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# Hydrologic and Geochemical Cycling within Karst Versus Non-Karst Basins within the Interior Low Plateau Province of South-Central Kentucky

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**Hydrologic and Geochemical Cycling within  
Karst versus Non-karst Basins  
within the Interior Low Plateau Province of South-central Kentucky**

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

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

By  
David A. Ek

December 2004

HYDROLOGIC AND GEOCHEMICAL CYCLING WITHIN KARST VERSUS NON-  
KARST BASINS WITHIN THE INTERIOR LOW PLATEAUS PROVINCE OF  
SOUTH-CENTRAL KENTUCKY

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This thesis summarizes my research in which I investigated differences and characteristics in hydrologic, nutrient and geochemical cycling between karst versus non-karst basins within the Interior Low Plateau Province. Field data including stream discharge, evapotranspiration, and dissolved major ion concentrations were collected for a period of one year for two basins within Mammoth Cave National Park. Twelve percent carbonate rocks underlie one basin, while the other consists of 48 percent carbonate rocks. The carbonate rock exposures within both basins exhibit karstification. The hydrologic and geochemical differences between these basins were compared to determine to what extent that cycles are modified or altered within karst terrains. The characteristics of these cycles within both basins were also compared.

I found that there were noticeable hydrogeochemical effects from the presence of karst within a basin. These effects were either the result of the presence of carbonate rocks within the basin or due to the presence of morphological karst features within the carbonate rocks. The presence of karst serves as a buffer by moderating temperature extremes, lessens the effect of acid precipitation, moderates discharges during storm surges, moderates/lessens a basin's evaporative losses, and affects available moisture and

nutrients to surface biological processes. These hydrologic effects in turn, also continue to affect the basin's geochemistry in noticeable ways. Findings included that it only takes a small percentage of carbonate rocks within a basin to produce an output stream with a calcium/bicarbonate geochemical signature. In these situations, the quantity of karst is perhaps not as important as spatial distribution. Therefore, the quantity of karst within a basin may be more critical to accurately assess when conducting geochemical modeling. Many global geochemical models do not factor in karst affects (Holmén, 1992). Considering the extent of carbonate rocks globally and their potential ability to affect hydrogeochemical cycles, future model modifications may need to factor in karst affects in order to more accurately represent actual real-world field conditions.

## PART I INTRODUCTION

Many articles have been written on basin and global-scale cycling of water and dissolved chemical species within non-karst watersheds (Likens and Bormann, 1995; Butcher *et al.*, 1992). Many other studies have focused upon specific and even landscape-scale karst research (Ford and Williams, 1989; White, 1989). However, few studies have linked the two, focusing upon how the degree and nature of karst development within a basin impacts hydrologic and geochemical cycling. The purpose of this research is to examine differences between hydrologic and chemical cycling within otherwise similar karst and non-karst basins within the humid Temperate Interior Low Plateau province of south-central Kentucky.

Karst is a German derivation of a name (Kras) for a relatively small region located near the northern Adriatic coast in Slovenia (Jakucs, 1977 and ASAK, 2003). Extensive sinkholes, sinking stream caves, and springs dominate the landscape within this region. Through popular usage in or before the nineteenth century, Europeans seeing similar landscapes in other regions began referring to the landscape type as 'karst.' This terminology was based entirely upon the form of the landscape, not any process-oriented functional basis. Eventually, the term 'karst' was applied to cave-bearing landscapes in other regions.

The primary source of water for any basin is precipitation, whether in the form of rain, ice, snow or fog drip. Typical outputs for water within a basin are the base-level stream and loss to the atmosphere via evapotranspiration. On a watershed-level scale, the principle agent for inorganic chemical species and nutrient loss is via the base-level

stream that flows out of the basin (Likens and Bormann, 1995; Butcher *et al.*, 1992). The chemical constituents within streams result from the physical and biologic interactions between the atmosphere and landscape, weathering of rocks in the basin and other watershed-scale reactions (Stumm and Morgan, 1970). Therefore, the knowledge of stream flow and evapotranspiration dynamics is key not only to understanding the hydrologic cycle within a basin but also the entire range of biogeochemical cycling and the ability to accurately model many natural processes.

Considering that over twelve percent of the earth's land surface is composed of karst (Ford and Williams, 1989), the effects that karst could play in modifying global processes could be significant. From a regional standpoint, the southeastern United States has a significant percentage of the global karst resources. One of the more dominant landscapes within the Interior Lowlands Province is karst. The Mammoth Cave region, located within the Interior Lowlands Province, is one of the most extensive, well known, and studied karst regions of the world.

As stated earlier, stream flow and evapotranspiration are the two primary means within the hydrologic cycle in which water leaves a basin. Along the way within each of these two final output mechanisms are a variety of other processes, as well as interactions with temporary storage mechanisms. For instance, vegetation distribution is closely related to soil type (Hem, 1989), which in turn is largely dependent upon geology and climate. Vegetation can play a role in modifying microclimate and soil development. Since karst affects the location and availability of water (Olsen and Franz, 1998), it is



possible that these differences could affect localized climate, vegetation and soil development, which in turn are factors in hydrologic and chemical cycles.

In many settings, a significant amount of water leaves the basins via evapotranspiration. In the Mammoth Cave region, evapotranspiration has been shown to range from about 50 to 80 percent of the total precipitation input into the basin (from precipitation values in Faller (1969) and evapotranspiration values in Hess and White (1989)). Evapotranspiration is largely a factor of climate, vegetation and the availability of water. Since the presence of karst can influence each of these three parameters, the nature and degree of these effects upon the hydrologic and chemical cycles warrants further investigation. Additionally, Likens and Bormann (1995) found that evapotranspiration significantly regulates and balances chemical and nutrient loss within a basin. This regulation and balancing is due to higher quantities of water loss via evapotranspiration that result in a lower quantity of water available for stream flow, which is the primary avenue for chemical and nutrient transport and subsequent loss from a particular watershed. Conversely, low evapotranspiration levels allow higher stream flows, which can transport larger amounts of nutrients and other dissolved substances from the basin. Since evapotranspiration levels in the south-central Kentucky karst range from approximately 50 to 80 percent of the annual total precipitation (Hess and White, 1989) factors that affect evapotranspiration could play a significant role in chemical and nutrient cycling within watersheds.

An ideal project site for this study would include the following parameters:

- the existence of sufficiently detailed dye tracing and other basin delineation investigations within the karst basin so that the basin's recharge area may be accurately determined;
- no complicated cross-basin transport of water during different flow regimes;
- basin divides composed of mostly non-karstic rocks to reduce complications in basin delineation;
- no significant water withdrawals or other human-related impacts;
- the two basins be of fairly equal size, elevation, slope and topography, aspect, and proximity;
- the basins be large enough to sustain streams that flow during the majority of the year, yet small enough to avoid the relatively complicated flow conditions that often occur within large catchment areas;
- other relevant data sets, preferably in geo-referenced digital form, exist, such as climate, precipitation, precipitation chemistry, geology, soils, and vegetation cover;
- the basins be of relatively easy access in order to allow frequent visits.

Based upon these considerations, two small watersheds located mostly within Mammoth Cave National Park were chosen for this study. The 6.6 square kilometer First Creek basin, located near Brownsville, Kentucky is underlain with the least amount of carbonate rocks (12.2 percent) of the watersheds occurring wholly or in part within Mammoth Cave National Park. The 6.9 square kilometer Dry Branch basin is located nearby and has relatively similar elevation, aspect and slope, but is underlain by 47.7 percent carbonate rocks (Figure 1). The exposed carbonate rocks within both basins are

primarily the Mississippian Glen Dean and Haney Limestones. The non-karstic rocks within the two study basins consist of the Pennsylvanian Caseyville Formation (sandstone), the Mississippian Leitchfield Formation (shale), the Mississippian sandstones of the Big Clifty Formation and the Hardinsburg Formation (Palmer, 1999). The Dry Branch basin was chosen to represent the more highly developed karst (the "karst" basin), while the First Branch ("non-karst") basin is almost totally developed in non-carbonate rocks.

Lithology is one of the dominant controls on a hydrograph response curve (Ford and Williams, 1989). Non-karstic rocks typically yield strongly peaked hydrographs due to relatively small amounts of groundwater storage and rapid surface runoff. Conversely, streams originating from karst aquifers typically yield flatter hydrographs with delayed responses of transmitting the storm pulse and existing groundwater storage through the myriad of conduits within a karstic system. Therefore, evapotranspiration, stream flow and other hydrologic factors are critical components of a complex network of hydrologic and biogeochemical cycles and that karst could potential affect these cycles and relationships.

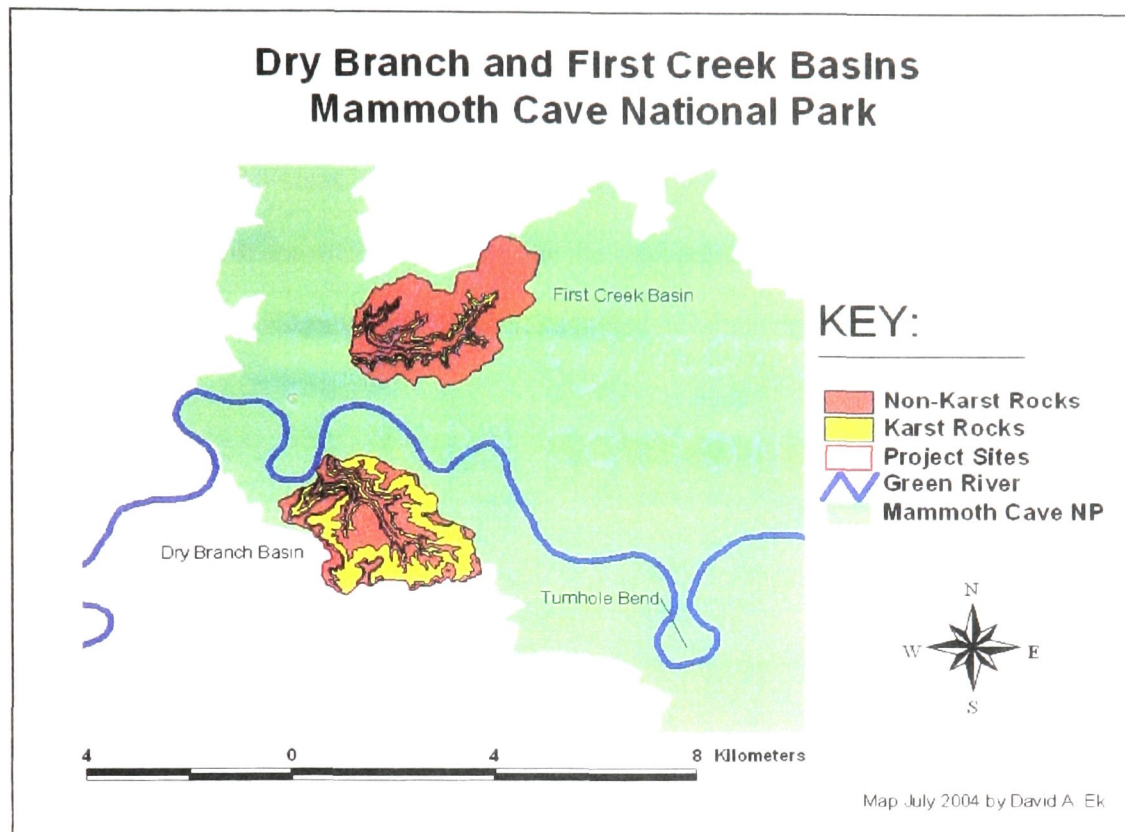


Figure 1. Study area location and extent of carbonate bedrock

### Statement of the Problem

My research proposed to test a hypothesis that there is a distinct and predictable difference in the hydrologic and chemical cycling between karst and non-karst basins.

Specifically, the research addressed the following:

- the degree of natural pH buffering of karst versus non-karst stream water;
- determination of statistical relations between various ions cycling through the basin under different hydrologic conditions;

- determination if the total net losses, gains or net balances for the various ions found by Likens and Bormann, (1995) in their non-karst basin study in New England are similar to the non-karst basin in the Mammoth Cave area project site;
- determination of the differences between the total net losses, gains, or net balances of the various ions and nutrients between karst and non-karst systems.

## PART II      GLOBAL PROCESSES

### **Subpart A: RESERVOIRS**

The beginning point in a discussion of global processes is the basic hydrologic cycle as depicted in Figure 2. The only water reservoirs depicted in figure 2 are the atmosphere and the oceans; however, other water reservoirs commonly exist, including groundwater, surface streams and lakes, biota, and soils. Movement of water between reservoirs, such as evapotranspiration and precipitation, are fluxes. Most substances on Earth cycle between their own reservoirs. Understanding global processes is largely an understanding of these reservoirs, fluxes, the nature and conditions that cause substances to move between reservoirs, and lastly the relationship and interaction between other substances and processes. Therefore, this section will begin with a basic description of each of the dominant water reservoirs.

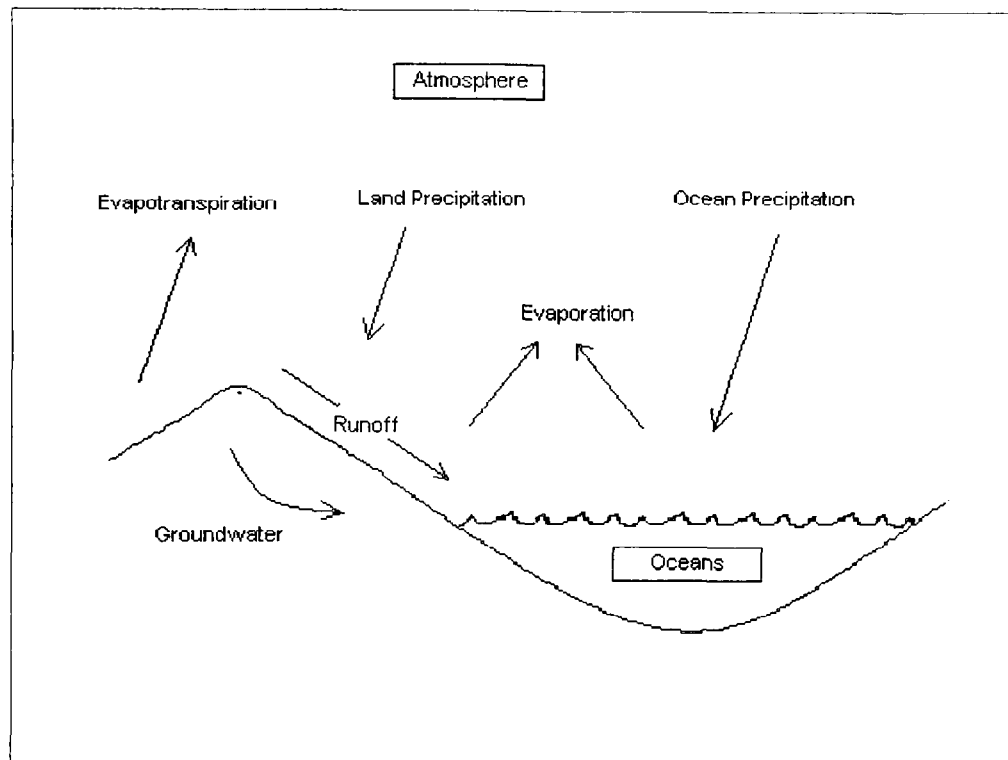


Figure 2 Generalized hydrologic cycle.

## ATMOSPHERE

The main ingredients of the atmosphere are nitrogen, oxygen, argon, carbon dioxide and water, but also include numerous minor constituents (Table 1). The atmosphere is not entirely homogeneous; therefore, the concentrations of some of the individual species vary in time and space.

Table 1. Mean Composition of the Atmosphere (Hem, 1989) [After Mirtov, 1961]

Gas	Percentage by Volume	Partial Pressure
N <sub>2</sub>	78.1	0.781
O <sub>2</sub>	20.9	0.209
Ar	0.93	0.0093
H <sub>2</sub> O	0.1-2.8	0.001-0.028
CO <sub>2</sub>	0.03	0.0003
Ne	1.8x10 <sup>-3</sup>	1.8x10 <sup>-5</sup>
He	5.2x10 <sup>-4</sup>	5.2x10 <sup>-6</sup>
CH <sub>4</sub>	1.5x10 <sup>-4</sup>	1.5x10 <sup>-6</sup>
Kr	1.1x10 <sup>-4</sup>	1.1x10 <sup>-6</sup>
CO	(0.006-1)x10 <sup>-4</sup>	(0.06-1)x10 <sup>-6</sup>
SO <sub>2</sub>	1x10 <sup>-4</sup>	1x10 <sup>-6</sup>
N <sub>2</sub> O	5x10 <sup>-5</sup>	5x10 <sup>-7</sup>
H <sub>2</sub>	~5x10 <sup>-5</sup>	~5x10 <sup>-7</sup>
O <sub>3</sub>	(0.1-1.0)x10 <sup>-5</sup>	(0.1-1.0)x10 <sup>-7</sup>
Xe	8.7 x 10 <sup>-6</sup>	8.7 x 10 <sup>-8</sup>
NO <sub>2</sub>	(0.005-2)x10 <sup>-6</sup>	(0.05-2)x10 <sup>-8</sup>
Rn	6x10 <sup>-18</sup>	6x10 <sup>-20</sup>

The concentration of solutes in rainfall often is different from the mean concentration within the atmosphere. Junge and Werby (1958), as reported by Whitehead and Feth (1964), show that the average U.S. solute concentration for rainfall for inland sampling stations is depicted in Table 2.

Table 2 Average solute concentration of rainfall for inland U.S. sites

Ca	1.41 mg/L
Na	0.42 mg/L
SO <sub>4</sub>	2.14 mg/L
Cl	0.22 mg/L

When studying geochemical cycling between reservoirs, one also often needs to consider the residence time within each respective reservoir. The atmosphere is no exception. Table 3 (from Butcher *et al.*, 1992, as modified from Margulis and Lovelock, 1974) depicts residence time within the atmosphere.



