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Hydrochemistry in an Alpine Karst System, Sequoia and Kings Canyon National Parks, California

Joel Despain
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HYDROCHEMISTRY IN AN ALPINE KARST SYSTEM,
SEQUOIA AND KINGS CANYON NATIONAL PARKS,
CALIFORNIA

A Thesis
Presented to
The Faculty of the Department of Geography and Geology
Western Kentucky University
Bowling Green, Kentucky, USA

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Geosciences

By Joel D. Despain

August 2006
Hydrochemistry in an Alpine Karst System,
Sequoia and Kings Canyon National Parks, California

Date Recommended

Dr. Chris Groves, Director of Thesis

Mr. Joseph Meiman, Hydrologist,
Mammoth Cave National Park

Dr. Stuart Foster

Dr. Nicholas Crawford

Dean, Graduate Studies and Research  Date
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Finally, I must thank my wife, Katherine Despain, for boundless support and encouragement, even though this thesis and degree has meant months of separation.
# Table of Contents

Signature Page ii

Direct Support Acknowledgements iii

Personal Acknowledgements iv

Table of Contents v

Illustrations vii

I. Abstract xi

II. Introduction
  1. Alpine Karst Aquifers 1

  2. Study Setting
     A. Regional Geology and Geography 3
     B. Spring Creek Watershed 5
     C. Mineral King Climate 11

  3. Problem Statement
     A. Hydrology and Chemistry of Alpine Karst System 17
     B. Alpine Karst and Atmospheric Carbon 18

III. Methods
  1. Site Development and Equipment Installation
     A. Introduction 23
     B. Installation 24
     C. Data Logger Programming and Outputs 27

  2. Data Collection
     A. Early Data 30
     B. Data Logger Management and Maintenance 31
     C. pH Equipment Maintenance 33

  3. Data Analysis
     A. Early Analysis 34
     B. Calculating Ion Constituents 36
     C. Calculating Discharge 41
IV. Results
1. Raw Data Graphs

2. Laboratory Results

3. Ion, discharge, and pH Values

4. C and Chemical Parameter Calculations

5. Regional Data for 2002

6. Data Comparisons

7. Flux Analysis

V. Discussion
1. Raw Data
   A. The Four Parameters
   B. Laboratory Data

2. Carbon Chemistry and Analysis
   A. Carbon Analysis Results
   B. Carbon Methods Compared

3. Calculated Data Sets
   A. Comparisons to Discharge
   B. Tufa Falls and SI
   C. Denudation Rate

4. Flux Analysis
   A. Flux Dependence
   B. Seasonal Variation in Flux

VI. Appendices
1. SigmaPlot Transform Formulas

2. Excel Calculations Table

VII. Bibliography
Illustrations

Figure 1: Location of the study site in California and Sequoia and Kings Canyon National Parks.

Figure 2: Cross section of the entire Spring Creek watershed.

Figure 3: Plan view map of the Spring Creek watershed.

Figure 4: Shane Fryer at a waterfall over bedrock schist just above the instrumented pool. Spring Creek is at base flow in this view. The karst resurgence lies approximately 200 m upstream.

Table 1: Temperature and precipitation sites used by Stephenson, 1988, and their relation to the Spring Creek Study site.

Figure 5: Precipitation in relationship to elevation in the southern Sierra Nevada, Sequoia National Park. Points with error bars reflect extrapolated total precipitation including snowfall. Filled circles are values from the Kaweah River watershed and open circles are from the Kern watershed. Data were corrected for under-reporting of snowfall values.

Figure 6: Mean summer and winter temperatures in relation to elevation in the southern Sierra Nevada, Sequoia National Park. Circles are values for July; Triangles are values from January. Filled symbols are from the Kaweah watershed and open symbols are values from the Kern River watershed. The x symbols are values from the White Mountain Research Station, the highest weather station in California located east of the Sierra Nevada.

Figure 7: Installation of the data logger and associated electrodes and equipment required several days of work in Three Rivers, California at Joel Despain's home and in Mineral King along Spring Creek. The installation took place in fall at a time of base-level flows in Spring Creek. Here discharge (including some flow out of view of the photo) is approximately 30 L/s.

Equation 1: Discharge calculation using sudden-injection tracer dilution method.

\[ Q = \frac{V_0 C_o}{\int_0^{\infty} (C - C_o) dx} \approx \frac{V_0 C_o}{\sum_{i=1}^{n} (C - C_o) \Delta t} \]

Figure 8: The winter approach to the Spring Creek study site.
Figure 9: Calcium vs. conductivity at the time of the water samples. The top graph includes all data points and had an $r^2$ of 0.601. The lower graph has two outliers removed one of which is from June 5, 2002 making an $r^2$ of .9445.

Figure 10: Magnesium vs. conductivity at the time of the water samples. The top graph includes all data points and had an $r^2$ of .74. The lower graph has one outlier removed from June 5, 2002 and an $r^2$ of 0.943.

Figure 11: Stage vs discharge using an exponential growth, single, 1 parameter regression. One outlier was removed to create the lower graph with an $r^2$ of 0.977. The upper graph with the outlier has fit of 0.874.

Table 2: 2002 values from pH regressions.

Equation 2: Relationship between Total Inorganic Carbon and its constituents.

$$\int_0^t \text{TIC} \, dt = \int_0^t C_a \, dt + \int_0^t C_b \, dt + \int_0^t C_m \, dt$$

Equation 3: Inorganic component of CO2

$$\xi = \frac{\left( \int_0^t C_a \, dt + \int_0^t C_b \, dt \right)}{tA}$$

Equation 4: Relationship of Total Inorganic Carbon to ion activities in groundwater.

$$\text{TIC} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3^-]$$

Equation 5: Calculating TIC components.

$$\int_0^t C_m \, dt = \int_0^t (\text{Ca}^{2+} + \text{Mg}^{2+}) \, dt$$

Equation 6: Calculating TIC components.

$$\int_0^t C_b \, dt = \int_0^t \text{TIC} \, dt - \left( \int_0^t (\text{Ca}^{2+} + \text{Mg}^{2+}) \, dt + \int_0^t C_a \, dt \right).$$

Figure 12: pCO2 vs. spC showing the extremely poor fit of this regression which has an $r^2$ value of 0.14.

Figure 13: Early data from the project.

Figure 14: Smoothed conductivity for 2002.

Figure 15: Discharge break-through curve from August 2002 showing
spC dropouts.

Figure 16: The Spring Creek data set during the period of data logger failure showing pH millivolts, conductivity, and stage.

Figure 17: Discharge of the Spring Creek Spring in 2002.

Figure 18: Spring Creek temperatures for 2002.

Figure 19: Spring Creek pH for 2002 showing data gaps and the effects of correlating the data to sets of calibration values determined on varying dates.

Table 3: Laboratory data for water samples from Spring Creek with values in mg/L. Ions detected more than twice are included. Values below detection limit and none detected are shown as nd.

Table 4: Laboratory data for primary ions from water samples above the karst from the basin's two perennial insurgent streams.

Table 5: Charge balance values for laboratory data for water samples from Spring Creek.

Figure 20: Bicarbonate vs. spC at the time that water samples were collected. No outliers were removed from this data set. The $r^2$ for the line is 0.983.

Figure 21: Calcium vs. conductivity at the time of the water samples. The line has an $r^2$ of 0.9445.

Figure 22: Magnesium vs. conductivity at the time of the water samples. The line has an $r^2$ of 0.943.

Table 6: Charge balance values for constituent ion data from the 2002 data set.

Figure 23: Stage vs discharge using an exponential growth, single, 1 parameter regression. One outlier was removed to create the lower graph with an $r^2$ of 0.977. The upper graph with the outlier has fit of 0.874.

Table 7: Comparison of field and laboratory pH values for 2002 from dates with available data.

Figure 24: spC vs TIC regressions from laboratory-derived data. The graph displays a fit of .97.
Figure 25: Saturation Index values for calcite vs. spC producing a fit of .86 with one outlier removed.

Table 8: Values for the sources of TIC in the waters of Spring Creek using three methods.

Figure 26: East Fork of the Kaweah Discharge for 2002.

Figure 27: Lower Kaweah precipitation for 2002.

Figure 28: Lower Kaweah daily mean temperature in C for 2002.

Figure 29: Spring Creek discharge and spC during 2002.

Figure 30: Spring Creek discharge and Total Inorganic Carbon for 2002.

Figure 31: Spring Creek discharge and Saturation Indices for calcite for 2002. The line indicates an SI value of 0.

Figure 32: Discharge and pCO₂ values for Spring Creek for 2002. Gaps in the data reflect periods with pH data.

Figure 33: Discharge and pH for 2002 at the Spring Creek resurgence.

Figure 34: Discharge and Spring Creek water temperatures in C for 2002.

Figure 35: The relationship between Ca²⁺ and Mg²⁺ flux vs. Ca²⁺ and Mg²⁺ concentration and Ca²⁺ and Mg²⁺ flux vs. discharge. The fit of the line to the discharge regression is 0.86.

Figure 36: The relationship between TIC flux vs. TIC concentration and TIC flux vs discharge. The fit of the line to discharge regression is 0.77.

Figure 37: Ion Concentrations in four time periods during spring run-off 2002 showing a decline in ion concentration through the period.

Figure 38 pH values through spring run-off partitioned into four time periods correlating to periods with varying ion concentrations.

Figure 39: Spring Creek Spring discharge, East Fork discharge, Lower Kaweah mean temperature, and Lower Kaweah daily precipitation for 2002.

Table 9: Daily discharge variance during three 10-day periods in 2002.
HYDROCHEMISTRY IN AN ALPINE KARST SYSTEM,
SEQUOIA AND KINGS CANYON NATIONAL PARKS, CALIFORNIA

Joel Despain  August 2006  101 pages
Directed by Chris Groves

Department of Geography and Geology  Western Kentucky University

This study uses high-resolution, long-term conductivity, temperature, discharge, pH, and laboratory data from 2001 through 2003 from an alpine karst spring located at 2,500 m amsl in Sequoia National Park, California to reveal detailed chemical parameters of this karst system. The data show a system with a pronounced spring run-off, extended periods of base flow quiescence, storm responses tied to precipitation as rain or as snowfall, and clear diurnal and seasonal patterns of discharge. pH and spC values show an inverse relationship to discharge and temperature, which are generally in phase. Total inorganic carbon (TIC) and the fraction of mineral-derived and biologically derived C were calculated using three methods. One provided values close to the theoretically likely ratio of 50:50 between the two C sources, while others showed ratios of greater biologically derived C, an unlikely possibility in groundwater chemistry. Saturation indices for the system vary seasonally, with base flow waters saturated at SI values between 0.2 and 0.5, and spring run-off (Q ≥ 100 L/s) waters under saturated and chemically aggressive with SI values as low as -1.2. Late summer rain storm events can return the system to an under saturated state. The denudation rate for the marble bedrock, which makes up approximately 8% of the basin, was found to be high at 148.6 mm/1000 years. Ion and TIC flux are shown to be determined by discharge and not ion concentration.
II. Introduction

1. Alpine Karst Aquifers

According to the Karst Waters Institute, karst aquifers cover approximately 20% of the surface area of the United States and provide 40% of the potable water consumed by Americans each year via springs and wells (What is Karst, p.1). The Floridian karst aquifer alone supplied 3.4 billion gallons of water per day in 1990 (Miller, 1999). These trends continue globally where karst covers vast landscapes. Karst recharge supplies fresh water to 25% of the world's people (Ford and Williams, 1989).

The widespread occurrence and size of karst aquifers allows their chemistry to significantly affect the transportation of water and the elements dissolved within it, including carbon, across large areas. Because of the ubiquity of atmospheric carbon in the form of CO₂ and the chemistry of karst processes, atmospheric carbon, as well as rock derived C and other ions, are sequestered in solution in karst waters where the material is ultimately transported to the oceans or internal basins in large quantities.

High resolution data is useful for understanding the movement of C and other ions in karst aquifers have numerous other applications. Such data can provide detailed information on the hydrology of a given karst system and more general information on the greater character of karst hydrology as a whole. It offers insights into the chemistry of ions, rates for conduit and landscape development, measures on anthropogenic acid deposition, and more. High-resolution data over relatively extended periods of time is a powerful tool for the overall assessment of karst watersheds and their respective hydrologies and chemistries allowing for a useful and detailed understanding of karst
systems. Such data sets are of particular value due to their paucity. Understanding the movement of carbon through natural systems is of particular importance at this time because of the prevalence of anthropogenic carbon in that Earth's atmosphere, which has been implicated in global climate change (Herzog, et al, 2000; Leggett, 2001). Specific effects may include shifting rainfall patterns, more extreme weather and rising mean temperatures world wide. Accurately understanding the impacts of karst geochemical processes on global carbon cycling will allow a better understanding of the global carbon cycle overall. Ultimately, this work originated in collaborations developed from the UNESCO International Geological Correlation Program Project #379: Karst Process and the Global Carbon Cycle.

