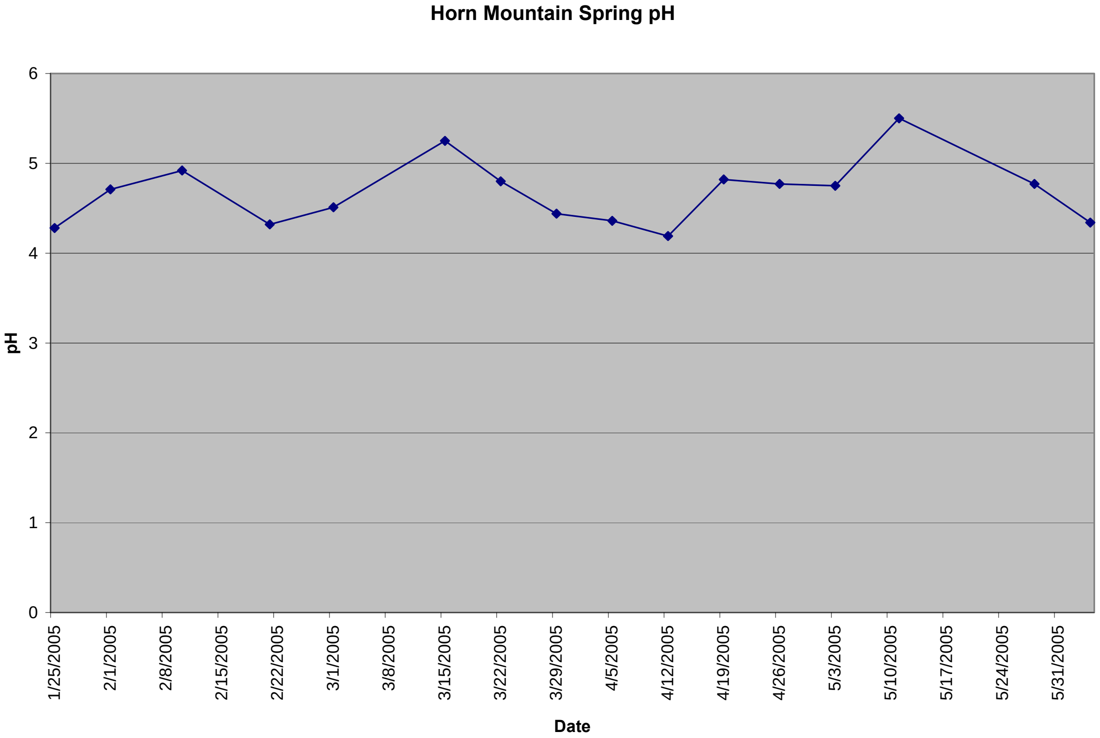

Figure 32: Horn Mountain Spring pH vs. Time

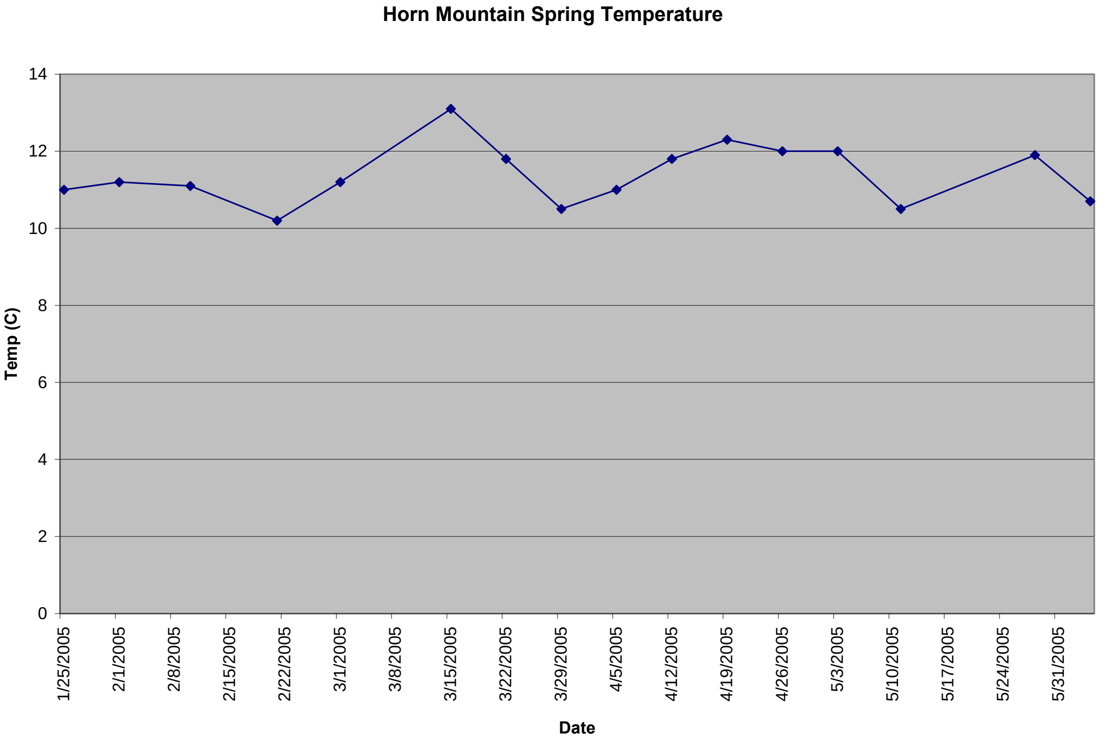

Figure 33: Horn Mountain Spring Temperature vs. Time

CHESTNUT MOUNTAIN SHOOTING RANGE FIELD DATA RESULTS

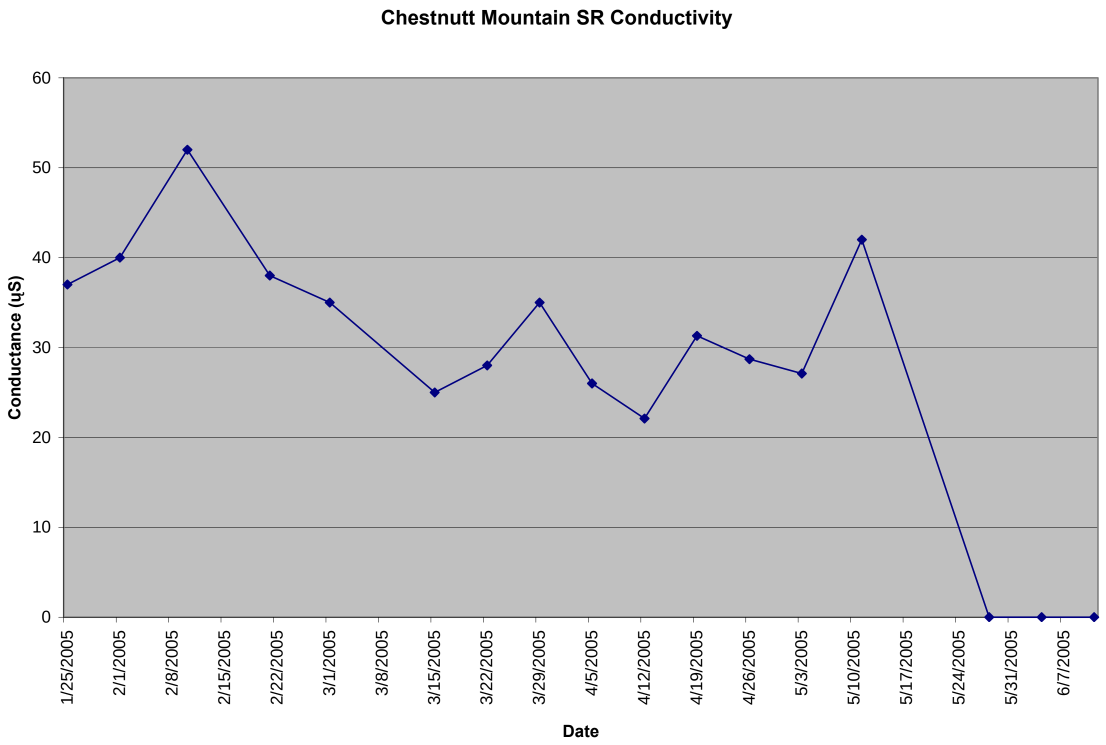

Figure 34: Chestnut Mountain Shooting Range Conductance vs. Time

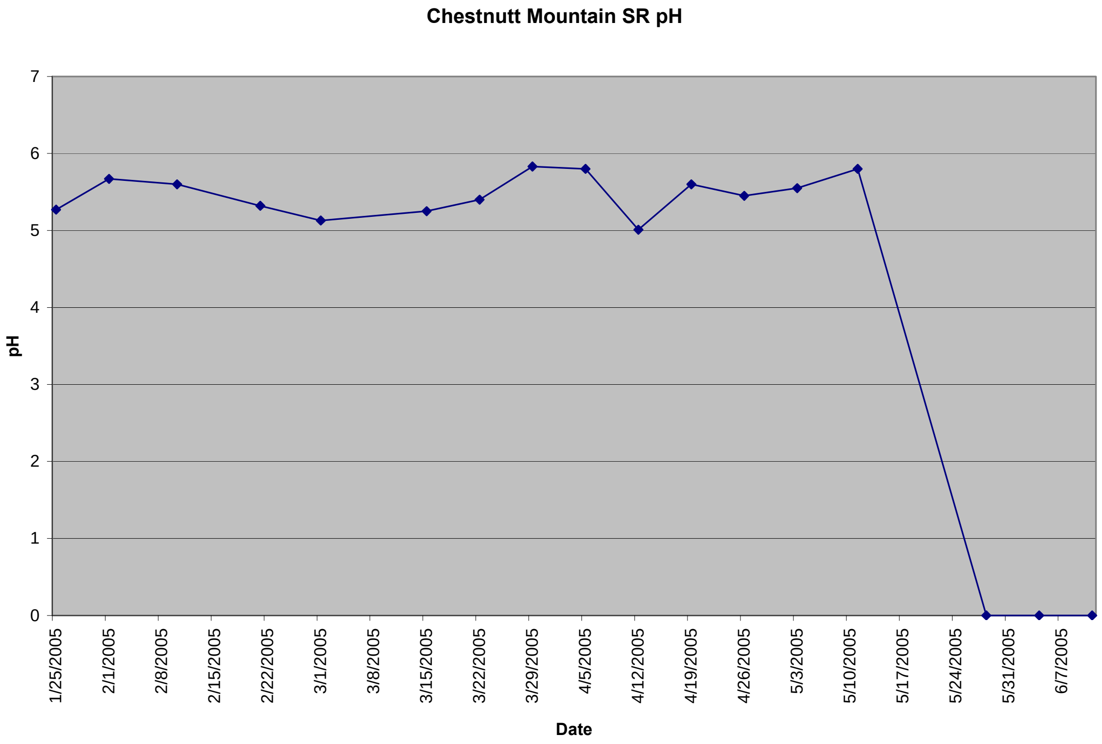

Figure 35: Chestnut Mountain pH vs. Time

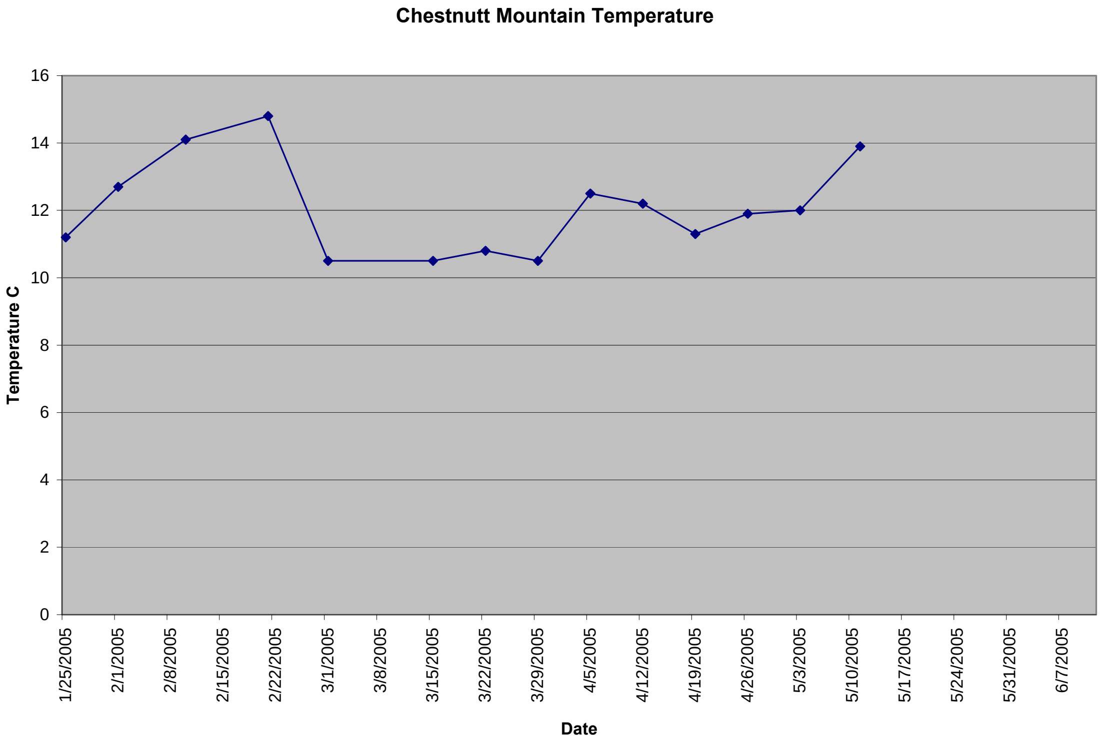

Figure 36: Chestnut Mountain Temperature vs. Time

EVERETT SPRINGS FIELD DATA RESULTS

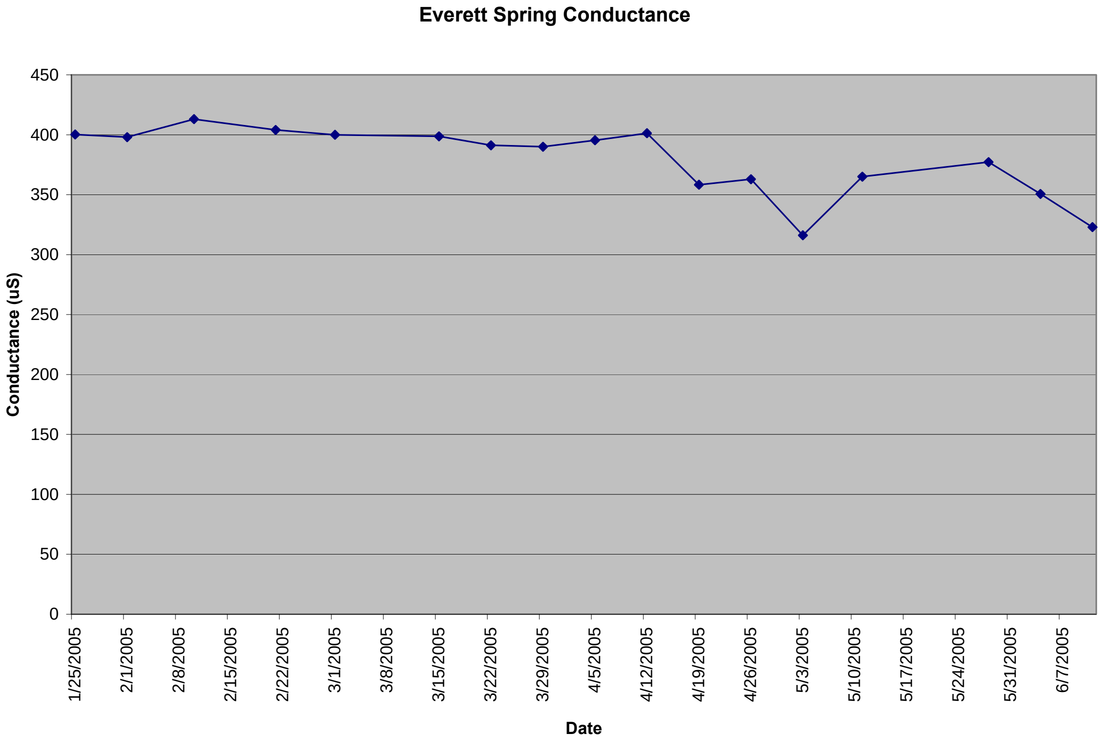

Figure 37: Everett Springs Conductance vs. Time

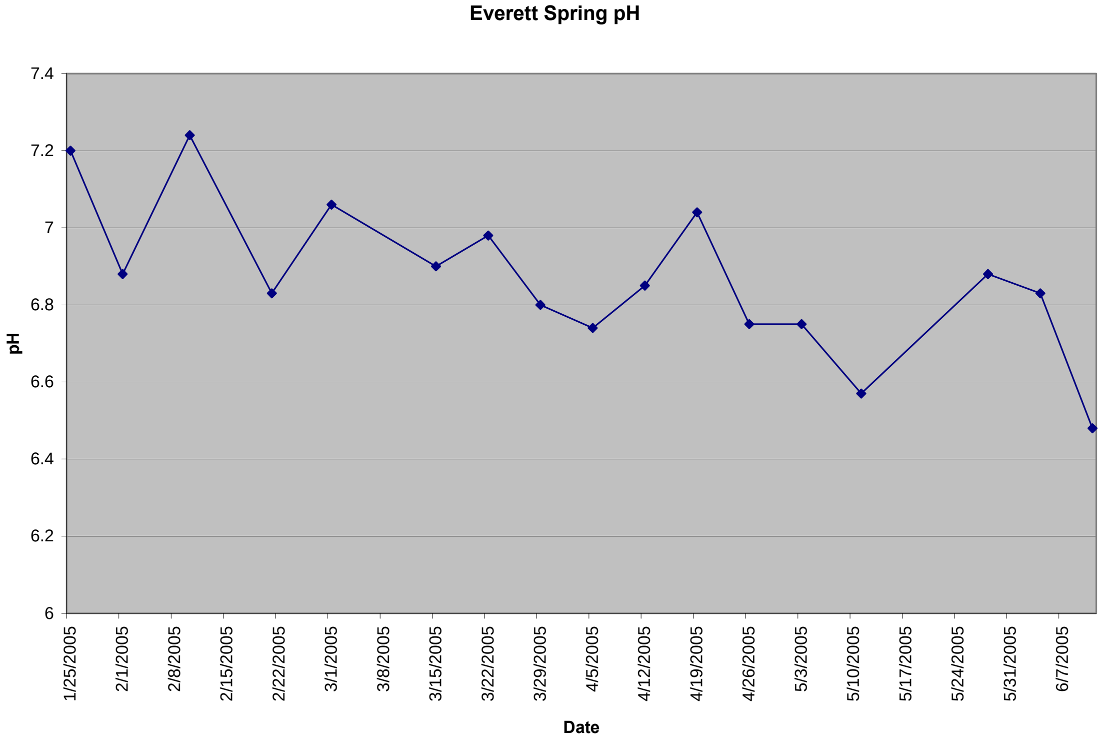

Figure 38: Everett Spring pH vs. Time

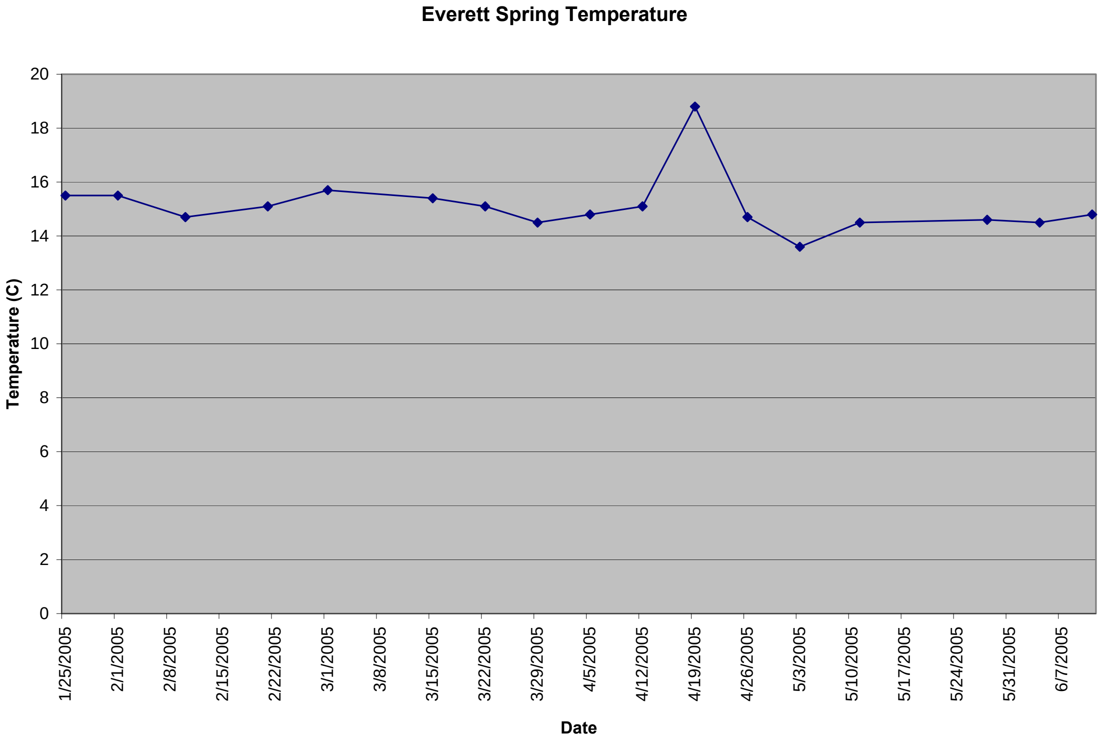

Figure 39: Everett Spring Temperature vs. Time

WEST ARMUCHEE FIELD DATA RESULTS