Table 3 Residence time of selected atoms

Nitrogen	107 to 109
Oxygen	thousands of years
Carbon dioxide	approximately 100 years
Carbon monoxide	a few months
Methane	a few years
Nitrous oxide	approximately 100 years
Ammonia	a few days
NO <sub>x</sub>	a few days
Hydrogen sulfide	a few days
Hydrogen	a few years

Precipitation is not only the principle source of water input into a particular watersheds but also serves as an important transport mechanism for air-borne particles via wet deposition (the other primary means is by dry deposition). Evaporation and transpiration are common avenues for water molecules to move from land and water surfaces into the atmosphere.

## LITHOSPHERE

The surface and near surface geologic makeup of a particular watershed has a very strong effect on the basin's weathering, stream chemistry and geochemical cycles. Before the discussion of the study area's geology and geography, a broader perspective will be presented by looking at the global perspective:

Area of continents  $149 \times 10^6 \text{ km}^2$  (29.2 % of surface of earth);  
 Area of world oceans  $361 \times 10^6 \text{ km}^2$  (E. Kossina, 1933, In: Weast & Astle, 1982)  
 Land area of earth  $148.847 \times 10^6 \text{ km}^2$  (Weast and Astle, 1982)  
 Ocean area  $361.254 \times 10^6 \text{ km}^2$  (Weast and Astle, 1982).

The Average Amounts of the Elements are located in Earth's Crust (Weast and Astle, 1982) are depicted in Table 4.

Table 4 Average concentration of the various components of the Earth's crust

<u>Element</u>	<u>ppm</u>
O	466,000
Si	277,200
Al	81,300
Fe	50,000
Ca	36,300
Na	28,300
K	25,900
Mg	20,900
Ti	4,400
H	1,180
P	1,180
Mn	1,000
S	520
C	320
Cl	314
Rb	310
F	300
Sr	300
Br	250
Zr	220
Cr	200
V	150
Zn	132
Ni	80
Cu	70
W	69
Li	65
N	46

Chemical composition of rocks (reprinted from "Sedimentary Rocks" (Weast and Astle, 1982) are depicted in Table 5:

Table 5 Chemical composition of selected rocks

Element	Average Igneous Rock	Average Shale	Average Sandstone	Average Limestone	Average Sediment
SiO <sub>2</sub>	59.14	58.10	78.33	5.19	57.95
TiO <sub>2</sub>	1.05	0.65	0.25	0.06	0.57
Al <sub>2</sub> O <sub>3</sub>	15.34	15.40	4.77	0.81	13.39
Fe <sub>2</sub> O <sub>3</sub>	3.08	4.02	1.07	0.54	3.47
FeO	3.80	2.45	0.30		2.08
MgO	3.49	2.44	1.16	0.89	2.65
CaO	5.08	3.11	5.50	42.57	5.89
Na <sub>2</sub> O	3.84	1.30	0.45	0.05	1.13
K <sub>2</sub> O	3.13	3.24	1.31	0.33	2.86
H <sub>2</sub> O	1.15	5.00	1.63	0.77	3.23
P <sub>2</sub> O <sub>5</sub>	0.30	0.17	0.08	0.04	0.13
CO <sub>2</sub>	0.10	2.63	5.03	41.54	5.38
SO <sub>3</sub>		0.64	0.07	0.05	0.54
BaO	0.06	0.05	0.05		
C		0.80			0.66
Total	99.56	100.00	100.00	99.84	99.93

Average composition, in parts per million, of igneous rocks and some types of sedimentary rocks (Hem, 1989) [In: Horn and Adams (1966)] are depicted in Table 6.

Table 6 Average composition of igneous and other selected rocks.

Element	Igneous Rocks	Sandstone	Shale	Carbonates
Si	285,000	359,000	260,000	34
Al	79,500	32,100	80,100	8,970
Fe	42,200	18,600	38,800	8,190
Ca	36,200	22,400	22,500	272,000
Na	28,100	3,870	4,850	393
K	25,700	13,200	24,900	2,390
Mg	17,600	8,100	16,400	45,300
Ti	4,830	1,950	4,440	377
P	1,100	539	733	281
Mn	937	392	575	842
F	715	220	560	112
Ba	595	193	250	30

S	410	945	1,850	4,550
Sr	368	28	290	617
C	320	13,800	15,300	113,500
Cl	305	15	170	305
Cr	198	120	423	7.1
Rb	166	197	243	46
Zr	160	204	142	18
V	149	20	101	13
Ce	130	55	45	11
Cu	97	15	45	4.4
Ni	94	2.6	29	13
Zn	80	16	130	16
Nd	56	24	18	8.0
La	48	19	28	9.4
N	46		600	
Y	41	16	20	15
Li	32	15	46	5.2
Co	23	0.33	8.1	0.12
Nb	20	0.096	20	0.44
Ga	18	5.9	23	2.7
Pr	17	7.0	5.5	1.3
Pb	16	14	80	16
Sm	16	6.6	5.0	1.1
Sc	15	0.73	10	0.68
Th	11	3.9	13	0.20
Gd	9.9	4.4	4.1	0.77
Dy	9.8	3.1	4.2	0.53
B	7.5	90	194	16
Yb	4.8	1.6	1.6	0.20
Cs	4.3	2.2	6.2	0.77
Hf	3.9	3.0	3.1	0.23
Be	3.6	0.26	2.1	0.18
Er	3.6	0.88	1.8	0.45
U	2.8	1.0	4.5	2.2
Sn	2.5	0.12	4.1	0.17
Ho	2.4	1.1	0.82	0.18
Br	2.4	1.0	4.3	6.6
Eu	2.3	0.94	1.1	0.19
Ta	2.0	0.10	3.5	0.10
Tb	1.8	0.74	0.54	0.14
As	1.8	1.0	9.0	1.8
W	1.4	1.6	1.9	0.56
Ge	1.4	0.88	1.3	0.036
Mo	1.2	0.50	4.2	0.75
Lu	1.1	0.30	0.28	0.11

Tl	1.1	1.5	1.6	0.065
Tm	0.94	0.30	0.29	0.075
Sb	0.51	0.014	0.81	0.20
I	0.45	4.4	3.8	1.6
Hg	0.33	0.057	0.27	0.046
Cd	0.19	0.020	0.18	0.048
In	0.19	0.13	0.22	0.068
Ag	0.15	0.12	0.27	0.19
Se	0.050	0.52	0.60	0.32
Au	0.0036	0.0046	0.0034	0.0018

The type of exposed rocks within a basin is important due to its effect upon weathering and other chemical reactions that occur as a result of the basin's geologic and the hydrologic system. For example, sources of solutes in natural water are largely the net effect of a series of antecedent chemical reactions that have dissolved material from another phase, altered previously dissolved material, or eliminated them from solution by precipitation or other processes (Hem, 1989).

### **Weathering**

Weathering is the chemical and/or physical breakdown of substances such as rocks within a particular watershed. In general, chemical weathering becomes more dominant in warm, moist regions, while physical weathering dominates in cold and dry regions. Similarly, chemical weathering dominates in regions with much vegetation, while physical weathering dominates in steep terrain (Butcher *et al.* 1992). Weathering is an important process that allows substances held in the lithosphere reservoir to move to other reservoirs or partake in local, regional or global processes.

While all minerals can weather, some are much more susceptible than others to both the physical and chemical forms of weathering. The products of weathering may be smaller-sized particles (associated with physical) or dissolved species (associated with chemical). In many situations, some of the more easily dissolved elements of bedrock may go into solution, thereby changing the material and leaving the least soluble particles to remain in the stream bed or on slopes.

The processes of rock weathering are strongly influenced by temperature and the amount and distribution of precipitation (Hem, 1989). Climatic patterns tend to produce characteristic plant communities and soil types, and the composition of water draining these systems could be thought of as a product of the ecological balance (Hem, 1989).

Bicarbonate tends to predominate in water in areas where vegetation grows profusely (Hem, 1989). Some metals are accumulated by vegetation and may reach peak concentrations when plant-decay cycles cause extra amounts of these metals to enter the circulating water (Hem, 1989).

Low temperature inhibits weathering reaction rates (Hem, 1989). The ultimate sources of most dissolved ions are near-surface rocks (Hem, 1989); however, the nature of the rocks, for instance the purity and crystal size, rock texture and porosity, regional structure, degree of fissuring, and exposure time also have an effect.

Chemical weathering involves the alteration of bedrock, largely by solution. The products are determined by the mineral present in the bedrock, water pH, bonding strength of the ions, and the movement and redox potential of the solvent (Butcher *et al.* 1992). Weakly bonded ions are removed by solution, while the strongly bonded ions precipitate out of solution thereby they are preferentially retained within the basin.

Within the last 100 years, increases in carbon dioxide and other anthropomorphic changes in the atmosphere have affected weathering rates and types (Butcher *et al.*, 1992).

The less soluble components of rocks are either flushed out of a basin via water or wind action, or are retained, even temporarily, within the basin. These retained and accumulated non-soluble particles contribute to soil development. Even soluble rocks such as limestone generally contain at least a small fraction of insoluble products that contribute to and influence soil development.

## **PEDOSPHERE**

Although not requiring the presence of biota, such as vegetation, soil development is significantly accelerated by the presence of organic material. Well-developed soil retains nutrients and moisture better than less developed soils; therefore one would typically find a greater loss of chemical elements from a basin in less well-developed soils.

An average temperate soil contains approximately 40 percent inorganic solid material, 10 percent organic solid material, 15 to 35 percent liquid (mostly water), and 15 to 35 percent gas (Jackson, 1964). The inorganic component is dominated by oxygen, silicon, aluminum, iron, magnesium, calcium, sodium, and potassium (Jackson, 1964). These chemical elements are similar to the constituents of the igneous rocks that dominate the Earth's crust.

Soils in temperate deciduous forests tend to be rich in nitrogen, but poor in lignin (Butcher *et al.*, 1992). In these forest soils humic acid/fulvic acid ratios tend to be low in the higher soil horizons. The lower soil horizons are dominated by carbonic acid weathering reactions, with some minor organic acid reactions (Butcher *et al.*, 1992).

There are several important factors for the type and concentrations of ions in stream water. These factors often overwhelm the influence of the local soil and its constituents. Therefore, the type of soil often has little relation to the soluble products found in nearby streams. The soil profile/layer with which the water is in contact has the greater bearing upon water chemistry. The chemistry of the upper layers of a soil varies from soil type to soil type, whereas the lower layers are fairly similar; therefore, streams in contact with these similar lower layers will often have relatively similar water chemistry, even when separated for some distance. Similarly, streams in contact with the upper soil layers of soil may have dramatically different water chemistry, even in relatively close proximity to each other (Butcher *et al.*, 1992).



## BIOSPHERE

As the lithosphere and hydrosphere affect the pedosphere, the pedosphere and hydrosphere affect the biosphere. One may consider a basin's vegetation to be a reflection of the many geochemical processes occurring within the basin.

Net Primary Production is defined as total photosynthesis minus respiration. The Net Primary Production values of the Earth's major ecological regions (after Rodin et al., 1975) are summarized in Table 7 [The study area is a small part of the Temperate ecological zone].

Table 7 Net primary production values of the Earth's major ecological regions

Zone	Area (106 km <sup>2</sup> )	Mass of Plants (106 tonnes)	Primary Production (106 tonnes C)
Polar	8.1	13.8	1.3
Coniferous forests	23.2	439.1	15.2
Temperate	22.5	278.7	18.0
Subtropical	24.3	323.9	34.6
Tropical	55.9	1347.1	102.5
Total land	133.9	2402.5	171.5
Glaciers	13.9	0.0	0.0
Lakes and rivers	2.0	0.04	1.0
Total continents	149.3	2402.5	172.5
Oceans	361.0	0.2	60.0
Earth's total	510.3	2402.7	232.5

## HYDROSPHERE

In many ways the hydrosphere ties and links the earth processes occurring in the atmosphere, lithosphere, pedosphere, and biosphere together. As I had earlier, the hydrosphere discussion will begin with a global perspective. The oceans are by far the

most dominant reservoir for water on the Earth's surface accounting for 99.9 percent of the total (Table 8).

Table 8 Reservoirs of water (from Butcher *et al.*, 1992), units are  $10^{18}$  g  $H_2O$  (burdens) and  $10^{18}$  g  $H_2O$ /year (fluxes)

Oceans	=	1,370,000
Ocean Evaporation	=	383
Ocean Precipitation	=	347
Land Precipitation	=	99
Evapotranspiration	=	63
Runoff	=	36
Atmosphere	=	13
Total		<u>1,370,941</u>

### **Solute**

Water forms a very important solvent for many chemical species. Water has even been called “the universal solvent.” Water’s ability to serve as a highly effective solvent is due largely to the fact that water molecules are large and dipolar and have an ability to form hydrogen bonds (Butcher *et al.*, 1992).

### **Transport**

An important characteristic of water is its ability to function as a transport mechanism for soluble and non-soluble material. Commonly the by-products of erosion and weathering are eventually transported to the ocean reservoir via surface streams. The hydrosphere’s significant role in transporting weathering products cannot be underestimated.

## **Evapotranspiration**

The evaporation of water is the largest transfer of energy from the surface of the Earth to the atmosphere (Butcher *et al.*, 1992); therefore, its role in hydrogeochemical cycles cannot be understated. One common means of measuring evaporation is with the National Oceanic and Atmospheric Administration (NOAA) evaporation pan. However, evaporation pan measurements typically overestimate lake evaporation (Lee and Swancar, 1996), and a correction factor is commonly used. The energy-budget and mass-transfer methods are two theoretically based techniques used to estimate evaporation.

## **Subpart B: KARST PROCESSES**

Various authors, including Ford and Williams (1989), reported that the majority of carbonate dissolution within karst terrains occurs within the epikarst (surface and near surface) zone. This information coupled with an understanding of carbonate dissociation and acid creation depicted above might lead a person to believe that karst dissolution only lowers, on a continuing basis, the carbonate landscape surface. With this information alone, dissolution type caves within karst would not exist. Such caves however are the most common type of cave; therefore, there is more to the story. Many, if not most, carbonate rocks contain either large or minute cracks, joints, fissures, fractures, bedding planes, and faults. These structures provide an avenue for corrosive (acid) water to penetrate and dissolve limestone beyond the surface and epikarst zones. Furthermore, as dissolution occurs along one of these features, the feature becomes larger and thus allows more water to penetrate. In addition, once one of these growing karst conduits becomes large enough (approximately 1 cm in diameter (White, 1988)) turbulent flow commences.

Turbulent flow may or may not aid in the dissolution process, but it does aid in mechanical weathering and sediment transport. Although the majority of dissolution occurs in the epikarst, as karst waters become closer to saturation with respect to calcite, there is still enough aggressiveness to the water to create and enlarge these karst conduits, which eventually become known as caves. One factor contributing to extensive dissolution-type cave development is for the cave conduit to grow at a sufficiently fast rate in comparison to the rate of surface lowering. Rapid surface lowering and surface erosion may dissolve and remove slow developing proto cave passages before the cave becomes extensive. For that reason many caves are located below non-carbonate caprock. In these situations, the surface non-carbonate rocks (in the case of the Mammoth Cave region, it is sandstone, shale and conglomerate) provide partial protection to the underlying carbonate rock which continues to have its conduits enlarge from the discrete water entry points through the surface caprock material.

### PART III LITERATURE REVIEW

#### **Subpart A: STREAM CHEMISTRY**

Like Likens and Bormann (1995), I am assuming that the streams contain a mixture of both surface water and groundwater sources. Stream water chemistry is also a reflection of these two sources of water. Stream water chemistry varies depending upon a variety of factors such as geology, precipitation, and season. Likens and Bormann (1995), while studying streams in New Hampshire, found that stream water chemistry was fairly constant, independent of stream water discharge. Johnson and Swank (1973) found similar results in their North Carolina study. Likens and Bormann (1995) maintained that this is caused by stream water chemistry being largely established in the soil zones within eastern deciduous forests containing granitic bedrock. In these situations, chemical equilibrium is reached quickly in the soil zone, based upon the ecological conditions of the watershed. Therefore, the chemistry of a headwater-type stream is the product of the natural ecosystem. Although the chemistry may be altered by disturbances, the natural condition of the ecosystem forms the basis of stream water chemistry in eastern deciduous forests containing granitic rocks. While the streams in this study are within eastern deciduous forests, they are dominated by sedimentary rocks, and not igneous. Additionally Stumm and Morgan (1970) have demonstrated that high rates of dissolution of carbonate rocks, compared with granitic rocks, produces a much more varied stream water chemistry regime and one that is much more influenced by discharge (Ford and Williams, 1989). Before discussing these similarities and differences further, we should first look at the individual ions commonly found in

streams. The nature and characteristics of dissolved components within streams that are relevant to this study are discussed below:

### **Carbon**

In spite of carbonate rocks, including carbonate karst terrains, being globally the largest reservoir of carbon, this reservoir is commonly not included in global carbon cycle models due to the assumption that the fluxes to and from this reservoir are insignificant given the time frame that most of these models utilize (Holmén, 1992). However, karst terrain is largely a factor, through carbonate dissolution, of the release of carbon from these reservoirs into streams and groundwater which then becomes available to participate in global processes. Since twelve percent of the Earth's ice-free land surface contains karst (Ford and Williams, 1989), perhaps through karst processes, carbon within this large carbonate reservoir plays a larger role in global processes than what many of these models account for.

There are four main reservoirs of carbon: the atmosphere, biosphere, lithosphere and the ocean. These reservoirs and the common fluxes between them are depicted in Figure 3. The largest source of carbon within the lithosphere reservoir is contained within terrestrial carbonates, such as  $\text{CaCO}_3$  (calcite/aragonite) and  $\text{CaMg}(\text{CO}_3)_2$  (dolomite) (Butcher *et al.*, 1992).