An impact on carbon cycling and the mobilization and transportation of other ions in alpine karst systems is the inverse relationship between CO₂ solubility and water temperature. As is typical with gases, colder rain, snow and ground water generally contain more atmospheric dissolved CO₂ than would be the case with higher temperatures. This chemical variation makes alpine karst settings particularly worthwhile areas to study.

This study is an application of the high-resolution data collection methods conducted by Groves and Meiman and their colleagues (Groves and Meiman, 2000, 2001, in press; Groves et al. 2002; Liu et al. 2004a, 2004b, Raeisi et al, in review), but is set in an alpine valley at nearly 2,500 m amsl in the mountains of California. The Spring Creek research site in this work is part of what so far is three-site network of karst hydrologic processes monitoring sites in 1) a humid-subtropical system, Mammoth Cave,
Kentucky; 2) a tropical system, Spring 31, Guilin, China; and 3) an alpine system, Spring Creek. Climatic differences such as temperature and the distribution of precipitation between these sites, and karst areas in general, may lead to significant variance in the results of these studies. Of particular importance in this alpine setting may be the greater solubility of CO₂, the most significant source of rock-dissolving acid in karst systems in colder water.

2. Study Setting

A. Regional Geology and Geography

The Mineral King alpine valley is the source of East Fork of the Kaweah River within the boundaries of Sequoia National Park in the southern Sierra Nevada, California (Figure 1). The glaciated valley floor is orientated north to south and lies at approximately 2,400 m amsl. Parallel are the peaks of the Great Western Divide, a sub-range of the greater Sierra Nevada, separating the Kaweah from the Kern River watershed. To the west are lower mountains dividing the East Fork of the Kaweah from the South Fork. The valley and mountains are covered by scattered stands of coniferous trees and broad meadows of herbaceous annuals and perennial shrubs. There are numerous permanent snowfields in the area at higher elevations but no active glaciers. Bare bedrock is common at the highest altitudes.
Study Site in California and Sequoia and Kings Canyon National Parks

Well below Mineral King, the East Fork joins the main (Middle) Fork of the Kaweah near the Sequoia National Park entrance at an elevation of 350 m amsl. A few kilometers downstream from here, historically, the Kaweah left the mountains via a broad alluvial fan in the eastern San Joaquin Valley. The fan featured numerous river branches and arms many of which eventually reached very large Tule Lake, in an internal basin along the west side of the valley. Today, the Kaweah is used almost entirely for irrigation, and the Tule Lake bed is farmed.

Back within Mineral King, Jurassic plutonic rocks outcrop on the margins of the
valley including in the peaks of the Great Western Divide that reaches heights of more than 3800 m amsl to the east of the valley floor. Rocks in the central portions of the watershed, including the valley floor and adjacent tributaries, are largely of Mesozoic marine origin. These rocks reveal an altered but intact submarine volcanic center that forms a vertically-dipping, east-facing homocline with extensive local folding and faulting that is sub-parallel to the bedding (Busby–Spera, 1982). The Mesozoic rocks are largely meta-volcanic and metamorphosed volcanic sediments. They include meta-rhyolite and meta-andesite, phyllites, schists, quartzite, and also marble. The marble outcrops lie in narrow bands parallel to the valley floor. They are prominent in the White Chief hanging valley, near Timber Gap, along Crystal Creek, and in Panorama and Franklin valleys. The marbles are generally white calcite with only minor dolomitization and dark, carbon-rich foliations (Moore, 2000). Karst has developed in these areas producing dozens of springs, sinking streams, sinkholes and caves across the Mineral King area (Rogers, 1978).

The rocks of Mineral King are similar to those across the western sections of the southern Sierra Nevada and Sequoia and Kings Canyon National Parks. Plutonic rocks dominate, but Mesozoic marine rocks are also common and often contain carbonate units and caves and karst.

**B. Spring Creek Watershed**

Along the west side of Mineral King Valley lies the Spring Creek karst watershed. This basin, including the drainages of Eagle and White Chief creeks, is 7.8 square kilometers in size. The marble unit extends (including mantled areas) to 0.65 square
kilometers within the basin. This watershed begins at 3642 m amsl on the granitic, glaciated rocks of Vandever Peak. The watershed is fed by "Little Bear," a permanent snow field along the northwest slopes of Vandever. Runoff builds into a small stream and descends to the north and west to an elevation of approximately 3050 m amsl. There the stream encounters the White Chief marble and flows into the large southern entrance of 1,200-m-long Cirque Cave. The stream emerges at a spring below the cave, flows across the surface for 300 m and enters White Chief Cave. White Chief has 2,000 m of passage, much of it adjacent to the cave stream. The stream emerges onto the surface again at the lower end of the cave, crosses onto schist and phylite and plunges over a 30-meter waterfall (Rogers, 1978). At low flow, the stream crosses the surface for 400 m and sinks yet again into a shallow cave system (Middle Swallet caves #1 and #2) that is generally not human-sized. Underground, this main stream joins the creek from White Chief Lake to the west and quickly resurges and flows through White Chief Bogaz Cave. Another 500 m across the surface brings the stream to several sinks heavily mantled by plutonic glacial debris. There the White Chief stream sinks underground a final time and does not reappear on the surface in the valley (Figure 2). At high flow conditions recharge exceeds the capacity of the karst system and water also flows down the main surface stream channel.
Figure 2: Cross section of the Spring Creek watershed.

North of White Chief Valley, the marble is mantled by more than 150 m of Tioga stage glacial debris (Tinsley, 1999). One kilometer further north, five sinkholes appear in the surface along the valley of Eagle Creek at 2,700 m amsl. Eagle Creek, after flowing on the surface for 1.5 kilometers, disappears into a large sink where fractured pieces of marble, but no bedrock, crop out. Beyond Eagle Sinks, the narrow marble band can be followed on the surface for another 1.5 kilometers to the resurgence that creates Spring Creek. The marble unit also ends here. The spring lies in the steep, glaciated wall of Mineral King Valley and it emerges from among large marble boulders at an elevation of 2,500 m amsl. Lower elevations near the spring include heavier tree cover, scattered wet meadows and dry slopes of sage and other shrubs.

Upstream the creek and persistent airflow can be followed through a small cave among the boulders and bedrock along the south margin of the irregular passages for 50 m, ending in terminal breakdown. From the boulder choked spring, the stream descends over a series of steep runs and falls crossing phylite and schist bedrock, granitic boulders, and spring-deposited travertine for 300 m before braiding at an alluvial fan deposit 150 m
before the East Fork of the Kaweah (Figures 3 and 4).

Alpine White Chief Valley and the upper Eagle Creek watershed are characterized by sparse vegetation and widespread exposed bedrock, talus boulders, and glacial till. Vegetation includes meadows of grasses and annuals and a few scattered clumps of trees including lodgepole pines and western junipers below 2800 m. The bare marble bedrock of the area creates a classic example of alpine karst, with many surface karst features such as karren, joints enlarged by solution, sinkholes, blind pits, and collapses.
Figure 3: Plan view map of the Spring Creek watershed.
Figure 4: Shane Fryer at a waterfall over bedrock schist just above the instrumented pool. Spring Creek is at base flow in this view. The karst resurgence lies approximately 200 m upstream.
Flow at the resurgence varies seasonally with a peak, generally in late May, as high as 1,200 L/s. Late fall flows from the spring are generally much lower and in dry years may drop below 20 L/s (Black, 1994; Schultz, 1996). Previous work has shown that stream temperatures range between 2° and 9° C and pH values between 7.3 and 8.0 (Black, 1994; Schultz, 1996). Tinsley (1999) has demonstrated that the water at the spring originates from Eagle Sink and White Chief Valley. Sodium chloride and fluorescein were used in 1989 to document the connection to the White Chief stream. Transit time to the spring was 3.5 days. This work was completed during low flow conditions of late summer.

C. Mineral King Climate

Most of California displays a classic Mediterranean climate pattern – wet, cool winters and hot, dry summers. Southern California (including Sequoia National Park and Mineral King) also occasionally experience monsoon precipitation as very infrequent warm, summer rains. Vegetation and available water for plants and runoff are strongly affected by geography, elevation, aspect, and rain shadow effects in the mountains of Southern California. Stephenson (1988) carefully analyzed temperature and precipitation data for the Sequoia National Park area in his Ph.D. dissertation, *Climatic Control of Vegetation Distribution: The Role of the Water Balance with Examples from North America and Sequoia National Park, California*. Stephenson used temperature, snow course data, daily precipitation values, and annual precipitation values from 32 sites in or within a few miles of Sequoia and Kings Canyon National Parks, including three snow survey sites in Mineral King (Table 1).
Table 1: Temperature and precipitation sites used by Stephenson, 1988, and their relation to the Spring Creek Study site.

<table>
<thead>
<tr>
<th>Weather Station</th>
<th>Location from the Mineral King study area</th>
<th>Approximate elevation relative to the Spring Creek Spring</th>
<th>Within the parks?</th>
<th>Type of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grant Grove</td>
<td>50 km. northwest</td>
<td>400 m lower</td>
<td>yes</td>
<td>Temperature, snow course, daily precipitation</td>
</tr>
<tr>
<td>Big Meadows</td>
<td>40 km. northwest</td>
<td>100 m lower</td>
<td>no</td>
<td>Temperature, snow course, daily precipitation</td>
</tr>
<tr>
<td>Snow course 237</td>
<td>45 km. northwest</td>
<td>400 m lower</td>
<td>no</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 226</td>
<td>40 km. northwest</td>
<td>250 m higher</td>
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<td>Snow course</td>
</tr>
<tr>
<td>Mitchell Meadow</td>
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<td>200 m higher</td>
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<td>Snow course</td>
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<td>Beartrap Meadow</td>
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<td>500 m lower</td>
<td>yes</td>
<td>Daily precipitation</td>
</tr>
<tr>
<td>Lodgepole</td>
<td>25 km. northwest</td>
<td>400 m lower</td>
<td>yes</td>
<td>Temperature and daily precipitation</td>
</tr>
<tr>
<td>Giant Forest</td>
<td>25 km. northwest</td>
<td>550 m lower</td>
<td>yes</td>
<td>Temperature, daily precipitation, and snow course</td>
</tr>
<tr>
<td>Snow course 243</td>
<td>25 km. northwest</td>
<td>450 m lower</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Bear Hill</td>
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<td>Temperature, daily precipitation, and snow course</td>
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<tr>
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<td>Temperature, daily precipitation, and snow course</td>
</tr>
<tr>
<td>Three Rivers PH 1</td>
<td>20 km. west</td>
<td>2,200 m lower</td>
<td>no</td>
<td>Temperature and daily precipitation</td>
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<tr>
<td>Three Rivers 6 SE</td>
<td>20 km. west</td>
<td>1,700 m lower</td>
<td>no</td>
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</tr>
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<td>Atwell</td>
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<td>500 m lower</td>
<td>yes</td>
<td>Daily precipitation</td>
</tr>
<tr>
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<td>same</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 374</td>
<td>in Mineral King</td>
<td>same</td>
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<td>Snow course</td>
</tr>
<tr>
<td>Snow course 292</td>
<td>in Mineral King</td>
<td>same</td>
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<td>Snow course</td>
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<tr>
<td>Hockett Meadow</td>
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<td>Daily precipitation and snow course</td>
</tr>
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<td>Wet Meadow</td>
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<td>no</td>
<td>Temperature, daily precipitation, and snow course</td>
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<tr>
<td>Snow course 264</td>
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<td>200 m higher</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Location</td>
<td>Distance</td>
<td>Elevation</td>
<td>Yes/No</td>
<td>Measurement Details</td>
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<td>-----------</td>
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<td>----------------------------------------------------------</td>
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<tr>
<td>Chagoopa</td>
<td>14 km northeast</td>
<td>600 m higher</td>
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<td>Yearly Precipitation and snow course</td>
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<td>Upper Tyndall</td>
<td>30 km northeast</td>
<td>900 m higher</td>
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<td>Snow course</td>
</tr>
<tr>
<td>Tyndall Creek</td>
<td>30 km northeast</td>
<td>750 m higher</td>
<td>yes</td>
<td>Daily temperature and snow course</td>
</tr>
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<td>Snow course 250</td>
<td>30 km northeast</td>
<td>850 m higher</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 275</td>
<td>25 km northeast</td>
<td>850 m higher</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Crabtree Meadow</td>
<td>25 km northeast</td>
<td>650 m higher</td>
<td>yes</td>
<td>Temperature, daily precipitation, and snow course</td>
</tr>
<tr>
<td>Snow course 254</td>
<td>25 km northeast</td>
<td>800 m higher</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 256</td>
<td>25 km east</td>
<td>500 m higher</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 252</td>
<td>30 km east</td>
<td>1000 m higher</td>
<td>yes</td>
<td>Snow course</td>
</tr>
<tr>
<td>Cottonwood Lakes</td>
<td>35 km east</td>
<td>850 m higher</td>
<td>no</td>
<td>Temperature, daily precipitation, and snow course</td>
</tr>
<tr>
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<td>550 m higher</td>
<td>no</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 251</td>
<td>35 km east</td>
<td>900 m higher</td>
<td>no</td>
<td>Snow course</td>
</tr>
<tr>
<td>Snow course 260</td>
<td>22 km east</td>
<td>same</td>
<td>no</td>
<td>Snow course</td>
</tr>
<tr>
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<td>400 m higher</td>
<td>no</td>
<td>Temperature, yearly precipitation and snow course</td>
</tr>
<tr>
<td>Snow course 259</td>
<td>30 km southeast</td>
<td>500 m higher</td>
<td>no</td>
<td>Snow course</td>
</tr>
</tbody>
</table>
Figure 5: Precipitation in relationship to elevation in the southern Sierra Nevada, Sequoia National Park. Points with error bars reflect extrapolated total precipitation including snowfall. Filled circles are values from the Kaweah River watershed and open circles are from the Kern watershed. Data were corrected for under-reporting of snowfall values. 