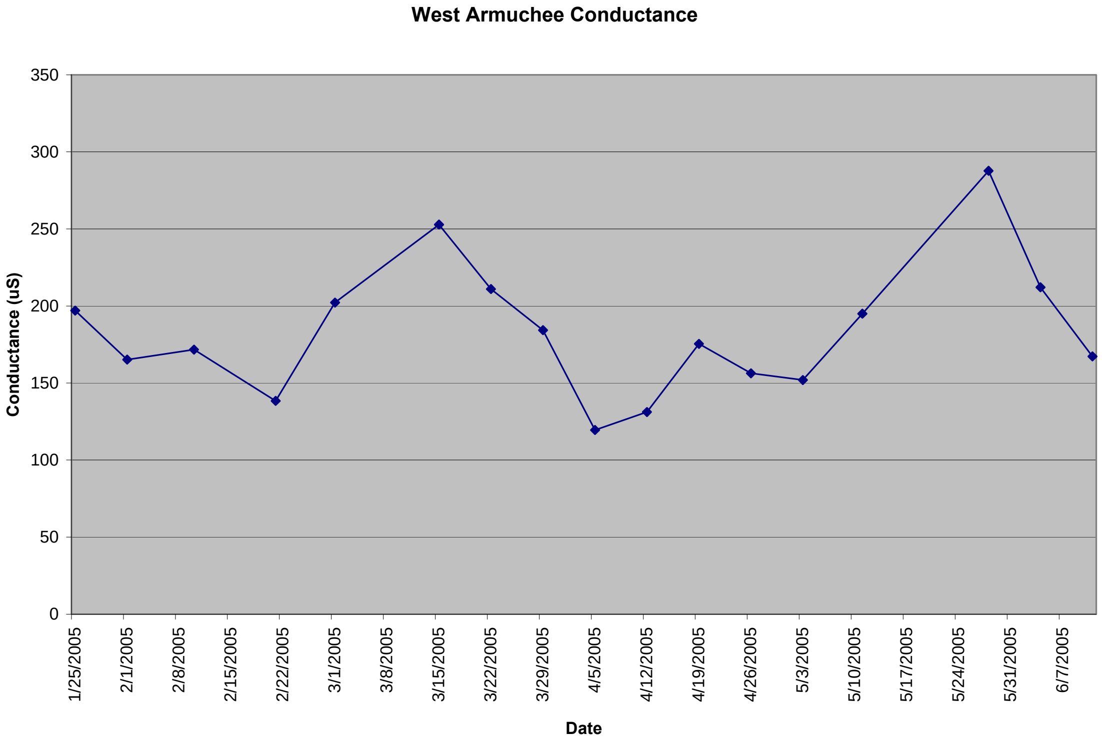

Figure 40: West Armuchee Conductance vs. Time

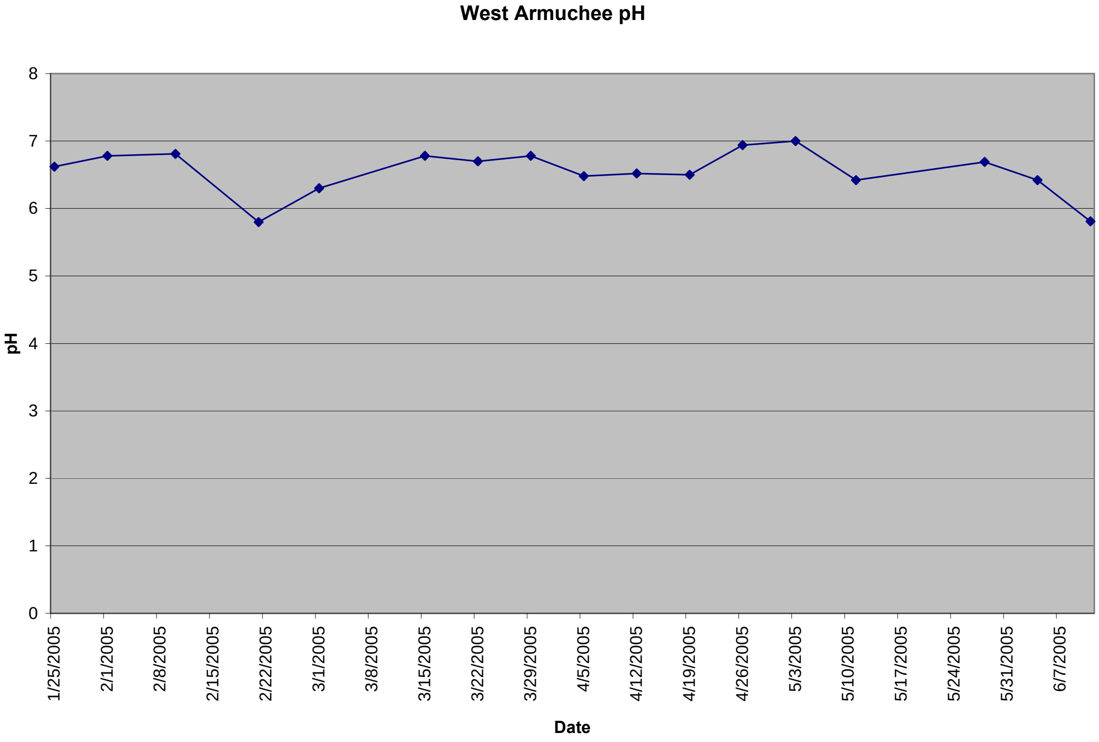

Figure 41: West Armuchee pH vs. Time

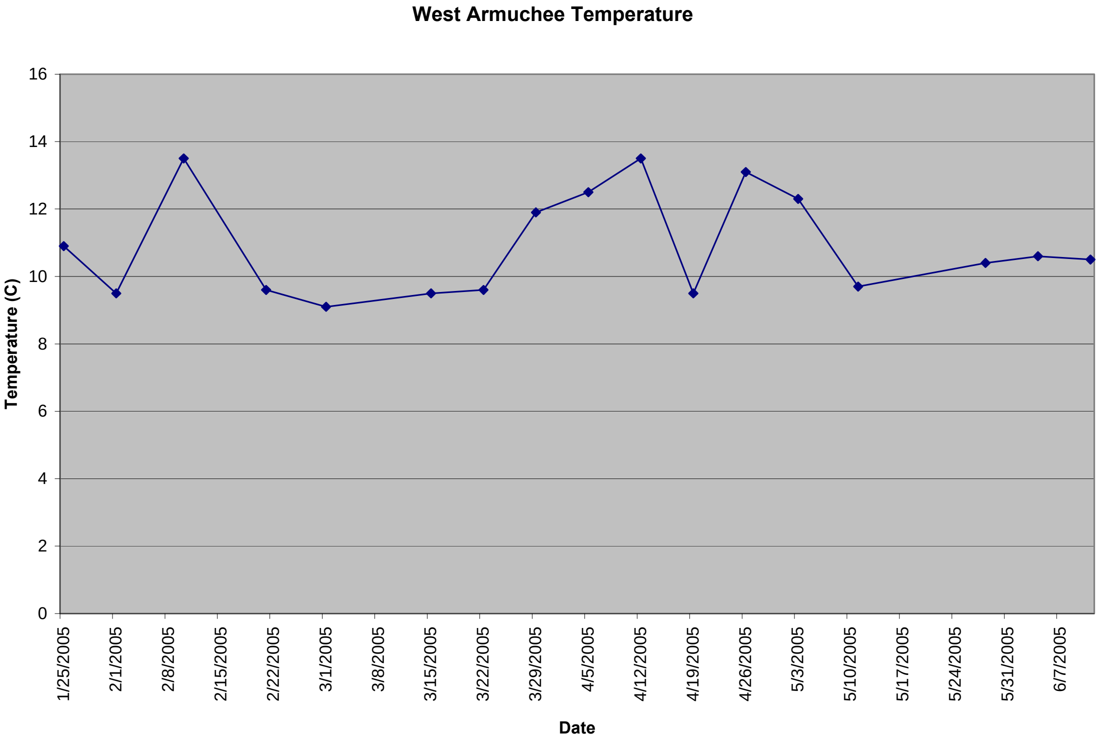

Figure 42: West Armuchee Temperature vs. Time

TURKEY MOUNTAIN FIELD DATA RESULTS

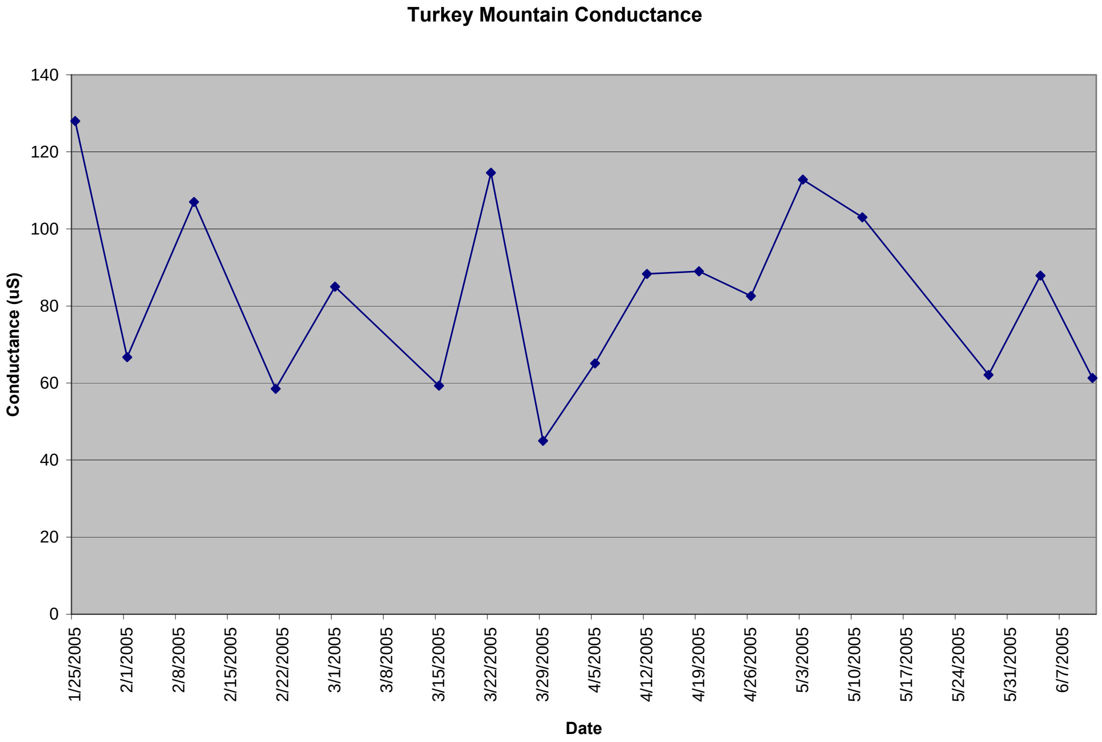

Figure 43: Turkey Mountain Conductance vs. Time

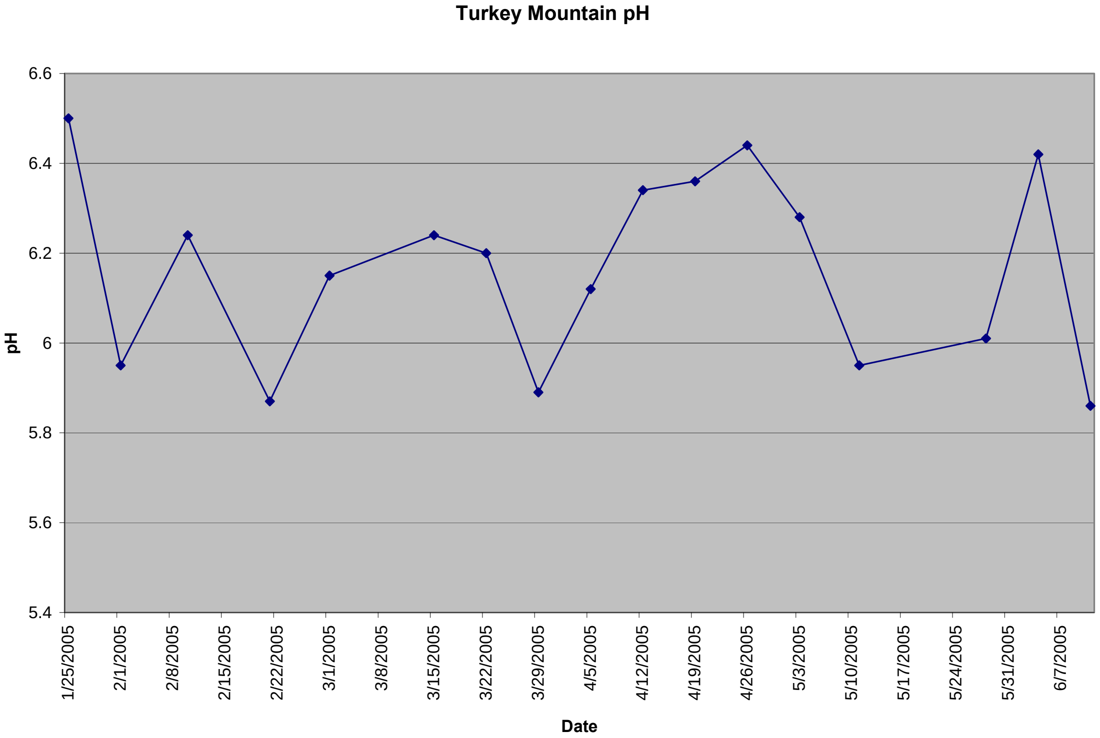

Figure 44: Turkey Mountain pH vs. Time

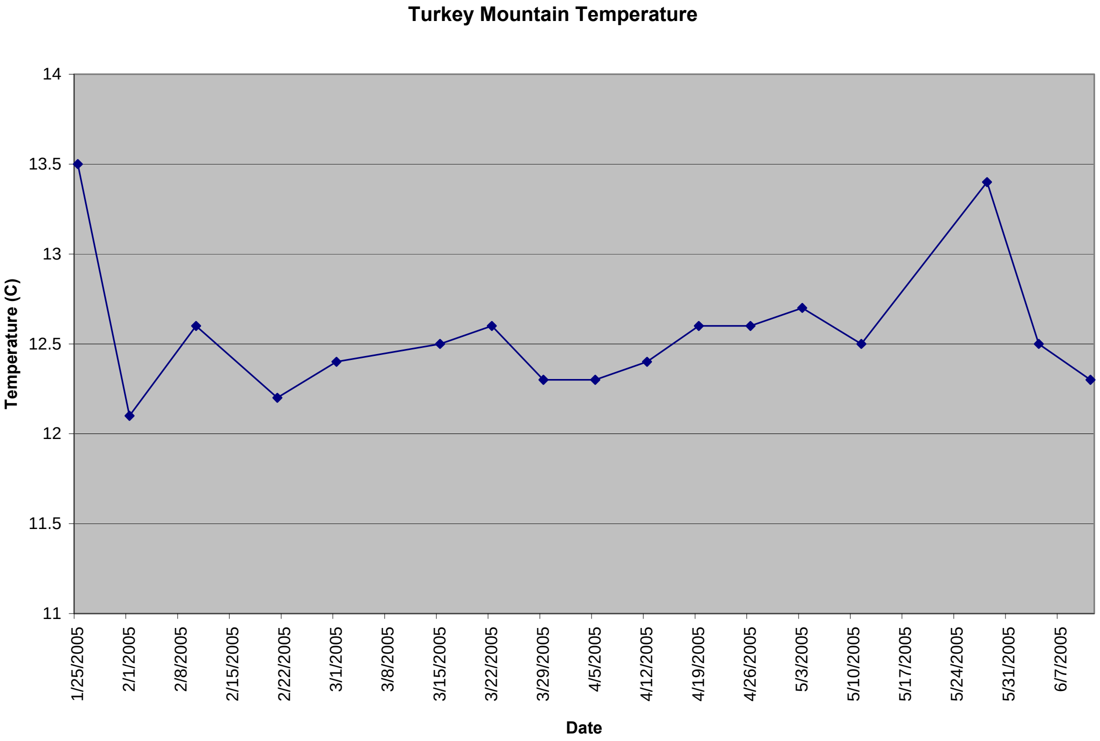

Figure 45: Turkey Mountain Temperature vs. Time

APPENDIX B: SPRING CHEMISTRIES

Chemistry of Cave Spring

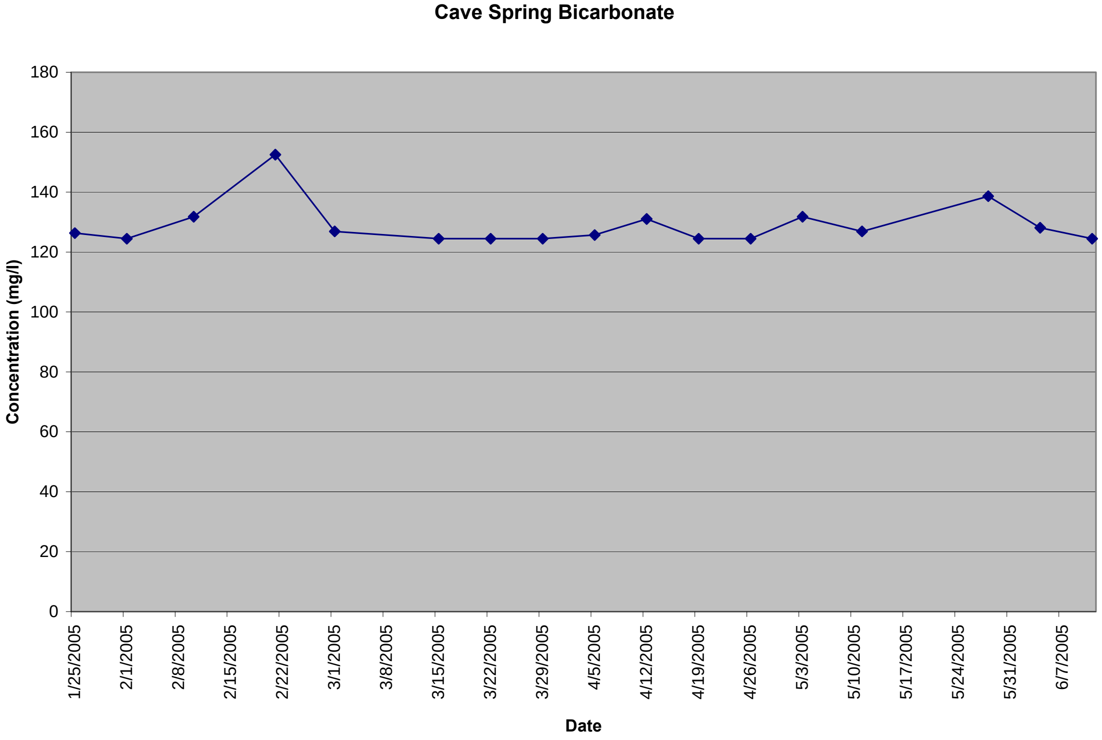

Figure 46: Cave Spring Bicarbonate Levels.

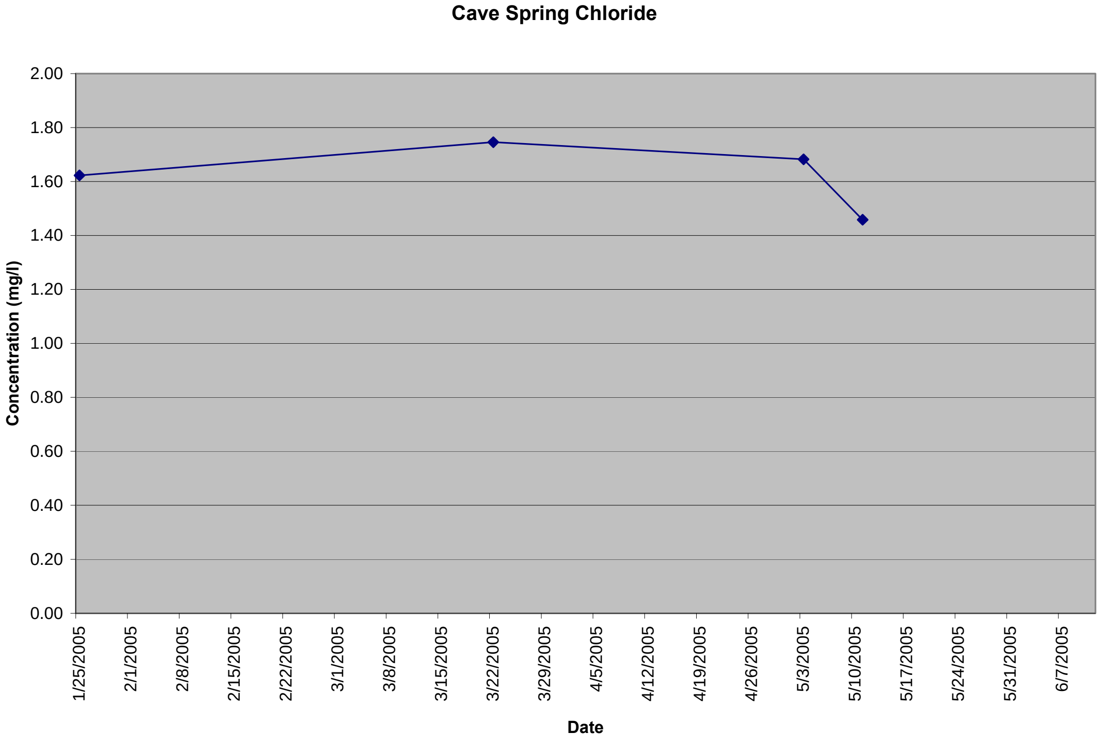

Figure 47: Cave Spring Chloride Levels.

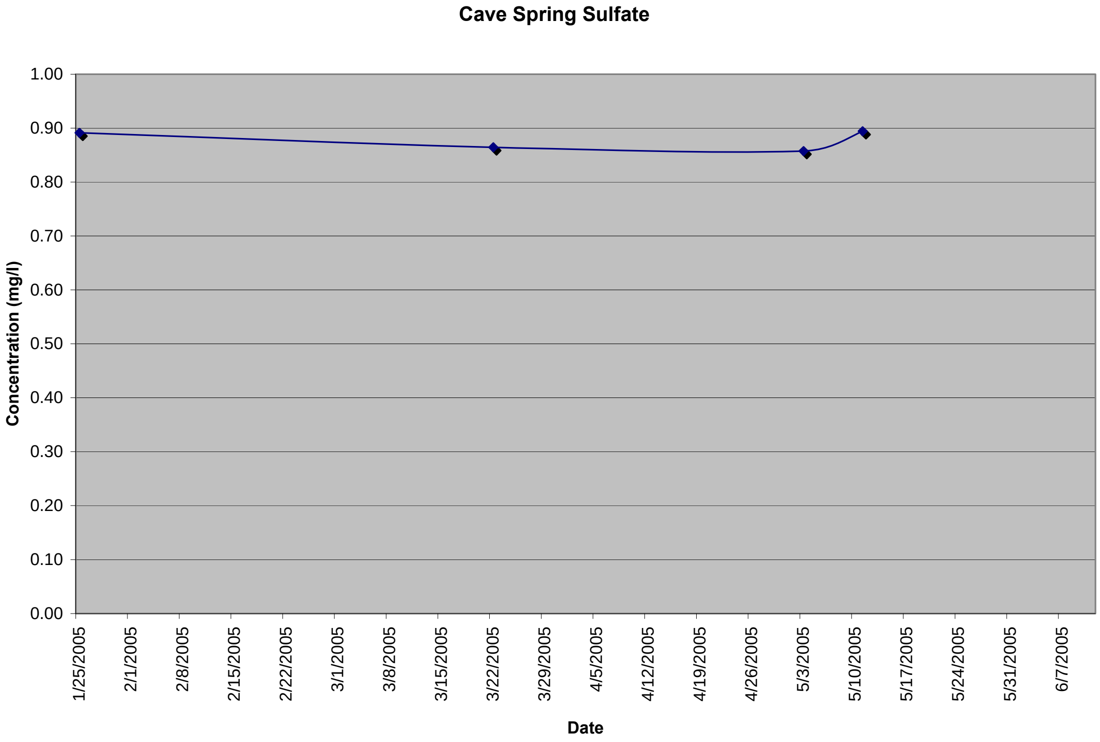

Figure 48: Cave Spring Sulfate Levels.