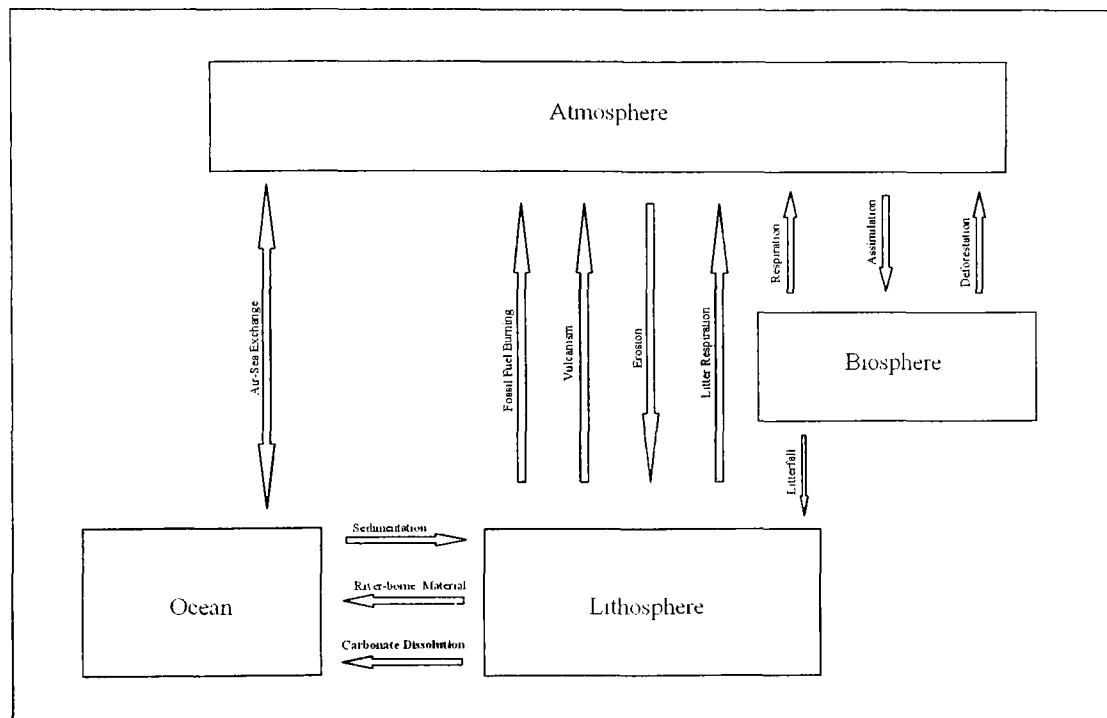


Figure 3 Major reservoirs and fluxes of the global carbon cycle (modified and adapted from Butcher *et al.*, 1992)

Carbon is the key element of life on Earth (Butcher *et al.*, 1992). Although it is an abundant element on Earth, elementary carbon (consisting of three forms- amorphous carbon, diamond and graphite) is rare. Carbon can exist in oxidation states ranging from +4 to -4; however, the most common is +4. The carbon found in CO<sub>2</sub> and carbonate rocks is in the +4 oxidation state. Methane (CH<sub>4</sub>), formed by the reduction of carbon, is in the -4 oxidation state.

Although there are seven isotopes of carbon, only two (<sup>12</sup>C and <sup>13</sup>C) are of significance to the carbon cycle. <sup>12</sup>C is by far the most common carbon isotope, accounting for 99 percent of the total carbon in nature (Butcher, Charlson, Orians, and Wolfe, 1992). The other five isotopes are radioactive and unstable within natural

systems. In addition, the half-life of these elements is much shorter than the turnover time of carbonate rock carbon reservoirs (Table 9); therefore, carbonate rocks typically contain no radioactive carbon isotopes.

Carbon dioxide fixation consists of the conversion of  $\text{CO}_2$  to organic material. This fixation process is conducted by photosynthetic organisms (i.e., plants, algae, bacteria), and chemoautotrophic organisms (i.e., nitrifying bacteria, some sulfur oxidizers, iron oxidizers, and hydrogen oxidizers) (Butcher *et al.*, 1992).

Aerobic respiration consists of the conversion of organic material and  $\text{O}_2$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This process is conducted by plants, animals and strictly aerobic microbes (Butcher *et al.*, 1992). Organic decomposition consists of the conversion of organic carbon and  $\text{O}_2$  to inorganic forms. This process is conducted by microorganisms, especially fungi and bacteria (Butcher *et al.*, 1992).

Methane is produced by the conversion of  $\text{CO}_2$  and  $\text{H}_2$  (or simple organic compounds such as acetate) to  $\text{CH}_4$  and  $\text{H}_2\text{O}$ . This process is conducted by methane producing bacteria (Butcher *et al.*, 1992). The energy is derived from the oxidation of simple organic compounds.



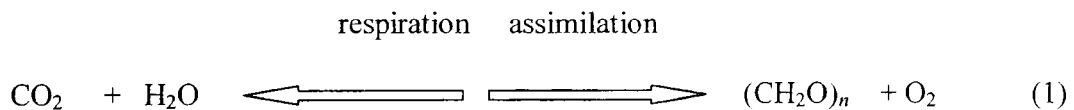
Table 9 Principal reservoirs and fluxes in the carbon cycle. Units are  $10^{15}$  g C (burdens) and  $10^{15}$  g C/year (fluxes). From Bolin (1986), In: *Butcher, et al.*, 1992.

Reservoirs	
Fossil Fuels	5,000 to 10,000
Intermediate and Deep Ocean	
Dissolved inorganic	36,700
Dissolved organic	975
Annual increase	~2.5
Soil	1,300 to 1,400
Atmosphere	725
Annual increase	~3
Surface water (fresh)	
Dissolved inorganic	700
Dissolved organic	25
Annual increase	~0.3
Long-lived terrestrial biota	~450
Annual decrease	~1
Peat	~160
Short-lived terrestrial biota	~110
Litter	~60
Surface oceanic biota	3
Fluxes	
Atmosphere to land	~120
Atmosphere to ocean surface	~ 93
Ocean surface to atmosphere	~ 90
Ocean surface to intermediate and deep ocean	~ 38
Ocean surface to ocean surface biota (primary production)	~ 40
Ocean surface biota to ocean surface (respiration & decomposition)	~ 36
Ocean surface biota to intermediate and deep ocean (detritus)	~ 4
Intermediate and deep ocean to ocean surface	~ 40
Fossil fuels to atmosphere	5
Short-lived terrestrial biota to atmosphere	~ 60
Short-lived terrestrial biota to ocean surface	~ 1
Short-lived terrestrial biota to long-lived terrestrial biota	~ 15
Short-lived terrestrial biota to litter	~ 40
Long-lived terrestrial biota to atmosphere (deforestation)	~ 1
Long-lived terrestrial biota to litter	~ 15
Litter to atmosphere (detritus decomposition)	54-50
Litter to peat	<1
Litter to soil	2-5
Peat to atmosphere	<1
Soil to atmosphere	2-5

Water in equilibrium with atmospheric  $\text{CO}_2$  at 25 degrees C has a pH of 5.65 (Butcher *et al.*, 1992). The partial pressure of  $\text{CO}_2$  within soil varies dramatically and

may be from 10 to 400 times greater than in the atmosphere (Holland, 1978). If the soil CO<sub>2</sub> partial pressure is ten times atmospheric levels, soil water pH would be 5.15. If the soil CO<sub>2</sub> partial pressure is 100 times atmospheric levels, soil water pH would be expected to be 5.15 and 4.65, respectively (Butcher *et al.*, 1992). The addition of other acids, such as organic acids, can also complicate these relationships. Therefore, one could see how dramatically the degree of acidification, and thereby its ability to dissolve rocks, is affected by the quantity of CO<sub>2</sub> derived from the soil. Complicating these relationships, the partial pressure of soil CO<sub>2</sub> varies greatly temporally and spatially. In addition, the partial pressure of soil CO<sub>2</sub> is difficult to measure accurately.

Sources of carbon include biota, the weathering of rocks, and the atmosphere. Carbon in the atmosphere exists primarily as CO<sub>2</sub>. Biologic uptake and storage of carbon is accomplished via photosynthesis. Through this process, atmospheric CO<sub>2</sub> is reduced by photosynthetic organisms and converted to a wide variety of organic substances that are stored in the plant tissues. This process is represented by the following equation:



When plants die or drop their leaves, this material is incorporated into the soil and becomes part of the pedosphere. Soil organic matter is primarily carbon, oxygen and hydrogen (Butcher *et al.*, 1992). Soil organic material near the surface generally contains an abundance of microorganisms. The metabolism of these organisms consumes soil

oxygen and produces carbon dioxide. As a consequence, the carbon dioxide partial pressure may be 10 to 100 times greater than the atmosphere (Holland, 1978). Water passing through the soil picks up this additional carbon dioxide, thus increasing its acidity.

To some degree all rocks and minerals can be dissolved (Jakucs, 1977), given either a strong enough acid or else by allowing sufficient time for a weak acid to proceed slowly. As regards rocks specifically, dissolution is a degenerative process that erodes the landscape and carries material to the ocean; therefore, in order for dissolution to be an important process on the landscape, there must be some rock types or environmental conditions in which the solution process outpaces not only rock-forming processes but also other rock degenerative processes.

If a particular rock or mineral type dissolves too slowly under natural conditions then it is unlikely that the solution process would play a significant role in natural geomorphic processes since other geomorphic processes would overwhelm and mask the minor contribution from dissolution. For instance, the majority of rocks on the earth's surface are silica-based. With a few exceptions, at the pH (acidity) of most natural waters, most silica-based rocks dissolve too slowly to be a significant factor in geomorphic processes.

On the opposite extreme, there are limiting factors if a particular rock or mineral type dissolves too quickly under natural conditions. For instance, sodium chloride

(halite) dissolves rapidly under natural conditions- too rapidly for it to play a dominant role in surface geomorphic processes except for a few extremely arid locations. If a buried layer of salt is exposed to degenerative processes on the earth's surface, in humid conditions the exposed salt dissolves so rapidly that its presence on the surface is so transitory that its influence upon the landscape is negligible, except under extreme conditions. Under very dry surface environments can one possibly find surface exposures of salt. In these extremely dry environments, one can find salt caves and karst features within the salt. There are salt caves in Israel, the former USSR, Rumania, Spain, Algeria, Hungary, and Chile (Frumkin, nd). However, there are no known natural surficial salt caves in the United States.

Within the dissolution continuum between silica on one extreme and evaporates on the other, there are particular rocks types that dissolve fast enough to outpace other degenerative processes while at the same time dissolve slowly enough that they are retained long enough on the surface that they may interact and affect other surface geomorphic processes. Limestone, composed mostly of the mineral calcite, is perhaps the most ideal rock type along this dissolution continuum. Limestone's frequency of occurrence coupled with its position along the dissolution continuum makes it a particularly ideal rock type for speleogenesis.

Limestone is not very soluble in pure water (Ford and Williams, 1989). However, limestone is highly soluble in even weak acids. The most abundant acid in natural water is carbonic acid (White, 1988). A weak carbonic acid solution is formed by placing

water in contact with carbon dioxide. Since carbon dioxide is a constituent of the atmosphere, and is respired by living organisms, as well as carbon being contained in many rocks and minerals, it is perhaps easy to see why carbonic acid is the most abundant acid in natural water (White, 1988). Therefore, limestone solution rates are closely related to the availability of carbon dioxide to coming in contact with water to form carbonic acid.

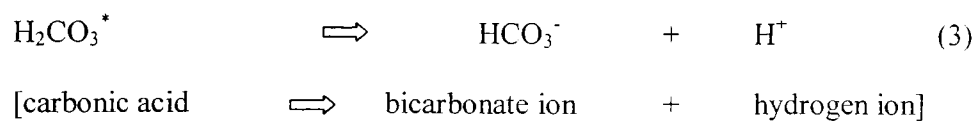
Within any natural karst system, carbon dioxide can be dissolved by water causing the water to become more acidic, or carbon dioxide may be released from the water, making it less acidic. There are many factors affecting the degree and rate of carbon dioxide gains and losses as water passes through a karst system. The term utilized to describe these carbon gains and losses within a given area is carbon flux. Since carbonic acid is the primary solvent of limestone, knowledge and an understanding of mechanisms that affect carbon flux within a karst system is important in any study of limestone solution and the evolution, growth and development of cave and karst systems.

Weak acids such as carbonic acid are abundant in the natural environment. Water on the earth's surface, groundwater and atmospheric water are in almost constant contact with atmospheric carbon dioxide (the principal 'greenhouse' gas, believed to be responsible for global-warming). Carbon dioxide ( $\text{CO}_2$ ) is absorbed by water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ). Carbonic acid, although a relatively weak acid under environmental conditions, is very effective in dissolving limestone. It is primarily a three-step chemical process. The first step involves the absorption of carbon dioxide to

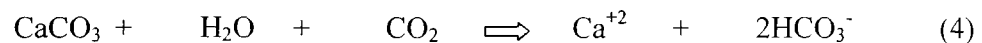
form positively and negatively charged ions in solution. The chemical equation for this process is as follows:



Where  $\text{H}_2\text{CO}_3^*$  is the sum of aqueous  $\text{CO}_2$ . Carbonic acid in turn, can dissociate to form separate ions, as depicted below in the second step:



The hydrogen ion makes the solution acidic, and in fact, pH is a measurement of the amount of hydrogen ions in solution. Ionic hydrogen is the primary factor that dissolves limestone. The final step in this process is listed below:

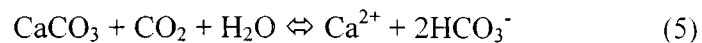


The above equation illustrates carbonate dissociation reactions involving limestone dissolution. A similar chemical process is also involved in the dissolution of dolostone (dolomite), however it differs due to the presence of a magnesium ( $\text{CaMg}(\text{CO}_3)_2$ ) atom within the mineral structure.

In these chemical processes, hydrogen ions (which make the solution acidic) combine with bicarbonate ions, thereby raising the pH, and making the solution more basic. Eventually the solution becomes saturated with respect to calcite.

## Calcium

Calcium is the fifth most abundance element in the earth's crust (Weast and Astle, 1982). It is essential for many biologic processes, being needed for many leaves, bones, teeth and shells (Weast and Astle, 1982). Calcium ions typically are derived from carbonate rocks (Hem, 1989), but also may originate from amphiboles, feldspar, olivine, pyroxenes, and clays (Pagenkopf, 1978). The solution of calcite follows the following chemical equation depicted in equation 5 (Stumm and Morgan, 1970).



It is important to realize that along with this dominant calcite dissolution reaction, there are other dissolution reaction products involving chemical species such as  $\text{H}_2\text{CO}_3$ ,  $\text{CO}_3^{2-}$ , and  $\text{CO}_2$  (aq) that are also occurring simultaneously, in varying degrees of importance under natural environmental conditions. Sources of calcium include the atmosphere and the weathering of rocks, particularly carbonate rocks.

## Bicarbonate

One of the most important constituents of carbonate dissolution is bicarbonate ( $\text{HCO}_3^-$ ). The actual dissolution process is discussed earlier. The presence of high concentrations of bicarbonate is one of the signatures of the dissolution process and a “karst water” (White, 1988). Alkalinity is defined as the sum of bicarbonate, carbonate, and hydroxide ion concentrations minus the hydrogen ion concentration. My study

measured bicarbonate ion concentration by the determination of alkalinity, expressed as  $\text{CaCO}_3$ .

### **Magnesium**

Magnesium ( $\text{Mg}^{2+}$ ) is the eighth most abundant element in the earth's crust (Weast and Astle, 1982). It is not found in nature uncombined, but rather occurs within dolostone or magnesite (Weast and Astle, 1982). Magnesium typically is derived from carbonate rocks, usually dolostone (Hem, 1989).

### **Hydrogen**

In natural waters the hydrogen ion ( $\text{H}^+$ ) is responsible for water's acidity. The sources of the hydrogen ion include volcanic gases, the combustion of fossil fuels, natural oxidation processes (such as the oxidation of the ferrous ion to the ferric ion) (Hem, 1989).

### **Silicon**

Silicon is the second most abundant element in the Earth's crust. The silica ion ( $\text{Si}^{4+}$ ) bonds well with oxygen; therefore, it is very stable and does not readily occur in ionized forms in natural waters (Hem, 1989). Silica in natural waters most readily exists in the non-ionized form  $\text{SiO}_2$ ,  $\text{H}_4\text{SiO}_4$  or  $\text{Si}(\text{OH})_4$ , however, convention often refers to these three forms as just  $\text{SiO}_2$  (Hem, 1989).



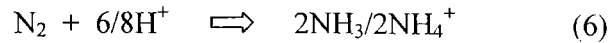
Silicon is a common component of quartz and many sandstones. The dissolution rate for silicon is typically low. Therefore, silica concentrations in natural waters typically range from 1 to 30 mg/L; but may be higher in some groundwaters (Hem, 1989). Silica is not analyzed as part of this study.

## **Nitrogen**

Nitrogen is the most abundant element in the Earth's atmosphere. It is also an essential nutrient to plant life. Nitrogen exists in the Earth's crustal, terrestrial, oceanic and atmospheric systems. On a global average, four percent of the Earth's nitrogen exists as organic terrestrial nitrogen and 6.5 percent as inorganic terrestrial nitrogen (Butcher *et al.*, 1992). Dissolved N<sub>2</sub> is the primary form of oceanic nitrogen. Nitrogen gas (N<sub>2</sub>) is the primary form of atmospheric nitrogen.

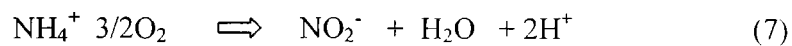
Nitrogen can exist in oxidation states ranging from +5 to -3. A significant percentage of the total reduced nitrogen contained in the atmosphere exists as the ammonium ion. Nitrogen also exists in nature in the form of proteins. Proteins are polymers of amino acids. The dominant forms of nitrogen discussed in this report are N<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>O, NH<sub>3</sub><sup>+</sup>, and NH<sub>4</sub><sup>+</sup>.