*Graph and regression by Dr. Nate Stephenson, Western Ecological Research Center, US Geological Survey; used with permission.*
Stephenson concluded that along the western side of the Great Western Divide at elevations between 1,800 m and 2,700 m amsl rainfall peaks in this region of the state at approximately 140 centimeters per annum and declines at both lower and higher elevations (Figure 5).

In the steep Sierra Nevada, this band of highest precipitation is very narrow, often less than 10 kilometers wide. Mineral King lies near the end of the Sierra. South of this valley, both the Great Western Divide and the peaks along the crest of the Sierra, further to the east, gradually shorten. Also, further south along the Pacific Coast in the middle latitudes of North America, precipitation declines as the effects of winter rainfall patterns weaken due to the semi-permanent high pressure systems associated with the northern hemisphere Subtropical High Pressure Zone, leading to the deserts of the Southwestern United States and Northwestern Mexico. Declining elevation and geographic climatic shifts place Mineral King on the edge of the region with plentiful rainfall.

However, this southerly locale also places the watershed within reach of summer monsoon weather patterns that bring infrequent thunderstorms to the region. These tropical storms occur June through September and are most common in August.

While most of the precipitation in Mineral King is winter snowfall (Figure 5), according to Stephenson (1988) the area remains relatively warm, compared to other montane regions of North America to the north and within the interior of the continent (Figure 6). Thus, the mean winter temperature at the study site at the downstream end of the Spring Creek Watershed at 2,400 m amsl is only 0° C.
Figure 6: Mean summer and winter temperatures in relation to elevation in the southern Sierra Nevada, Sequoia National Park. Circles are values for July; Triangles are values from January. Filled symbols are from the Kaweah watershed and open symbols are values from the Kern River watershed. The x symbols are values from the White Mountain Research Station, the highest weather station in California located east of the Sierra Nevada. *Graph and regressions by Dr. Nate Stephenson, Western Ecological Research Center, US Geological Survey; used with permission.*
Due to the Mediterranean climate with wet winters, the majority of precipitation in Mineral King and throughout the national parks is snowfall. In heavy precipitation years, the snow pack can exceed 12 m. However, the comparatively warm temperatures of the region lead to frequent melt-off during the winter months at elevations below 2,500 m amsl and on south-facing slopes, voluminous spring run-off, and the presence of very few glaciers within the southern Sierra Nevada even though elevations exceed 4000 m amsl on more than a dozen peaks.

3. Problem Statement

A. Hydrology and Chemistry of an Alpine Karst System

As in other karst settings, many questions remain about the character and aspects of alpine karst hydrology and the evolution of alpine karst topography. Karst springs exhibit their own unique patterns of discharge that vary in response to many environmental factors including diurnal effects, storm run-off, local climate, water retention within the karst, the influence of any epi-karstic aquifer, and much more. Few karst discharges, particularly in a cold-water, alpine setting, have been compared to greater watershed discharges or have been carefully studied for discharge patterns. Such work may reveal important environmental factors that control discharge in the karst and across a watershed and lead to a greater understanding of karst processes as a whole.

The high-resolution data of this study also allows a rare examination of the chemistry of this karst watershed. Again many factors can affect the overall chemistry of the watershed and the waters at its spring. This includes pCO₂ soil pressures, changing patterns of pH and conductivity, anthropogenic acid deposition, storm and spring runoff
dilution, the degree of dolomitization and other chemical parameters in the carbonate rock hosting the karst development, and much more. The high-resolution and long-term aspects of this study allow the chemical flux of this system to be followed through time and seasonal variances allowing insight into the factors driving the system and the development of this karst. Data on the Spring Creek karst hydrology and chemistry can reveal the details of rock/water interactions through time in alpine karst. Nutrient and chemical cycling can be quantified using hydrologic and spC data to determine parameter flux. This study seeks to examine the hydrochemical behavior of this system by determining the total inorganic carbon (TIC) flux, the calcite solution indices (SI) flux, and the pCO₂ flux within waters emerging from the spring. In turn, this information can be compared to discharge revealing the relationship between water flow and the changes in these chemical parameters through time.

Bare bedrock alpine karst is an unusual erosional setting where rates of denudation likely vary from low-elevation or non-carbonate settings. Understanding these rates of erosion has broad implications for landscape development and montane erosion.

B. Alpine Karst and Atmospheric Carbon

Carbonate rock karst systems, including those in alpine settings, play a role in the global carbon cycle. These systems operate under the chemical constraints of low water temperatures and generally weak ionic solutions, contrasting to the high solubility of carbon dioxide in cold waters producing lower pH values. In studies of TIC flux from carbonate rock drainage systems it has typically been assumed that of the inorganic carbon draining from carbonate rock basins, 50% is geologically derived carbon and 50
% is atmospherically derived carbon (e.g. Berner et al., 1983; Meybeck, 1987; Berner and Lasaga, 1989; Probst et al., 1994; Amiotte Suchet, P. and J.L. Probst, 1993, and 1995; Liu et al., 1998). However, recent work with high-resolution data sets by Groves and Meiman (2000, 2001) in the humid-subtropical Mammoth Cave karst, Kentucky, which considered the mechanistic kinetics interpretations of Plummer et al. (1978), has produced results that vary from this assumed 50:50 ratio, in their interpretation, resulting from strong acid contributions due to sulfuric anthropogenic acid rain. Groves and Meiman’s (2000, 2001) work involved a detailed chemical analysis of the Mammoth Cave karst hydrologic system and a careful recording of the system's discharge. This produced results of 57% inorganic carbon derived from carbonate mineral dissolution, 42% inorganic carbon produced by biological activity in the soils and vadose zone and 1% inorganic carbon entering the system as a component of recharge waters. Making an overall ratio of 57% carbon derived from bedrock and 43% derived from the atmosphere. Carbon from biological activities in soil and the vadose zone derives from the atmosphere as well. A question is whether the alpine karst system of the Mineral King Valley, with it's own unique chemistry, varies from the presumed 50:50 ratio and is likely to produce results significantly different from temperate systems due to the chemical impacts of significantly colder water.

Air quality with respect to strong acid rain, which Groves and Meiman (2000, 2001) identified as an influence on carbon source ratios, is also generally better (higher pH’s) in the study area compared to south central Kentucky where rainfall contaminated with sulfuric acid from coal-fired power plants often has a pH below 4.5.
Carbon dioxide's apparent role in modern climate change has made understanding the movement, retention and release of carbon compounds a priority. Work on the global carbon cycle has been a major focus of hydrologic, geologic, and atmospheric research for more than 10 years. Yet many questions concerning the detailed movements of carbon remain. These questions have led to varied, sometimes conflicting, models of global carbon cycling. Karst areas have been recognized as a global sink for carbon, through the incorporation of carbon dioxide into natural waters as carbonic acid and the subsequent weathering of calcite in limestone (Berner et al., 1983; Meybeck, 1987; Probst et al., 1994; Amiotte Suchet, P. and J.L. Probst, 1993, and 1995; Liu et al., 1998). This chemistry, occurring across an estimated 12% of the earth with karst processes (Ford and Williams, 1989) may well impact global carbon cycles. These results imply that an improvement of global carbon models may be realized with a better understanding of the details of the ways in which carbonate rock and natural water systems influence overall carbon cycling.

Overall, the greater Spring Creek karst hydrology offers an excellent opportunity to characterize the chemistry of an alpine karst stream. The well defined watershed (Schultz, 1996; Tinsley, 1999), previously mapped geology (Busby-Spera, 1982; Tinsley, 1999), well understood climate (Stephenson, 1988; Stephenson and Parsons, 1993), and reasonable winter access to the spring make this the ideal site for this work in the Sierra Nevada.

For this aspect of the study it is assumed that there are three sources of total inorganic carbon, TIC, leaving a limestone or marble groundwater basin (Groves and
Meiman, 2000, 2001). 1) Dissolved inorganic carbon in precipitation, in equilibrium with atmospheric background CO₂ that enters the aquifer as recharge; 2) biologically produced CO₂ gas in soil, vadose and saturated zones, including microbial respiration, oxidation of organic material, and plant root respiration; 3) carbonate mineral dissolution. These parameters can be determined through a series of calculations.

With considerations of time, sampling period, discharge, basin size, and biogeochemical processes the dissolved inorganic C in precipitation can be estimated by calculating a carbon mass flux leaving the basin. (Stumm and Morgan, 1981).

Both carbonate mineral dissolution C and the C component derived from biologically produced CO₂ gas can be derived because during dissolution of marble, limestone, or dolomite one mole of C is released from the mineral for each mole of Ca²⁺ + Mg²⁺, regardless of the elementary reaction involved (Berner et al., 1983; Busenberg and Plummer, 1982).

Meiman and Groves (2000, 2001) used ion activities at Mammoth Cave to determine groundwater ion constituents, TIC, and other parameters. This approach was rejected for this study because activity values include variables that account for the subatomic behavior of the ions in question in solution. These values would affect the results of this study. However, as a check on this work and to evaluate various approaches to high-resolution, long time-scale karst water chemistry data sets, three methods were used in this study to determine the ratio of atmospheric to rock-derived C and compared. 1) The first method uses laboratory derived data from occasional water samples from 2001 through 2003 to determine the ratio. 2) The second determines ion-constituents by using
the laboratory data to create regressions and line formulas applied to the spC values in the 
entire data set for 2002. 3) The third approach directly relates TIC and other parameters 
to spC using regressions and was again applied to the entire 2002 data set.

Thus, having recognized the need for a better understanding of the chemical and 
hydrological parameters of alpine karst systems and the sequestration of carbon in alpine 
karst, and to compare methods of data analysis, this study was initiated. Four parameters 
were identified as necessary for mathematically determining the chemical and hydrologic 
parameters of the waters emerging at Spring Creek Spring. 1) Conductivity of the spring 
waters supplied data used as an indicator of ionic strength. 2) Discharge data for the 
spring were used as a multiplier to calculate ion loadings and was examined 
independently to hydrologically characterize the spring and karst. 3) Temperature plays 
an important role in the chemistry of the spring and may influence the quantity of 
atmospheric carbon sequestered. 4) pH was also measured to quantify carbonate 
chemistry behavior.
III. Methods

1. Site Development and Equipment Installation

   A. Introduction

   For this thesis it was appropriate to manage a project near the investigator’s home and associated with his work as the Cave Specialist at Sequoia and Kings Canyon National Parks in the Sierra Nevada Mountains of California. Luckily, the karst of the two parks includes alpine areas and was appropriate as a new component of the research initiated at Mammoth Cave National Park, Kentucky, by Groves and Meiman (2000, 2001, in press Groves et al., 2002; Raeisi et al., in review). Their work documented years of water chemistry and discharge from remote-sensing wells installed in Hawkins and Logsdons rivers inside Mammoth Cave. These research methods are both the model and the impetus for the Spring Creek project, which adds alpine, cold-water data to this research, creating a more complete picture of karst system chemistry and the sequestration of atmospheric carbon worldwide.

   Karst within the two parks is found as low as 450 m amsl and is most common in mid elevations between 1,000m and 1,700 m elevation. At low elevations in the parks, the climate is warm and dry producing native vegetation of grasslands scattered with oaks and dense thickets of shrubs. This area has only a few caves and karst springs. The few caves that are here have temperatures of 16° C or more. Mid-elevation karst, where coniferous forests dominate, contain the longest caves in the parks, Lilburn, Crystal and Hurricane Crawl. But, these caves, and their associated springs, are still relatively warm, with temperatures of 10° C or higher. Alpine karst, where caves may have permanent ice
and temperatures as low as 1° C, is found in two areas in the parks: At the headwaters of the East Fork of the Kaweah, an area added to Sequoia National Park in the late 1970s, and in Paleozoic rocks near the crest of the Sierra in Kings Canyon National Park. This high-elevation karst south of Mt. Pinchot is limited in extent, contains only a few springs, and is very remote, particularly in winter. In Mineral King, at the headwaters of the East Fork, caves occur as high as 3,200 m and several caves longer than 1,200 m have formed. The valley has an average precipitation of more than 100 centimeters per year, compared with 65 centimeters at the park’s lower elevations. This area also has the park's highest road, reaching 2,400 m amsl (Despain, 2003).