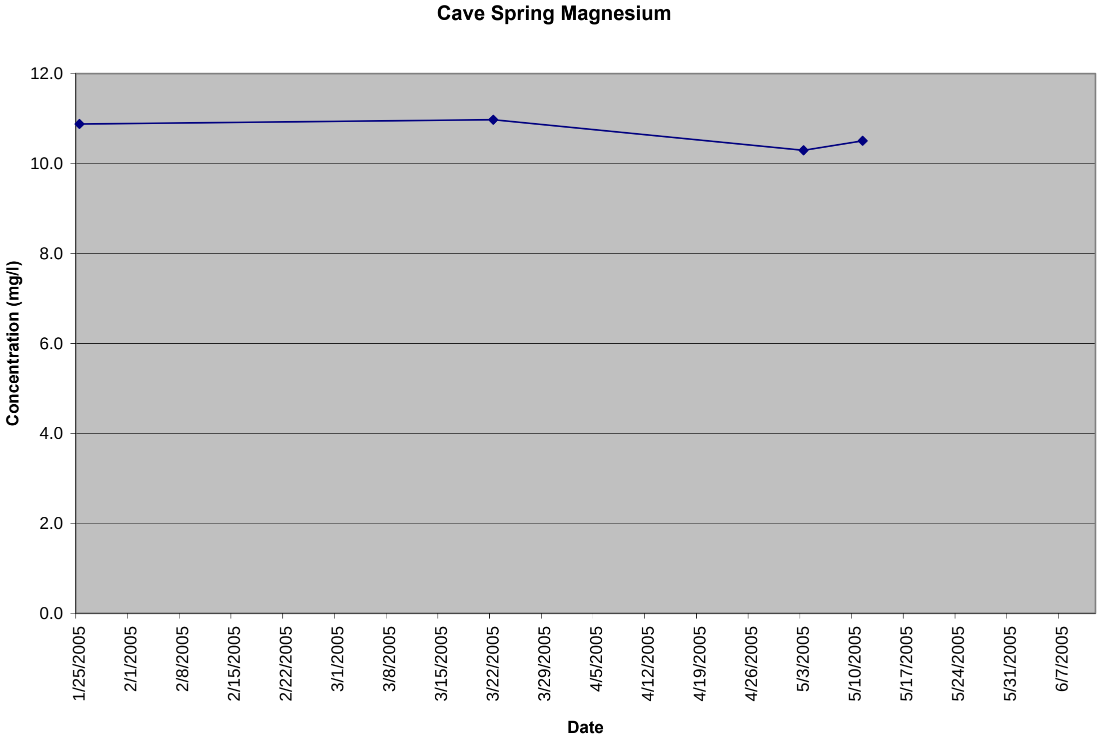

Figure 49: Cave Spring Magnesium Levels

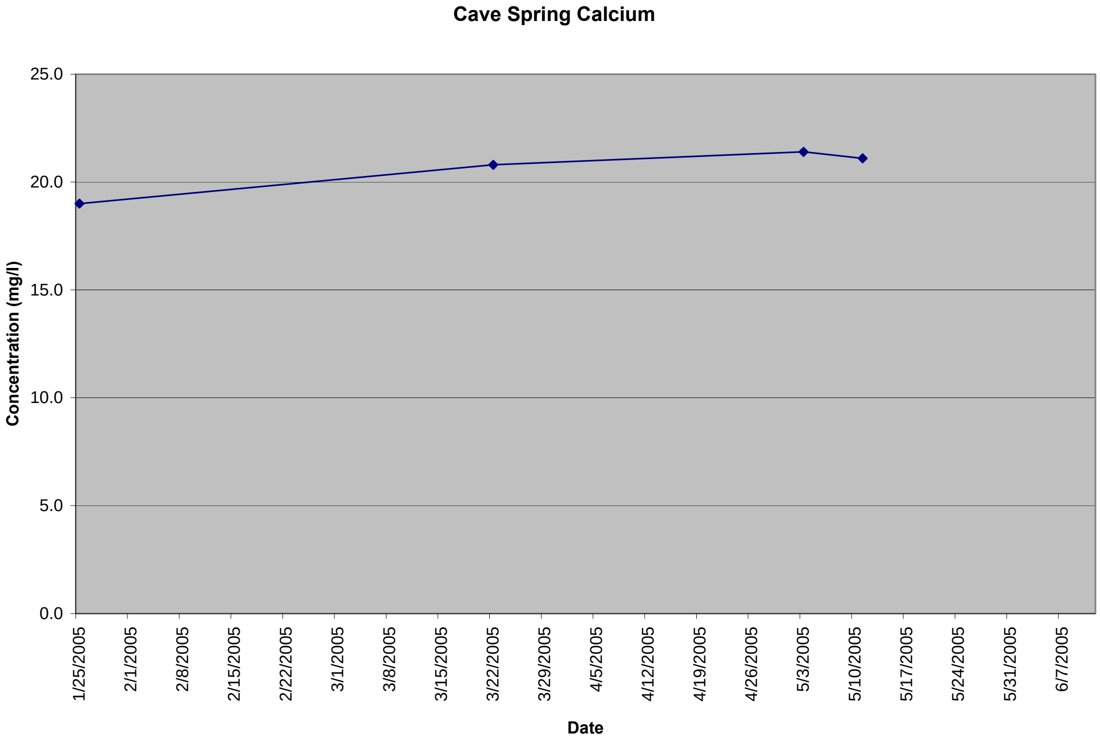

Figure 50: Cave Spring Calcium Levels.

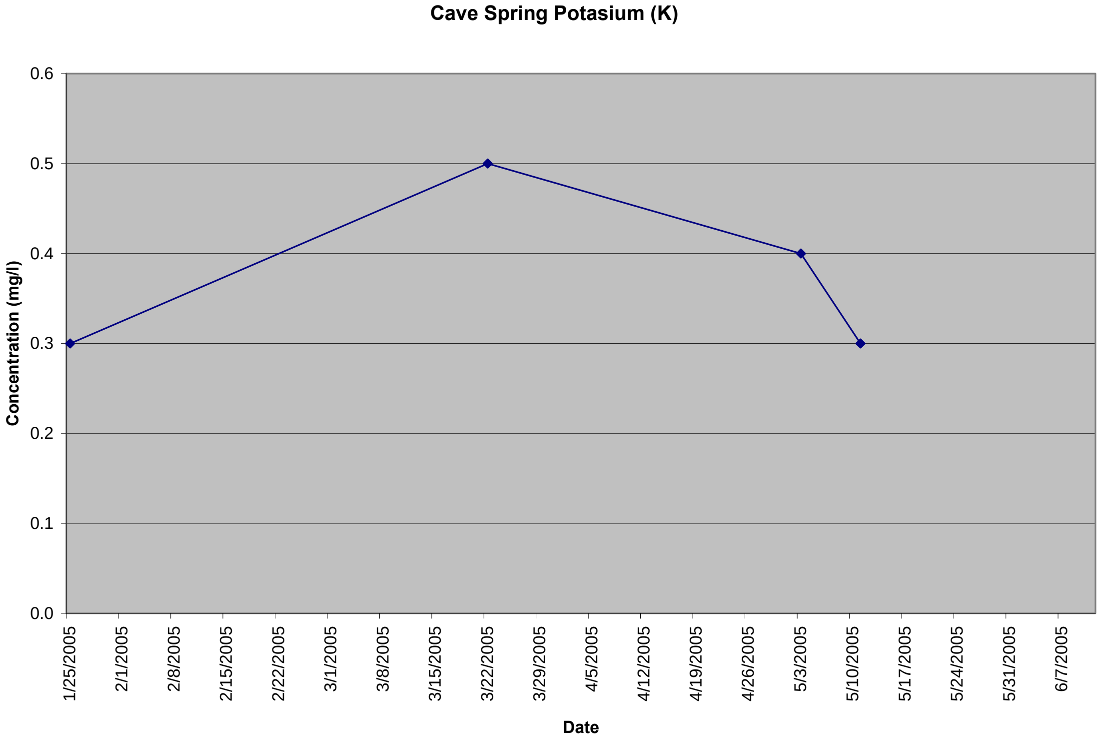

Figure 51: Cave Spring Potassium Levels.

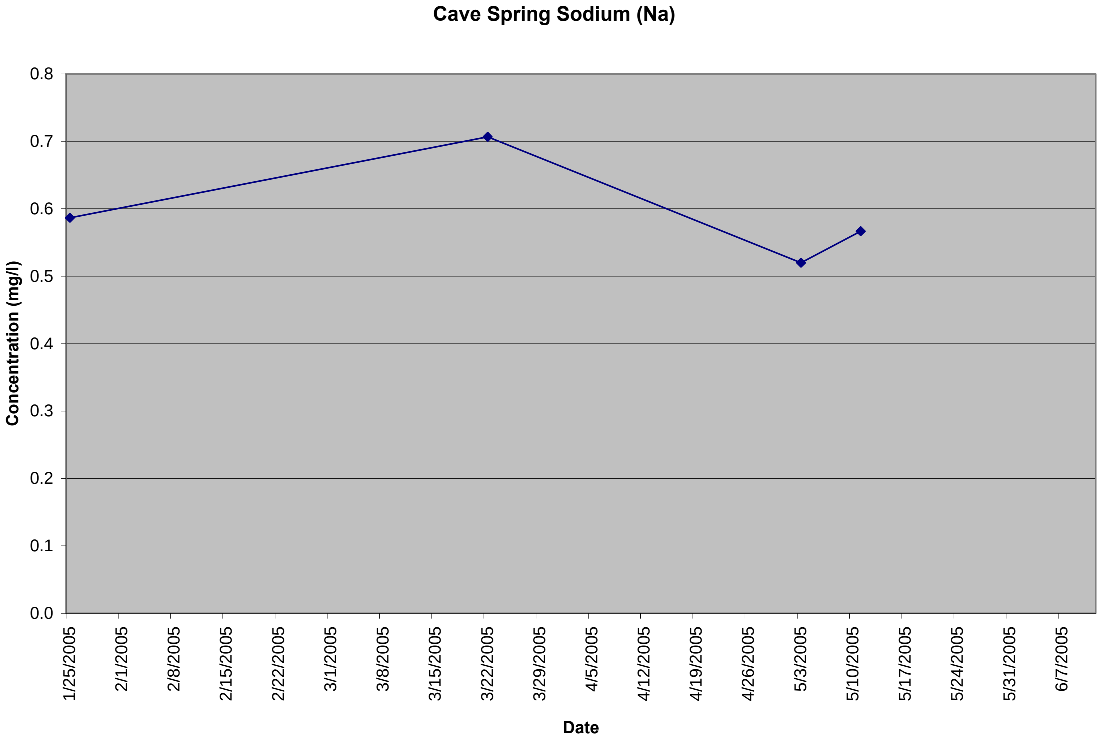

Figure 52: Cave Spring Sodium Levels.

Major Ion Chemistry of Sand Spring

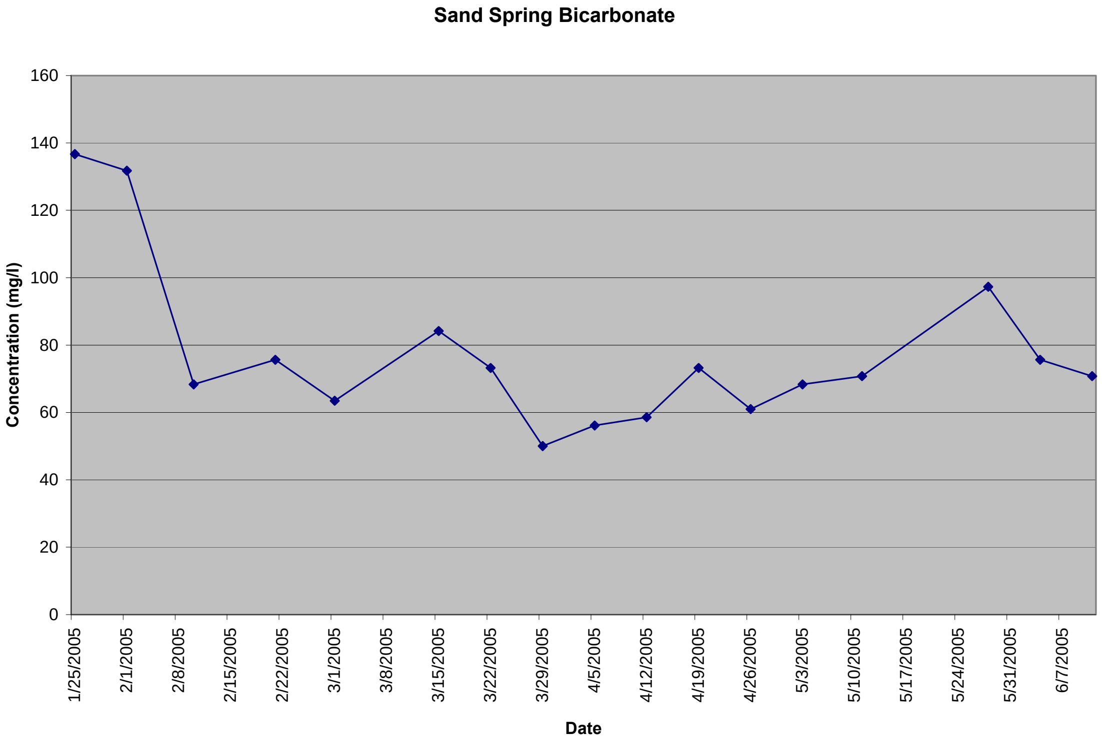

Figure 53: Sand Spring Bicarbonate Levels.

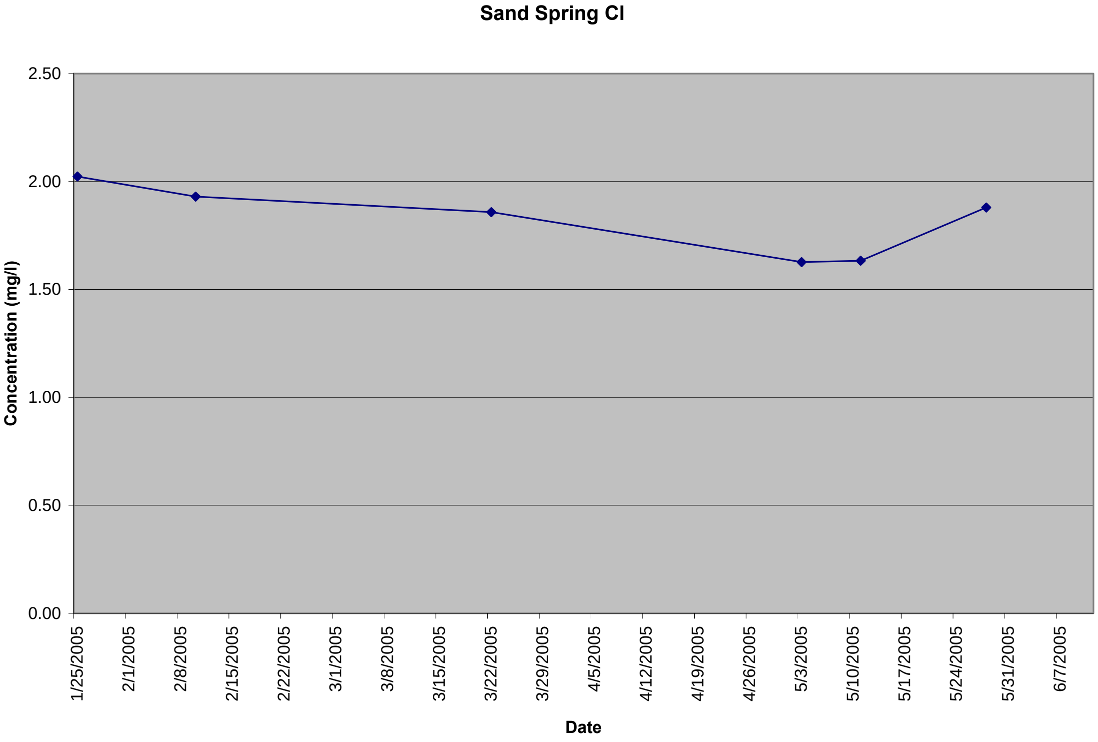

Figure 54: Sand Spring Chloride Levels.

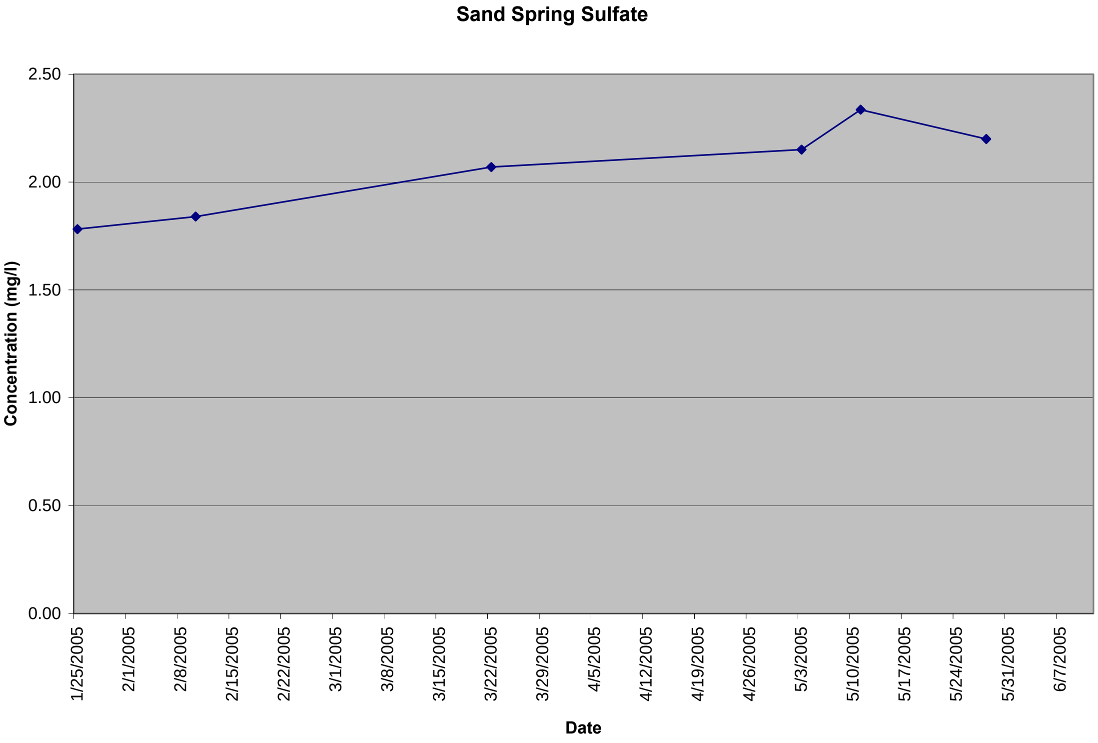

Figure 55: Sand Spring Sulfate Levels.

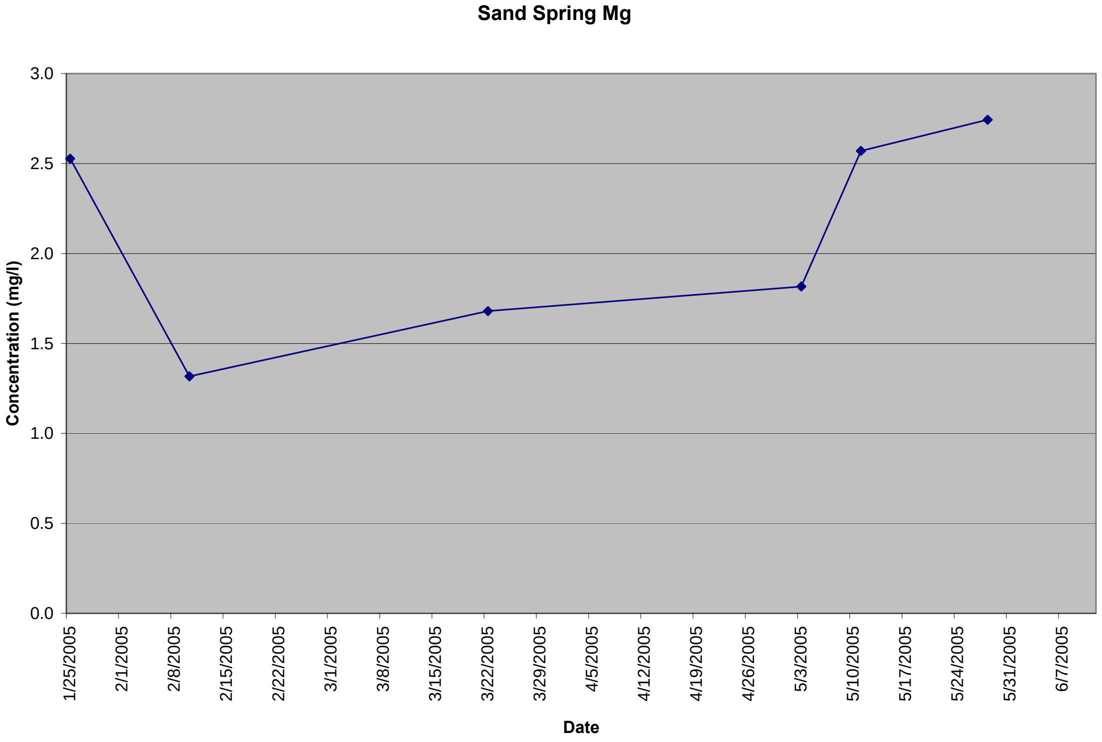

Figure 56: Sand Spring Magnesium Levels.

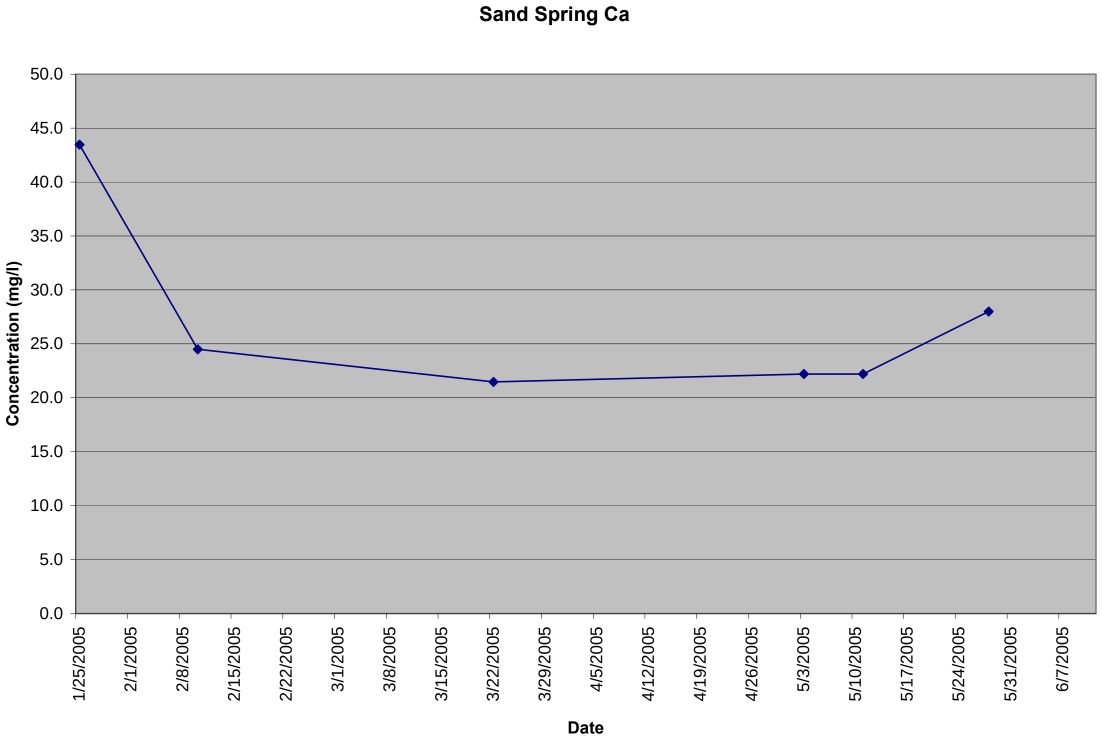

Figure 57: Sand Spring Calcium Levels.