Nitrogen fixation consists of converting N<sub>2</sub> to the organic amino group. This Nitrogen fixation is conducted by free-living prokaryotes: *Azotobacter* spp., some *Clostridium* spp., some *Cyanobacteria*, and photosynthetic bacteria (Butcher *et al.*, 1992) in a process represented by the following equation:



Nitrogen that has been fixed has two primary outcomes: it can be oxidized to  $\text{NO}_2^-$ , or  $\text{NO}_3^-$ , or it can be assimilated into an organism (Butcher *et al.*, 1992). In each situation, these dissolved forms of nitrogen either may be stored in the basin or be flushed from watershed via streams.

Nitrification consists of converting  $\text{NH}_3$  to  $\text{NO}_2^-$  and  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , as depicted in the following two equations:



Nitrification is conducted by chemoautotrophic nitrifying bacteria (Butcher *et al.*, 1992). The energy source is the oxidation of inorganic nitrogen compounds such as nitrite and ammonia.

McGarity and Rajaratnam (1973), referencing Arefyeva and Kolesnikof (1964), demonstrated that the freezing and thawing of soils promotes nitrification and the mobilization of nitrate into streams. This seasonal increase in nitrate mobilization is one reason that nitrate concentrations in streams typically reach a maximum in late winter (Likens and Bormann, 1995).

Dissimilatory denitrification (the reduction of nitrate to amino acids to be incorporated into proteins) converts  $\text{NO}_3^-$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$ . This process can be conducted

primarily by anaerobic respiring bacteria (Butcher *et al.*, 1992). Energy is derived from the oxidation of anaerobic organic compounds. Ammonification is the conversion of organic nitrogen to  $\text{NH}_3$ . Many microbes, especially bacteria, can conduct ammonification (Butcher *et al.*, 1992).

From an analytical standpoint, nitrogen can be in four forms: ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), and inorganic nitrogen (Allen and Kramer, 1972). Kjeldahl nitrogen is the sum of all ammonia and organic nitrogen (Allen and Kramer, 1972).

Most nitrogen loss from soil via leaching is in the form of nitrate (99 percent). Almost one percent that is lost is in the form of ammonium, and just a trace is in the form of nitrite (Pierre *et al.*, 1966). The reason for these differences is that ammonium is absorbed and retained by vegetation and the initial nitrite concentrations are typically quite low.

Nitrate ( $\text{NO}_3^-$ ) generally exists in natural surface waters in trace amounts, however concentrations may be high in some groundwater (American Public Health Association, 1995). It tends to be very stable and easily transported by water (Hem, 1989). Conversely, nitrite ( $\text{NO}_2^-$ ) and ammonium ( $\text{NH}_4^+$ ) are less stable and thereby less common in natural waters (Hem, 1989). Ammonium concentrations in groundwater tend to be low due to the molecule's ability to be readily absorbed by clay, sediment and soils (American Public Health Association, 1995). Nitrite and ammonium are more closely

associated with polluted waters since the primary sources involve industrial, wastewater, agricultural and other anthropomorphic operations. The USGS (1999) specifically lists karst as one of the risk factors for landscapes in which there is a greater potential for nitrate to enter groundwater. Anthropomorphic activities such as clear cutting forests, agricultural fertilization, and draining of wetlands can also produce high  $\text{NO}_3^-$ .

The presence of karst may influence a stream's velocity, and thus the residence time, within the basin, of an individual parcel of water. Kolpin and Kalkhoff (1991) and Hill (1988) found that biologic processes such as assimilation, denitrification and periphyton (Duff *et al.*, 1984) that remove nitrogen from a stream are affected by residence time. Therefore, the presence of karst that may reduce the stream's velocity which may ultimately cause a reduction in the stream's dissolved nitrogen concentrations (Kalkhoff, 1995). Only nitrate, nitrite and ammonium are analyzed as part of this study.

### **Chloride**

Although chloride ion can exist in various oxidation states ranging from  $\text{Cl}^-$  to  $\text{Cl}^{7+}$ , the  $\text{Cl}^-$  form known as chloride is by far the most abundant in natural waters (Hem, 1989). Some igneous rocks contain chlorine however it is usually more abundant within sedimentary rocks, particularly evaporites such as gypsum (Hem, 1989). Shale and other sedimentary rocks also contain small quantities of chlorine molecules.

Salt spray in the proximity of the ocean can be a significant source of chloride ions in natural water, however the concentrations decrease rapidly as one moves inland

(Hem, 1989). Gambel and Fisher (1966) and Fisher (1968) found concentrations of chloride ions in North Carolina streams much higher than could be attributed to atmospheric sources alone. They attributed this increased chloride concentrations on either the weathering of crystalline rocks or from human sources such as pollution or highway de-icing. Similar higher concentrations of chloride ions in waters in the western United States above and beyond expected atmospheric sources were found by Van Denburgh and Feth (1965) and Junge and Werby (1958). These additional sources were also attributed to the weathering of sedimentary rocks and from human sources. Industrial operations and wastewater can also be a significant source of chloride in natural waters (American Public Health Association, 1995).

### **Bromide**

Bromide can occur in rainwater and snow (Hem, 1989), but sea-spray and seawater intrusions are the dominate sources of bromide (American Public Health Association, 1995). Beyond close proximity to ocean water and salt spray, the main source of the bromide ion in the atmosphere appears to be from anthropomorphic sources (Hem, 1989). Oil field brines are also a potential source of bromine (American Public Health Association, 1995). There are operational oil fields within the Dry Branch basin.

### **Fluoride**

Low quantities of fluoride are found in a variety of rock types. Fluoride atoms within these rocks do not readily dissolve in the presence of water under typical environmental conditions (Hem, 1989). Therefore, fluoride typically is a minor

constituent of natural stream water. Brown and Roberson (1977) found that waters containing high calcium concentrations have lower concentrations of fluoride as a result of equilibrium and complexing effects.

### **Sodium**

Sodium occurs in natural waters in the  $\text{Na}^+$  oxidation state. The sodium ion is quite stable; therefore in the environment surrounding the project sites, it usually does not reprecipitate or form other mineral complexes (Hem, 1989). Sodium is contained in a variety of minerals, including feldspar (Pagenkopf, 1978); as a consequence, it is a typical constituent of natural stream water. However salts from winter de-icing and salts used in certain oil well operations can also be sources of sodium (Hem, 1989).

### **Potassium**

Like sodium, potassium is a rather common constituent of a variety of minerals, such as some feldspars and clays (Pagenkopf, 1978). In waters in contact with certain rocks such as sandstone, quartzite and dolostone, potassium concentrations may exceed that of sodium; however, potassium's abundance in natural stream water is usually less than sodium, due to potassium's tendency to be reincorporated into insoluble products, particularly clays. Additionally, potassium is an essential nutrient for most forms of vegetation. Therefore, generally there is more storage of potassium within biota than sodium (Hem, 1989), thereby lowering potassium's concentration in stream water relative to sodium.

## Iron

Although iron is abundant within the Earth's crust, it is a minor ion within natural waters (Hem, 1989). Where it does exist within natural waters, the  $\text{Fe}^{2+}$  ferrous ion is much more common than the  $\text{Fe}^{3+}$  ferric ion (Hem, 1989). Ferrous ions are more common within natural waters due to the fact that when ferric ions are exposed to oxygenated water with pH near 7.0 the ferric ion hydrolyzes, causing iron to precipitate as ferric oxide (Pagenkopf, 1978).

Under reducing conditions, iron exists in the ferrous state (American Public Health Association, 1995). The ferric ion is not very soluble (American Public Health Association, 1995). On exposure to air or oxygen rich waters, the ferrous ion is oxidized to the ferric state.

Many rocks and minerals contain iron. When in contact with water, iron can reprecipitate within other minerals such as hematite ( $\text{Fe}_2\text{O}_3$ ), siderite ( $\text{FeCO}_3$ ) and goethite ( $\text{FeOOH}$ ) (Hem, 1989). Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of iron released into the atmosphere was 0.39, meaning that anthropogenic sources are relatively minor when compared with natural sources.

The typical ionic forms of the ferric ion are  $\text{Fe}^{3+}$ ,  $\text{FeOH}^{2+}$ , or  $\text{Fe}(\text{OH})_2^+$ , while the typical form of the ferrous ion is  $\text{Fe}^{2+}$  (Hem, 1989). Higher concentrations of iron are usually found in groundwater in comparison with surface waters (American Public

Health Association, 1995); therefore, it could be a potential indicator of the source of the water (e.g., direct surface runoff versus groundwater).

### **Manganese**

Manganese occurs as a minor component of many rock types, including basalt, amphibole, limestone, and dolostone (Hem, 1989). Like iron, manganese commonly reprecipitates to form other minerals or clays. However it tends to be a little more stable, and is sometimes more common in natural waters than iron (Hem, 1989).

Manganese is typically a minor constituent of natural waters (Hem, 1989).

Although the manganese ion can exist in oxidation states ranging from  $Mn^{2+}$  to  $Mn^{4+}$ , the  $Mn^{2+}$  form is by far the most abundant in natural waters (Hem, 1989).

Domestic wastewater, industrial effluent (American Public Health Association, 1995) and certain mining operations (Hem, 1989) are also sources of manganese. However, Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of manganese on release into the atmosphere was 0.52, meaning that anthropogenic sources are nearly half as important as natural sources.

### **Aluminum**

Although aluminum is abundant within the Earth's crust (the third most abundant element in the Earth's crust), it is a minor ion within natural waters (Hem, 1989). Similar to iron, the pH of natural waters is typically too high for aluminum to exist in



concentrations much greater than a few tenths of a mg/liter (Hem, 1989). Feth and others (1964) found the maximum aluminum concentrations in runoff from granite surfaces to be only a few hundredths of a milligram per liter.

Many rock types, especially igneous rocks, contain aluminum. These include the feldspars, granites, mica, and amphiboles (Hem, 1989). During the weathering of rock, at the pH range most typical of natural waters, aluminum does not go into solution, but rather precipitates and forms other solid minerals or forms or bonds with clays and other sediments (Hem, 1989). Aluminum may also form complexes with fluoride ( $\text{AlF}^{2+}$ ), phosphate ( $\text{AlPO}_4$ ) and sulfate ( $\text{AlSO}_4^+$ ). Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of aluminum release into the atmosphere was 0.15, meaning that anthropogenic sources are relatively minor when compared with natural sources. Aluminum is not analyzed as part of this study.

### **Lithium**

Several minerals contain lithium. It can also be substituted for magnesium within individual minerals (Hem, 1989). The common-ion exchange minerals typically found in soils absorb lithium to a lesser degree than other common elements (Hem, 1989). Therefore, lithium tends to stay in solution longer than other common ions.

### **Phosphorus**

Phosphorus is generally thought to be limiting for the majority of vegetative biomass. Some phosphorus originates from the weathering of bedrock, especially

sedimentary rocks. However, this trend or relationship can be masked or overwhelmed by anthropomorphic sources, principally from agricultural areas. Additionally, airborne particulate phosphorus sources may be significant in some areas, particularly from industrial regions. Often, these anthropomorphic sources are so high that it is often meaningless to predict the geologic sources of stream water phosphorus except for very isolated and uninhabited regions (Gibson, 1997).

From an analytical standpoint, there are three forms of phosphorus: soluble orthophosphate, inorganic phosphate, and total phosphorus (Allen and Kramer, 1972). Total phosphorus consists of both soluble orthophosphate and inorganic phosphate (Allen and Kramer, 1972).

Phosphorus is an essential element for the growth of most plant life forms, and it has been found to be a leading factor in limiting primary production within many ecosystems (Schindler, 1977; Smith *et al.*, 1986). The largest natural source of phosphorus within a watershed is the weathering of rocks. Direct anthropogenic sources such as livestock wastes, detergents, fertilizers and other industrial applications can affect localized and regional phosphorus concentrations within surface and groundwaters (Butcher *et al.*, 1992). Walker (1933) found that the available phosphorus content of the soils within Mammoth Cave National Park, while all low, were higher for the soils overlying carbonate rocks.

Phosphorus never is found free in nature, although it is widely distributed in a variety of minerals (Weast and Astle, 1982), including igneous and carbonate rocks (Butcher *et al.*, 1992). The atmosphere plays a minor role in the transport and storage of phosphorus, due to the limited gaseous forms of phosphorus (Butcher *et al.*, 1992).

Within the biosphere, phosphorus consists primarily of inorganic or organic phosphate (Butcher *et al.*, 1992). Being nonvolatile, phosphorus is not readily transported to the atmosphere, but instead is transported to other reservoirs by soil processes and water (Butcher *et al.*, 1992). "Microorganisms are able to store phosphate as a polymer inside their cells" (Butcher *et al.*, 1992). Phosphorus usually exists in natural water in the form of phosphate ( $\text{PO}_4^{3-}$ ). Only the phosphate form ( $\text{PO}_4^{3-}$ ) is analyzed as part of this study.

## **Sulfur**

Sulfur is an abundant element on Earth and essential to numerous organic and inorganic processes. Sulfur can exist in oxidation states ranging from -2 to +6. The most oxidized state,  $\text{SO}_4^{2-}$  is the most abundant anion in rivers, next to the bicarbonate ( $\text{HCO}_3^-$ ) ion and the most abundant anion in the ocean next to  $\text{Cl}^-$ . The  $\text{SO}_4^{2-}$  ion is also one of the primary causes of acidity in natural waters (Butcher *et al.*, 1992).

Sulfur oxidation consists of the conversion of  $\text{H}_2\text{S}$  to  $\text{S}$ ,  $\text{S}$  to  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_4^{2-}$ . Sulfur oxidation is conducted by purple and green sulfur photosynthetic bacteria, and some cyanobacteria (Butcher *et al.*, 1992).

Dissimilatory sulfate (the reduction of sulfate to the sulfhydryl level where it is incorporated into the sulfur amino acids of proteins) is the conversion of  $\text{SO}_4^{2-}$  to  $\text{H}_2\text{S}$ . This process is conducted by sulfate reducing bacteria (Butcher *et al.*, 1992). Dimethyl sulfide production is the conversion of  $\text{SO}_4^{2-}$  to  $(\text{CH}_3)_2\text{S}$ . This process is conducted in the oceans by certain marine algae (Butcher *et al.*, 1992). Sulfate concentrations typically reach a minimum within late winter (Likens and Bormann, 1995).

The largest sulfur reservoir is the lithosphere; however since this residence time is quite long, the hydrosphere, atmosphere and biosphere are where most sulfur transfer occurs (Butcher *et al.*, 1992). The burning of sulfur-containing fossil fuels causes sulfur to oxidize thus forming  $\text{SO}_2$  gas. Due to the nature of the kinetics of this reaction and the frequency of precipitation, the residence time for this gas in the atmosphere is on the order of days. Therefore, the concentration and distribution of the  $\text{SO}_2$  gas in the atmosphere is largely local and regional in effect (Butcher *et al.*, 1992).

Sulfur is widespread in many rock types, particularly igneous and sedimentary rocks (Hem, 1989). However, sulfur in its reduced forms are fairly insoluble. When rocks containing reduced forms of sulfur weather and oxidize as a result of being exposed to oxygenated water, then these oxidized sulfur forms readily dissolve and go into solution. The mineral pyrite is commonly a source. A major source of sulfate in natural waters is from the atmosphere as a result of human's combustion of fossil fuels. Only the sulfate form ( $\text{SO}_4^{2-}$ ) is analyzed as part of this study.

## Bicarbonate

Alkalinity is defined as water's ability to neutralize acid. In most natural waters, alkalinity is largely a function of the combined carbonate and bicarbonate species (Hem, 1989). These species may be differentiated by calculation, based upon the water's temperature and pH; however within the pH range normally encountered in natural waters, the dominant species accounting for alkalinity is the bicarbonate ion (Hem, 1989) (Figure 4).

The primary source of bicarbonate ion is the atmosphere, carbon enriched soils and carbonate rocks. However, other sources include outgas from the Earth's mantle and the decarboxylation of acetate and other short-chain aliphatic acids within and near oil and gas fields (Hem, 1989).

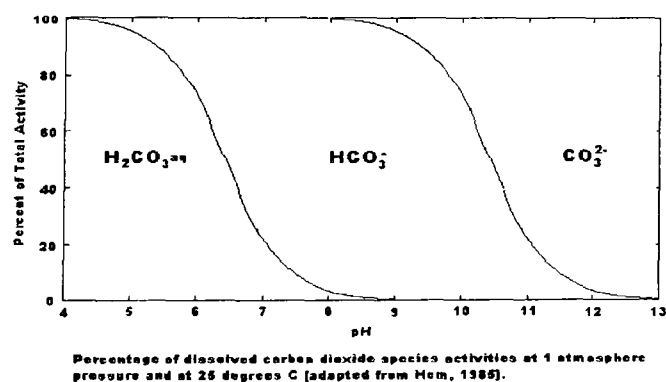


Figure 4 CO<sub>2</sub> species distribution diagram

## Copper

Copper occur in water in either the cuprous ion ( $\text{Cu}^+$ ) or the cupric ion ( $\text{Cu}^{2+}$ ) oxidation states; however its ability to disproportionate ( $2\text{Cu}^+ \Rightarrow \text{Cu}^0 + \text{Cu}^{2+}$ ) thereby favors the more oxidized state ( $\text{Cu}^{2+}$ ) (Hem, 1989). Copper concentrations in waters greater than a few hundreds of a milligram per liter are potentially harmful to many fish species (Hem, 1989).

The atmospheric source of copper ions is largely from solid particulate matter resulting from fossil fuel burning and certain smelting operations (Butcher *et al.*, 1992). These airborne particulates are mostly in the form of copper carbonates, sulfate hydroxides and oxides. Of these particulates, approximately 50 percent have been found to be soluble, depending upon the pH of rainwater. Since the quantity of particulate matter able to dissolve is dependent upon the pH of the precipitation, the concentrations of copper ions in precipitation can vary widely, especially locally (Butcher *et al.*, 1992).