There are many karst springs in the montane valleys of Mineral King. Numerous springs along Franklin, Farewell, Monarch, and Crystal creeks and the East Fork have been identified by Black and Rogers (Rogers, 1978, 1980; Black, 1994). However, one of these was an obvious choice for the project. The largest karst spring in Mineral King, at the head of Spring Creek, had been studied by the Cave Research Foundation (Rogers, 1978; Schultz and Tinsley, 1996; Tinsley, 1999) and lay close to the end of the road in Mineral King Valley, thus removing any need to backpack to the site while the road was open and providing closer access during the snow-burdened winter months.

**B. Installation**

The original site visit to Spring Creek, by Chris Groves and Joel Despain, was in May 2001. Installation of the equipment for the study took place early in October 2001, a period of seasonal low flows. Joe Meiman from Mammoth Cave National Park oversaw the installation and the programming of the data logger. Meiman completed the wiring
and data logger programming at Despain's home, which conveniently lies along the Kaweah River. Using the river, the equipment was tested before it was installed in Mineral King.

Spring Creek is a short and very steep run from the spring mouth to the East Fork of the Kaweah River. Over a distance of 250 m, the stream drops 140 m. The instruments for the study were sited in one of the few pools along this stream. However, the overall chaotic nature of the steep stream, particularly, during spring runoff, precluded traditional methods for calculating discharge, such as pygmy meters and weirs.

Installed into the stream was a Campbell Scientific CS547-L conductivity and temperature probe, a Druck 13824 pressure transducer with a 15 m cable for stage, and a Cole-Parmer U-59002-72 pH electrode. The conductivity equipment included a Campbell Scientific A547 conductivity interface, and the pH equipment included a submersible housing, a pH cable, and a U-27007-10 probe amplifier. All of the equipment was connected to a Campbell Scientific CR10X-2M datalogger.

This equipment was installed in the stream inside stainless-steel pipes that were in turn bolted to a large boulder adjacent to the creek. The pH and pressure transducer were installed along the margins of the pool closest to the data logger. The combined conductivity and temperature probe was installed into a turbulent section of the stream just above the pool using a steel pipe bolted to a rock in mid-stream to insure representative spC values for the creek (Figure 7).
Figure 7: Installation of the data logger and associated electrodes and equipment required several days of work in Three Rivers, California and in Mineral King along Spring Creek. The installation took place in fall at a time of base-level flows in Spring Creek. Here discharge (including some flow out of view of the photos) is approximately 30 L/s.

The data logger, batteries, and pH amplifier were stored in a Pelican waterproof case hung in a small western juniper tree approximately three m above the ground. A second Pelican case stored extra cable between the instruments and data logger as well as extra batteries. A small solar panel was integrated into the data logger and provided additional power to the system and batteries throughout the study. It was simply draped over branches of the juniper tree. After the cables from the instruments emerged from the steel pipes they were strung inside 15 m of flexible conduit leading to the Pelican cases where the conduit was attached to the cases with rotating plastic connectors and silicon sealant gel. We protected the equipment well due to the deep snows and forceful runoff.
found at the site, and also due to the activities of animals, including black bears and yellow-bellied marmots, both of which are very prone to chew on field equipment throughout the parks. Luckily, these animals caused no damage during the study.

C. Data Logger Programming and Outputs

Two programming tables regulated the activities of the data logger. Program table one was set to record two-minute averages of the four values (stage, temperature, pH and conductivity) based upon four readings taken every 30 seconds. In order to conserve memory and to assure high temporal resolution an activity-triggered program was written. The datalogger queried each of the four sensors every 30 seconds and cumulates values of each sensor. After a two-minute interval, each cumulative value is divided by four to produce a current average. Next, each current average is subtracted from each average of the previous two-minute value. The absolute value of each result is then compared to a pre-programmed small range that indicates changing conditions. During relatively static periods, the program records the unchanging two-minute values at the beginning of each hour, producing an hourly base-line data record during times of little hydrologic activity. If, however, any sensor value is found to exceed its preprogrammed range, all current two-minute data from each sensor are placed in final storage. In this way we achieve two-minute data resolution even during hourly recording periods since we know from inference the values between hourly recording while achieving efficiency with regard to data storage.

Program table two recorded conductivity values every second and was activated, while program table one was deactivated, during discharge measurements. These data
were used to calculate discharge in the stream using salt dilution conductivity breakthrough curves (Cobb and Bailey, 1965; Rantz et al., 1972). On each site visit, program table two was activated before a high-conductivity salt solution was added to the stream above the data logger and equipment. Later these spC readings were used to generate curves integrated to produce the discharge, which in turn was used to develop a discharge rating curve for the conversion of stage measurements to discharge throughout the data set.

There are two methods for tracer dilution, including constant-injection and sudden-injection (Cobb and Bailey, 1965; Rantz et al., 1972). While each has advantages, the sudden-injection method using sodium chloride is particularly useful for remote field studies, and was used here. A concentrated salt solution of known volume is mixed and the conductivity is measured along with the background concentration of the stream. The slug is quickly introduced into the stream and timing started. Some distance downstream, far enough for the slug to become well-mixed in the stream, the conductivity is measured at frequent intervals noting the time for each observation since the injection of the slug. These concentrations should be measured until the slug has passed, although in practice the tail of the time-conductivity curve can be very drawn-out due to dispersion of the tracer within the stream. Only a small error is introduced by ending when the conductivity returns close to pre-injection levels. From these data, discharge can be calculated using the relationship:
\[ Q = \frac{V_0 C_o}{\int_0^x (C - C_b) \, dx} \approx \frac{V_0 C_o}{\sum_{i=1}^n (C - C_b) \Delta t} \] (1)

where \( Q \) is discharge, \( V_0 \) and \( C_o \) are the volume and concentration of the injection tracer slug, respectively, \( C_b \) is the background tracer concentration in the stream before injection, \( C \) is the observed tracer concentration, and \( t \) is time. The integral in the denominator of the middle term of the equation above, is the area under the tracer concentration-time curve as it passes the measurement point, which in practice can be estimated using the summation in the right-hand term, where \( C \) is the observed concentration of each measurement and \( \Delta t \) the time interval between measurements. Any concentration units appropriate to the particular choice of tracer can be used (i.e. \( \mu \text{S cm}^{-1} \) for conductivity, fluorescence intensity for dyes, or \( \text{mg/L} \) for other tracers). Since the units of concentration in the numerator and denominator cancel, the resulting discharge units depend on those of the tracer slug and time intervals. Expressing the tracer volume in litres and the time intervals in seconds, for example, gives discharge in L/s.

Values for ions of interest, \( \text{Ca}^{+2} \), \( \text{Mg}^{+2} \), and \( \text{HCO}_3^- \), and others were calculated in a multiple step process using the spC and water sampling. Water samples collected on site 14 times throughout the study were analyzed at the Mammoth Cave National Park water quality laboratory for their constituent ions using a Varian AA240SS flame atomic absorption spectrometer. In addition water samples for analysis were collected late in the study during a period of base flow at the two insurgence streams into the system, Eagle Creek and White Chief Creek. Two liters were collected each time in two Nalgene
bottles, which were triple rinsed in the spring water before filling, and which were kept cold in a cooler during the warmer months. Later the concentration values generated by the Mammoth Cave water laboratory were used in regressions between the spC values recorded during the site visit and the laboratory values and applied to all spC data recorded by the data logger.

Raw pH data were recorded in pH millivolts. It was expected that values from the pH probe would drift over the course of the study. Thus, during each of the 14 site visits, the pH probe values were recorded for each of three calibration buffer solutions of 4.01, 7.00, and 10.00. Later the calibration values were used to calculate actual pH using regressions and line formulas applied to blocks of data delineated by the mid-way point between calibration times.

2. Data Collection

A. Early Data

With the help of Shane Fryer and Joe Meiman, the equipment was fully installed by October 3, 2001. It should be noted that both pH and spC values were temperature-compensated at the time of measurement beginning with the initial installation of the equipment. Initial data from the equipment appeared excellent and site visits to calibrate pH, collect water samples, calculate discharge, and download the data were made on October 10 and on October 23.

This early data set (Figure 13) included expected characteristics of the data gathered along Spring Creek, confirming the validity of the methodology employed and the proper installation of the equipment. Included were appropriate instrument readings,
and a repeated daily pattern for stage and temperature attributed to snow melt in the basin.

The spC data exhibited a common challenge throughout the entire Spring Creek data set—dropouts. These sudden declines in spC values occur when air bubbles enter the flow-through cell of spC sensor. When air bubbles enter the cell, the volume of water drops precipitously, and thus, so do the spC values. To remove this bias, smoothing functions were applied to the spC data when it was processed.

**B. Data Logger Management and Maintenance**

On November 2, the data logger malfunctioned. Initially values for spC dropped below 0.1 and pH millivolts values increased by more than an order of magnitude. By November 11, the stage was reading 1300 m—the maximum value for the pressure transducer, and the stream temperature registered a consistent 340° C (Figure 16)!

Through site visits on November 5 and 28 and December 17 attempts were made to correct the problems by checking all wiring, reinstalling program table one and via numerous phone calls from California to Kentucky. Meiman provided the project with another data logger in early January, saving the alpine effort.

From May through November, accessing the Spring Creek site required only a 15 minute hike from the end of the Mineral King road. However, the Mineral King area is known for its harsh winters, heavy snows, and avalanches. Winter snowfall totals may exceed 12 m on the valley floor, and winds during storms may be very strong due to the high elevation. Avalanches have killed numerous miners, destroyed dozens of buildings, and also killed a Walt Disney Corporation engineer who was surveying the site for a ski
resort in 1972. The Spring Creek study site was not in a prevalent avalanche corridor, but snow conditions, snow depth, wind speed and temperature played a large role in determining when we could access the site in winter.

Access to the trailhead near the site was possible in early November, using a 4WD Jeep and chains. Skiing was required later in the month. The December 18 trip required the use of a snowmobile and skis. Fryer and Despain were forced to dig the snowmobile out of snow banks on two occasions and endured several miles of scenic, but grueling skiing with lots of new snow and heavy packs, as well as an overnight stay in Mineral King in the winterized ranger station (Figure 8). The January 11 trip, with the new data logger, was completed in a day via riding in the park Snow Cat, snowmobiling, and skiing. Meiman had charged the new data logger and entered both program table one and program table two into the device. It was installed by carefully and systematically rewiring it into exactly the same configuration as the first logger. The new logger immediately began working. The previous data logger was returned to Campbell Scientific who found no problems with the machine.
The pH electrode was replaced at this time, and the conductivity and temperature sensor was cleaned on the December trip.

This repair began the most extensive period of good data collected during the project. The next real problem came following a site visit on March 13, when the values from the data logger again became clearly incorrect. However, the logger began functioning correctly five days later when appropriate values were again generated for the four study parameters (Figures 18 and 34).

Following this incident 111 days of good data were collected. This period includes spring run-off and large increases in discharge. The discharge peaked on day 136, May 16, at 903 L/s (Figure 17).

C. pH equipment maintenance

The next significant data failure was on day 189, when the pH probe failed.
During the failure, pH millivolts calibration readings ranged from 750 to 600, when previously they had ranged from 100 to -175. On the August 31 site visit, the pH electrode was replaced, but this did not correct the problem.

Meanwhile, in Kentucky, Meiman had been working on a more robust design for pH sensing equipment. He mailed this equipment with instructions for its installation in early October, approximately one year since the initiation of the project. Fryer and Despain completed the installation. The most challenging aspect was threading the new cables and wiring through the pipes and conduit already in place along Spring Creek. Another important component of the work was moving the Campbell pH amplifier from the data logger Pelican case to nearer the probe within a PVC housing (Figure 19).

This new equipment immediately corrected the problem and pH millivolt readings returned to their previous range. The conductivity and temperature probe was cleaned for the third time on this visit, also. Good data were produced for all four parameters for most of the rest of 2002. However, clearly erroneous data appeared again on December 13. At this point in the project, little effort was made to correct data problems, although the data were collected on several occasions through 2003. On site visits, salt dilution discharge measurements were made and water samples were collected for analysis.

Overall, the cleanest data during the project were from days 276 to 308, 2001 and 11 to 348, 2002, giving us a nearly complete year of data for analysis.

3. Data Analysis

A. Early Analysis

Initial analysis of the data began immediately. This work sought to confirm that
the equipment on Spring Creek operated correctly. These checks were made through reviewing consistency of the values, patterns in the values, and the validity of the values generated compared to other karst water springs and groundwater in general (Figure 13).

All work done to organize, transform, and generate statistics on the data set has been completed using the SigmaPlot software package from SPSS.