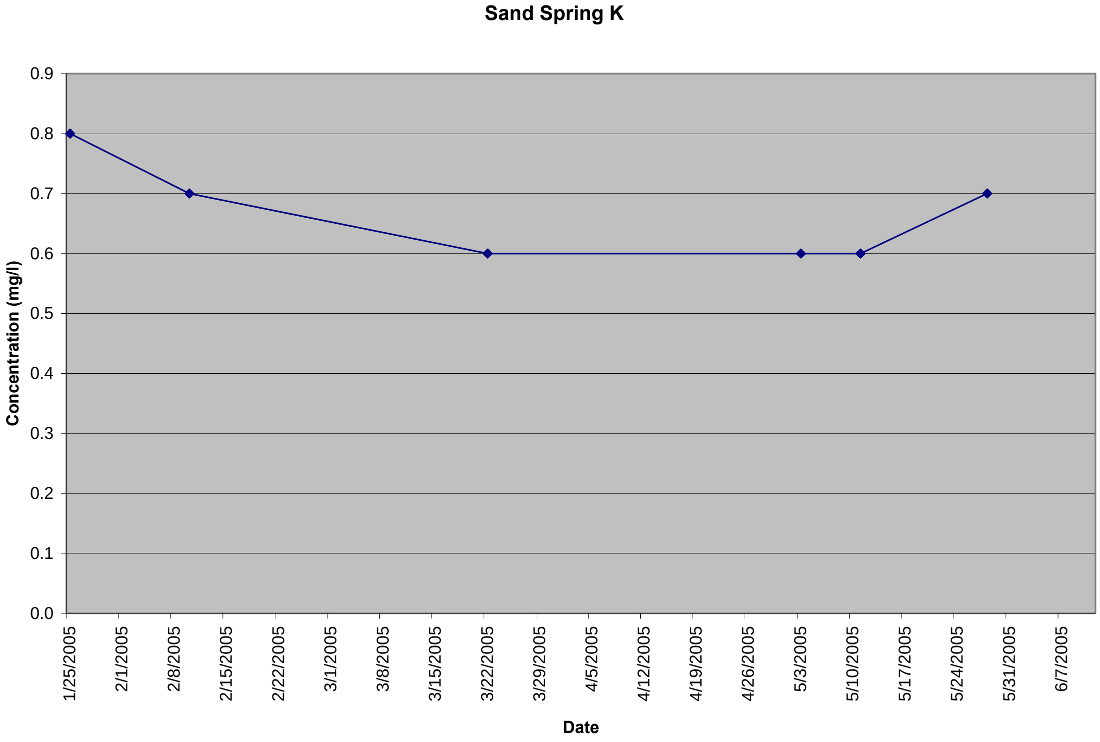

Figure 58: Sand Spring Potassium Levels.

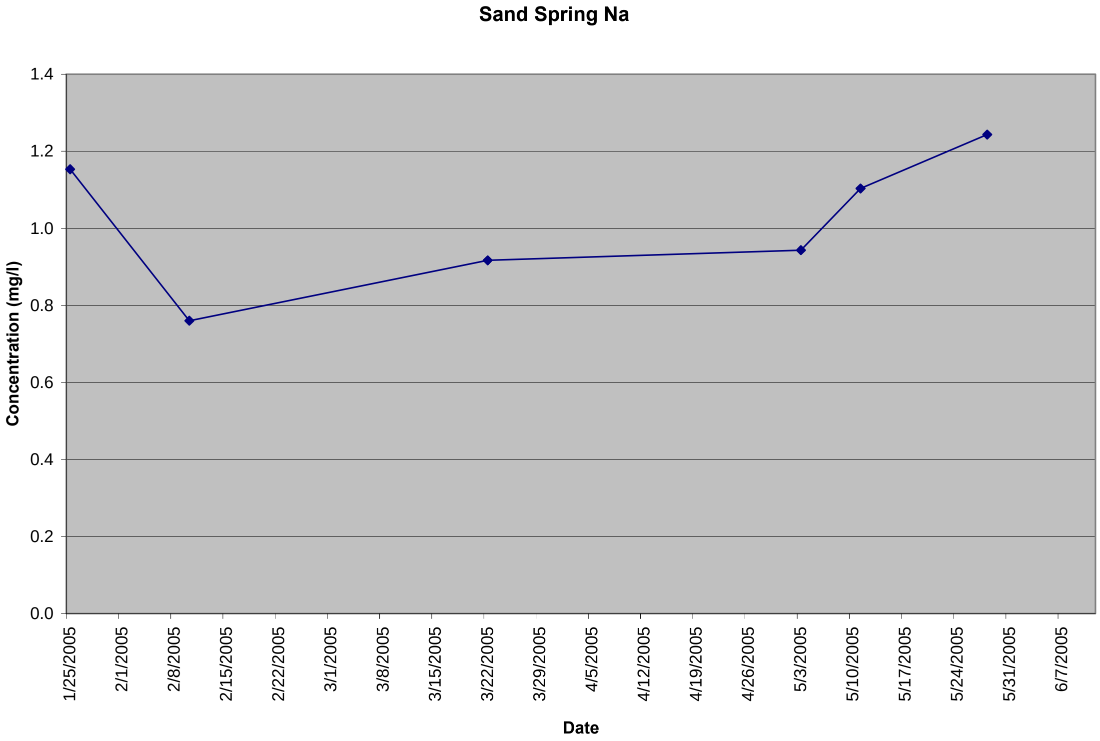

Figure 59: Sand Spring Sodium Levels.

Major Ion Chemistry of North John's Mountain

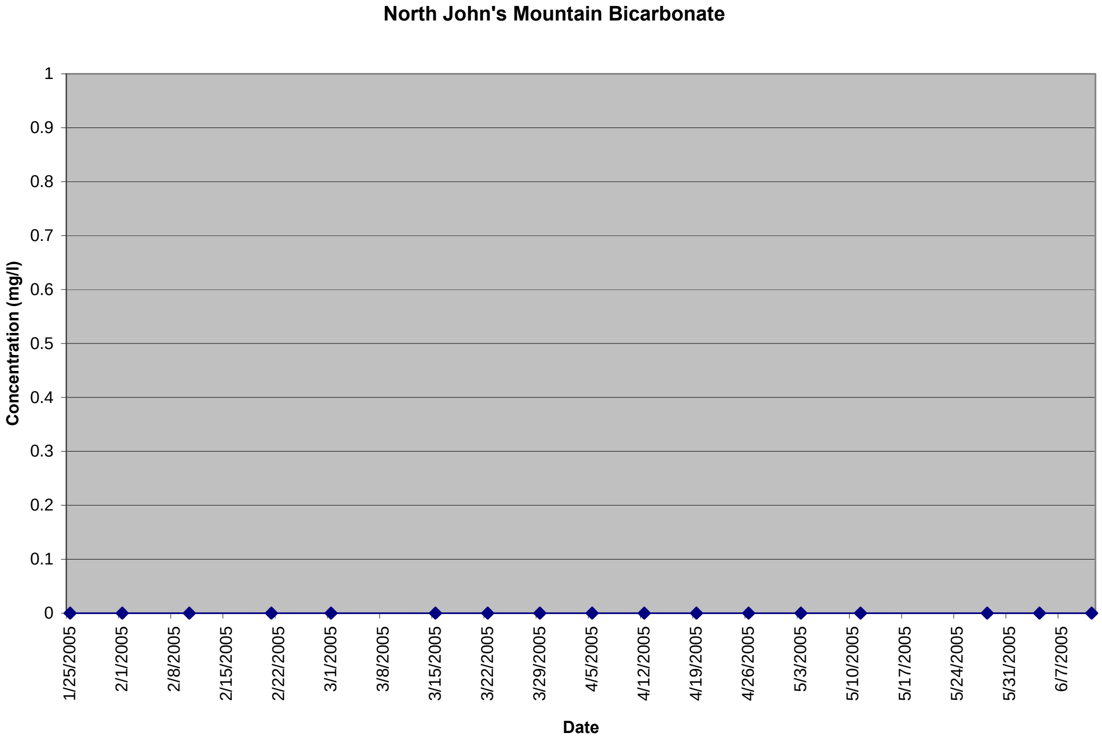

Figure 60: North John's Mountain Bicarbonate Levels.

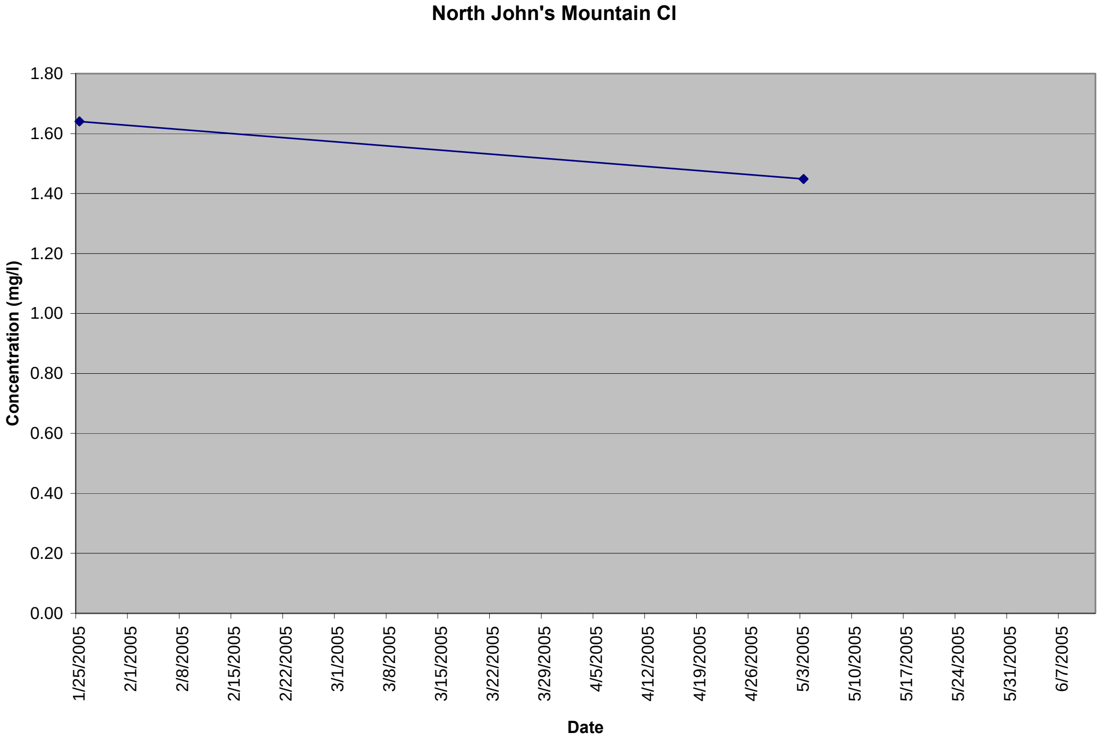

Figure 61: North John’s Mountain Chloride Levels.

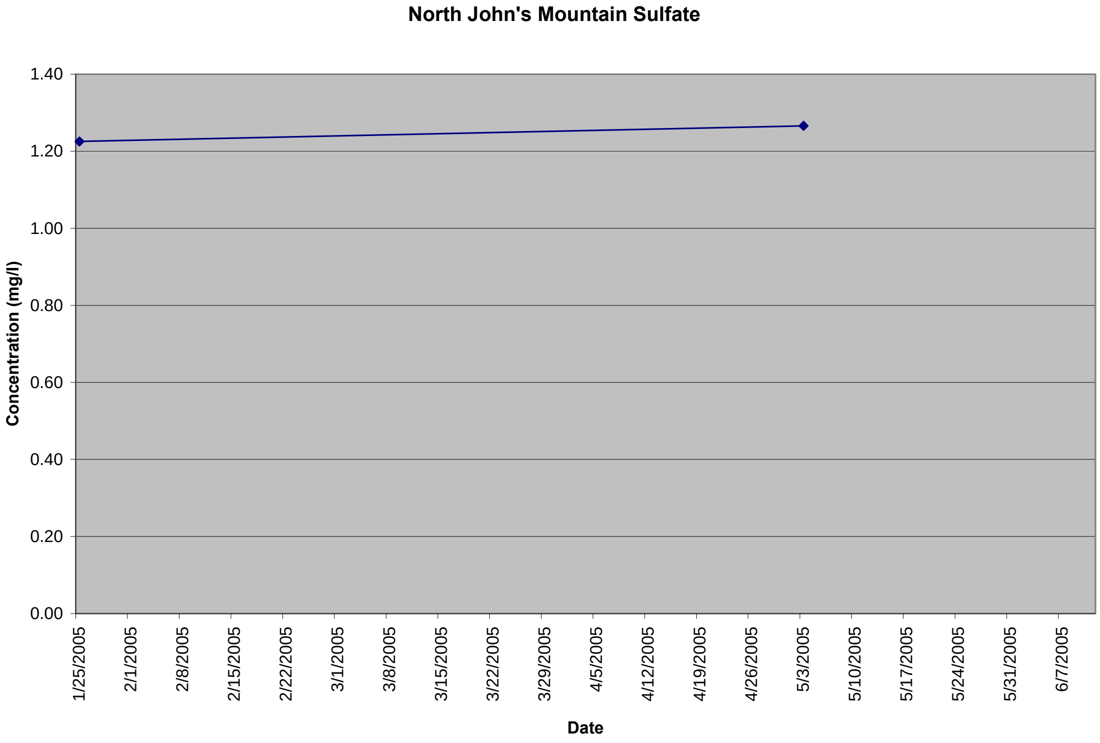

Figure 62: North John’s Mountain Sulfate Levels.

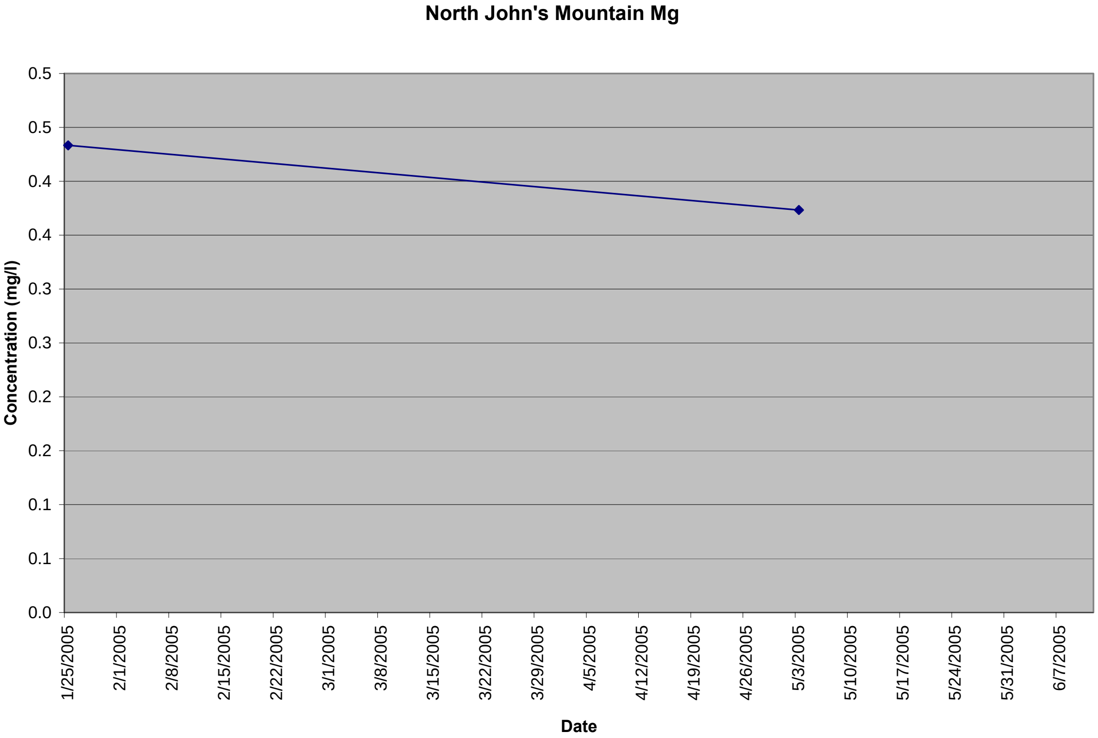

Figure 63: North John’s Mountain Magnesium Levels.

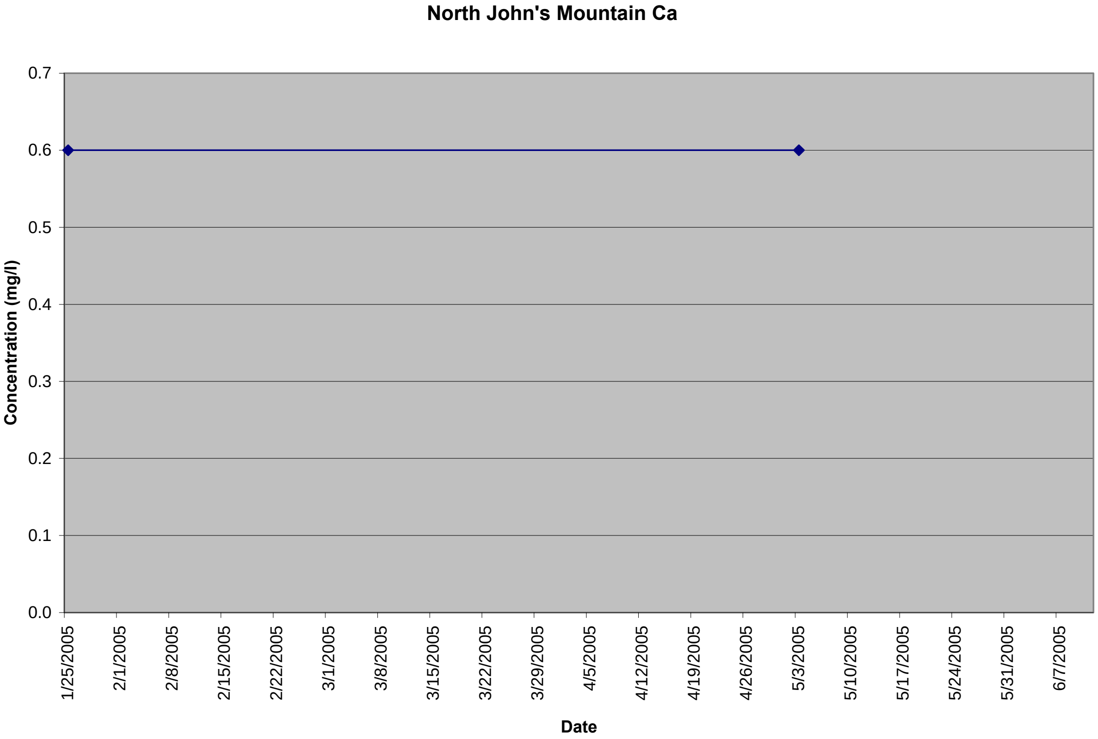

Figure 64: North John’s Mountain Calcium Levels.

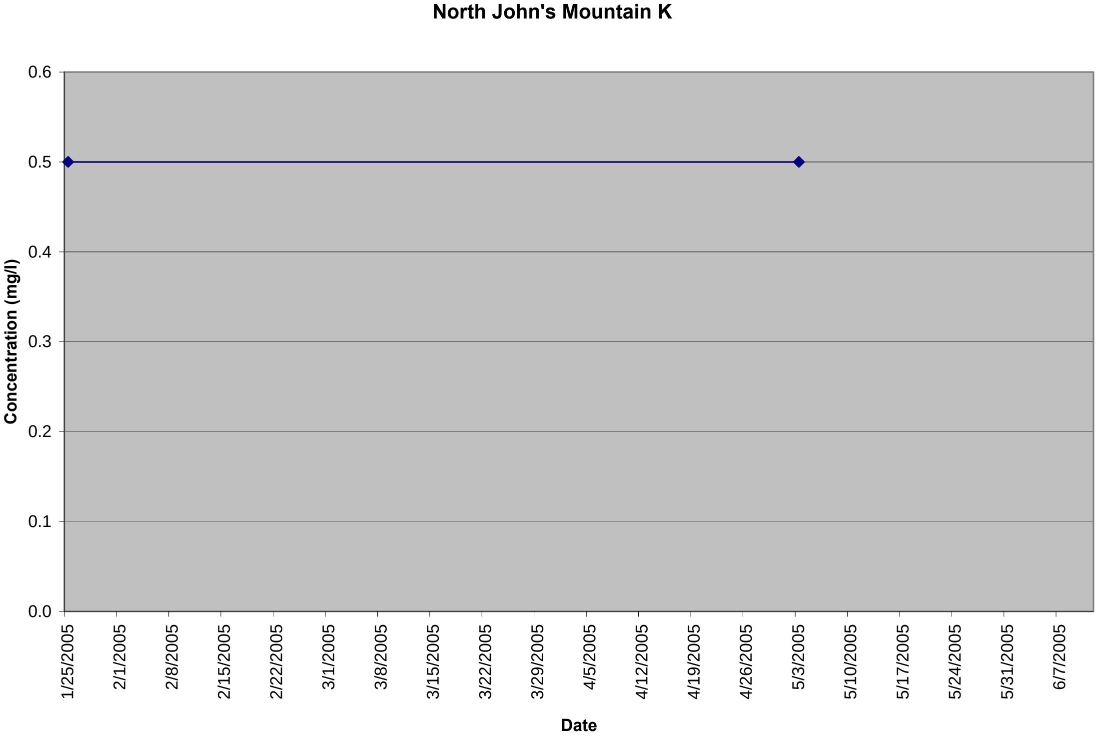

Figure 65: North John's Mountain Potassium Levels.

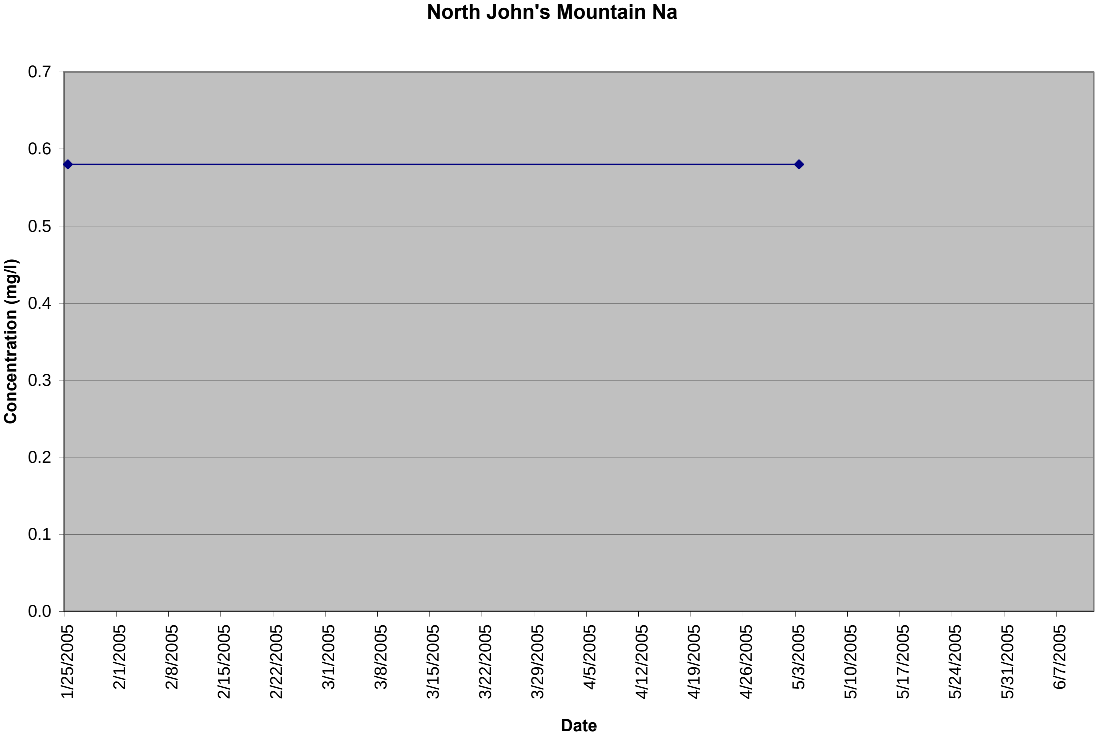

Figure 66: North John's Mountain Sodium Levels.