The cupric ion is among the most strongly sorbing of the heavy metals; thus it sorbs onto both organic and inorganic solids such as oxides and clays (Butcher *et al.*, 1992). Natural complexing agents can bind  $\text{Cu}^{2+}$  so strongly that nearly all copper remains bonded to organic matter. Therefore, the  $\text{Cu}^{2+}$  sorbs only under conditions in which organics sorbs (Butcher *et al.*, 1992). One could therefore infer that if  $\text{Cu}^{2+}$  is present in natural waters that some organic acids may also exist.

Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of copper release into the atmosphere was 13.6, meaning that anthropogenic sources are greater than natural sources.

### **Nickel**

Nickel primarily exists in the  $\text{Ni}^{2+}$  oxidation state (Hem, 1989). Nickel exists as a minor constituent of minerals; since it is used in a variety of industrial applications, it exists in wastewater and other byproducts. Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of nickel release into the atmosphere was 3.5, meaning that anthropogenic sources are greater than natural sources.

### **Zinc**

Sources of zinc in natural waters are largely from industrial operations and contamination (American Public Health Association, 1995). Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of zinc released into the atmosphere was 23.5, meaning that anthropogenic sources are greater than natural sources. Of the ions analyzed as part of this study, zinc has the highest anthropogenic/natural ratio, thereby indicating the dominance of the anthropogenic sources.

### **Cobalt**

Cobalt can occur in either 2+ or 3+ oxidation states. Co precipitation or adsorption of cobalt by oxides of manganese and iron appear to be important in

determining the concentration of dissolved cobalt in natural waters (Hem, 1989). Cobalt is only a minor constituent of carbonate rocks (Graf, 1962).

Natural waters contaminated with wastewater may contain high concentrations of cobalt (American Public Health Association, 1995). Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of cobalt released into the atmosphere was 0.63, meaning that anthropogenic sources are slightly more than half as important as natural sources.

### **Cadmium**

Cadmium is commonly found in low concentrations in the natural environment. It can enter the atmosphere because of certain industrial processes and by the combustion of fossil fuels (Hem, 1989), or via industrial discharges (American Public Health Association, 1995).

Lantzy and Mackenzie (1979) found that anthropogenic/natural ratio of cadmium release into the atmosphere was 19.0, meaning that anthropogenic sources are greater than natural sources. Of the ions analyzed as part of this study, only zinc had a higher anthropogenic/natural ratio. The indication is that anthropogenic sources dominate in comparison to natural sources of cadmium.



## **Subpart B: STUDY AREA BACKGROUND INFORMATION**

The Mammoth Cave karst is one of the most heavily investigated karst systems in the world. Modern karst research within the Mammoth Cave region began with Davis (1930), Swinnerton (1932) and Bretz (1942). These researchers were primarily concerned with explaining the theory of cave origin. Modern hydrologic research really began with the set of geologic maps and other water resource investigations produced in the 1960s and 1970s (e.g., Brown and Lambert, 1963; Cushman *et al.*, 1965; Brown, 1966; and Lambert, 1976). Additionally, Thraikill (Thraikill, 1968; Thraikill, 1972; and Thraikill and Robl, 1981) conducted a variety of karst hydrologic research for the Mammoth Cave and Central Kentucky karst region, some focusing upon evapotranspiration.

Perhaps the most extensive dye-tracing project in the world was conducted by Quinlan and Ray (1989) within the Mammoth Cave region during the 1970s and 1980s. These dye traces and others are depicted on the hydrologic maps produced by Ray and Currens (1998). However, the majority of this research focused on the Mammoth Cave system. There are many small-to-large watersheds basins within the Mammoth Cave region that are not part of the Mammoth Cave hydrologic system. Additionally, extensive dye tracing has occurred in many of the basins within Mammoth Cave National Park located north of the Green River (Meiman and Ryan, 1990-94).

Palmer (1981, 1999) provided some of the most detailed mapping of the stratigraphy of the various geologic units within Mammoth Cave National Park.

A few researchers, such as Hess (1974) and Hess and White (1988), have investigated karst geochemical effects as a function of spatial and temporal changes. Shuster and White (1971), for example, investigated the seasonal fluctuations of the geochemistry of a karst aquifer in Pennsylvania.

Hem (1989) found that although weathering of rocks within a basin is an important aspect of the resulting chemical composition of surface waters, a direct relationship is complicated by various factors, including the many independent variables that are at play within a basin. Although clear relationships often cannot be made between the rock types within a basin and the dissolved minerals in surface streams, some generalizations can be made (Hem, 1989). For example, Horn and Adams (1966) found that the average composition of siliclastic sandstone includes 35.9 percent silica versus only 0.0034 percent within carbonate rocks. Similarly, siliclastic sandstone contained on average 0.387 percent sodium, while carbonate rocks contained 0.0393 percent. Conversely, carbonates contained on average 4.53 percent of magnesium compared with 0.81 percent for siliclastic sandstone. Additionally, Weller (1927) detailed mineral compositions of the various rock units that exist within the study area during his geologic reconnaissance of Edmonson County, Kentucky.

Likens and Bormann in 1963 initiated a long-term watershed-scale biogeochemical flux study in Hubbard Brook Ecosystem Study in the White Mountains of New Hampshire (Likens and Bormann, 1995). This project quantified the mineral and

nutrient inputs into, and output from, a non-karstic basin and investigated the long-term trends in the cycling and total fluxes of these constituents (Table 10). They arrived at several important conclusions. Among these are:

- precipitation provides an important source of mineral inputs into the basin;
- forests acted as a filter for atmospheric pollutants, especially H, N, S and P;
- evapotranspiration was relatively constant over a wide range of precipitation and environmental conditions, and served to regulate certain aspects of the hydrologic cycle;
- stream-water chemistry was highly predictable, based upon given environmental conditions. Although it was recognized in this study that fixed-time series type of monitoring schedules do not accurately represent actual conditions for highly variable parameters, it was found that while stream-water chemistry did vary with the seasons, the short-term fluctuations were so small that bi-weekly or even monthly sampling was sufficient to characterize the chemistry of that (non-karst) system;
- the output of most individual nutrients can be closely predicted from the annual output of water alone;
- many of the minerals and nutrients within the basin, when comparing the total input (such as from precipitation or the weathering of rocks) into the basin's streams versus the total dissolved output being removed from the basin by the basin's streams, experienced some form of net gain or loss;
- Dissolved species experiencing net losses include Si, Ca, Na, Al, Mg, and K. Net gains were found for C, N, S, P and Cl;

- the input/output budgets for many (non-karst) vegetated watersheds throughout the world show many similar patterns as those of Hubbard Brook.

Table 10 Annual biogeochemical fluxes within Hubbard Brook, NH

	Hubbard Brook, NH (Likens & Bormann, 1995)- Annual mean kg/ha
Calcium:	
Input	2.2
Output	13.7
Net	-11.5
Magnesium:	
Input	0.6
Output	3.1
Net	-2.5
Potassium:	
Input	0.9
Output	1.9
Net	-1.0
Sodium:	
Input	1.6
Output	7.2
Net	-5.6
Aluminum:	
Input	Trace
Output	2.0
Net	-2.0
Ammonium:	
Input	2.9
Output	0.34
Net	2.6
Hydrogen:	
Input	0.96
Output	0.10
Net	0.86
Sulfate:	
Input	38.0
Output	52.8
Net	-14.8
Nitrate:	
Input	19.0
Output	16.1
Net	2.9
Chloride:	
Input	6.2
Output	4.6
Net	1.6
Phosphate:	
Input	0.11
Output	0.020
Net	0.09
Bicarbonate:	
Input	Trace
Output	7.7
Net	-7.7
Dissolved silica (SiO <sub>2</sub> ):	
Input	Trace
Output	37.7
Net	-37.7

Although Likens and Bormann (1995) found that the stream chemistry of Hubbard Brook did not greatly vary except with the seasons, so that the streams could be accurately characterized by even a once a month sampling schedule, this same approach does not appear to be the case for many karst systems. Since slightly acidic waters found in the natural environment can readily dissolve carbonate rocks, hydrologic conditions can rapidly cause noticeable chemical fluctuations within karst stream waters (White, 1988; Worthington, 1991; Groves and Meiman, 2000, 2001).

No hydrologic study has taken place in the First Creek basin. Studies conducted within Dry Branch have been related to either dye tracing (Ray and Currens, 1998) or hydrogeologic inventory and assessments of the potential threat posed by oil wells located within the basin adjacent to the park (Ek *et al.*, 1999 and 2000).

## PART IV    STUDY AREA

The study area consists of two small watersheds located mostly within Mammoth Cave National Park: the 6.6 square kilometer First Creek basin and the 6.9 square kilometer Dry Branch basin. Both of these basins are located in South-central Kentucky (Figure 5) entirely within the Interior Low Plateau Province (Figure 6).

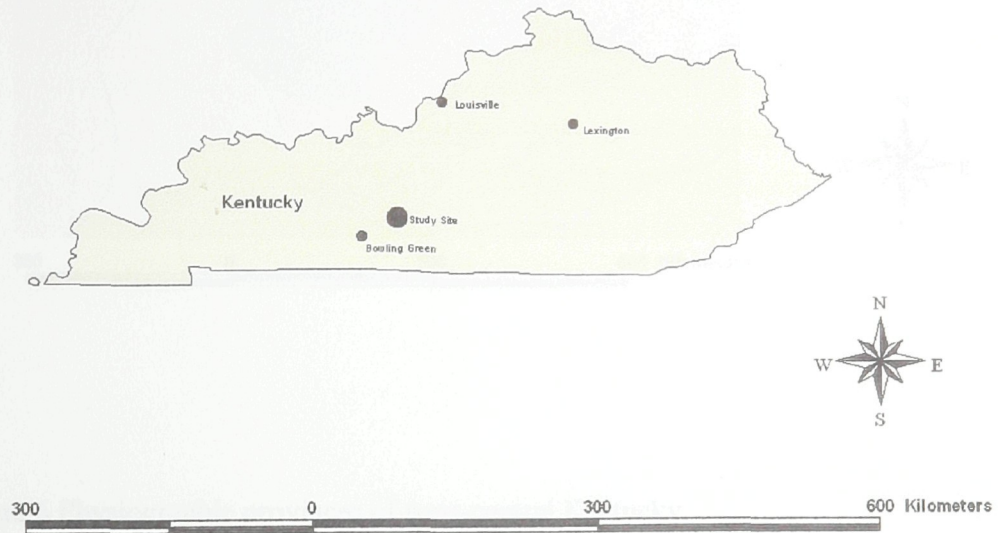


Figure 5 Study area location

### Physiographic Provinces- West-central Kentucky

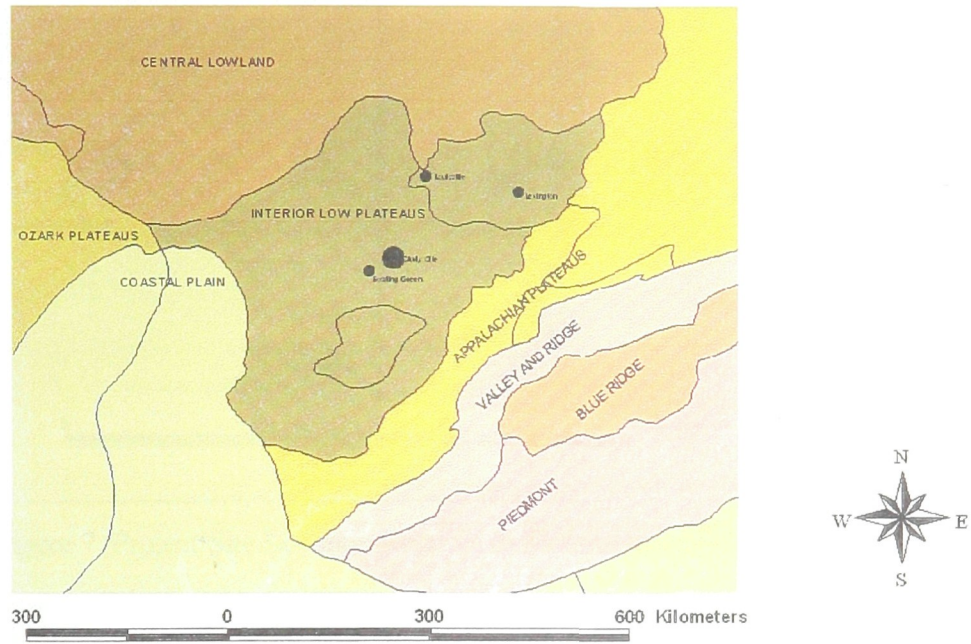


Figure 6 Physiographic provinces of west-central Kentucky

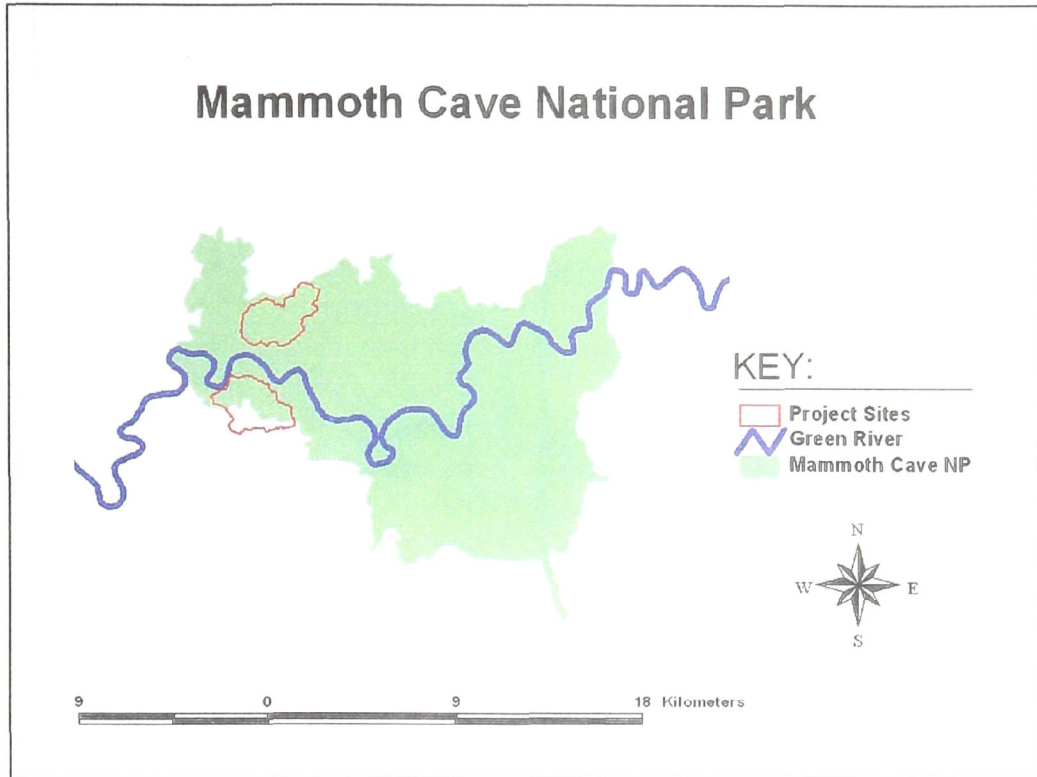


Figure 7 Project Site Location Relative to Mammoth Cave National Park



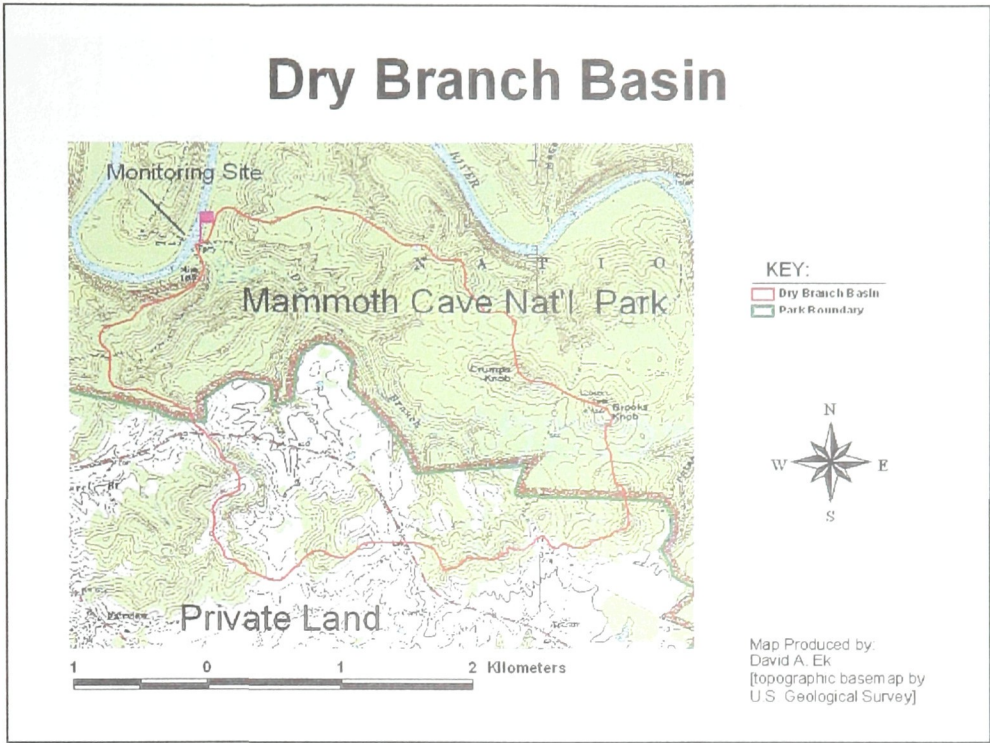


Figure 8 Dry Branch basin

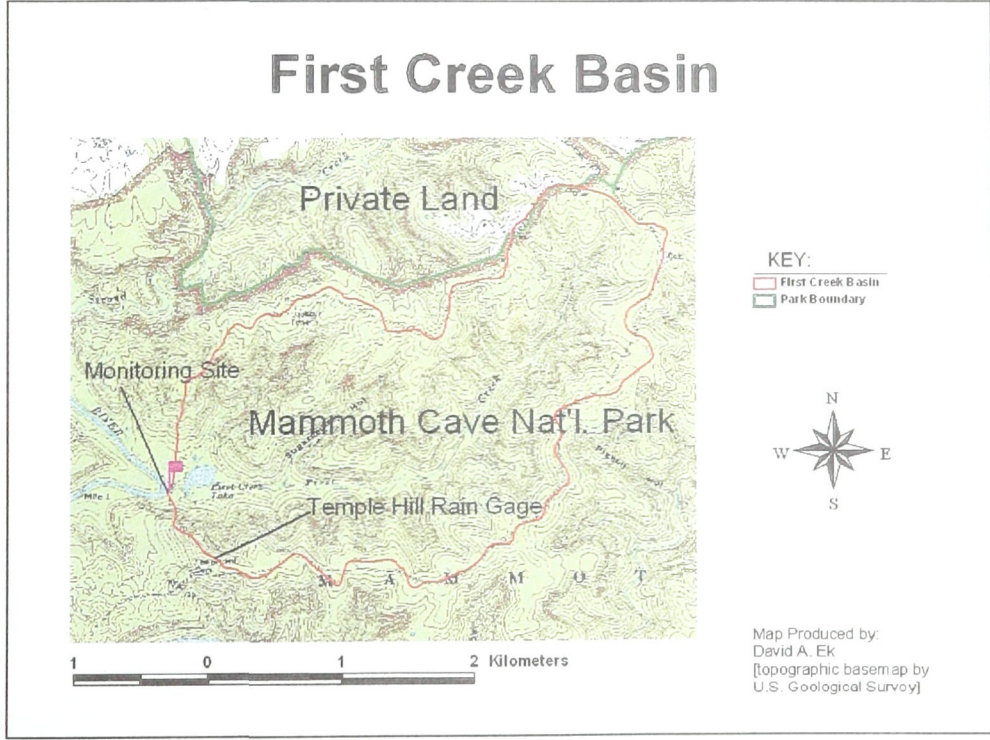


Figure 9 First Creek basin





Figure 10 Photo of First Creek sampling station



Figure 11 Photo of Dry Branch sampling station in flooded condition

## TEMPERATURE/HUMIDITY

Mean annual relative humidity of Kentucky is approximately 70 percent (Hill, 1976).