Efforts to turn large segments of the data set into usable values began in April 2002 when the author visited Bowling Green for this purpose. Meiman, Groves, and Despain were assisted by Jonathan Jernigan of the Mammoth Cave National Park staff for two days of using and creating SigmaPlot transforms. This work smoothed spC values and produced the first measurements of discharge from the project. When completed, this work would produce values for the mass of the ion constituents that exit the spring in solution, the percentage of atmospheric, rock-derived, and soil-derived C leaving the karst in solution, detailed hydrologic data showing multiple time series patterns, other chemical parameters of interest, such as solution indices, dissolution rate, and pCO2 values for the time period, and other calculations of interest such as denudation rate.

Transforms completed in 2002 were as follows:

- Changed Julian day and time to a single value of decimal Julian days;
- corrected a 12-hour time discrepancy created by a time-of-day entry error when the new data logger was put in place in January 2002;
- smoothed the spC discharge breakthrough curve values, which suffered from the same problems as the rest of the spC data, low anomalous values generated due to air bubbles;
• calculated the area under the spC curves from salt dilutions and processed these data with stage data yielding discharge;

• smoothed spC data from the program table one data set used later to calculate ion concentrations.

The discharge transform used the minimum time unit, one second, to define areas under the curve for each datum as trapezoids that were then totaled. This value then divides the multiplication product of the volume and spC of the known solution added to the stream to produce discharge, or Q (Formula 1).

After several iterations, the final spC smoothing transform limited values in subsequent cells to a change of less than or equal to 0.004 mS compared to the previous cell. If the change in values exceeded 0.004 mS then the value from the previous cell was placed in the subsequent cell.

The first transform created to smooth spC values from program table one replaced anomalously low values generated due to air bubbles with zero. The transform was applied only to data sets from 2001 and very early 2002. The transform created zero values for ion constituents for those time periods, requiring corrections during later data processing (Figures 14, 15 and 29).

B. Calculating Ion Constituents

During three trips to Kentucky in November 2002, June 2003 and February 2004, the author traveled to Bowling Green and the Mammoth Cave area to continue efforts to process the data with the project collaborators. The following section describes that work.

Values for ions of interest – Ca$^{+2}$, Mg$^{+2}$, and HCO$_3^-$, and others – were calculated
in a multiple step process using the spC values recorded by the data logger and water samples gathered periodically at the site. Water samples were collected 14 times throughout the study at the spring and once at the insurgence streams, Eagle and White Chief creeks, just above the karst in each basin. Samples were analyzed at the Mammoth Cave National Park water quality laboratory for their constituent ions using a Varian AA240SS flame atomic absorption spectrometer (Tables 3 and 4). Bicarbonate was calculated in Sequoia at the Ash Mountain water chemistry laboratory using burette titrations calculated by the inflection point method to determine mg/L as HCO₃⁻. Also at Ash Mountain, samples for Mammoth Cave were filtered and a filtered archive frozen. Samples were shipped to Mammoth Cave overnight by Federal Express and were packaged in coolers with Blue Ice.

Charge balance checks of ionic charges for each of the spring water samples were completed from the lab results. Eleven of the 12 results are within 80% of agreement and five are within 90%. A final sample from June 2002 had very poor agreement. Results from this lab run were outliers when graphed and were not used in further analysis (Table 5).

The ion values were used in linear regressions against the spC of the spring water measured in the field at the time of sample collection to establish the relationship between ion values and the spC. For two of three ions of greatest interest, outliers were eliminated (Figure 9). Two were removed from the Ca⁺² calculation, and one from Mg⁺². Resulting r² values for the regressions are 0.9445 for Ca⁺², 0.943 for Mg⁺², and 0.983 for HCO₃⁻. (Figures 9, 10, 20, 21 and 22)
One outlier removed for the Ca\(^{+2}\) and all outliers removed from Mg\(^{+2}\) calculations as well as the Na, K regressions were generated on the same day from the same sample processed at the Mammoth Cave lab in June 2002. These values were the highest recorded in the sample set for Ca\(^{+2}\) and Mg\(^{+2}\). The charge balance values from the lab data for this sample also show by far the worst agreement with a percentage of only 19.3%. This value points to a problem with this particular sample or with this particular chemistry run, justifying the removal of this datum.
Figure 9: Calcium vs. conductivity at the time of the water samples. The top graph includes all data points and had an $r^2$ of 0.601. The lower graph has two outliers removed one of which is from June 5, 2002 making an $r^2$ of .9445.

Mg vs spC with an outlier
Figure 10: Magnesium vs. conductivity at the time of the water samples. The top graph includes all data points and had an $r^2$ of .74. The lower graph has one outlier removed from June 5, 2002 and an $r^2$ of .943.

All ion values were calculated to be equal to the intercept plus the slope multiplied by the conductivity at that time. For Ca$^{+2}$ the intercept was 4.505 and the slope was 144.5. For Mg$^{+2}$ the slope was 17.92 and the intercept was -.4192. Finally, the HCO$_3^-$ calculation had a slope of 640 and an intercept of -2.232.

A review of the procedures for determining ions revealed two problems that were corrected. Independent and dependent axis were switched during ion vs spC regressions for Mg$^{+2}$ and the HCO$_3^-$ regression was calculated using Meq/L instead of mg/L of HCO$_3^-$, producing the wrong intercept in the line formula lowering HCO$_3^-$mg/L values.

Following the transformation from spC values to constituent ions, these values
were multiplied by the duration of each time segment between each data logger-recorded value for spC to generate the total of each ion in mg/L for each time period. Finally, the total values for all of the 2002 days with data were tabulated by summing the columns for each ion using additional transforms.

Three sets of ion concentrations expressed as units of equivalents (from days 11, 190, and 339, 2002) and the 2002 totals from the spring were charge balance checked to determine if final values generated through spC regressions were reasonable. The validity of the data set was confirmed by charge balance errors between 9.9% and 7.6% for the three randomly selected time periods and an error of 4.7% for the total eq of the ions emerging in solution from the spring for all of 2002. These calculations include data for ions determined through conductivity measurements (Ca$^{2+}$ Mg$^{2+}$, and HCO$_3^-$) and do not include all ion species likely present in Spring Creek and found by lab analysis, but they do represent the far most dominant ions in the stream (Table 6).

**C. Calculating Discharge**

Discharge values were calculated from the salt dilution spC curves using the transforms developed earlier. There were varied problems calculating discharge from the spC field data. In some cases the data set did not include an obvious curve to attribute to the salt slug breakthrough. In other cases the curve was poorly formed with few data points to define it. Finally, other data sets were lost to the varied data logger problems that occurred during the data collection, particularly in 2003. The rating curve was developed with 13 remaining discharge measurements. One outlier was also identified and eliminated from the data set. The reason for this outlier is unclear, but may relate to
anomalously low stage values during a time of very high discharge (day 189, 2002 during spring runoff) and chaotic white water in the stage pool.

The regression relating stage to discharge was an exponential growth, single, one parameter regression with a formula of $Y = e^{ax}$. An exponential growth discharge likely exists at the Spring Creek site due to a stream channel that rapidly widens with increased height. One half meter above the base-flow pool level, the stream channel is six m wide, while the stage pool itself is just over one m across. (Figures 11, 13)

Stage values were combined with the line slope value of 13.3964 to create an exponent value equal to discharge. This process produced discharge in L/s for a particular second and was multiplied by the time interval between each measured stage and discharge values to produce Q over longer time periods and an actual volume of water emerging from the spring.

![Stage vs Discharge with an outlier](image)
Figure 11: Stage vs discharge using an exponential growth, single, 1 parameter regression. One outlier was removed to create the lower graph with an $r^2$ of .977. The upper graph with the outlier has fit of .874.

D. Calculating pH

The first step to calculating pH data was to divide the pH milivolt data into blocks centered around each site visit when pH calibration values were generated. For each visit and set of calibration data, regressions between calibration fluid values (10.00, 7.00, and 4.01 SU) and millivolts recorded for each of these calibration fluids were generated. These line formulas were then used in transforms to calculate pH values. Because each regression has only three points, corresponding to each calibration fluid value, $r^2$ values were consistently close to one for all pH regressions, and no outliers were removed from any of the regression calculations (Table 2).

Table 2: 2002 values from pH regressions.
pH values from the laboratory measured for bicarbonate titrations were also compared to values from the data set at the time of sampling (Table 7). Value agreements ranged from a high of 100% to a low of 98.07%. While the values are generally close in agreement, due to the logarithmic nature of pH values in activity calculations, a small change can have a large effect. pH values for the year were also compared to discharge (Figure 33).

E. Data Analysis for the Source of Karst Aquifer Inorganic Carbon

This study has considered three sources of total inorganic carbon, TIC, leaving a limestone or marble groundwater basin, leading to the following formulas and calculations for this research (Groves and Meiman, 2000, 2001).

1) Dissolved inorganic carbon in precipitation, in equilibrium with atmospheric background CO₂ that enters the aquifer as recharge, Cₐ (MT⁻¹);

2) biologically produced CO₂ gas in soil, vadose and saturated zones, including microbial respiration, oxidation of organic material, and plant root respiration, C₅ (MT⁻¹), and;

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</table>
3) carbonate mineral dissolution, $C_m(MT^{-1})$. Thus, during a specified time interval, $t$ (T).

$$\int_0^t \text{TIC} dt = \int_0^t C_a dt + \int_0^t C_b dt + \int_0^t C_m dt \quad (2)$$

Since $C_a$ and $C_b$ originate in the atmosphere as CO$_2$ gas, and leave the karst system as dissolved inorganic carbon species, the inorganic component of the CO$_2$ sink was defined by Groves and Meiman as $\zeta(MT^{-1}L^{-2})$ due to flow and biogeochemical processes within the karst landscape and aquifer system as:

$$\zeta = \left( \frac{\int_0^t C_a dt + \int_0^t C_b dt}{tA} \right) \quad (3)$$

where $t$ is the length of the sampling period (T) and $A$ is the drainage basin area ($L^2$). $C_a$ is estimated by calculating a carbon mass flux leaving the basin using measured stream discharge and assuming TIC in equilibrium with a constant representative atmospheric CO$_2$ pressure, nominally set at 360 parts per million over the study period, where

$$\text{TIC} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3^+] \quad (4)$$

with activities denoted by square brackets and where $\text{H}_2\text{CO}_3^+$ is the sum of $\text{H}_2\text{CO}_3^0$ and aqueous CO$_2$ (Stumm and Morgan, 1981). As described above, two-minute to one hour resolution of chemical and flow conditions using electrodes and data loggers were obtained within Spring Creek a short distance downstream from the resurgence of the karst system. This records all significant features of storm-scale and seasonal variation so that close estimates of the appropriate integers can be obtained.

To obtain both $C_m$ and $C_b$, make use of the fact that during dissolution of marble,
limestone or dolomite one mole of C is released from the mineral for each mole of Ca$^{2+}$ + Mg$^{2+}$, regardless of the elementary reaction involved (Berner et al., 1983; Busenberg and Plummer, 1982), so that

$$\int_0^t C_m dt = \int_0^t (Ca^{2+} + Mg^{2+}) dt,$$  \hspace{1cm} (5)

and by substituting (5) into (2) and rearranging,

$$\int_0^t C_b dt = \int_0^t TIC dt - (\int_0^t (Ca^{2+} + Mg^{2+}) dt + \int_0^t C_a dt).$$  \hspace{1cm} (6)

Finally having determined $C_a$ and $C_b$, we can obtain a value for the inorganic carbon sink using (2).

### F. Calculating Atmospheric C

Within this mathematical framework several approaches may be taken to determining total atmospheric C:

Activities of the constituent ions are determined using mols per liter, the ionic strength, and calculated equilibrium constants. Total inorganic carbon is then totaled from the activities of the bicarbonate, carbonic acid and carbonate using the Debeye Huckel equation. TIC, calcium and magnesium mols, and atmospheric TIC are each totaled after their flux is calculated using the appropriate time interval and discharge. Total atmospheric carbon then equals TIC minus the atmospheric derived TIC and the rock derived C, which is equal to the calcium and magnesium values (Groves and Meiman, 2000, 2001). This approach was rejected for this study because activity values include variables that account for the sub-atomic behavior of the ions in question in
solution. Also, there are problems with the pH data in this study, an important value in these calculations. 1) There are gaps in the data – day 0 to day 11, day 189 to 282, and day 348 to 365, 2002. 2) Some blocks of pH data varied significantly in ending or starting values from the previous or subsequent block of data. For example 8.44 was the ending value in the data set from days 11 to 25, 2002, and the starting value for days 26 to 58, 2002 was 8.29. 3) Lab and field pH data vary and due to the logarithmic nature of pH values in activity calculations a small variation in value can have a large effect (Table 7).

As a check on this work and to evaluate various approaches to high-resolution, long time-scale karst water chemistry data sets, three methods were used in this study, however, to determine the ratio of atmospheric to rock-derived C and compared. 1) The first method uses laboratory derived mg/L data from the water samples from 2001 through 2003 to directly determine TIC and the ratios.