Major Ion Chemistry of Horn Mountain

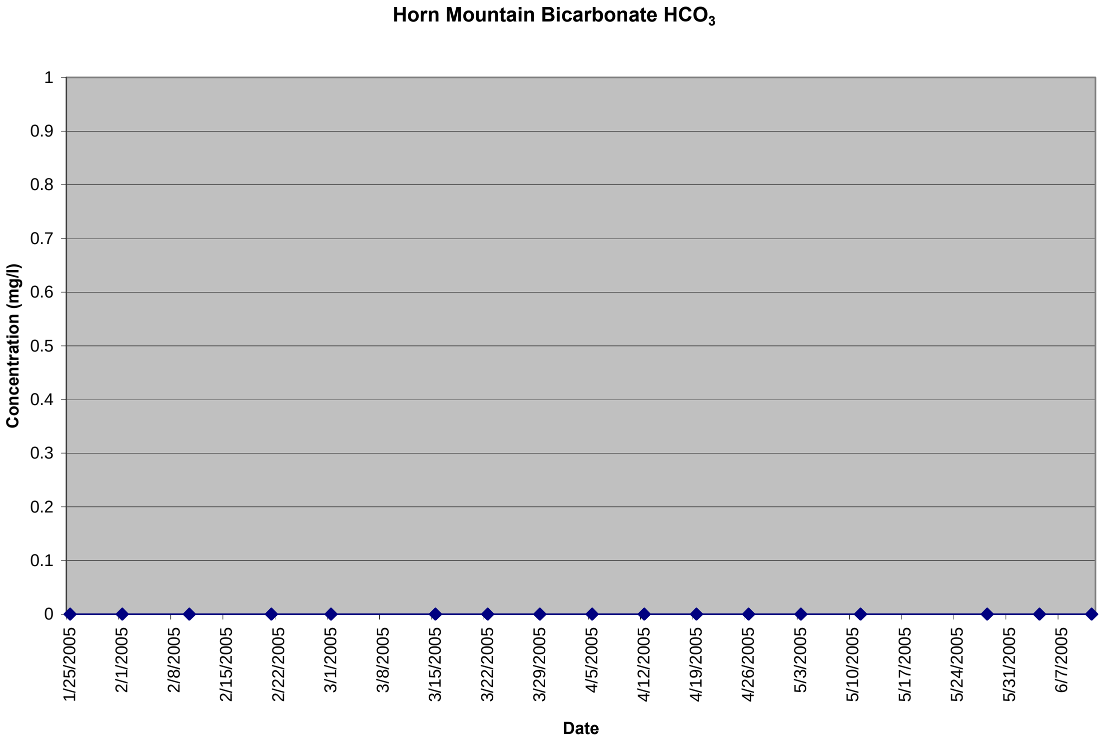

Figure 67: Horn Mountain Bicarbonate Levels.

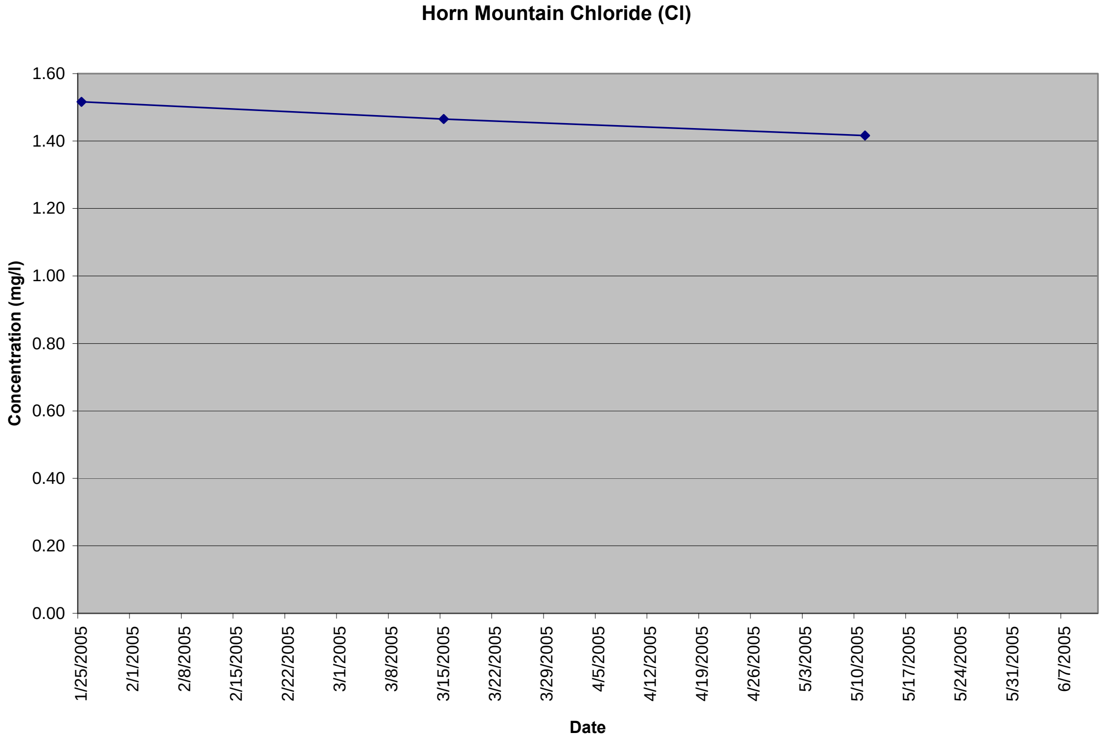

Figure 68: Horn Mountain Chloride Levels.

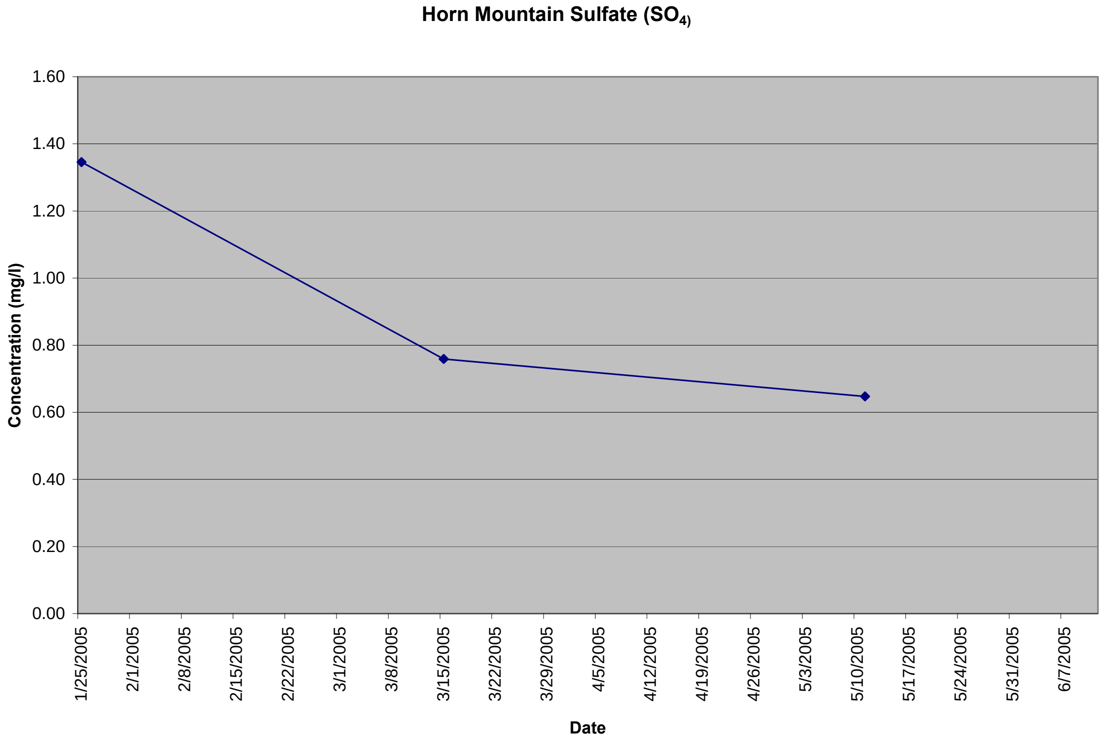

Figure 69: Horn Mountain Sulfate Levels.

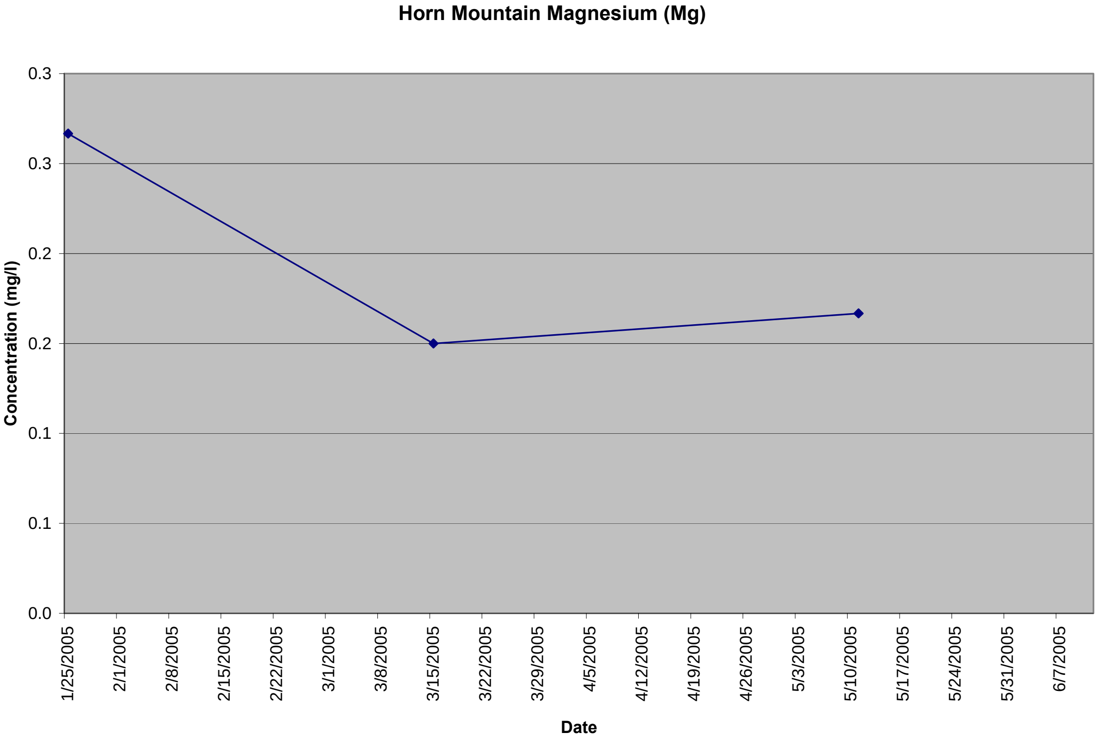

Figure 70: Horn Mountain Magnesium Levels.

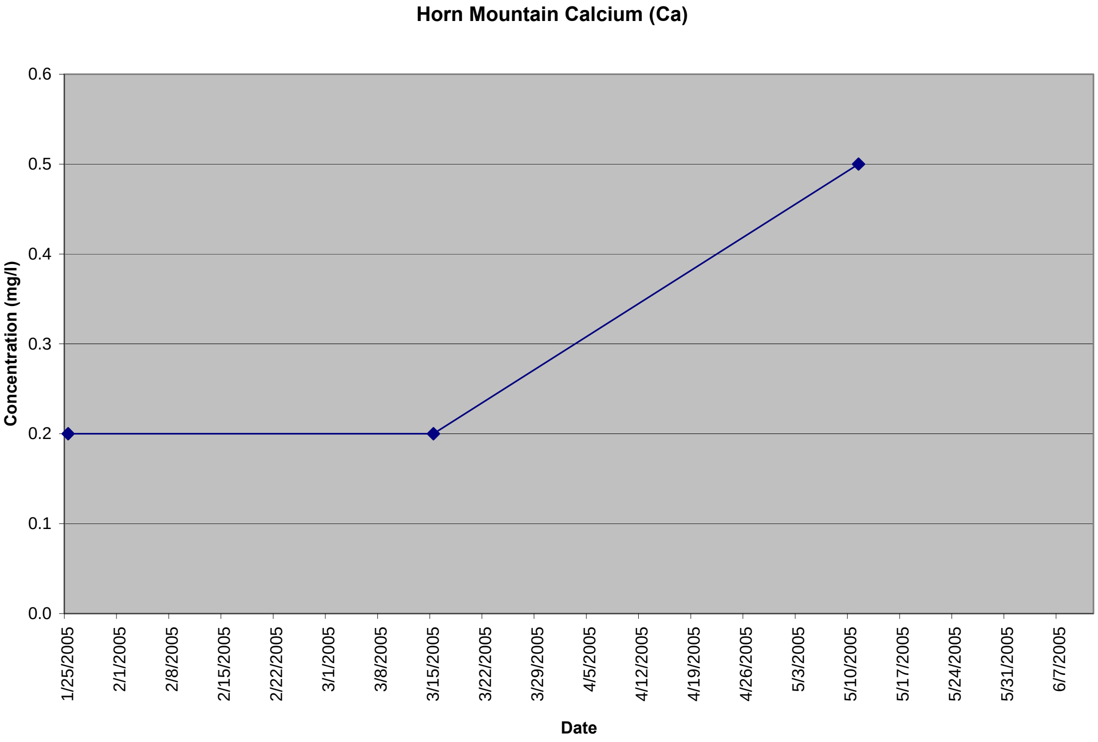

Figure 71: Horn Mountain Calcium Levels .

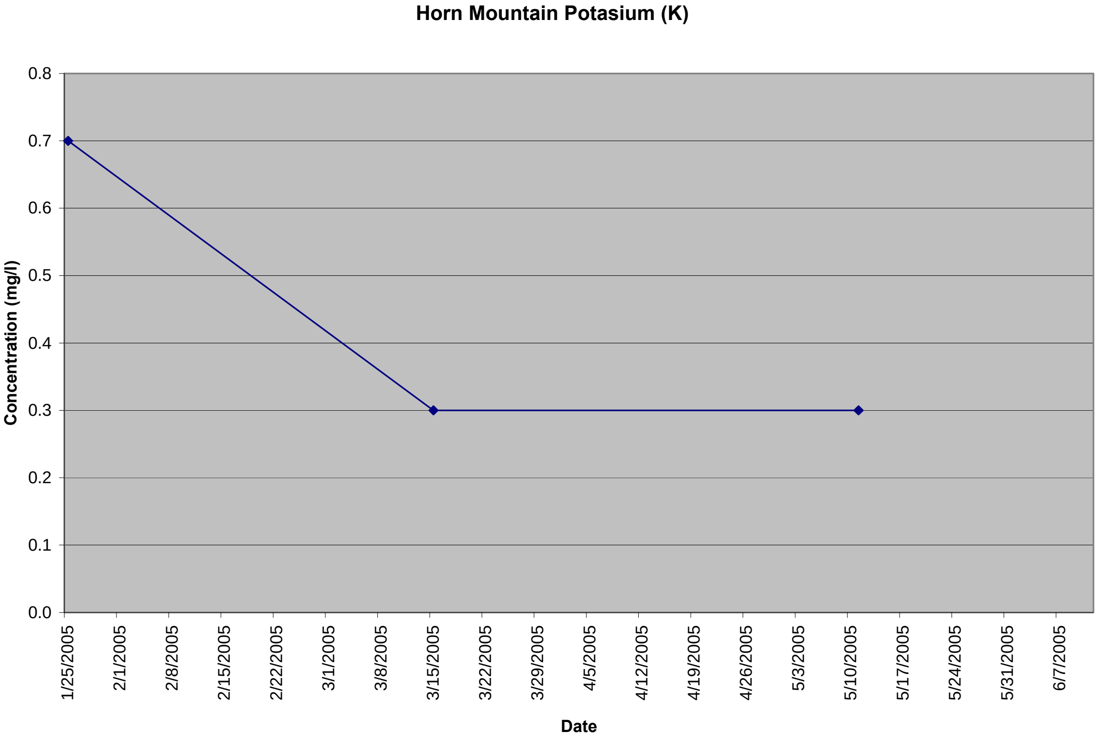

Figure 72: Horn Mountain Potassium Levels.

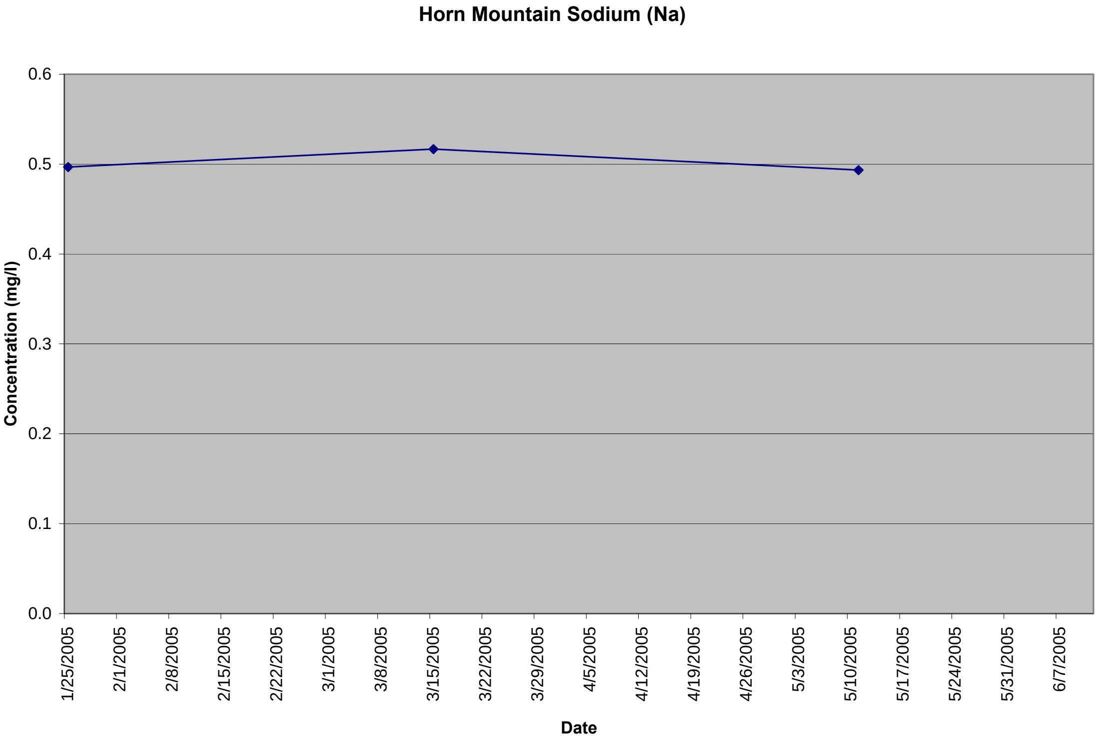

Figure 73: Horn Mountain Sodium Levels.

Major Ion Chemistry of Chestnut Mountain Shooting Range

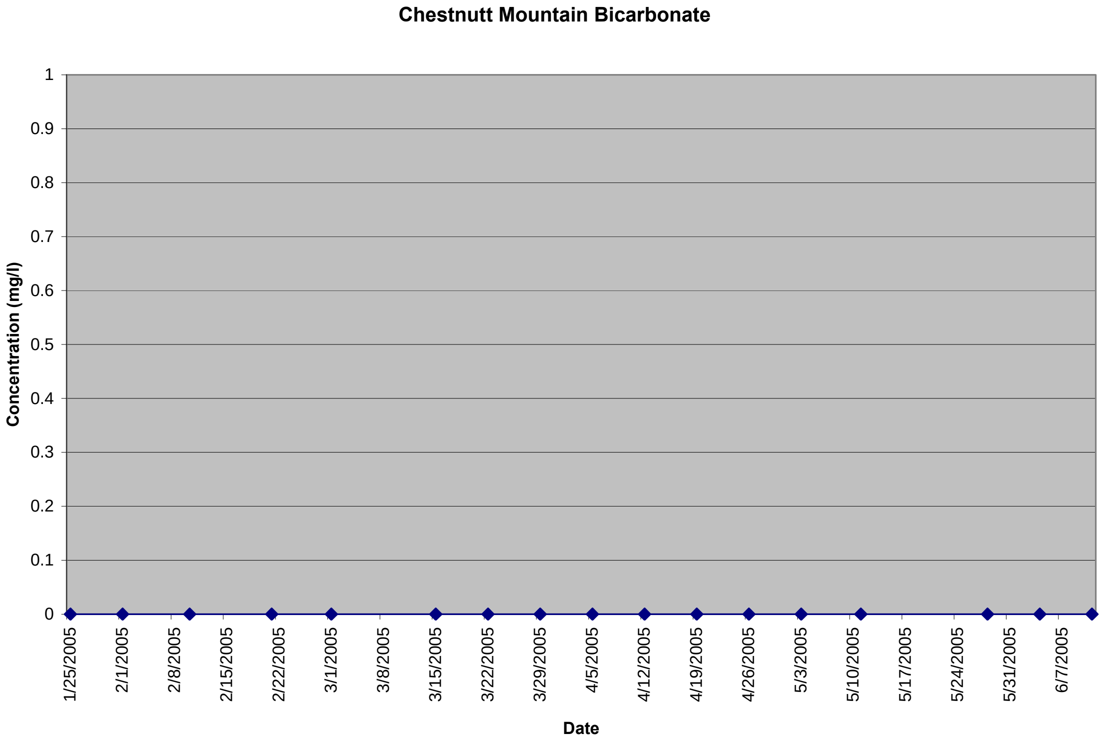

Figure 74: Chestnut Mountain Shooting Range Bicarbonate Levels.

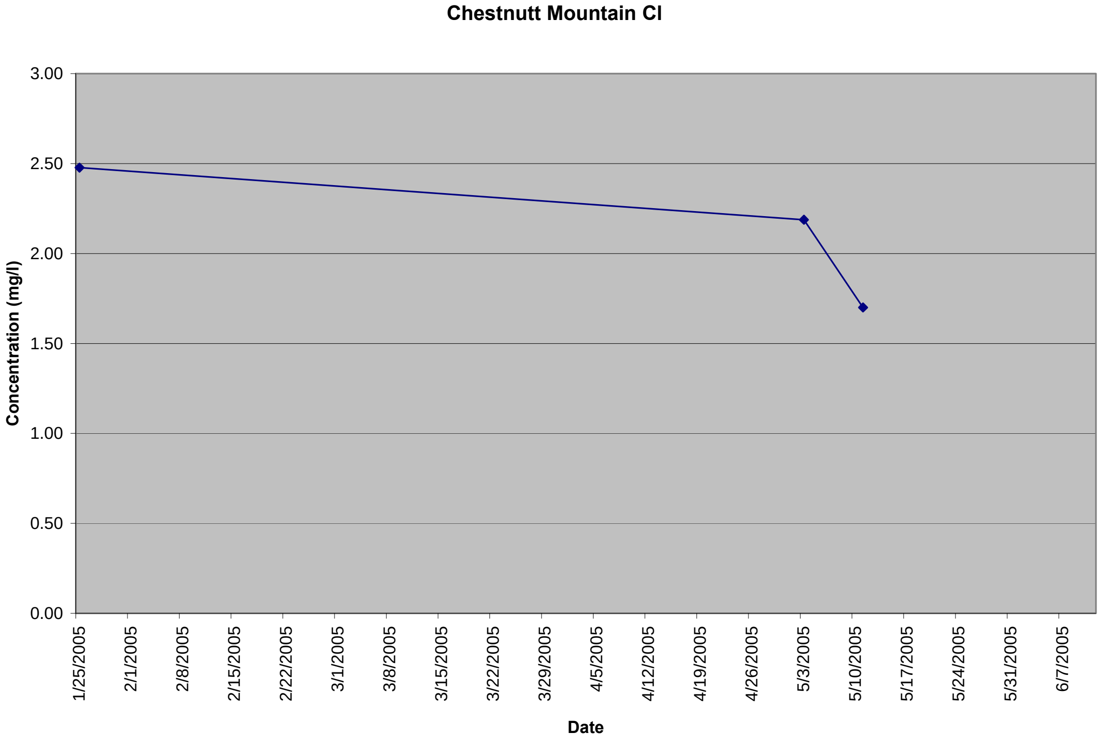

Figure 75: Chestnut Mountain Shooting Range Chloride Levels.