The relative humidity of Kentucky typically experiences a daily cycle. The highest relative humidity (90 percent in the spring and summer) corresponds with the lowest temperatures of the day, therefore immediately before sunrise (Hill, 1976). The lowest daytime relative humidity during the year (approximately 60 percent) is typically in the winter (Hill, 1976).

There are climatic factors affecting evaporation, chiefly solar energy (Hill, 1976). Climatic conditions most favorable toward evaporation are high temperature, low relative humidity, minimum cloud cover, and strong winds (Hill, 1976).

Within Kentucky, evaporation is greatest in the western and central portions of the state (Hill, 1976). The average evaporation losses within Kentucky's Central Division are depicted within Table 11 and the average daily soil temperatures are depicted in Table 12 (Hill, 1976).

Table 11 Average evaporation losses within Kentucky's Central Division.

April	May	June	July	August	September	October	Total
143.8mm	168.4mm	177.3mm	191.5mm	165.4mm	117.1mm	96.3mm	1059.7mm

Table 12

Average daily soil temperature (degrees C) within the Central Division of Kentucky.

January	February	March	April	May	June
4	4	6	12	17	22
July	August	September	October	November	December
24	26	23	20	11	6

A summary of the average temperature and precipitation for Mammoth Cave National Park and Bowling Green, Kentucky is depicted in Table 13 (Hill, 1976).

Table 13 Average temperature and precipitation for Mammoth Cave National Park and Bowling Green, KY [Kentucky Climate Center]

Month	Mean Monthly Temperature (deg. F) for Bowling Green, KY	Mean Monthly Temperature (deg. F) for Mammoth Cave National Park	Mean Monthly Precipitation (inches) for Bowling Green, KY	Mean Monthly Precipitation (inches) for Mammoth Cave National Park	Mean Monthly Snowfall (inches) for Bowling Green, KY
January	35.6	35.1	4.52	4.90	3.8
February	38.4	37.8	4.25	4.40	2.4
March	46.3	46.0	5.23	5.45	2.5
April	57.8	57.8	4.15	4.28	0.1
May	66.7	65.3	4.00	4.17	
June	75.0	72.7	4.35	4.68	
July	78.1	75.6	3.86	4.19	
August	76.9	74.6	3.27	4.02	
September	70.3	68.7	2.83	3.39	
October	59.1	58.4	2.47	2.55	
November	46.4	46.1	3.68	4.22	0.5
December	37.7	37.5	4.38	4.35	1.8
TOTAL	57.4	56.3	46.99	50.60	11.0

Approximately 85 to 90 percent of the total annual evaporation occurs during the months of April through October (Hill, 1976). The greatest is in July, where evaporation can be as much as 5.1 to 7.6 mm (0.2 to 0.3 inches) per day (Hill, 1976). When comparing methods of determining evaporation rates, it has been shown that water loss

from natural lake surfaces was approximately 75 percent of the losses from standard evaporation pans (Hill, 1976).

The rate of evaporation from bare soil that is moist on the surface is approximately the same as the rate of evaporation from a lake surface (Pierre *et al.*, 1966). As vegetation begins to grow on bare soil, the vegetation shades the soil, thus reducing the rate of evaporation from the soil surface. However, water loss begins to occur via transpiration from the vegetation. It has been demonstrated that amount of water loss via evaporation that is saved due to vegetation cover is approximately balanced by the water loss from transpiration (Pierre *et al.*, 1966). Therefore, according to this source, the evaporation rate from a water surface is comparable to the water loss via a combined evaporation and transpiration (ET). However, it appears that other studies may disagree.

#### **AREA/TOPOGRAPHY/ASPECT**

The Dry Branch watershed encompasses 6,890,730 square meters compared to the First Creek watershed's 6,593,177 square meters. Therefore, First Creek's watershed is four percent smaller. The sampling stations were located at the terminus of each respective watershed. The Dry Branch sampling station was located at the same elevation as the First Creek station; however it was located 2,670 meters south-southwest. Dry Branch drains directly into the Green River, while First Creek drains into the Nolin River, which in turn drains into the Green River a short distance downstream of the Dry Branch confluence.

Both sampling stations are located at an approximate elevation of 130 meters above mean sea level (msl). The highest point in the Dry Branch basin is Brooks Knob at 260 meters above msl. The highest point in the First Creek basin is the survey station site name "Ollie Station" at 270 meters above msl.

Because First Creek is on the north side of the Green River and Dry Branch on the south, each basin has nearly a mirror-image aspect. Dry Branch faces largely west-northwest, while First Creek faces west-southwest. There is a small difference in each basin's total length. Measured in a straight line from the highest divide above each respective creek to the mouth, Dry Branch is 3.884 meters long versus First Creek's 4.219 meters; therefore the length of Dry Branch is 92 percent shorter than the length for First Creek.

In summary, the two basins are similar in area, topography and aspect. They do have a different stream profile (Figure 12). The First Creek watershed is slightly smaller in area, but is slightly longer and narrower than Dry Branch's watershed. They are at nearly the same elevation and both face west (however Dry Branch faces northwest versus First Creek's southwest). They are both located only 2.67 km apart on nearly the same longitude on the western edge of Mammoth Cave National Park.



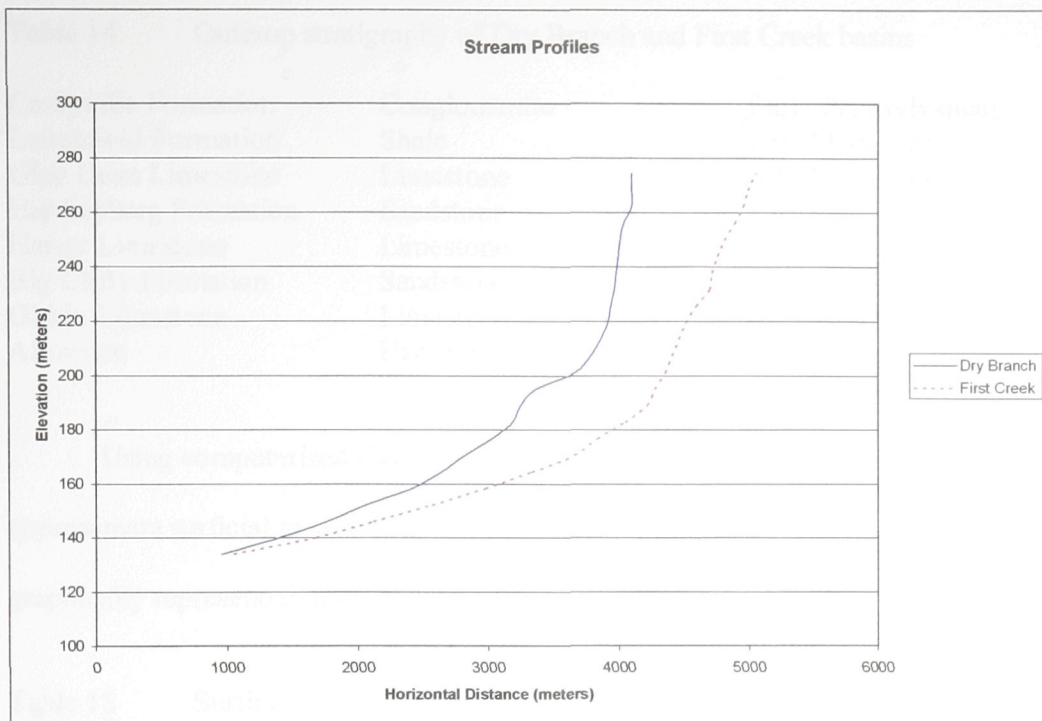


Figure 12 Cross-sectional stream profiles (vertical scale is exaggerated by 15 times)

## GEOLOGY

Although these two basins are similar in area, topography and aspect, they differ significantly in geology. Both field sites are located in the dissected Mammoth Cave Plateau within the Mississippian Section of the Interior Low Plateaus.

Six of the eight geologic formations found exposed within the project areas are depicted in Figure 13. The entire eight formations are listed in Table 14 (USGS National Geologic Map Database, Geolex Database, 2002) and in Figure 14.

Table 14 Outcrop stratigraphy of Dry Branch and First Creek basins

Caseyville Formation	Conglomerate	Early Pennsylvanian
Leitchfield Formation	Shale	Late Mississippian
Glen Dean Limestone	Limestone	Late Mississippian
Hardinsburg Formation	Sandstone	Late Mississippian
Haney Limestone	Limestone	Late Mississippian
Big Clifty Formation	Sandstone	Late Mississippian
Girkin Limestone	Limestone	Late Mississippian
Alluvium	Unconsolidated Sediment	Recent/Quaternary

Using computerized Geologic Information System (GIS) technology, the approximate surficial area of each of these formations is listed in Table 15 and graphically represented in Figures 15 and 16.

Table 15 Surficial area of each of the geologic formations exposed in the project areas

Geologic Unit	First Creek Watershed (area-square meters)	Dry Branch Watershed (area-square meters)
Caseyville Formation	4,574,980	872,646
Leitchfield Formation	0	512,272
Glen Dean Limestone	330,021	2,704,423
Hardinsburg Formation	454,407	1,586,978
Haney Limestone	410,659	415,528
Big Clifty Formation	570,411	493,646
Girkin Limestone	66,592	163,369
Alluvium	185,957	141,779
Water	150	88
<b>TOTAL</b>	<b>6,593,177</b>	<b>6,890,729</b>

The Leitchfield Formation is known to be largely absent from the general area of the two project sites, having been removed by pre-Pennsylvanian erosion (Weller, 1927).



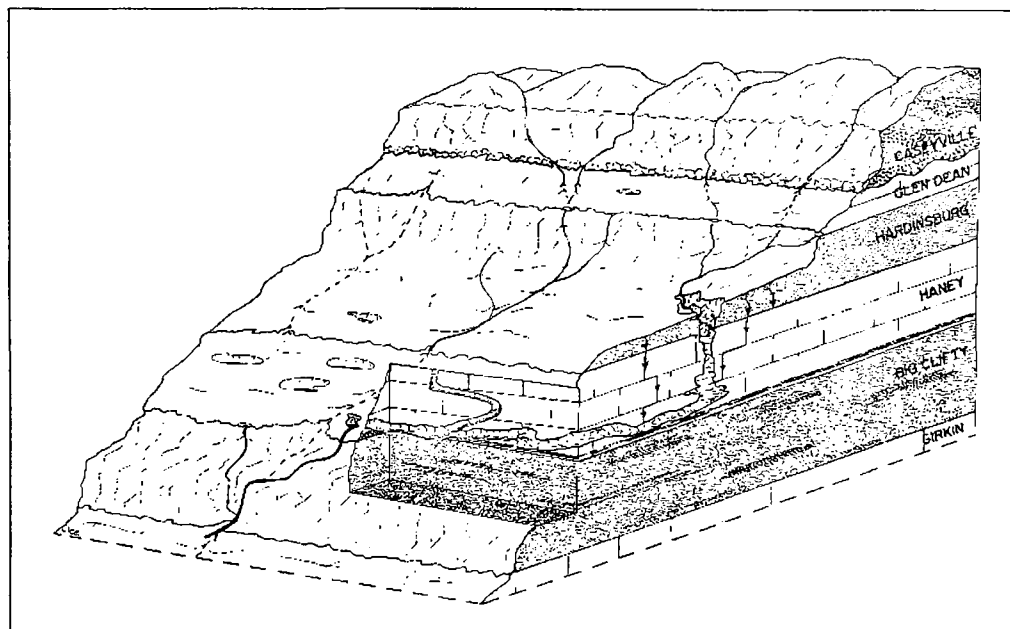


Figure 13 Drawing depicting typical stratigraphy within the First Creek and Dry Branch basins (drawing by Joe Meiman, used by permission)

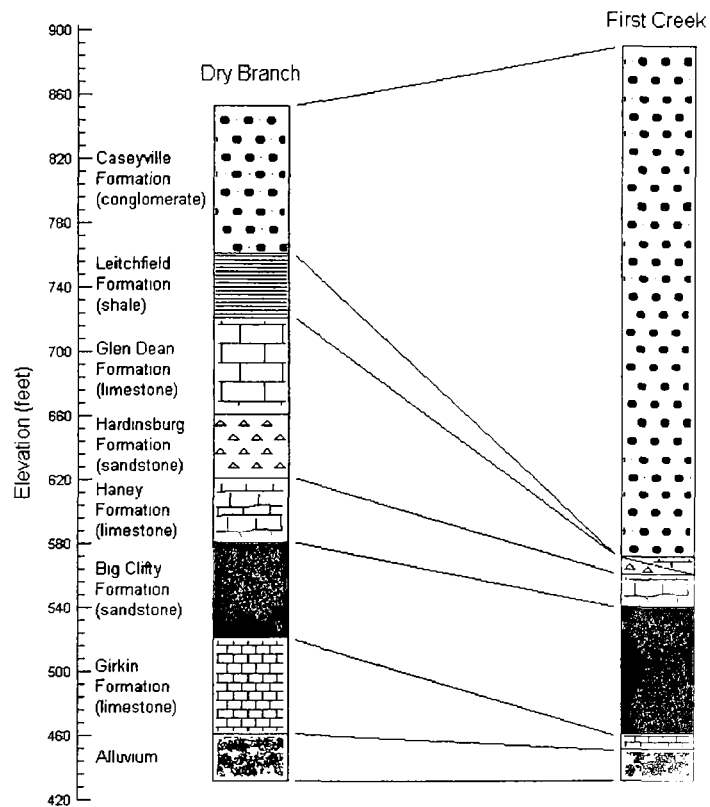


Figure 14 Basin-wide stratigraphic columns- (compiled from geologic and topographic maps) following along creek/valley bottom, beginning at the sampling station(s). [Note: there is an unconformity in the First Creek basin between the Caseyville Formation and the Glen Dean Formation].