2) The second determines ion-constituent concentrations and TIC by using the laboratory data for mg/L values of the respective ions and TIC (Appendix B). These are then used in a regression vs. field-data spC values to create regressions and line formulas applied to the spC values in the entire data set for 2002. spC data exists for all of 2002 except day 0 to day 11 and 348 to 365 (17 days) and was directly measured, avoiding the problems of post-processing data gaps. The regression between lab derived TIC values and spC had a fit of 0.972 with one outlier removed. This produced a line formula with an intercept of 0.00006918 and a slope of 0.009576 (Figures 12, 24). Regressions between spC and the concentrations of Ca$^{+2}$ and Mg$^{+2}$ (to account for magnesium-bearing dolomite within the marble) were required in order to subtract these components from
TIC to account for rock derived C. For Ca\(^{+2}\) the intercept was 0.0001122 and the slope was 0.003609. For Mg\(^{+2}\) the intercept was -0.00001531 and the slope was 0.0007196. Thus, biologically derived inorganic carbon was derived by subtracting the mg/L values for Ca\(^{+2}\) and Mg\(^{+2}\) from TIC.

3) The third approach uses transforms and calculations similar to those created for the activity calculations but substitutes ion concentration values for the activities. This method still uses pH data to calculate concentrations for CO\(_3^-\) and H\(_2\)CO\(_3\). This fact, and poor agreement between parts of the pH dataset, limited the time period used for analysis to day 24 to day 191 and day 285 to day 348.

For all methods, dissolved inorganic carbon in precipitation in equilibrium with atmospheric background CO\(_2\) that enters the aquifer as recharge was calculated using a 2nd order regression of a plot of TIC with an assumed atmospheric chemistry where pCO\(_2\) = 0.000360 and as a function of temperature (Table 8).

One method was also used to check for seasonal variation in the proportion of atmospheric C. This involved two 30-day data sets, day 12 to 42, 2002 for winter conditions and day 210 to 240, 2002 for summer conditions and associated increased soil and water temperatures (Table 8).

**G. Calculating other key chemical parameters and flux analysis**

The direct regression method was found to produce a good fit and result for one key chemical parameter used to determine C values, TIC, and was, thus, also used to calculate the calcite Saturation Index (SI) (Appendix B). With the same outlier removed as was removed for the TIC calculation, the linear regression between spC data collected
at the time of the water samples and SI data determined from the water samples using the Debeye-Huckel equation (White, 1988) produced a fit of 0.86 with an intercept of -1.68 and a slope of 8.98 (Figure 25). pCO₂ values did not produce a good fit (.14) when compared to spC. However, a strong correlation was found between pCO₂ and Ionic Strength (IS) with a fit of 0.975 with an intercept of 0.95 and a slope of 10484.2. These parameters were also compared to discharge (Figures 30, 31 and 32).

Also, the flux of ions and flux of TIC in the waters of the spring were compared with discharge to examine causation of changes in ion concentrations (Figures 35 and 36). Seasonal shifts in the concentrations at varying discharges were noted and isolated graphically (Figure 37).

Figure 12: pCO₂ vs. spC showing an r² value of 0.14.
The 2002 data set was also used to calculate the denudation rate for the carbonate bedrock in the Spring Creek basin.

**H. Other data sets**

The Lower Kaweah site in the Giant Forest area of Sequoia National Park is closest complete weather station to Mineral King and Spring Creek. It lies 25 kilometers to the northwest and is at an elevation 300 meters below Mineral King Valley, and thus is likely a slightly warmer and drier site. This site provided temperature and precipitation data for this study for 2002. Discharge data for the entire East Fork of the Kaweah watershed is also available from a gauging station operated by Southern California Edison Corporation in the town of Three Rivers. This data was also used in this work. (Figures 26, 27 and 28)
IV. Results

1. Raw Data Graphs

The early data set from Spring Creek (Figure 13) included expected characteristics of these data confirming the validity of the methodology employed and the proper installation of the equipment. This included appropriate instrument readings, and a repeated daily pattern for stage and temperature attributed to the diurnal snow melt in the basin. However, on November 2, 2001 the data logger malfunctioned. Initially values for spC dropped below 0.1 and pH millivolts values increased by more than an order of magnitude. By November 11, the stage was reading 1300 m – the maximum value for the pressure transducer, and the stream temperature registered a consistent 340° C (Figure 16).

All spC data exhibited a common challenge throughout 2001 and 2002 – dropouts (Figure 15). These sudden declines in spC values occur when air bubbles enter the flow through cell of spC sensor, precipitously reducing the volume of water in the sensor, and thus, momentarily reducing so the spC values. To remove this bias, smoothing functions were applied to the spC data when it was processed (Figure 14).

Temperature and stage data used to calculate discharge did not suffer from the problems of the spC and pH data and are generally complete except for time periods of complete data logger failure (Figures 17, 18 and 34).
Figure 13: Early data from the project.
Spring Creek Discharge for 2002

Figure 14: Smoothed conductivity for 2002.

Figure 15: Discharge break-through curve from August 2002 showing spC dropouts.
Figure 16: The Spring Creek data set during the period of data logger failure showing pH millivolts, conductivity, and stage.
Spring Creek Discharge for 2002

Figure 17: Discharge of the Spring Creek Spring in 2002.

Spring Creek Temperatures for 2002

Figure 18: Spring Creek temperatures for 2002.
Figure 19: Spring Creek pH for 2002 showing data gaps and the effects of correlating the data to sets of calibration values determined on varying dates.

2. Laboratory Results

Water samples were collected 14 times throughout the study. Samples were analyzed at the Mammoth Cave National Park water quality laboratory and at the Ash Mountain water chemistry lab at Sequoia National Park. Results were generally in agreement with expected values for karst ground water at the pH values of this spring.

Charge balance checks of ionic charges for each of the spring water samples were completed from the lab results. Eleven of the 12 results are within 80% of agreement and five are within 90%. A final sample from June 2002 had very poor agreement. Results from this lab run were outliers when graphed and were not used in further analysis (Table
Table 3: Laboratory data for water samples from Spring Creek with values in mg/L. Ions detected more than twice are included. Values below detection limit and none detected are shown as nd.

<table>
<thead>
<tr>
<th>Date</th>
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<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
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<td>69.0</td>
<td>61.0</td>
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<td>61.0</td>
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<td>69.0</td>
<td>61.0</td>
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Table 4: Laboratory data for primary ions from water samples above the karst from the basin's two perennial insurgent streams.

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Table 5: Charge balance values for laboratory data for water samples from Spring Creek.

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3. Ion, Discharge, and pH Values

Laboratory ion values were used in linear regressions against the spC of the spring water measured in the field at the time of sample collection to establish the relationship between ion values and the spC. Resulting $r^2$ values for the regressions with the ions of greatest interest are 0.9445 for Ca$^{+2}$, 0.943 for Mg$^{+2}$, and 0.983 for HCO$_3$$. Ion values in the greater data set were calculated to be equal to the intercept plus the slope multiplied by the conductivity at that time. For Ca$^{+2}$ the intercept was 4.505 and the slope was 144.5. For Mg$^{+2}$ the slope was 17.92 and the intercept was -.4192. The HCO$_3$$^-$ calculation had a slope of 640 and an intercept of -2.232 (Figures 20, 21 and 22).

Three ion concentrations (from days 11, 190, and 339, 2002) and the 2002 totals
from the spring produced nearly balanced charge values (Table 6).

![HCO₃ vs spC graph]

Figure 20: Bicarbonate vs. spC at the time that water samples were collected. The $r^2$ for the line is 0.983.

![Ca vs spC graph]

Figure 21: Calcium vs. conductivity at the time of the water samples. The line has an $r^2$ of 0.9445.
Figure 22: Magnesium vs. conductivity at the time of the water samples. The line has an $r^2$ of .943.

Table 6: Charge balance values for constituent ion data from the 2002 data set.

<table>
<thead>
<tr>
<th>Date</th>
<th>$\sum eq$ cations</th>
<th>$\sum eq$ anions</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002 total</td>
<td>5365.6</td>
<td>5628.9</td>
<td>4.7 %</td>
</tr>
<tr>
<td>Day 11, 19.02, 2002</td>
<td>.0020774</td>
<td>.00223</td>
<td>7.8 %</td>
</tr>
<tr>
<td>Day 190, 7.93, 2002</td>
<td>.0011388</td>
<td>.001035</td>
<td>9.9 %</td>
</tr>
<tr>
<td>Day 339, 14.00, 2002</td>
<td>.0021488</td>
<td>.0023257</td>
<td>7.6 %</td>
</tr>
</tbody>
</table>

Discharge was calculated in a comparison with stage using an exponential growth, single, 1 parameter regression and a fit of 0.977. One outlier was removed from this data set (Figure 23). This regression was applied to the 2002 data set to calculate discharge throughout the year. pH Laboratory and field values were compared and found to
generally be in agreement (Table 7).

Stage vs Discharge regression

Figure 23: Stage vs discharge using an exponential growth, single, 1 parameter regression and a fit of 0.977.

Table 7: Comparison of field and laboratory pH values for 2002 from dates with available data.

<table>
<thead>
<tr>
<th>Date</th>
<th>Field</th>
<th>Laboratory</th>
<th>Percentage agreement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16/02</td>
<td>8.36</td>
<td>8.44</td>
<td>99.05</td>
</tr>
<tr>
<td>2/13/02</td>
<td>8.28</td>
<td>8.41</td>
<td>98.45</td>
</tr>
<tr>
<td>3/13/02</td>
<td>8.17</td>
<td>8.33</td>
<td>98.07</td>
</tr>
<tr>
<td>4/11/02</td>
<td>7.99</td>
<td>7.99</td>
<td>100</td>
</tr>
<tr>
<td>5/13/02</td>
<td>7.60</td>
<td>7.75</td>
<td>98.06</td>
</tr>
<tr>
<td>6/5/02</td>
<td>7.78</td>
<td>7.64</td>
<td>98.2</td>
</tr>
<tr>
<td>7/8/02</td>
<td>7.55</td>
<td>7.41</td>
<td>98.14</td>
</tr>
</tbody>
</table>
Denudation of the Spring Creek basin was calculated using the 2002 data set and the ion values generated by the previously mentioned regressions. Rainfall values for ions from Lower Kaweah for the time period were very low – Ca\(^{+2}\) averaged 0.0558 mg/L for 2002 – and, so, were not included in this analysis. 1,688,023 mols or 62.57 m\(^2\) of CaCO\(_3\) were removed from the basin during 2002. Divided by the surface area of the carbonate bedrock, this produces a denudation rate of 148.6 mm/1000 years.

4. C and Chemical Parameter Calculations

Three methods were used to determine C. For one a direct linear regression between spC and TIC produced a fit of 0.97, an intercept of 0.00006918 and a slope of 0.009576 (Figure 24). Saturation indices for 2002 were calculated using a regression between spC and SI values from days when spring waters were sampled. The SI regression had a fit of 0.86 with an intercept of 0.95 and a slope of 10484.2 (Figure 25). pCO\(_2\) values did not produce a good fit (0.14) when compared to spC. However, a strong correlation was found between pCO\(_2\) and Ionic Strength (IS) with a fit of 0.975 an intercept of 0.95 and a slope of 10484.2. Partitioned TIC values were calculated for each of these three methods (Table 8). The regression method was also used to examine the variation in C partitioning seasonally.
Figure 24: spC vs TIC regressions from laboratory-derived data. The graph displays a fit of 0.97.

Figure 25: Saturation Index values for calcite vs. spC producing a fit of .86 with one outlier removed.

Table 8: Values for the sources of TIC in the waters of Spring Creek using three methods.
<table>
<thead>
<tr>
<th>Method</th>
<th>Mineral derived C</th>
<th>Biologically derived C</th>
<th>Atmospheric C as recharge</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laboratory data method</td>
<td>39.7%</td>
<td>58.7%</td>
<td>1.4%</td>
<td>100%</td>
</tr>
<tr>
<td>Concentration method using pH</td>
<td>34.3%</td>
<td>64.3%</td>
<td>1.4%</td>
<td>100%</td>
</tr>
<tr>
<td>Regression Method</td>
<td>48.1%</td>
<td>49.9%</td>
<td>1.9%</td>
<td>100%</td>
</tr>
<tr>
<td>Regression Method - Summer</td>
<td>46.4%</td>
<td>52.2%</td>
<td>1.3%</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>45.3%</td>
<td>53.6%</td>
<td>1.2%</td>
<td></td>
</tr>
</tbody>
</table>

5. Regional Data for 2002

Data from the Sequoia National Park weather station at Lower Kaweah and data from Southern California Edison Corporation gauging stations in Three Rivers were tabulated and processed to show discharge from the entire East Fork of the Kaweah, precipitation, and daily mean temperature for 2002 (Figures 26, 27 and 28).