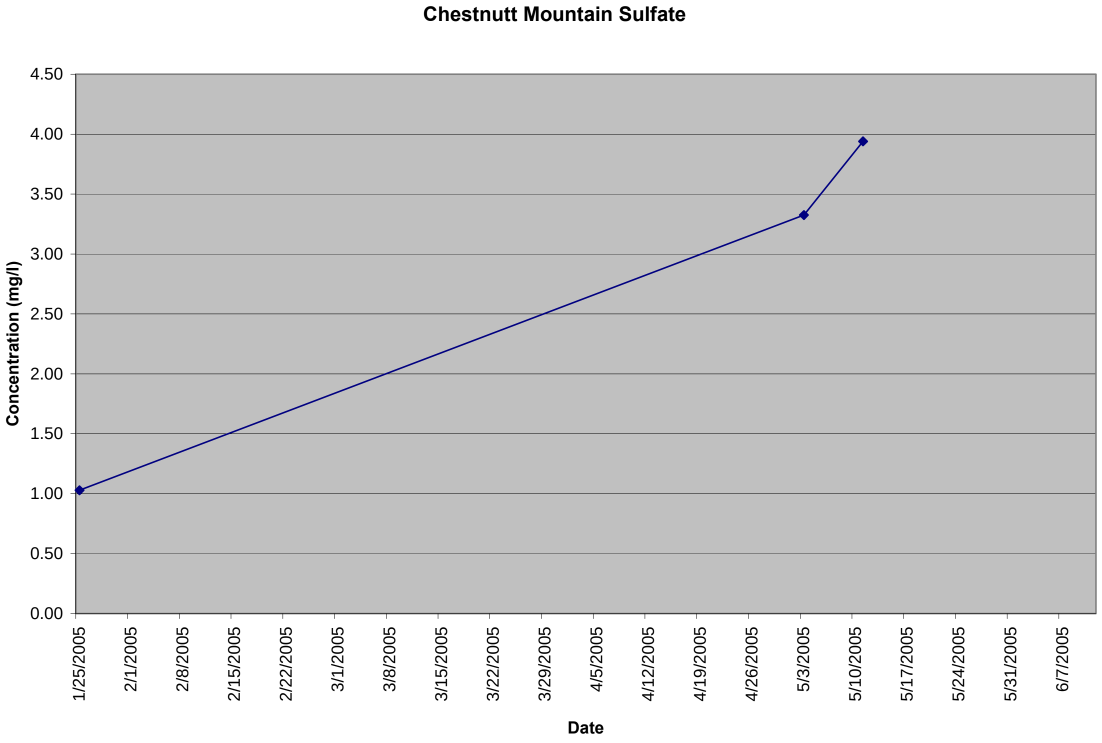

Figure 76: Chestnut Mountain Shooting Range Sulfate Levels.

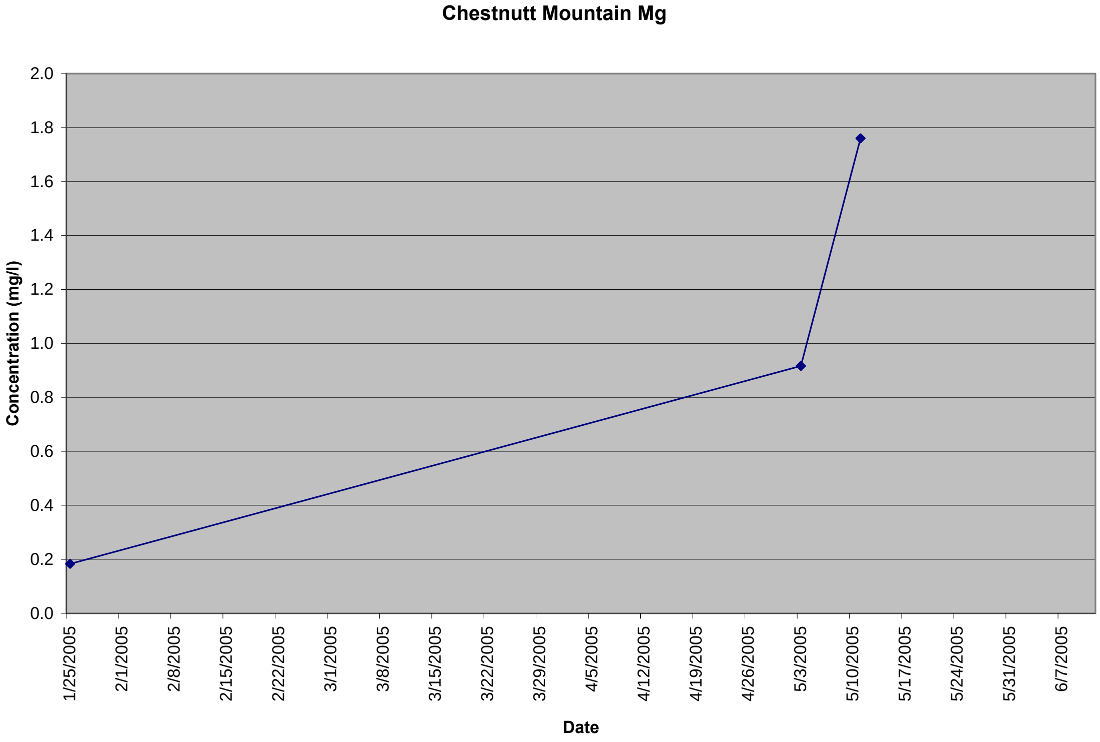

Figure 77: Chestnut Mountain Shooting Range Magnesium Levels.

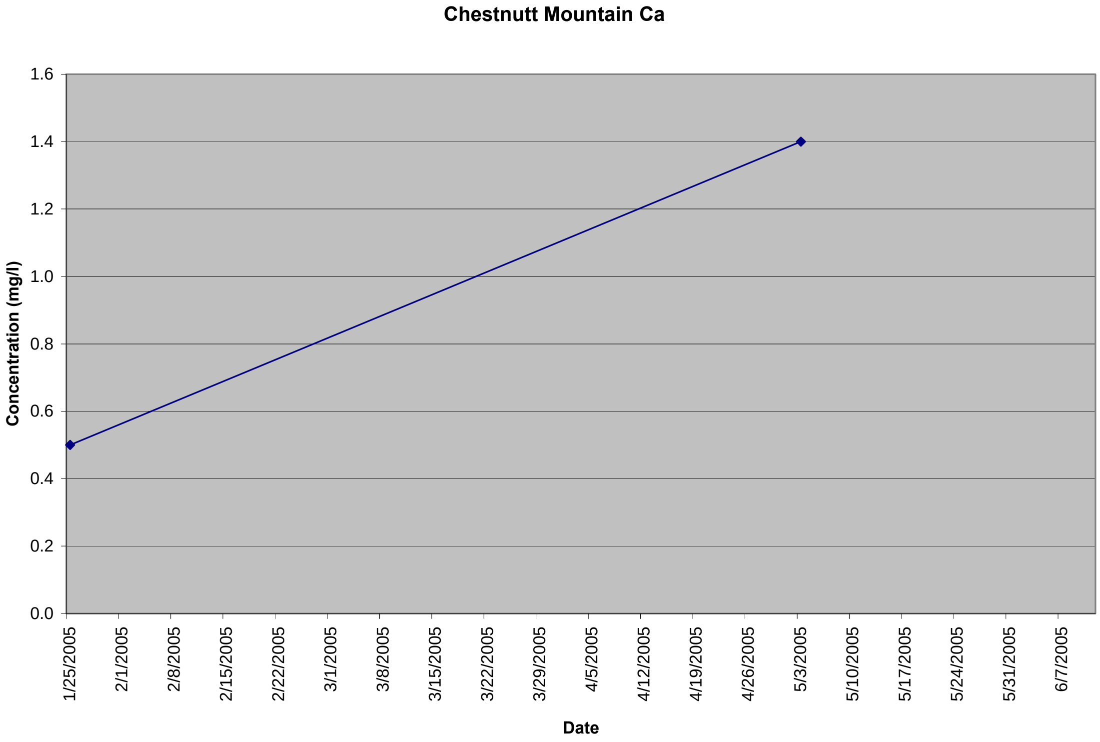

Figure 78: Chestnut Mountain Shooting Range Calcium Levels .

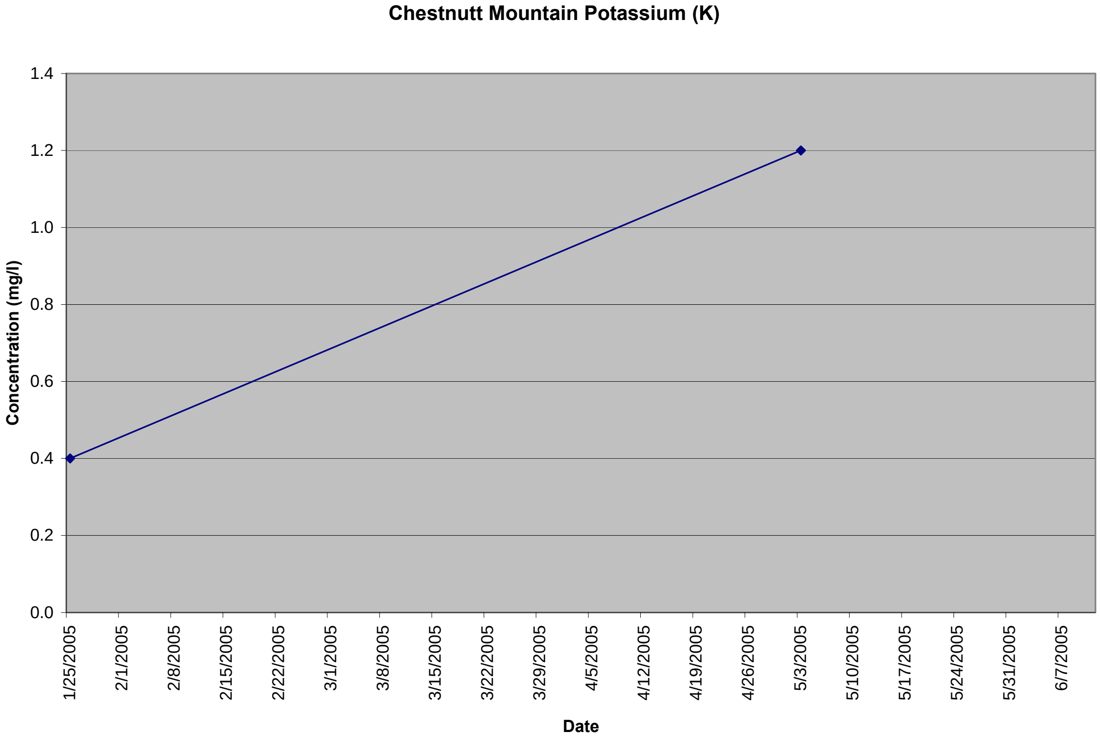

Figure 79: Chestnut Mountain Shooting Range Potassium Levels.

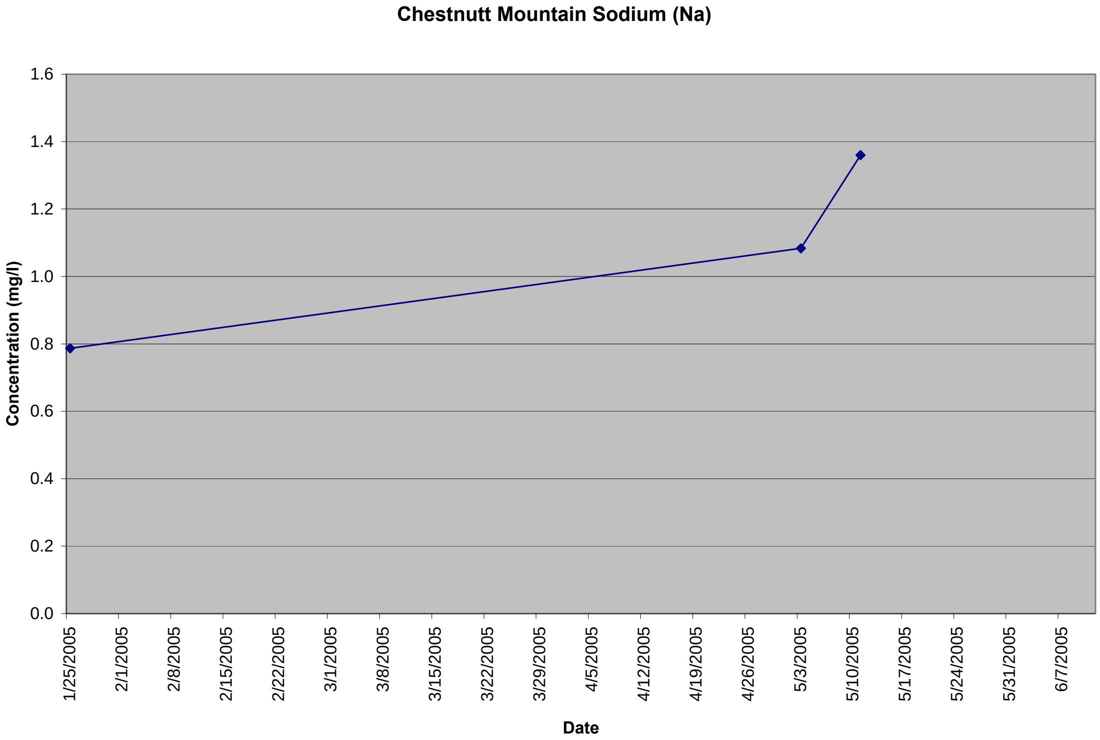

Figure 80: Chestnut Mountain Shooting Range Sodium Levels.

Major Ion Chemistry of Everett Springs

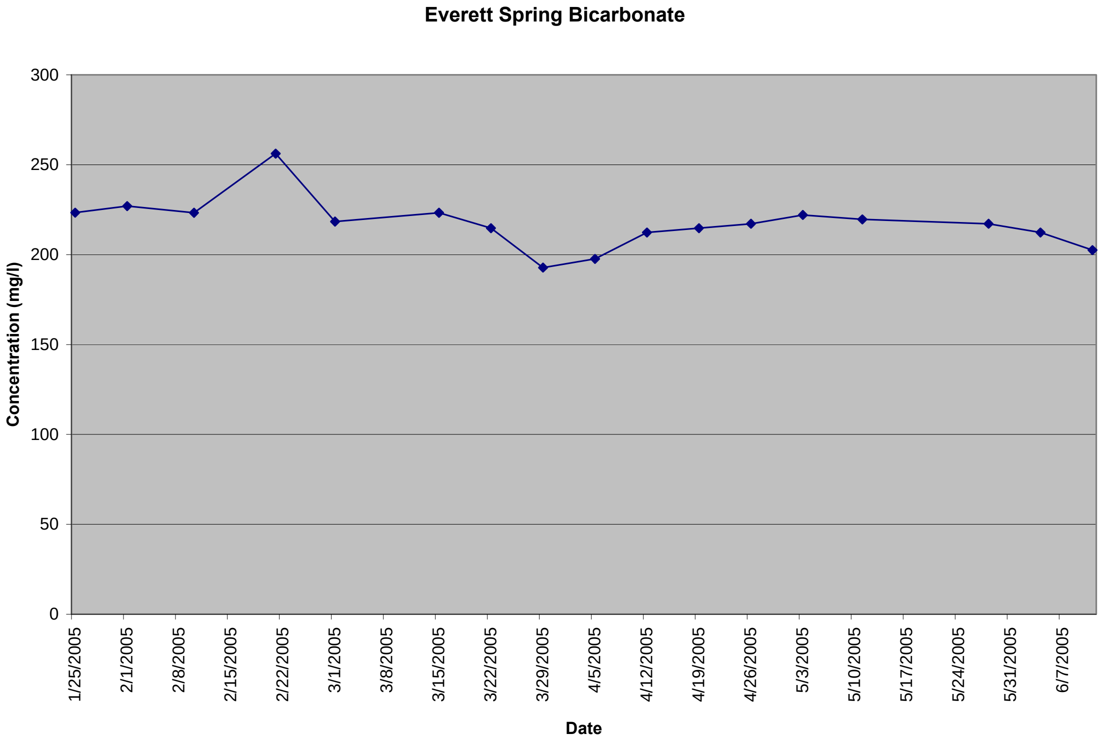

Figure 81: Everett Springs Bicarbonate Levels.

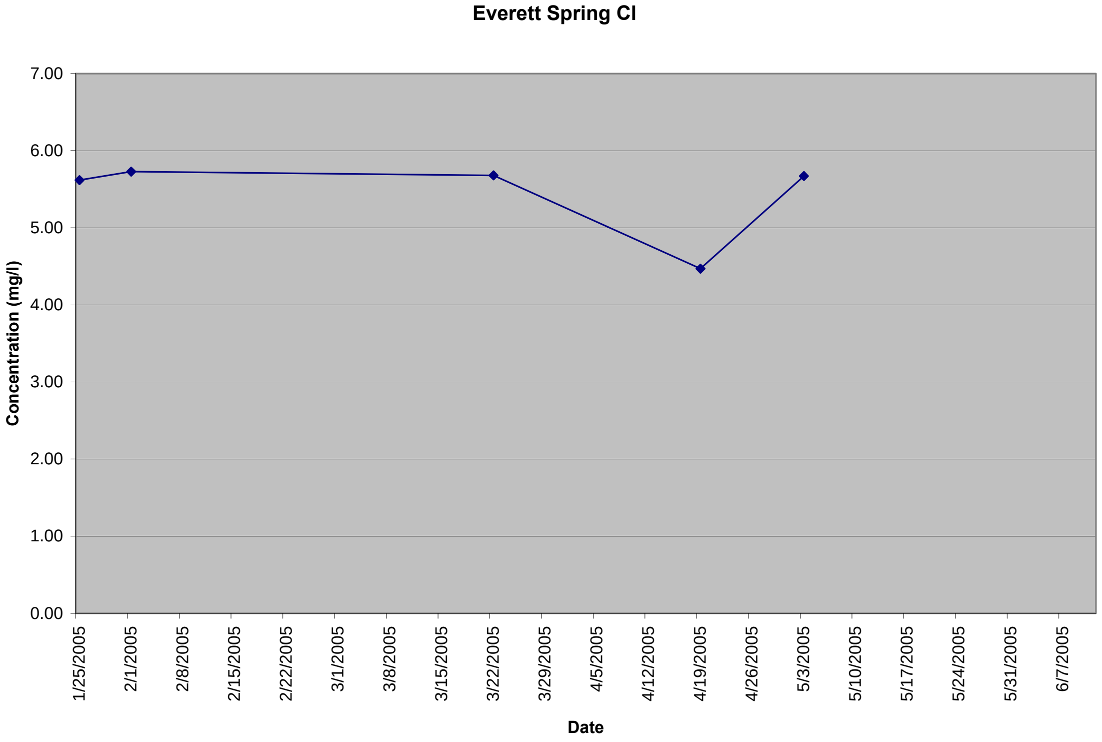

Figure 82: Everett Springs Chloride Levels.

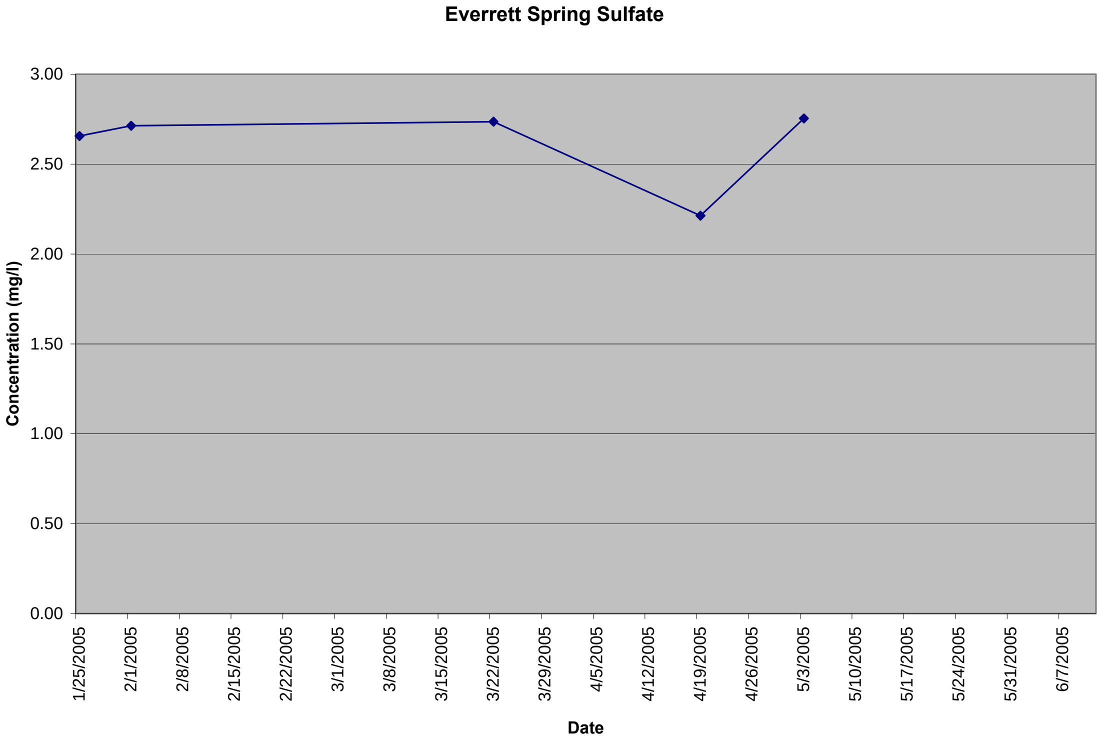

Figure 83: Everett Springs Sulfate Levels.