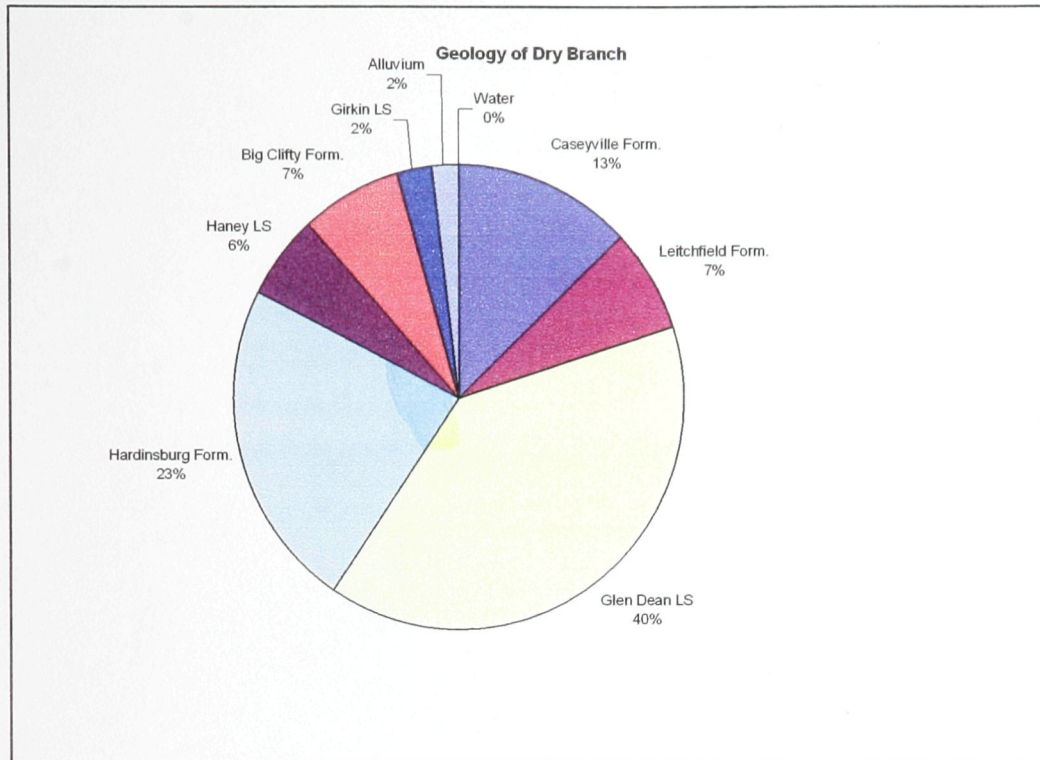


Figure 15 Surficial area of the various stratigraphic units within Dry Branch

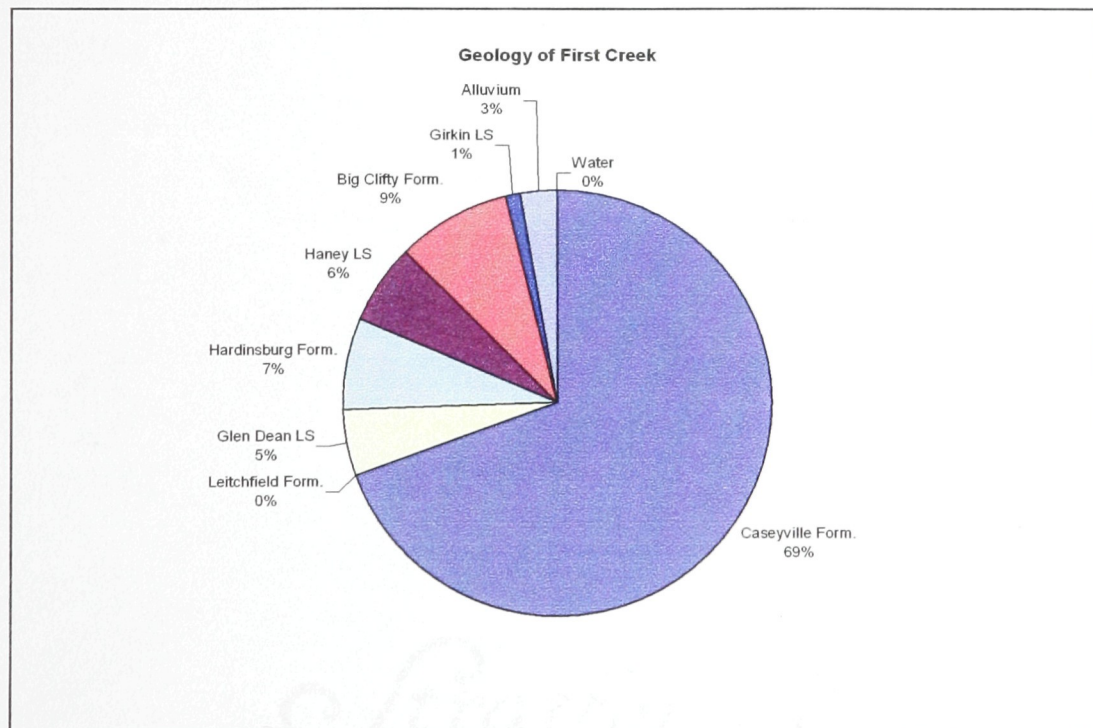


Figure 16 Surficial area of the various stratigraphic units within First Creek

The Dry Branch watershed is underlain by 47.7 percent carbonate rocks (Figure 17), while the First Creek watershed is underlain with only 12.2 percent carbonate rocks (Figure 18).

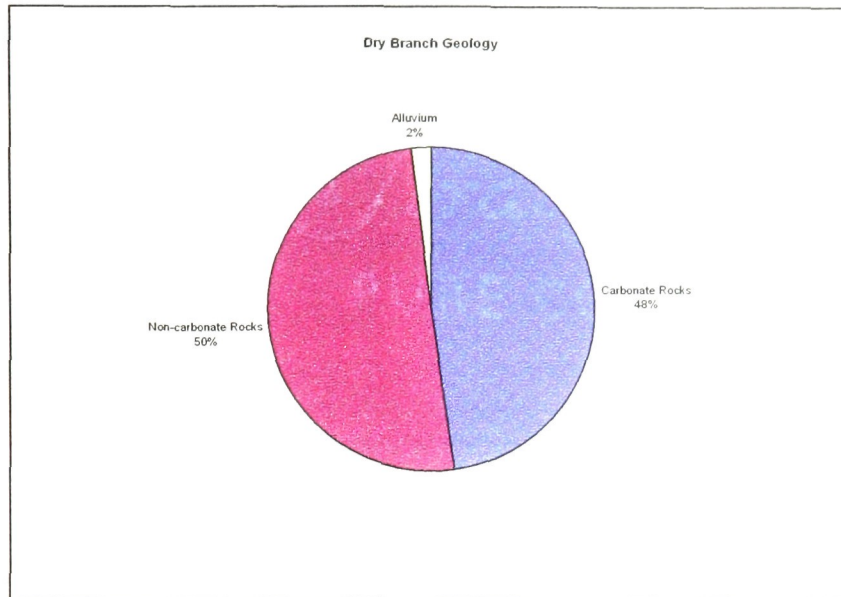


Figure 17 Extent of exposed carbonate rocks in Dry Branch

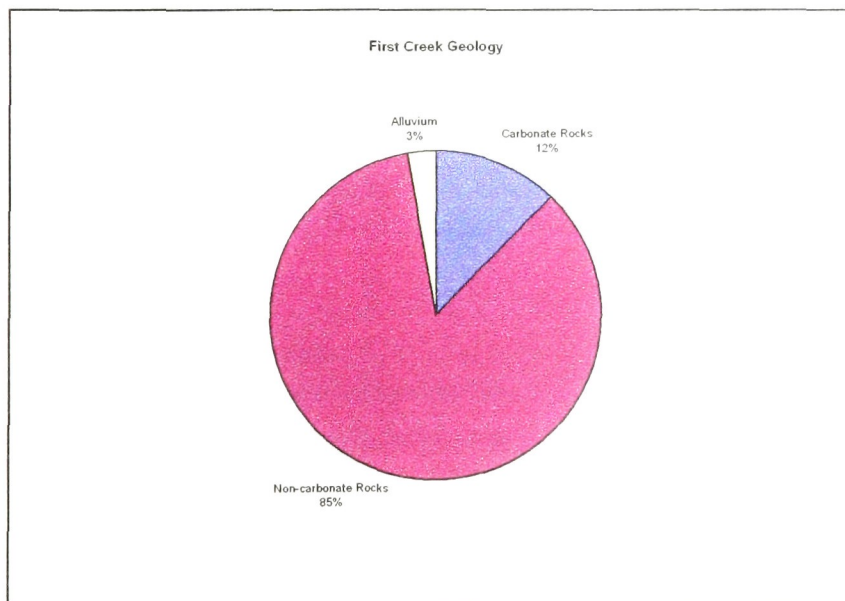


Figure 18 Extent of exposed carbonate rocks in First Creek

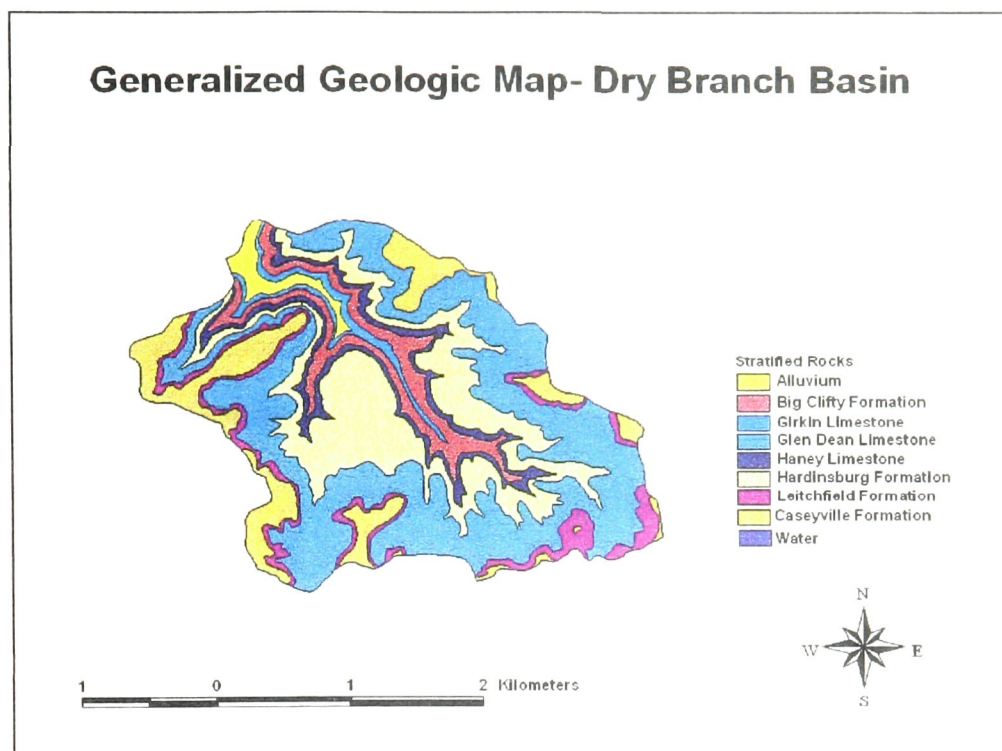


Figure 19 Generalized geologic map- Dry Branch basin

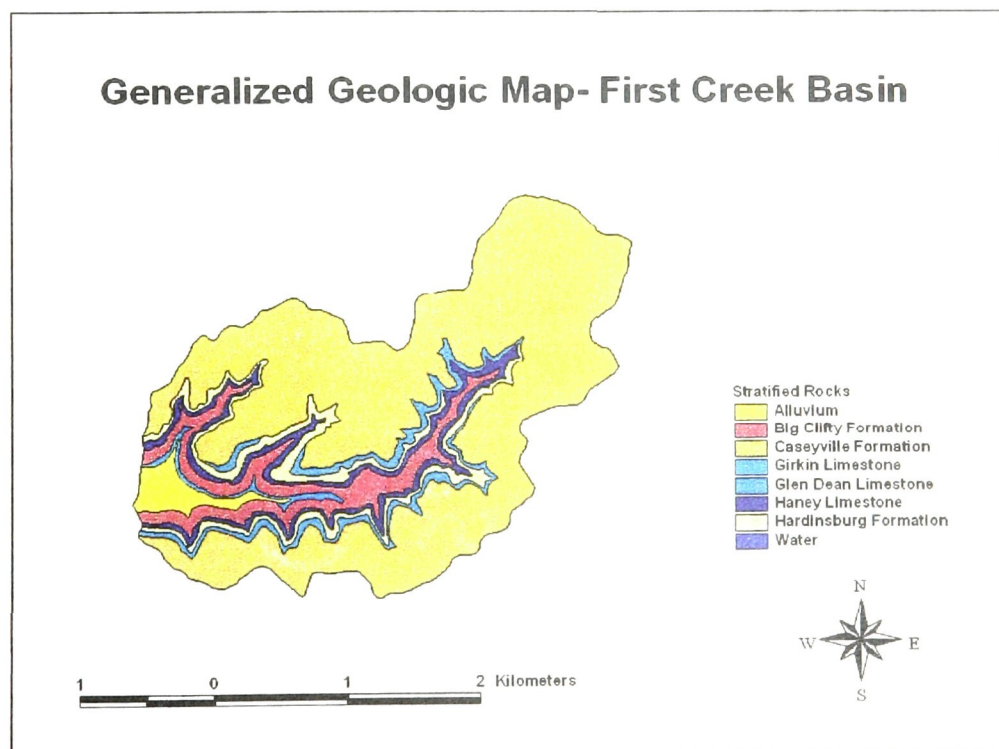


Figure 20 Generalized geologic map- First Creek basin

## HYDROLOGY

The Dry Branch sampling site was located near the confluence with the Green River. Conversely, the First Creek site was located near the confluence with the Nolin River. As a consequence, the hydrology of these sites are affected not solely by streams in the basins (e.g., Dry Branch and First Creek) but also by the adjacent river systems. One area of effect includes occasional back-flooding from the river systems, up to and beyond the sampling site. Therefore, a brief discussion of the basic hydrologic conditions of these two river systems is warranted.

The nearby Nolin Reservoir was impounded in 1963. This multilevel release dam was constructed by the US Army Corps of Engineers. Nolin River rises in Hardin County, Kentucky and flows approximately 196 kilometers to its mouth in Edmonston County, Kentucky. The drainage area is approximately 1,883 square kilometers, 62 of which are below the Nolin Dam. The drainage area above the dam is a combination of karstic and non-karstic terrain. Upland soils mostly Westmoreland and Muskingum associates derived from acidic siltstones, sandstones and shales (Carter, 1968). The Tailwater Soil is located in the western Coalfield Physiographic Province, overlying mostly sandstone and shale (U.S. Department of Interior, 1960- as presented in Carter, 1968). Downstream of the Nolin River Dam, the river's gradient averages 0.38 meters per kilometer. The Nolin River's flow is influenced by backwater resulting from Green River's Lock and Dam Number 6, located on the Green River 3.2 kilometers downstream of the confluence with Nolin River (Carter, 1968).

## **DISTURBANCES**

First Creek basin contains no buildings, homes, or any form of significant development. However, Dry Branch basin lies partly outside of Mammoth Cave National Park and is partly developed. Besides several home sites and roads, there are also approximately 44 oil wells (Figure 21).

Besides the storm events that are mentioned in other parts of this paper, the only other known disturbance of note within the project areas during the durations of the study was on April 23, 2002 (day number 203) when a 30-acre controlled burn (fire) was lit by National Park Service staff within the First Creek basin. The author had no previous knowledge of this control burn being planned; therefore no special monitoring activities were planned to precisely assess what, if any, effect this fire may have had upon basin-wide hydrologic or geochemical cycling.



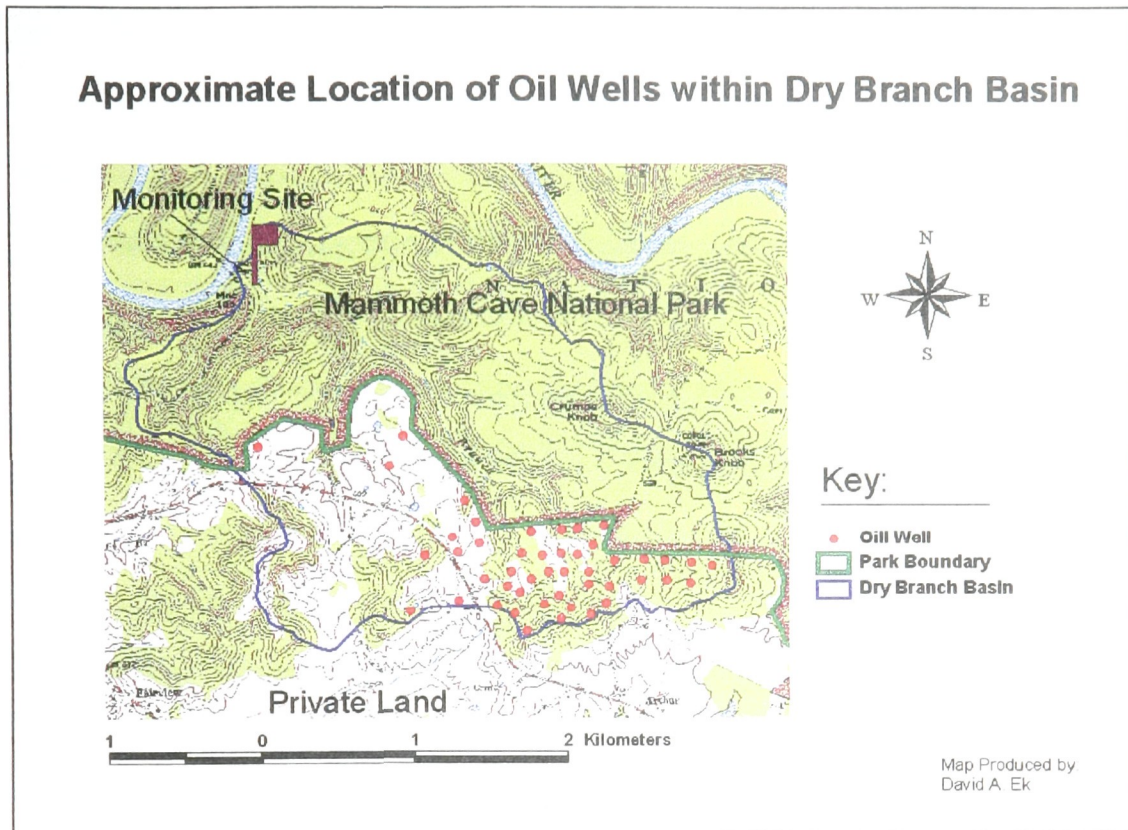


Figure 21 Location of oil wells in Dry Branch basin



## PART V      METHODOLOGY

A thorough karst inventory was conducted for both basins. A geographic information system (GIS) dataset will be compiled and developed. Geology maps will be field checked for accuracy, primarily the location and distribution of carbonate rocks.

Two main dataloggers were deployed, one for each of the two basins. Each datalogger was connected to temperature, pH and conductivity probes and a pressure transducer. The dataloggers and probes were placed at the downstream end of each respective basin. A Marsh-McBirney current meter was utilized to develop a rating curve (relation between stage and discharge) for the flow for these particular streams.

The monitoring schedule consisted of three distinct components: 1) synoptic sampling; 2) storm event sampling; and 3) a detailed time-series analysis of one storm event in each season. The synoptic sampling was on a regular biweekly schedule. Likens and Bormann (1995) found that although in general sampling schedules based upon regular time-series sampling have proven to either over or under predict the actual values in highly variable systems, in the case of their detailed work on Hubbard Brook they have shown that the geochemical factors did not vary significantly. Therefore, their data indicate that biweekly or even monthly sampling would suffice for synoptic sampling of the non-karst basin. The synoptic sampling in this study was conducted on a bi-weekly schedule.