![East Fork of the Kaweah Discharge for 2002](image)

Figure 26: East Fork of the Kaweah Discharge for 2002.
Figure 27: Lower Kaweah precipitation for 2002.

Figure 28: Lower Kaweah daily mean temperature in C for 2002.
6. Data Comparisons

The data sets generated by this work are most illuminating when compared (Figures 29, 30, 31, 32, 33 and 34).

Figure 29: Spring Creek discharge and spC during 2002

Figure 30: Spring Creek discharge and Total Inorganic Carbon for 2002.
Figure 31: Spring Creek discharge and Saturation Indices for calcite for 2002. The line indicates an SI value of 0.

Figure 32: Discharge and pCO$_2$ values for Spring Creek for 2002. Gaps in the data reflect periods with no pH data.
Figure 33: Discharge and pH for 2002 at the Spring Creek resurgence.

Figure 34: Discharge and Spring Creek water temperatures in C for 2002.
7. Flux Analysis

Flux calculations can provide insight into the driving force in a system and can explain what drives changes in ion concentrations. Flux in ion concentrations and TIC concentrations were examined in this study with comparisons between concentrations and discharge. Lines of fit were applied to the discharge relationship points. For the ion concentrations graph the fit of the line to the discharge vs flux points was 0.86. For the TIC concentrations graph the fit of the line to the discharge vs TIC flux points was 0.77.

Figure 35: The relationship between Ca\(^{+2}\) and Mg\(^{+2}\) flux vs. Ca\(^{+2}\) and Mg\(^{+2}\) concentration and Ca\(^{+2}\) and Mg\(^{+2}\) flux vs. discharge. The fit of the line to the discharge regression is 0.86.
Figure 36: The relationship between TIC flux vs. TIC concentration and TIC flux vs discharge. The fit of the line to discharge regression is 0.77.

Changes in the ion concentration flux for the spring run-off period for 2002 were noticed during the above analysis of what drives changes in concentrations of constituent ions. In general, ion concentrations lower as run-off continues through the spring of 2002. Values for four periods defined by the multiple peaks of the spring run-off discharge values were examined. For example at a discharge of 200 liters per second ion concentrations are near 0.30 mols/L around day 100, but are near 0.15 mols/L around day 150 (Figure 37). pH during this period does show a steady decline (Figure 38). These periods are days 88 to 104 during rising discharge; days 112 to 122, which includes a period of rising and declining discharge during a relatively small spike in the discharge; days 122 to 143, which captures the apex of the 2002 spring run-off; and days 143 to 174, which captures the final peak in the discharge associated with spring run-off.
Figure 37: Ion Concentrations in four time periods during spring run-off 2002 showing a decline in ion concentration through the period.

Figure 38: pH values through spring run-off partitioned into four time periods correlating to periods with varying ion concentrations.
Spring Creek discharge, E. Fork discharge, mean temperature, and precipitation for 2002
Figure 39: Spring Creek Spring discharge, East Fork discharge, Lower Kaweah mean temperature, and Lower Kaweah daily precipitation for 2002.
V. Discussion

1. Raw Data

A. The Four Parameters

The raw data for this study reveals a great deal about the chemical and hydrologic aspects of the Spring Creek karst basin and the Spring Creek Spring. Daily cycles for all four initial parameters are evident (Figure 13). Temperature and stage are in phase with each other. As water volume increases so does temperature; when volume declines the water cools. Increases in discharge and temperature appears to be caused by the daily melting of snow in the upper basin.

This pattern is retained throughout the year, but there is less variance in the daily pattern during the winter months. Daily discharge variances were calculated for three 10-day time periods for mid-winter, spring run-off, and late summer base flow (Table 9). The lowest variance (and lowest discharge) was seen in late summer when snow and ice in the basin are at their annual minimums, and, thus, have the least effect on the daily change in discharge.

Table 9: Daily discharge variance during three 10-day periods in 2002.

<table>
<thead>
<tr>
<th>Julian Days</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>53 to 62</td>
<td>13.017</td>
</tr>
<tr>
<td>127 to 136</td>
<td>280.305</td>
</tr>
<tr>
<td>260 to 269</td>
<td>3.429</td>
</tr>
</tbody>
</table>

A moderate variance was seen in late winter when snow covers the basin, but cold temperatures preclude large-scale melting. The highest values were seen for the period of spring run-off, when higher temperatures and longer sunny days lead to a large daily
variance in flow.

There is a clear correlation with a time lag between water temperature at the spring and spring run-off as seen in Figure 34. Rising temperatures starting on approximately Day 82 and which peak on Day 96 with the highest water temperatures of the year by that date at 8°C, are parallel to rising discharges that initiate on Day 87 and peak on Day 105. Through the spring run-off and snow-melt period, water temperatures remain low. Water temperatures at the spring do not return to 8°C until Day 180, as spring run-off is rapidly fading and discharges are declining steeply. Also, during this time period weekly patterns show a partially inverse relationship between discharge and temperature. These patterns are likely due to the high discharges and reduced transit time through the karst system, which allows for greater retention of water temperatures closer to 0°C – the melting point of snow. From Day 180 forward, temperatures rise steadily and peak at about 11.5°C on Day 220 and remain largely above 8°C for two months, before declining with the onset of colder weather and the first precipitation events of the year. Discharge during this period is nearly flat at base level.

Inverse to temperature and stage (discharge) are spC and pH. These two parameters are generally in phase with each other and drop as water temperatures and volume increases at the spring. Schultz and Tinsley (1996) found that transit time to the spring from the upper basin swallet was 3.5 days. These patterns in the data are roughly in phase with this transit time to the spring with 86% of low flows within two hours of midnight.

Seasonal patterns are also evident in the data, with the strongest patterns
associated with spring run-off and early season storms in late summer and early fall. In comparisons between discharge and other parameters we see a variety of patterns. Through spring run-off, spC retain a nearly perfect inverse pattern when compared to discharge.

A late summer event on day 248 caused a precipitous decline in these chemical parameters, with a surprisingly small rise in discharge for the same event at the spring. Discharge doubled from approximately 10 L/s to 20L/s, but spC declined by 250% dropping nearly as low as it had during the height of spring run-off. However, the East Fork of the Kaweah discharge rose nearly an order of magnitude in association with the event (Figure 39). The Lower Kaweah weather station did not record any rainfall with this event, but a strong decline in temperature was documented. Late summer storms are often localized thunderstorms with a limited extent. It is hypothesized that the East Fork of the Kaweah basin, including the Spring Creek watershed, was hit by a large but localized thunderstorm, which, as the first rain event of the year, flushed anthropogenic acidic dry deposition and acid from basin soils, causing the particularly steep decline in spC. Such flushes of acidic waters have been documented in other park watersheds and are associated with anthropogenic acid deposition (Sickman, 1998).

Early in the fall a rare rainfall event occurred when more than 20 centimeters of rain fell on the Lower Kaweah weather station and across the two parks in a single day. Discharge at the spring rose from 10 L/s to approximately 140 L/s in a few hours. The event did cause a concurrent decline in spC of approximately 60%.

In general, storm responses in this hydrologic system vary. The data shows a very
strong storm response for late summer storms, with precipitation likely occurring as rain. But, not surprisingly, winter storms, where precipitation in the basin is likely snow, produce little to no response in the system's discharge.

**B. Laboratory Data**

Values from the Spring Creek Spring consistently showed high pHs from 7.41 to 8.41 and a mean of 8.1075 from laboratory data and 8.0213 for the 2002 data set. Ion values generally agree with these high pH values with bicarbonate concentrations varying from a low 41.6 mg/L during spring run off to 194.2 mg/L during base flow and a mean of 119.117 from the laboratory data and 107.140 for the 2002 data set. Calcium values range from 46.56 mg/L to 14.74 mg/L during run-off. Magnesium values are generally low, pointing to low dolomitization of the bedrock as reported by Moore (2000). Magnesium values range from 4.02 mg/L to .94 mg/L during run-off (Table 3).

These values contrast with the water samples from the two insurgent streams in the Spring Creek basin – Eagle and White Chief creeks (Table 4). At base flow, when Spring Creek Spring ion concentrations are at their highest, the two streams carried bicarbonate loads of 20.9 and 6.9 mg/L, respectively, and Calcium and Magnesium values of 3.93 and 2.64 and 0.345 and 0.19 mg/L, respectively. These values, from above the karst and marble in the basin, clearly show the chemical effects of groundwater retention in a karst system with an overall enrichment in the Ionic Strength (IS) of an order of magnitude from insurgence to resurgence. Mean IS for Eagle and White Chief Creeks is 0.00030048 while for Spring Creek it is 0.002977.

Greater concentrations of ions in the waters of Eagle Creek may be explained by
the lower elevation of this sink (110 m lower) and the more extensive forest cover and soil development in the watershed, leading initially to more acidic conditions and overall greater ion loading.

2. Carbon Chemistry and Analysis Methods

A. Carbon Analysis Results

The three methods employed to determine the constituents of Total Inorganic Carbon in the Spring Creek system did not agree (Table 8). The regression method produced results consistent with 50:50 ratio for rock to biologically derived C assumed in the literature (e.g., Berner et al., 1983; Meybeck, 1987; Berner and Lasaga, 1989; Probst et al., 1994; Amiotte Suchet, P. and J.L. Probst, 1993, and 1995; Liu et al., 1998). The two other methods, which used the limited data set generated by the laboratory results and an analysis of ion concentrations reliant upon pH, respectively, both produced results showing an enrichment of biologically derived C – 66% for the laboratory data and 34% for the concentration method. Generally assumed chemical conditions for soil and groundwater chemistry do not provide for a ready mechanism for the enrichment of biologically derived C, which is believed to be largely driven by soil CO2 pressures, which vary significantly. Thus, these results are suspect, and it is believed that the regression method produced the most accurate results, which correlate with the literature and a ratio of 50:50 for rock and biologically derived carbon. These results also imply that the overall basin is not strongly affected by anthropomorphic acid deposition.

The regression method was used to examine two 30 day periods for indications of seasonal variation in atmospheric C (Table 8). Both 30 day periods days 12 to 42, 2002
and days 210 to 240, 2002 did not show a significant variation from the annual ratio of 50:50. However, both 30 day periods showed slight enrichment in the biologically derived C and no seasonal variation in the partitioning of C.

**B. Carbon Methods Compared**

Of the three methods used to determine the partitioning of TIC in Spring Creek, the direct regression method, which utilized the entire 2002 dataset was deemed most accurate and reflective of the chemistry of the spring in question. The other two methods, which relied upon pH values and a much smaller data set, appear to have produced poorer, less accurate results.

**3. Calculated Data Sets**

**A. Comparisons to Discharge**

Figures 29 through 33 compare the Spring's discharge to spC, TIC, SI, pCO₂, and pH through 2002. TIC and SI, which are strongly related to spC, show an inverse relationship to discharge and drop during periods of high flow. SI and TIC both show the same precipitous drop in values as spC around Day 248 as was described and discussed above. The SI appears to be particularly sensitive to discharge and varies through only a few weeks of increasing discharge from a saturated value of 0.5 to a chemically-aggressive, undersaturated value of -1.2 during spring run-off.

pCO₂ and pH do not show as strong a relationship to discharge as do other parameters. pCO₂ values appear unchanged during the initiation of spring run-off, but show an inverse relationship to discharge after the peak of run-off on Day 135. The relationship may be explained by a flushing effect as the peak of spring run-off saturates
soils and dissolves most readily available CO₂, leaving less CO₂ within soils and producing a more direct correlation between discharge and calculated pCO₂ values. As run-off declines, pCO₂ values rise steadily presumably due to rising soil temperatures and increased soil microbial activity. pCO₂ shows a strong response to the late summer rain event on day 248 with rising values that remain high through the rest of the available data set. With the first rain of the returning winter season after months without precipitation, increased soil moisture following the precipitation event likely allows microbes to become more active and reproduce, thereby increasing pCO₂.

On a seasonal basis, pH shows an inverse relationship with discharge and drops steadily with increasing discharge as spring run-off begins. Yet, pH values remain low and even decline further as spring-off declines and discharge drops. pH also shows a strong response to the storm event on Day 248. From a high of 8.35 it drops as low as 7.7 and then rebounds to values of approximately 8.0.

**B. Tufa Falls and SI**

The waterfalls between the Spring Creek resurgence and study site pool are known as Tufa Falls, for the prominent deposits of tufa found in the area. The current stream channel is incised into this rock as it crosses the deposit. The current, ongoing erosion of this material is supported by the SI values determined in this study. Tufa deposits are generally associated with SI above 1, which the spring waters never attained in 2002 (White, 1988). The tufa at the falls cannot be of great age because the canyon into which the spring emerges contained a glacier as recently as 12,000 years ago. If the tufa is relatively young, then the current chemical conditions in the spring, which are
eroding the tufa, must be even younger. Sometime in the relatively recent past, hydrologic conditions within the interior of the Spring Creek karst conduit changed allowing CO₂ to outgas within the cave system, permanently lowering pH and SI values for these waters.