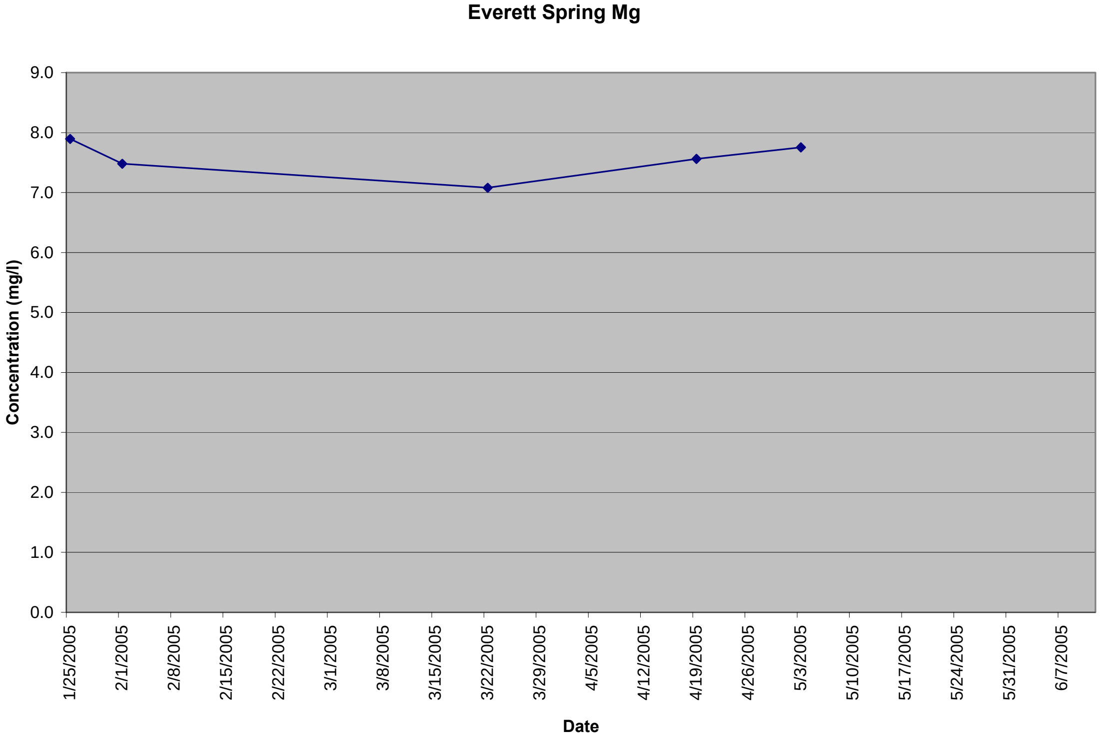

Figure 84: Everett Springs Magnesium Levels.

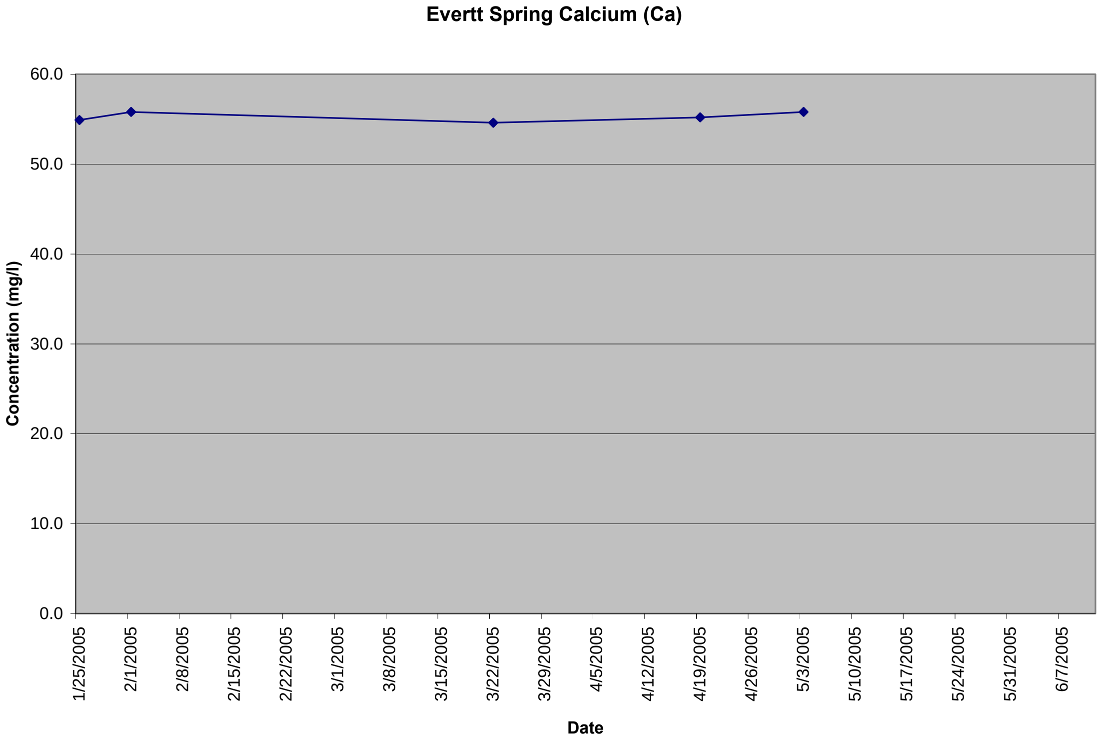

Figure 85: Everett Springs Calcium Levels.

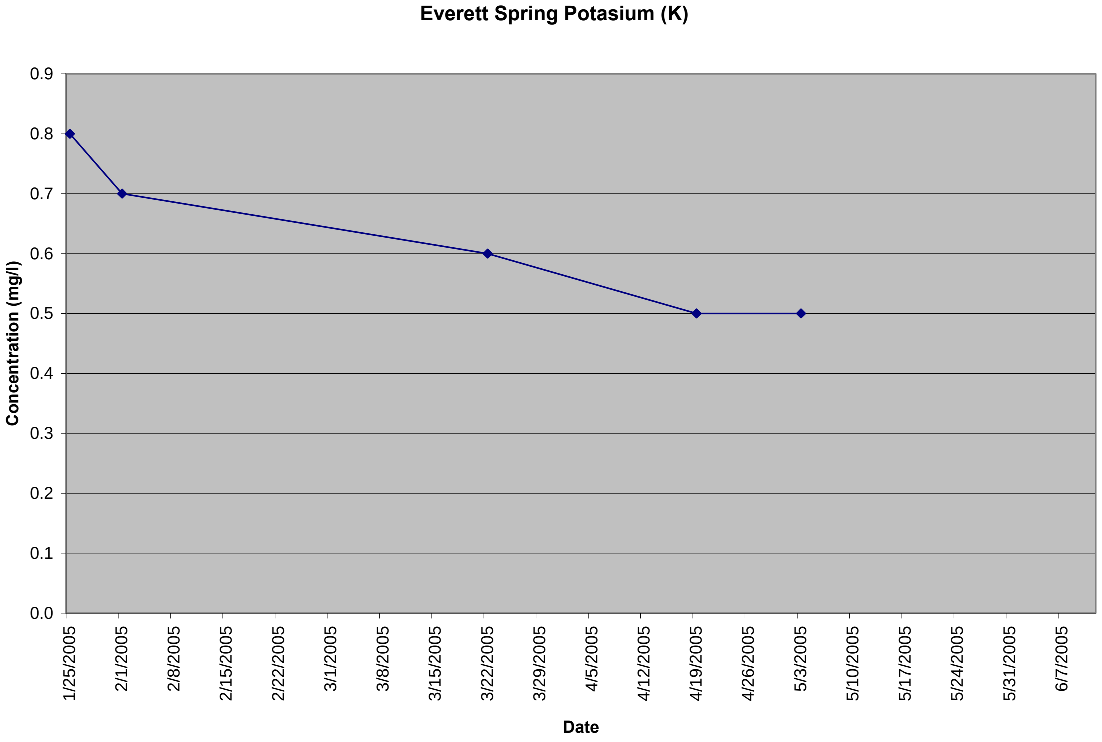

Figure 86: Everett Springs Potassium Levels.

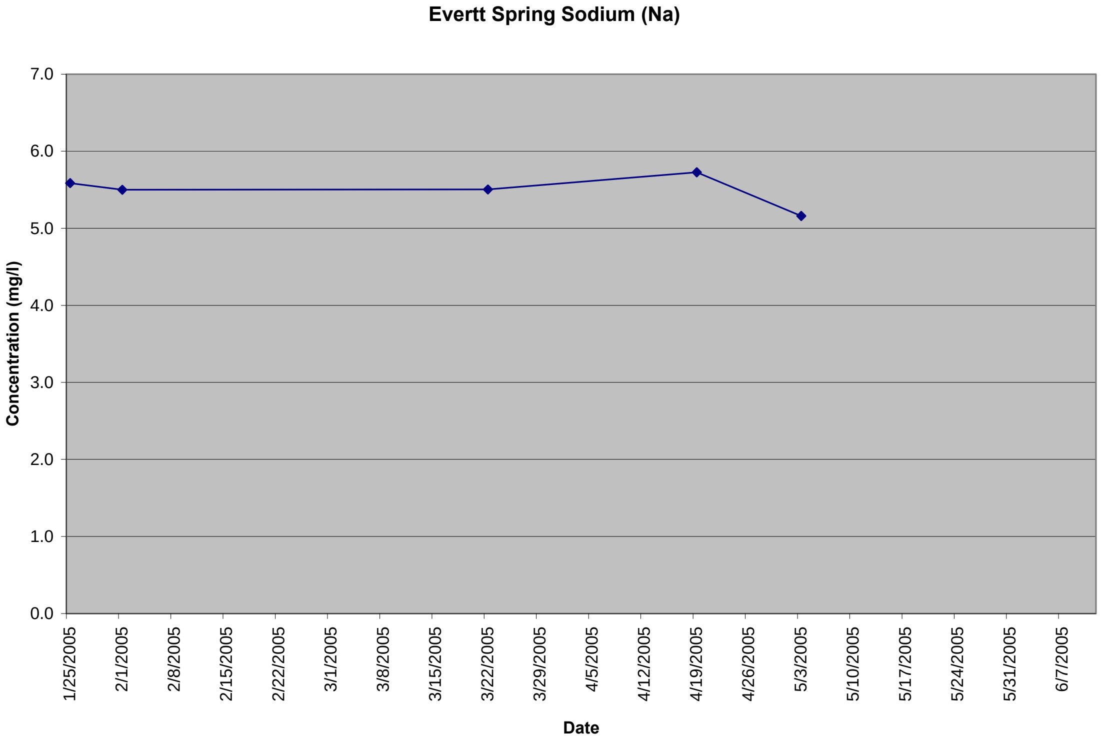

Figure 87: Everett Springs Sodium Levels.

Major Ion Chemistry of West Armuchee

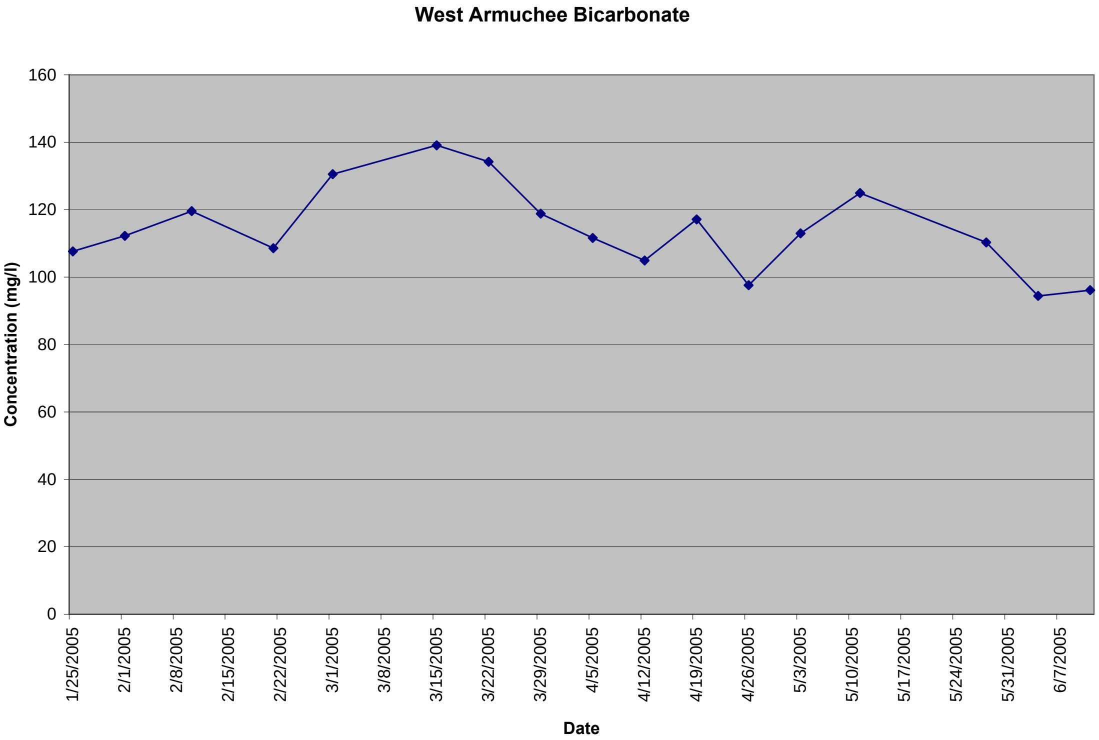

Figure 88: West Armuchee Bicarbonate Levels.

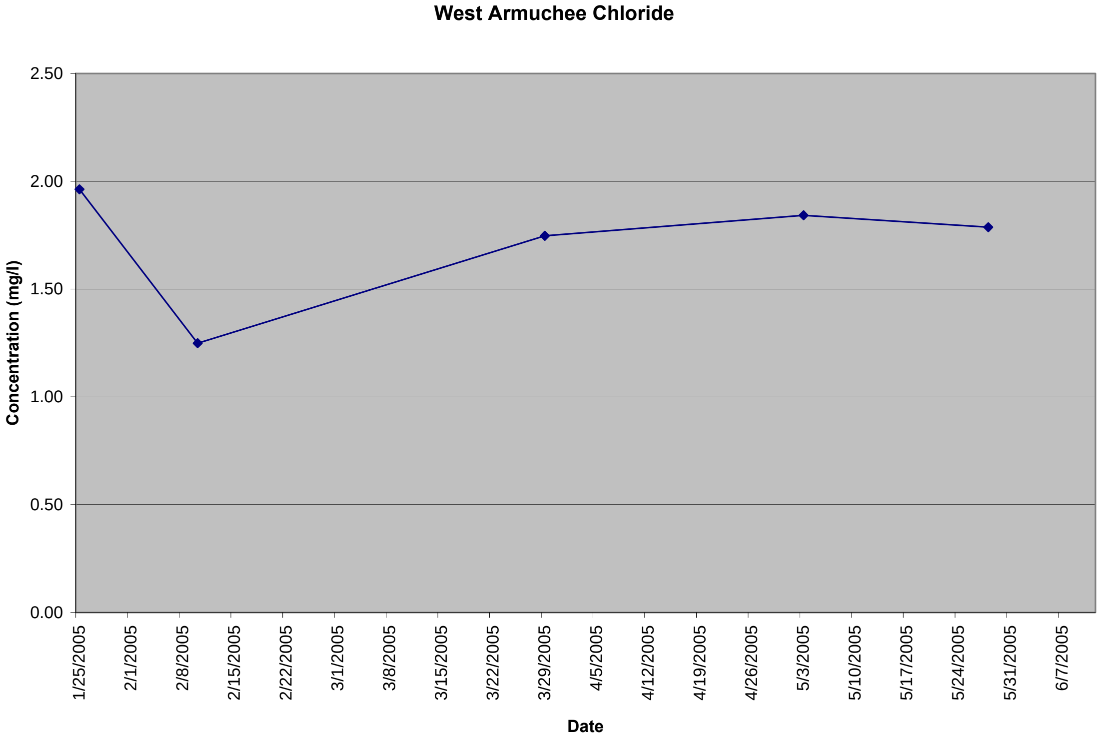

Figure 89: West Armuchee Chloride Levels.

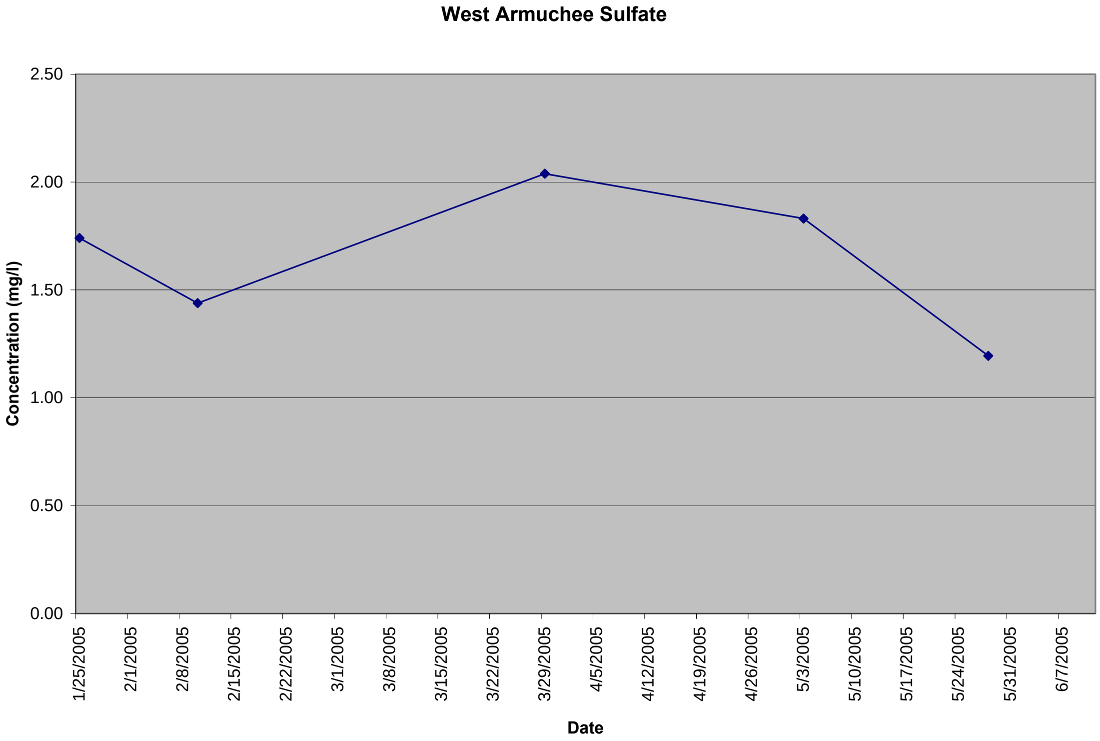

Figure 90: West Armuchee Sulfate Levels.

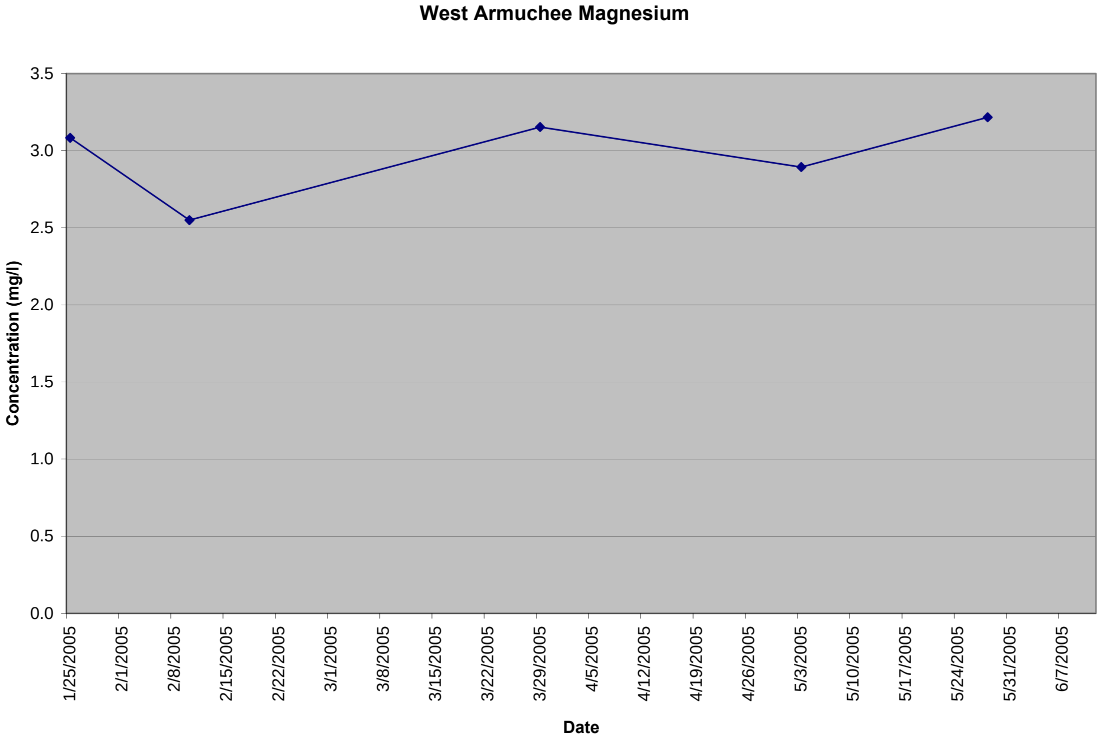

Figure 91: West Armuchee Magnesium Levels.

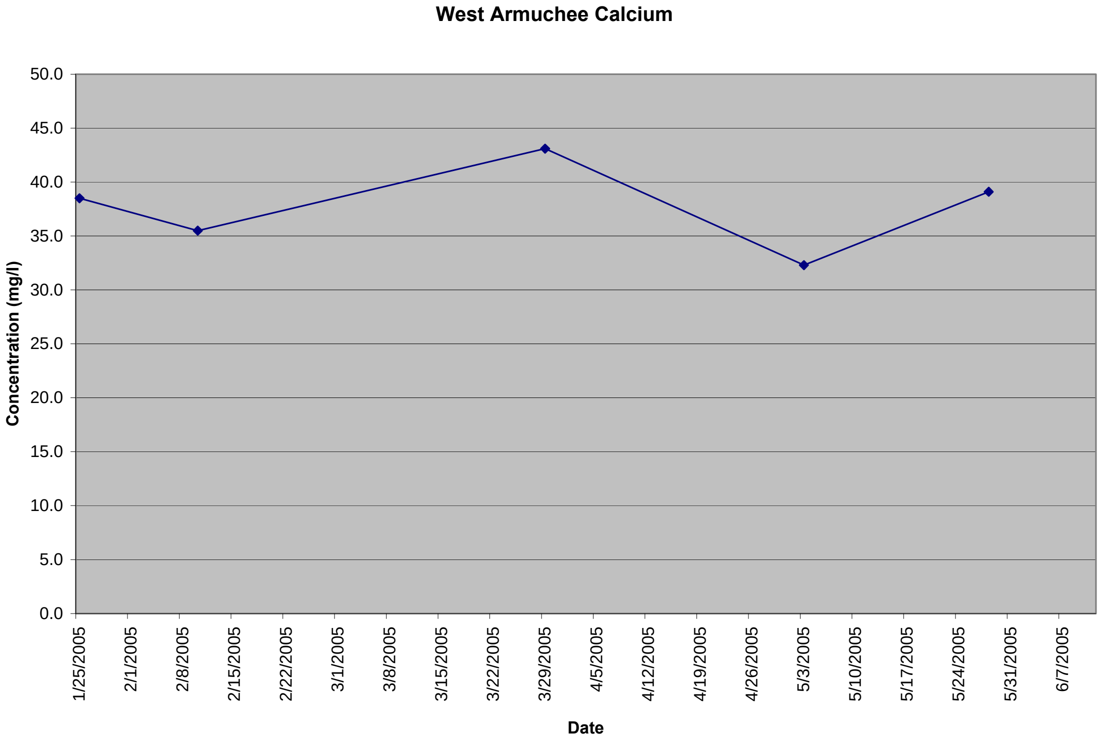

Figure 92: West Armuchee Calcium Levels.

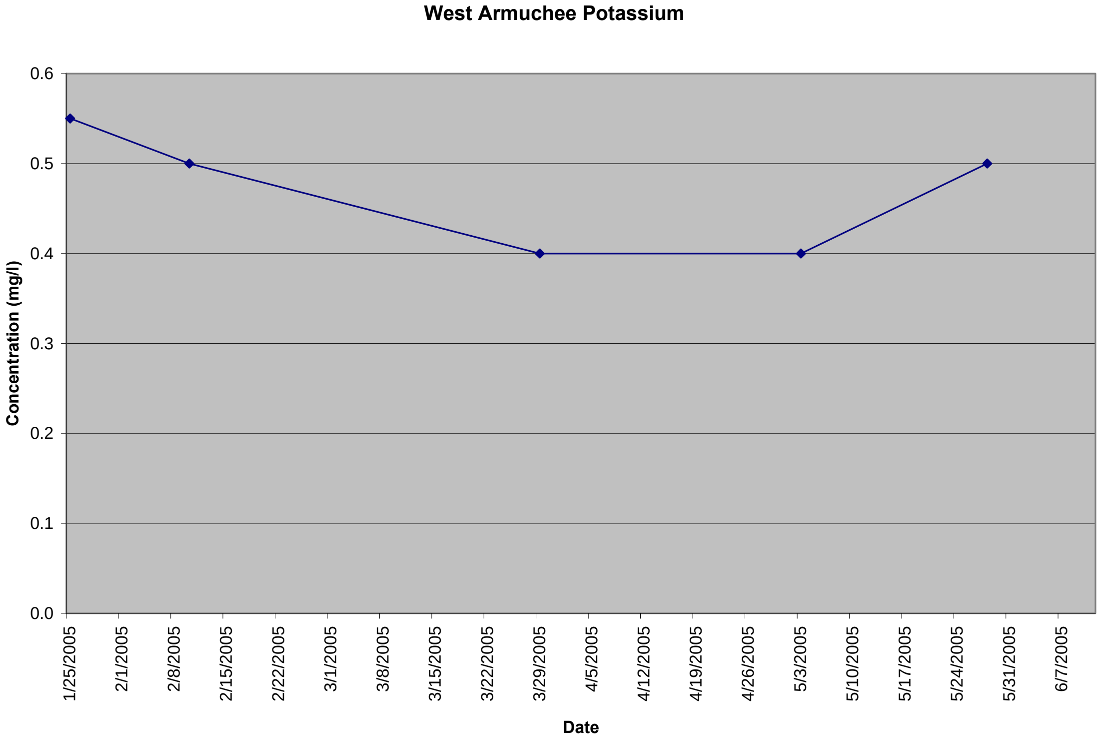

Figure 93: West Armuchee Potassium Levels.

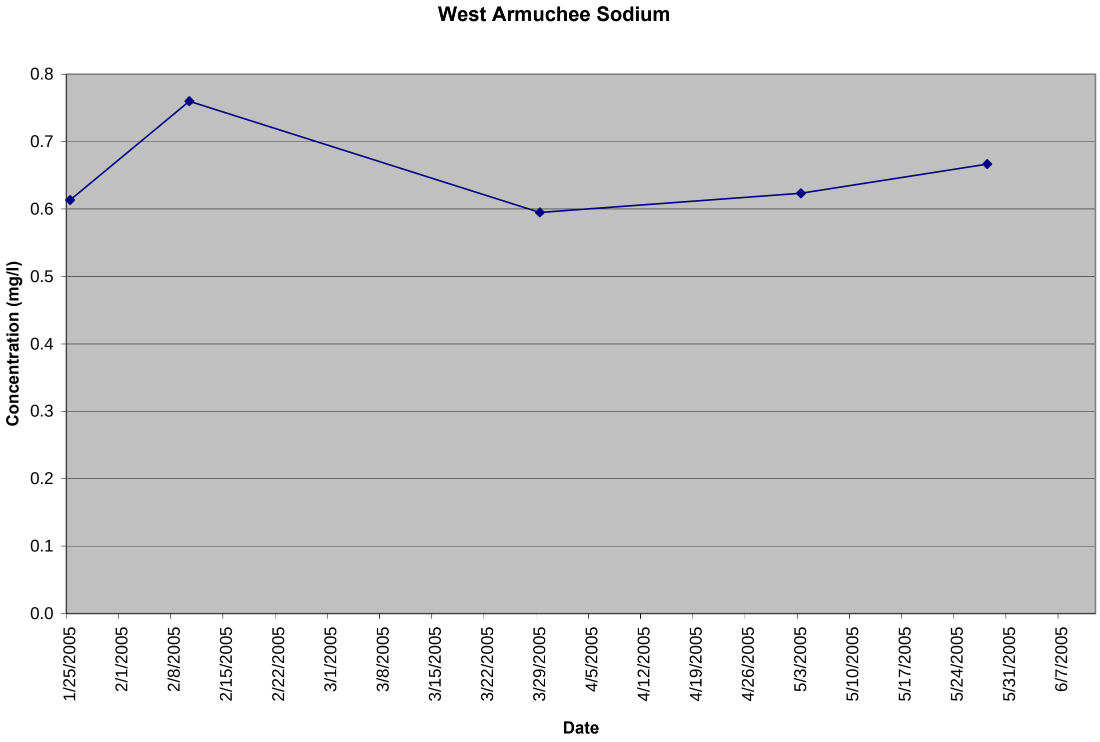

Figure 94: West Armuchee Sodium Levels.

Major Ion Chemistry of Turkey Mountain

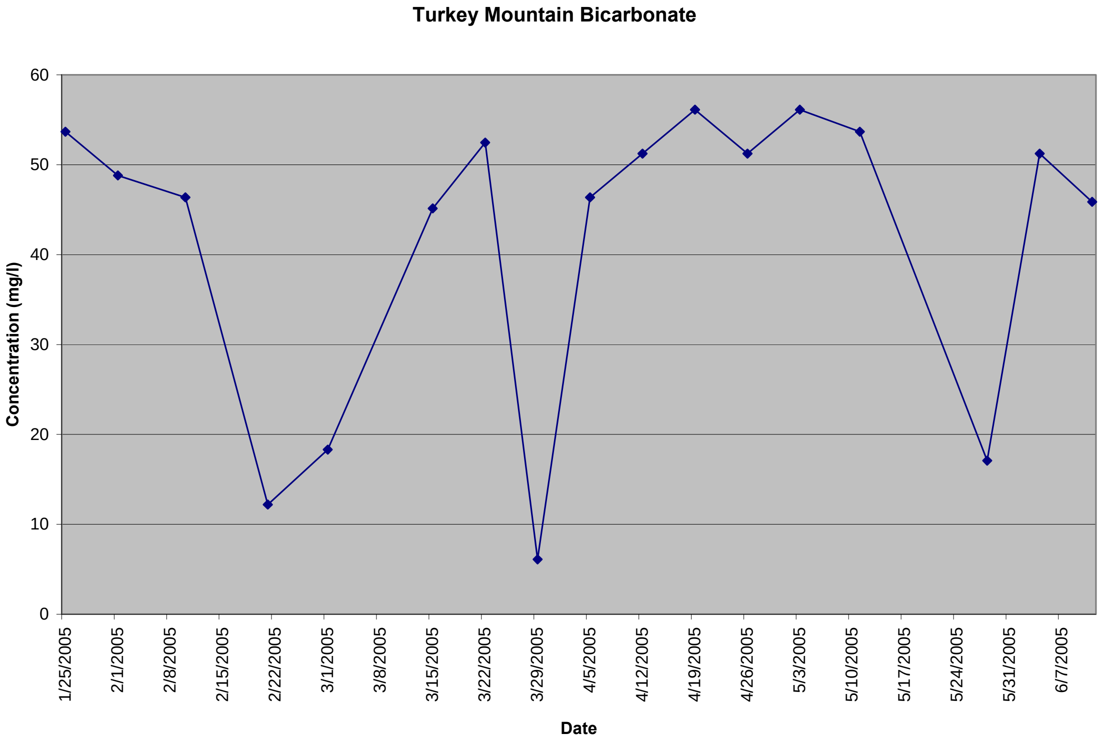

Figure 95: Turkey Mountain Bicarbonate Levels.

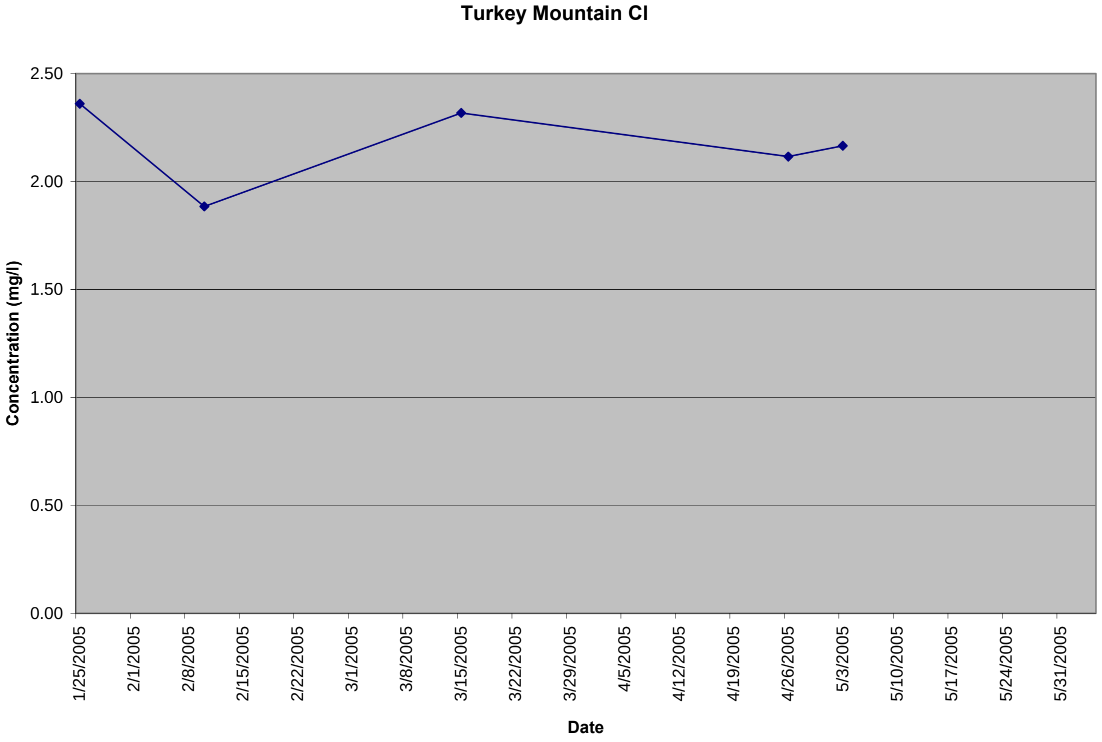

Figure 96: Turkey Mountain Chloride Levels.

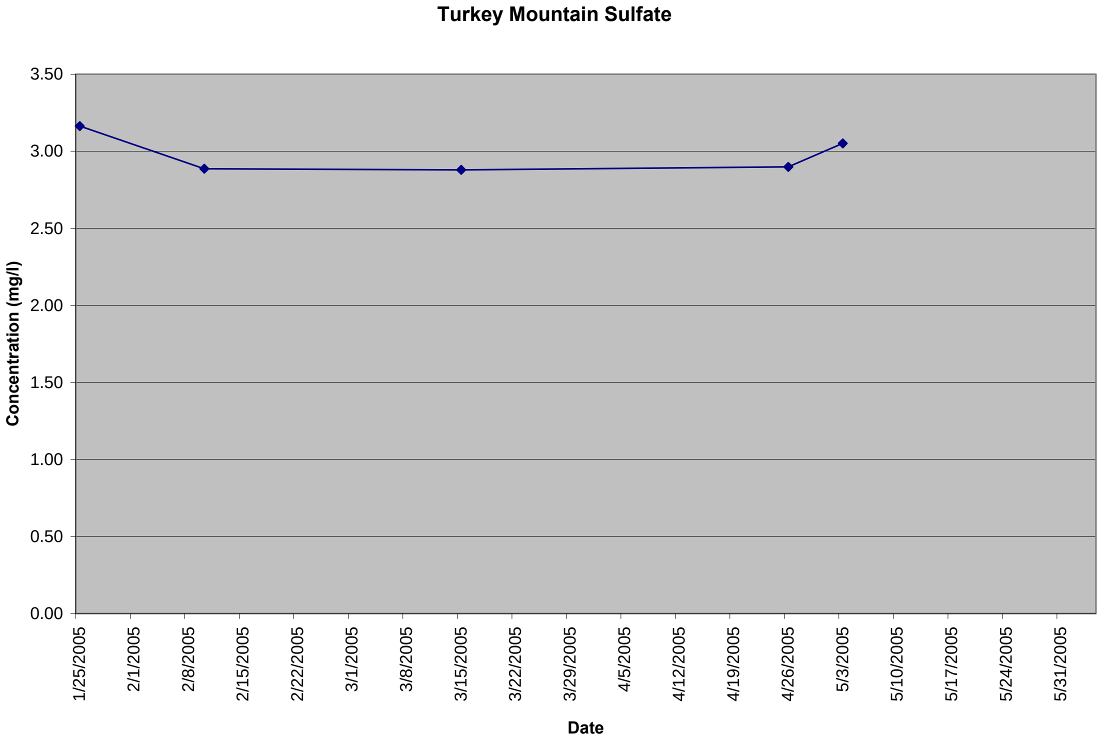

Figure 97: Turkey Mountain Sulfate Levels.

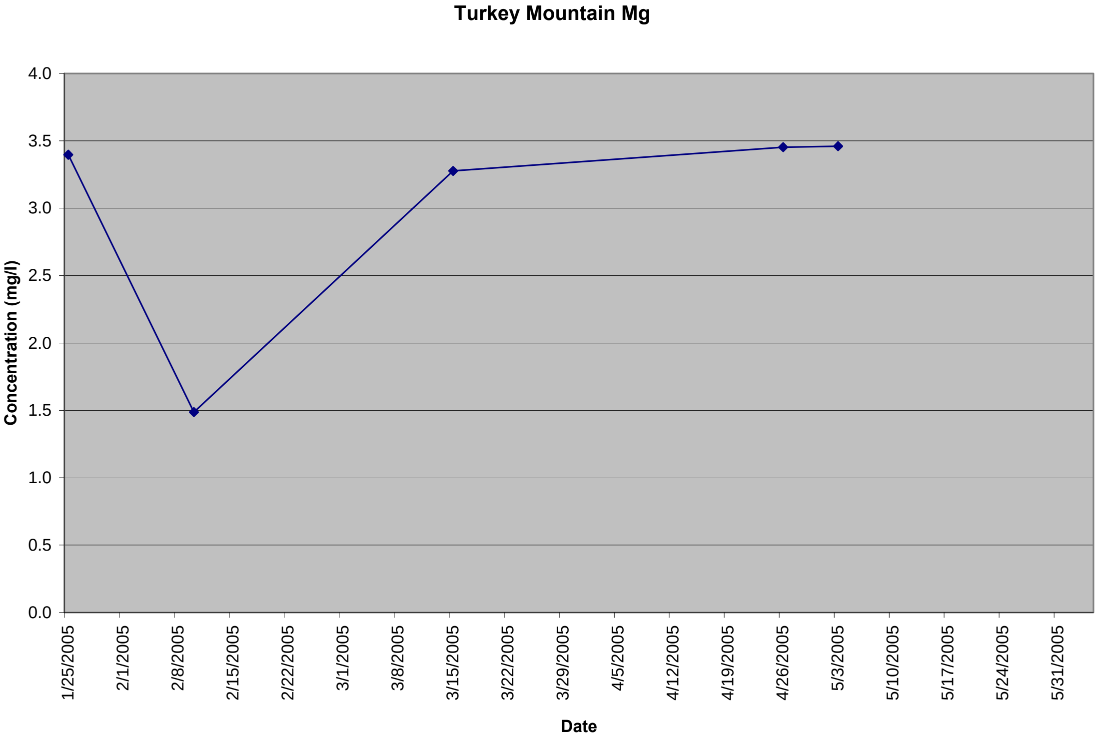

Figure 98: Turkey Mountain Magnesium Levels.

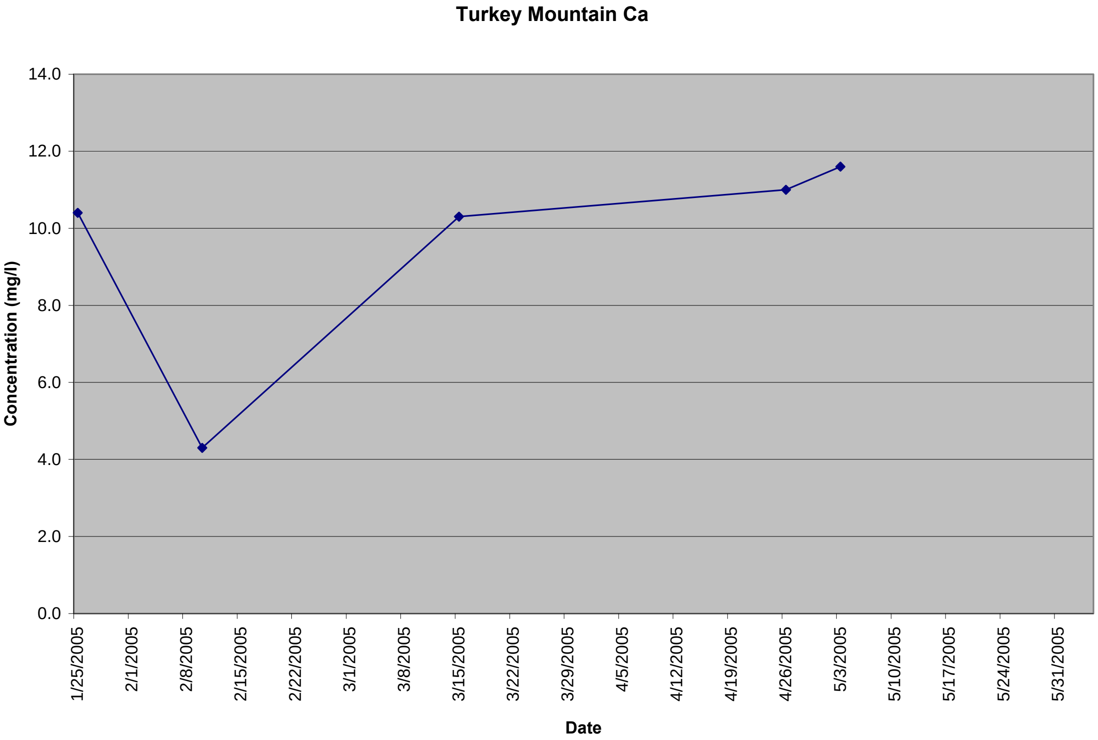

Figure 99: Turkey Mountain Calcium Levels.

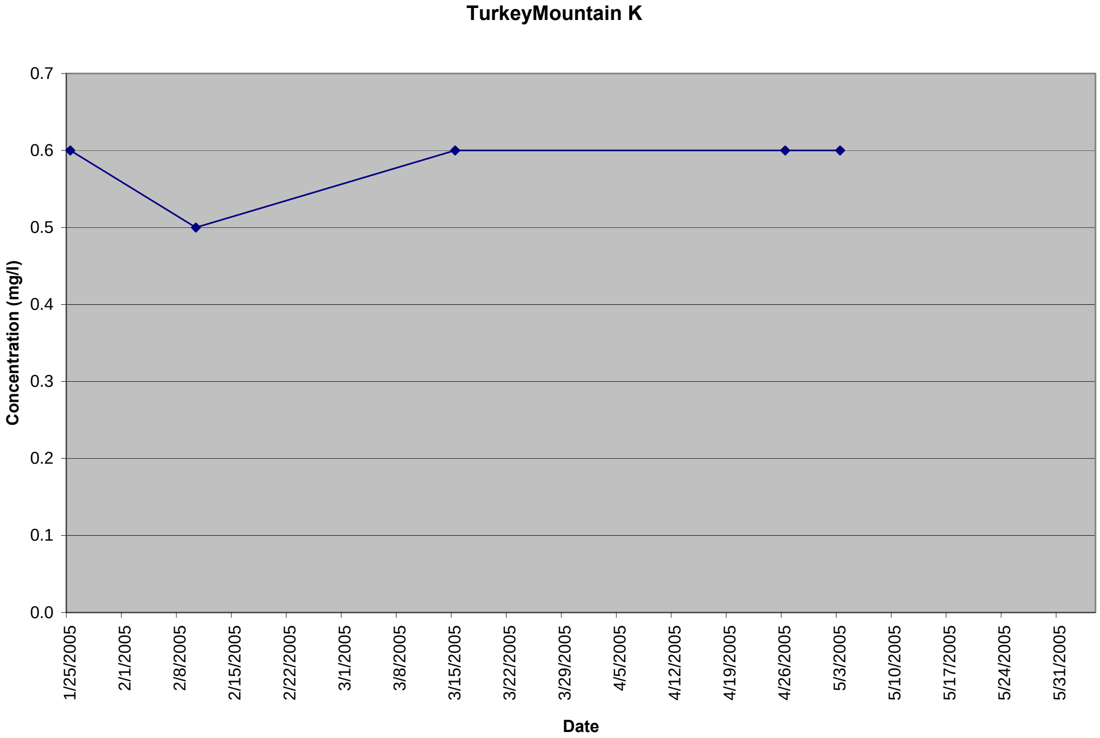

Figure 100: Turkey Mountain Potassium Levels.

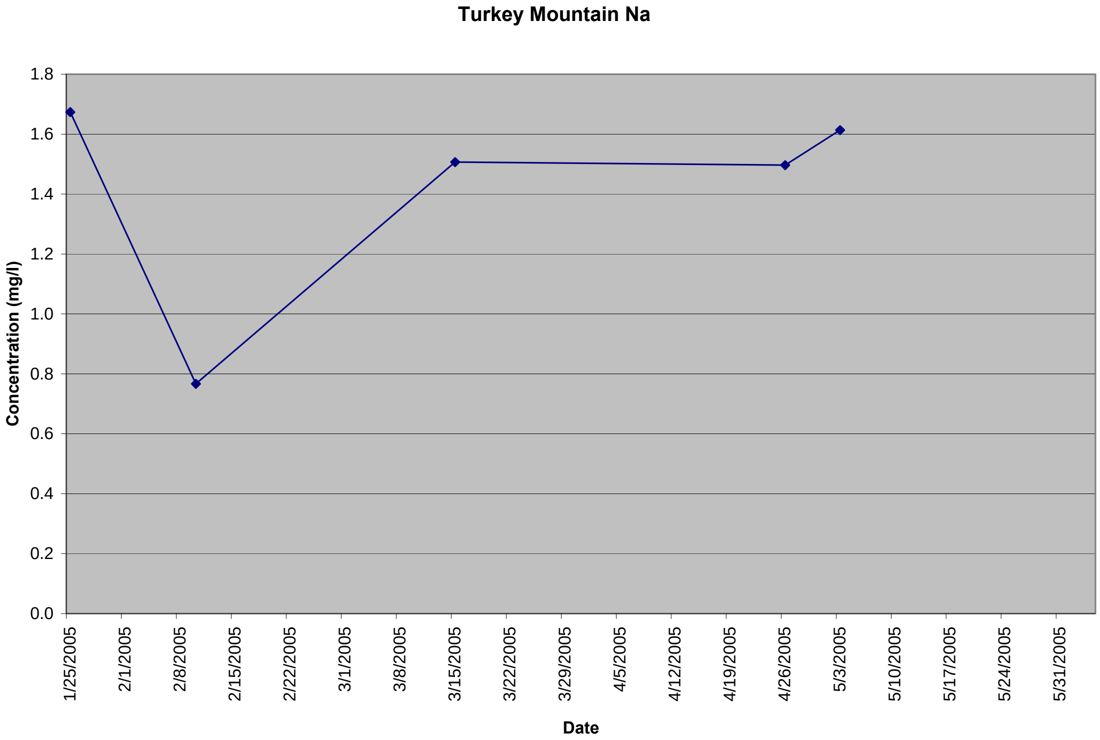

Figure 101: Turkey Mountain Sodium Levels.