**C. Denudation Rate**

The denudation of the Spring Creek karst landscape was calculated using the 2002 data set and the ion values generated by the previously mentioned regressions for a rate of 148.6 mm/1000 years. This very high rate points to the rapid erosion of this small body of carbonate bedrock by karst processes in the Spring Creek watershed. Even with limited soil cover and alpine climatic conditions, rapid dissolution and erosion are occurring owing to the active chemical and hydrologic nature of the Spring Creek karst.

**4. Flux Analysis**

**A. Flux Dependence**

Flux in ion concentrations and TIC concentrations were examined in this study with comparisons between concentrations and discharge. The relationship between Ca⁺² and Mg⁺² flux vs. Ca⁺² and Mg⁺² concentration and Ca⁺² and Mg⁺² flux vs. discharge was examined, as was the relationship between TIC flux vs. TIC concentration and TIC flux vs. discharge (Figures 35 and 36). In both instances, the graphs reveal that discharge is the driving force in ion concentrations and flux and TIC concentrations and flux. The fit of the line to the discharge regression is 0.86 for the ions and is 0.77 for TIC. This result is not unexpected because ion concentrations vary little compared to discharge, which has a larger relative range. Since discharge most directly determines ion concentrations, this
analysis is potentially widely applicable to larger areas and other karst regions using rainfall and GIS computer analysis, providing a potentially important short cut in determining karst denudation rates, the role of karst in atmospheric C and other chemical parameters of interest.

**B. Seasonal Variation in Flux**

A review of Figures 35 and 36 showed that the ion flux values in relation to discharge were clumped into several areas of the graph. Further analysis temporally defined these areas and showed a clear decline in the ion concentrations through the spring run-off period. For example at a discharge of 200 liters per second ion concentrations are near 0.30 mols/L near day 100, but are near 0.15 mols/L around day 150 (Figure 37). In an attempt to explain this change over time, pH values for the same four time periods were defined and examined in Figure 38. This graph shows a clear overall decline in pH values through the period although, there was some rise in pH between days 142 and 152. These declining pH values likely account for increasing dilution of spring solutions. This decline in pH may be associated with spring run-off saturation and the flushing of basin soils, as was hypothesized for pCO₂ values, or may be the product of a flush of anthropogenically acidic enriched snowmelt as was found in the Emerald Lake Basin by Sickman (1998). In these cases, acidic deposition accumulates in the snow through the winter and is released in a single pulse as spring snow melt begins.
VI. Appendices
A: SigmaPlot™ Formulas

1. Discharge from salt dilution transform

Variables:

- $c_0 =$ spC of known solution that was added to the stream above the data logger;
- $v_0 =$ volume of the known solution
- $x_{\text{min}} =$ starting row number for the calculation
- $x_{\text{max}} =$ ending row number for the calculation
- $\text{data}_{\text{col}} =$ the data column with values under which the areas is to be calculated
- $\text{placed}_{\text{data}} =$ the column where data are placed.

The formula using these variables is:

$$\text{for } i = x_{\text{min}} \text{ to } x_{\text{max}} - 1 \text{ do}$$
$$\text{cell}(\text{placed}_{\text{data}}, 1) = \text{cell}(\text{placed}_{\text{data}}, 1) + 0.5(\text{cell}(\text{data}_{\text{col}}, \text{i}) + \text{cell}(\text{data}_{\text{col}}, \text{i} + 1) - 2 \times \text{cell}(\text{data}_{\text{col}}, x_{\text{min}}))$$
$$\text{end for}$$
$$\text{cell}(\text{placed}_{\text{data}}, 2) = (c_0 \times v_0) / (\text{cell}(\text{placed}_{\text{data}}, 1))$$

2. Stage to discharge regression transform

$$Q = \exp (13.3964 \times x)$$

3. spC smoothing transform

for $i = 1$ to size(2) - 1 do
$$\text{if } (\text{cell}(2, i + 1) - \text{cell}(2, i)) < 0.004 \text{ then}$$
$$\text{cell}(2, i + 1) = \text{cell}(2, i)$$

4. spC to HCO₃ regression transform

$$\text{col}(14) = -2.232 + (640 \times \text{col}(9))$$

5. spC to Ca regression transform

$$\text{col}(15) = 4.505 + (144.5 \times \text{col}(9))$$

6. spC to Mg regression transform

$$\text{col}(16) = -0.4192 + (17.92 \times \text{col}(9))$$
col(16) = -0.4192 + (17.92 * col(9))

7. spC vs TIC regression transform

col(4) = 0.0001 + (.009 * col(3))

8. Calculating C, method 1

; this transform does carbon summaries for Spring Creek SEKI

; mg/L to mol/L

BICARB = COL(5) / 61000
CALCIUM = COL(6) / 40080
MAGNESIUM = COL(7) / 24305
HYDROGEN = 10^(-(COL(4)))

; calculate calcium, bicarbonate and magnesium activities

IONSTR = 0.5 * ((CALCIUM * 4) + (BICARB) + (MAGNESIUM * 4))
GAMCAL = 10^(-(0.4921 * 4 * SQRT(IONSTR)) / (1 + (SQRT(IONSTR) * 0.3249 * 5)))
GAMBIC = 10^(-(0.4921 * SQRT(IONSTR)) / (1 + (SQRT(IONSTR) * 0.3249 * 5.4)))
GAMMAG = 10^(-(0.4921 * 4 * SQRT(IONSTR)) / (1 + (SQRT(IONSTR) * 0.3249 * 5.5)))

ACTCAL = GAMCAL * CALCIUM
ACTBIC = GAMBIC * BICARB
ACTMAG = GAMMAG * MAGNESIUM

; calculate equilibrium constants as f(temperature)

TEMPK = COL(2) + 273.15
KH = 10^((108.3865 + (0.01985076 * TEMPK) - (6919.53 / TEMPK) - (40.45154 * LOG(TEMPK)) + (669365 / (TEMPK^2)))
K1 = 10^((-356.3094 - (0.06091964 * TEMPK) + (21834.37 / TEMPK) + (126.8339 * LOG(TEMPK)) - (1684915 / (TEMPK^2)))
K2 = 10^((-107.8871 - (0.03252849 * TEMPK) + (5151.79 / TEMPK) + (38.92561 * LOG(TEMPK)) - (563713.9 / (TEMPK^2)))
KCAHCO = 10^((1209.120 + (0.31294 * TEMPK) - (34765.05 / TEMPK) - (478.782 * LOG(TEMPK))))
KCACO3 = 10^((-1228.732 - (0.299444 * TEMPK) + (35512.75 / TEMPK) + (485.818 * LOG(TEMPK))))
KMGHCO = (3.585864e-5 * col(2)^2) - (3.041197e-3 * col(2)) + (0.160404)
KMGCO3 = (-2.361508e-7 * (COL(2)^2)) - (1.082416e-5 * (col(2)) + (1.750207e-3)

; calculate species activities and sum up carbon
ACTH2CO3 = (HYDROGEN * ACTBIC) / K1
ACTCO3 = (K2 * ACTBIC) / HYDROGEN
ACTCAHCO = (ACTCAL * ACTBIC) / KCAHCO
ACTCACO3 = (ACTCAL * ACTCO3) / KCACO3
ACTMGHCO = (ACTMAG * ACTBIC) / KMGHCO
ACTMGCO3 = (ACTMAG * ACTCO3) / KMGCO3
TIC = ACTBIC + ACTH2CO3 + ACTCO3
COL(12) = TIC

DISCHARGE = COL(3)

; sum up the total carbon, mineral dissolution carbon, gas carbon, and biological carbon
; interval * 86,400 for units of seconds
INTERVAL = DIFF(COL(1)) * 86400
CARBFLUX = (TIC * INTERVAL * DISCHARGE)
CALFLUX = (ACTCAL + ACTMAG) * INTERVAL * DISCHARGE

; the following equation for gascarb comes from 2nd order regression of plot of TIC in
; equilibrium with an atmosphere with PCO2 = 0.000360, as a function of temperature
GASTIC = (1.040e-8 * col(2)^2) - (8.990e-7 * col(2)) + 3.027e-5
GASFLUX = GASTIC * INTERVAL * DISCHARGE

col(13) = CARBFLUX
col(14) = CALFLUX
col(15) = GASFLUX

TOTCARB = TOTAL(CARBFLUX)
cell(16,1) = TOTCARB
CALCARB = TOTAL(CALFLUX)

cell(17,1) = CALCARB
GASCARB = TOTAL(GASFLUX)
cell(18,1) = GASCARB
BIOCARB = TOTCARB - (CALCARB + GASCARB)
cell(19,1) = BIOCARB

; sum up carbon percentages

cell(21,1) = (CALCARB / TOTCARB) * 100
cell(21,2) = (GASCARB / TOTCARB) * 100
cell(21,3) = (BIOCARB / TOTCARB) * 100
cell(21,4) = cell(21,1) + cell(21,2) + cell(21,3)
9. Calculating SI
\[\text{col (6)} = -1.68 + (8.98 \times \text{col(3)})\]

10. Calculating pCO₂
\[\text{col (7)} = 0.95 + (10484.2 \times \text{col (5)})\]

### Appendix B: Microsoft Excel™ Calculations Table

<table>
<thead>
<tr>
<th>sample date</th>
<th>pH</th>
<th>T (°C)</th>
<th>Ca</th>
<th>HCO₃</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
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<tr>
<td>10/10/2001</td>
<td>8.23</td>
<td>6.7</td>
<td>34.69</td>
<td>125</td>
<td>3.12</td>
<td>3.52</td>
<td>0.38</td>
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<th>Ca</th>
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<th>Mg</th>
<th>Na</th>
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<th>SO₄</th>
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<td>K</td>
<td>L</td>
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<th>K</th>
<th>Li</th>
<th>Mg</th>
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<th>K</th>
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<td>S</td>
<td>T</td>
<td>U</td>
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\[
\begin{align*}
\text{AE} &= \left(0.4921 \times 4 \times \text{AA}^2 \right) \\
\text{AG} &= \left(0.4921 \times 4 \times \text{AA}^2 \right) \\
\text{AH} &= \left(0.4921 \times 4 \times \text{AA}^2 \right) \\
\text{AI} &= \left(0.4921 \times 4 \times \text{AA}^2 \right) \\
\text{AJ} &= \left(0.4921 \times 4 \times \text{AA}^2 \right)
\end{align*}
\]
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<th>Mg activity</th>
<th>Na activity</th>
<th>Activity of CO₃</th>
<th>IAP Calcite</th>
<th>Omega calcite</th>
<th>IAP Dolomite</th>
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<td>AL</td>
<td>AM</td>
<td>AN</td>
<td>AO</td>
<td>AP</td>
<td>AQ</td>
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\[ P²A²G² = Q²A²H² = R²A²L² = 10.55 \times A²K² \times 10^{(-B²)} = A²J²A²N² = A²O²/10^{(-8.39)} \]

<table>
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<tr>
<th>SI</th>
<th>Cal</th>
<th>Si Dol</th>
<th>pK1</th>
<th>K1</th>
<th>pKCO2 constant</th>
<th>aH</th>
<th>aH₂CO₃</th>
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<tr>
<td>AR</td>
<td>AS</td>
<td>AT</td>
<td>AU</td>
<td>AV</td>
<td>AW</td>
<td>AX</td>
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<tr>
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<td>3.76726E-05</td>
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**Notes**

- **Kh** (for PCO₂)

\[ T in K = 10^{(0.78365 + (0.01985076 \times A²Y²) - (6919.53 \times A²Y²) - (40.45154 \times \text{LOG}(A²Y²)))} \]

\[ = (C²) + 273.15 + (669365/(A²Y²)^2)) = (A²X²)/(A²Z²) = (A²X²)+(A²K²)+(A²N²) \]

<table>
<thead>
<tr>
<th>T in K</th>
<th>Kh (for PCO₂)</th>
<th>PCO₂</th>
<th>TIC</th>
<th>Notes</th>
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<tbody>
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<td>AV</td>
<td>AZ</td>
<td>BA</td>
<td>BB</td>
<td>BC</td>
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- **Notes**
<table>
<thead>
<tr>
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<th>Temperature near 10°C</th>
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<td>278.94 0.062417585 0.000444438 0.002196709</td>
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<td>277.69 0.065366641 0.000523205 0.002255654</td>
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<td>278.67 0.063038232 0.000675482 0.000766859</td>
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<td>278.77 0.062807337 0.000940611 0.002162159</td>
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VII. References


Groves, C, and J. Meiman, 2001, Inorganic carbon flux and aquifer evolution in the south

Groves, C. and J. Meiman, in press, Weathering, geomorphic work, and karst landscape evolution in the Cave City groundwater basin, Mammoth Cave, Kentucky. Invited manuscript accepted for publication by *Geomorphology*.


Rogers, Bruce, 1978, Mineral King Update, *California Caver*, v. 29, p. 4-12.