Although a biweekly time series sampling schedule for low-variability parameters such as stream water chemistry in non-karst basins appears to be sufficient (Likens and Bormann, 1995), as mentioned earlier, this approach may not be sufficient in the more highly variable environment of karst streams. Therefore, some form of adjustments to the sampling scheme will need to be made in order to accommodate these differences. Besides the biweekly chemical analysis, two-minute resolution readings of temperature, pH and conductivity were obtained from the dataloggers. From the datalogger readings coupled with results obtained from the water lab, statistical relations were developed between flow and conductivity values and concentrations of each of the ions. If these relations indicate reliable and predictable relationships, then calculated ion concentrations were utilized along with the actual concentrations obtained from the lab as part of the synoptic sampling.

Several storm events occurring during different seasons throughout the year were analyzed. All samples were analyzed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Li}^{+}$ ,  $\text{Cl}^{-}$ ,  $\text{F}^{-}$ ,  $\text{Br}^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{NO}_2^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^{+}$ ,  $\text{H}^{+}$ ,  $\text{HCO}_3^{-}$ , and  $\text{PO}_4^{3-}$ . These ions were chosen based upon the geology within the study area basins, as well as being similar ions investigated as part of the extensive Hubbard Brook study (Likens and Bormann, 1995). Charge balancing was conducted to serve as an accuracy check, as well as a means of determining if other untested ions were present in significant concentrations. National Park Service and Western Kentucky University lab technicians within the Mammoth Cave National Park water lab determine ion concentrations (for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Li}^{+}$ ,  $\text{Cl}^{-}$ ,  $\text{F}^{-}$ ,  $\text{Br}^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{NO}_2^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^{+}$ , and  $\text{PO}_4^{3-}$ ) using their Dionex ion chromatograph (IC). The detection

limit for this lab equipment varied with the ion and during the course of the study (Table 16).

Table 16 Instrument (IC) detection limit during the course of this study

<b>Ion</b>	<b>Instrument Detection Limits (mg/L) [values changed through course of study]</b>
F <sup>-</sup>	0.012, 0.200
Li <sup>+</sup>	0.025, 0.050
NO <sub>3</sub> <sup>-</sup>	0.059, 0.991
Cl <sup>-</sup> , Br <sup>-</sup>	0.060, 0.996
SO <sub>4</sub> <sup>2-</sup>	0.060, 1.000
NO <sub>2</sub> <sup>-</sup>	0.061, 1.015
Na <sup>2+</sup>	0.1000, 0.200
PO <sub>4</sub> <sup>3-</sup>	0.1200, 1.998
Mg <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup>	0.1250, 0.250
Ca <sup>2+</sup> , K <sup>+</sup>	0.2500, 0.500

*In situ* pH was measured utilizing a portable pH meter, calibrated prior to each sampling event. HCO<sub>3</sub><sup>-</sup> concentrations were also measured in the field using a digital titrator.

The rain gage near the Mammoth Cave visitor center was utilized for rainfall, as well as an additional rain gage deployed in or near the study basins. This rain gage was an automated tipping type rain bucket connected to a datalogger. Precipitation chemistry

data for all the eleven ions discussed earlier is routinely collected by the National Park Service at the Mammoth Cave weather station.

One evaporation pan was deployed at the Mammoth Cave visitor center's weather station. This evaporation pan was placed out in the open, and served as the "standard" for the Mammoth Cave region. Evapotranspiration was calculated by subtracting stream discharge leaving the basin from the total input because of precipitation.

Data obtained from continuous-reading probes attached to dataloggers drift over time. To account for this drift, probes must be occasionally cleaned and recalibrated and the data recorded on the datalogger must be adjusted accordingly. To account for the drift in the various data, I assumed that the drift was linear. Site visits and probe calibration and cleaning were conducted on average every two weeks. Data obtained from the datalogger between each of these two week segments was adjusted separately. For every data segment (approximately on a two-week average), I determined what the datalogger read at the beginning point ( $DL_0$ ) and at the end point ( $DL_1$ ), and what the actual reading was according to the calibrated field probes brought on site ( $P_0$  for the beginning point of each line segment, and  $P_1$  for each line segment ending point). The line segments span a given time increment. The time of the beginning point of each line segment is represented by  $X_0$ , and the end point is  $X_1$ . Therefore, each line segment is  $X_1 - X_0$  time interval long. Each data point, at time  $X$ , was adjusted using the formula listed in equation 9.

$$y = [[(DL_0 - P_0) - (DL_1 - P_1)] / (X_1 - X_0)] * (X - X_0) + (P_0 - DL_0) \quad (9)$$

The "y" in the above equation is the amount to add to the respective DL reading to correct the datalogger values in order to correct and better represent the actual/true values.

This equation was applied to all the data obtained from the datalogger in order to adjust the data to the proper field calibration data and to account for normal linear drift of the pH and specific conductance probes.

## PART VI RESULTS

### **Morphology**

As mentioned earlier (Figure 12), the two study basins have different stream profiles. The profile of the Dry Branch basin is less concave than First Creek basin's profile. I conclude that the greater concavity of the First Creek basin is a direct result of surface erosion operating preferentially within the First Creek basin compared with the Dry Branch basin. Water flowing on the surface within a non-carbonate karst watershed causes erosion and the lowering of the basin, which in turn would create a more concave stream profile. Conversely, water flowing in subsurface karst conduits would not lower the basin's surface as much as enlarge the subsurface conduits. Under this scenario, one would expect to have the surface stream profiles of non-karst basins more concave than the surface stream profile of a similar karst basin. This conclusion is reinforced by similar observations and measurements that I have conducted in within different basins within the United States and Canada (not associated with this study). Therefore, the difference in stream profiles between these two basins is a karst phenomenon.

### **Precipitation and Precipitation Chemistry**

Precipitation data were obtained from Bowling Green, Kentucky (maintained by Western Kentucky University and the Kentucky Climate Center), Nolin Reservoir (maintained by the United States Corps of Engineers, Mammoth Cave National Park (maintained by the National Park Service), and the authors' automated rain gage located at the Temple Hill Cemetery (Figures 22 and 23) in the First Creek Basin. During the course of this one-year study, each of these stations experienced appreciable differences

(Table 17). Therefore, during many hydrologic studies within the region, the use of non-site specific precipitation data may be inappropriate. However, it was found that if data are averaged from stations located in different directions/sides from the study area, then close approximations of the actual site-specific averages may be obtained.

Table 17 Precipitation values for the Mammoth Cave area [Sources: Kentucky Climate Center for the Mammoth Cave data, while the Temple Hill data is from my study]

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Total
Mammoth Cave Normal Precipitation (mm)	124	112	138	109	106	119	106	102	86	65	107	110	1284 $\bar{X}=107$ (mm/mn.)
Mammoth Cave Precipitation 10/01- 9/02 (mm)	98	110	115	78	36	176	107	119	83	90	86	225	1323 $\bar{X}=110.3$ (mm/mn.)
Temple Hill Precipitation 10/01-9/02 (mm)	107	162	101	86	30	184	114	57	96	127	109	225	1398 $\bar{X}=116.5$ (mm/mn.)
Temple Hill Storm Events ( $\geq 25.4$ mm (1 inch) /day)	1	2	1	0	0	2	2	1	1	2	0	2	14 $\bar{X}=1.17$ (events/mn.)
Temple Hill # Days of Precipitation	7	9	11	12	10	14	13	14	11	10	14	11	136 (37.3% of the year)

As the above table indicates, Temple Hill (First Creek) received more precipitation than the Mammoth Cave Station. This table also shows that the period from October 1, 2001 to September 30, 2002 did not closely match the average annual precipitation values. Precipitation within the study basins in Autumn began and ended drier than average, but the study basins were wetter than average within the Winter and Spring. Precipitation within the study basins in March was wetter than average as it was

in July. In addition, there was an atypical storm the very last part of the study period (the end of September 2002) that produced the highest amount of precipitation (129 mm in a period of two days) for the study year. The annual precipitation graph for the average year appears to be much flatter than what occurred in the 2001-2002 hydrologic year.

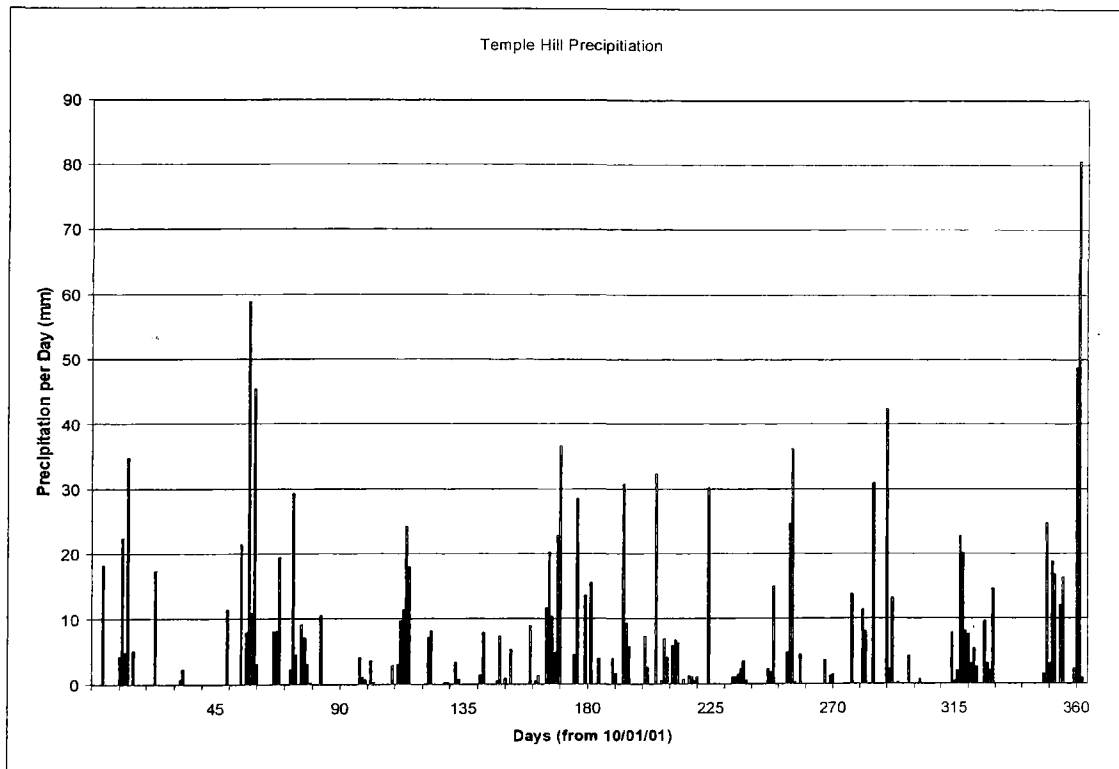


Figure 20 Daily precipitation for the Temple Hill station

There were three distinct and noticeable precipitation peaks: one in November, one in March, and the last in September. Troughs in the precipitation graph existed in late January and May. Overall, precipitation at Mammoth Cave (for an average year and this particular year) does not experience dramatic seasonal trends.



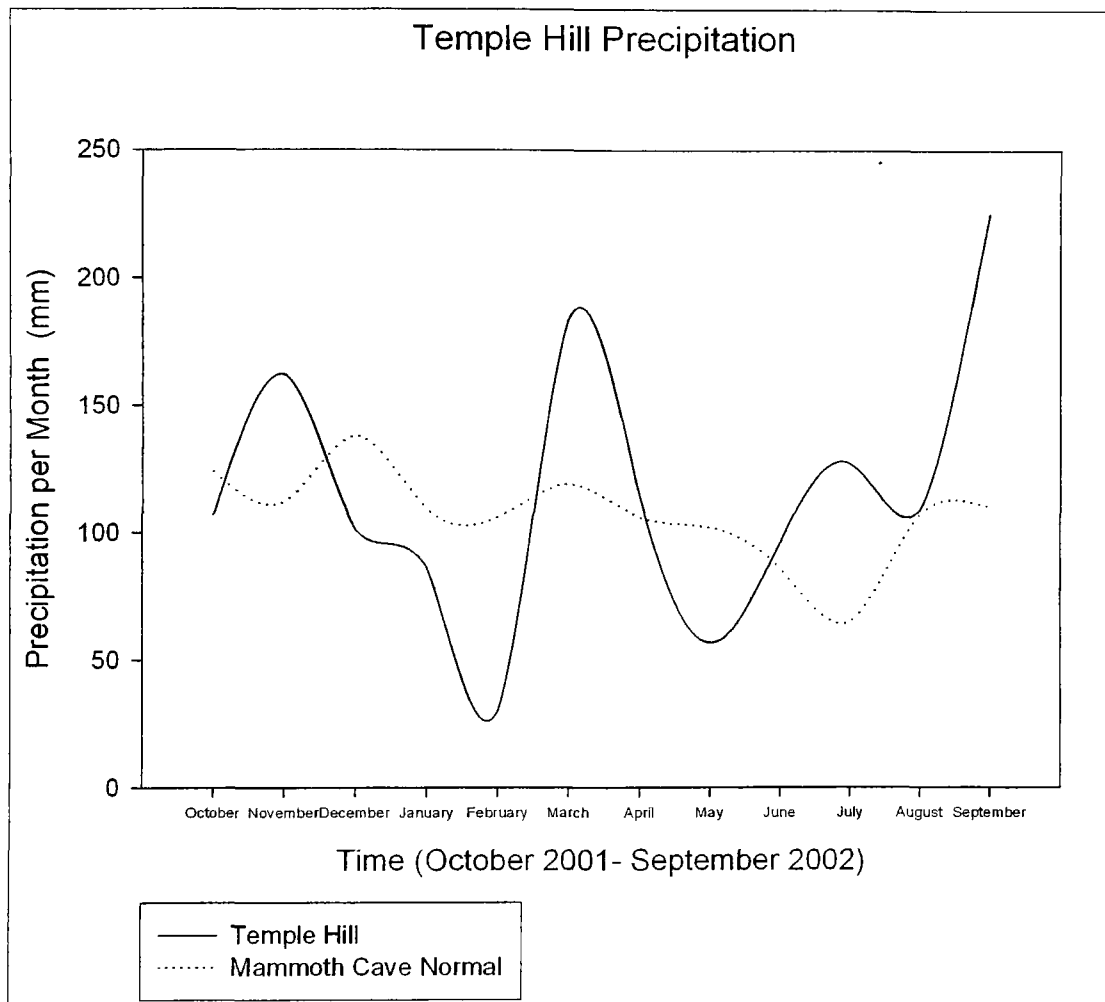


Figure 23 Monthly precipitation for the Temple Hill station

The region's precipitation chemistry was obtained from the nearby Mammoth Cave National Park wet deposition monitoring station located adjacent to the southwest portion of the park near Pig, Kentucky. These values were utilized along with the area of the two study basins to estimate the total annual chemical input into these basins from precipitation (Table 18).

Table 18 Precipitation chemistry- total input from wet deposition

	Dry Branch (grams)	First Creek (grams)
Ammonium	2,508,927.7	2,400,588.1
Calcium	1,707,599.3	1,633,862.3
Chloride	2,786,144.5	2,665,834.2
Magnesium	745,895.6	713,686.6
Nitrate	8,109,554.3	7,759,370.5
Potassium	113,227.0	108,337.7
Sodium	619,096.1	592,362.5
Sulfate	11,930,045.8	11,414,886.9

### Discharge

Discharge values were obtained by using a stream gage during several different stream levels (stage). From this information, I used power functions to develop stream rating curves (Figures 24, 25 and 26). I then applied the stream rating curves to the stage data recorded on the automated dataloggers (Figure 27). The discharge rating curve for Dry Branch fit well for all data points gathered; however a power function for the First Creek data fit well for only the lower and moderate flow values. The two higher flow data points ranged well above the rating curve. The meaning is that for the higher flows within First Creek, the data represented in this report is slightly underrepresented.

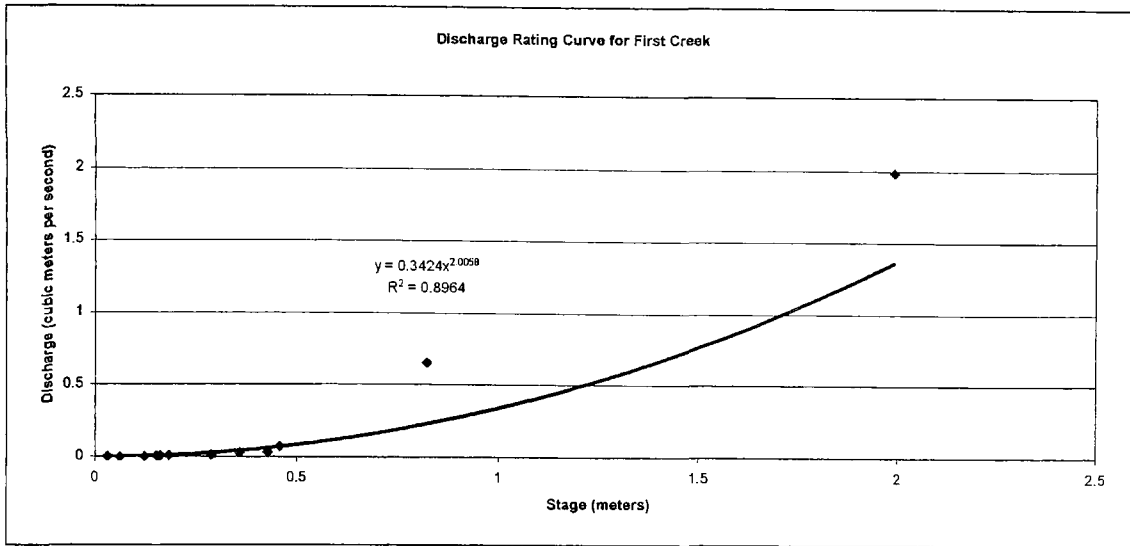


Figure 24 Discharge rating curve for First Creek

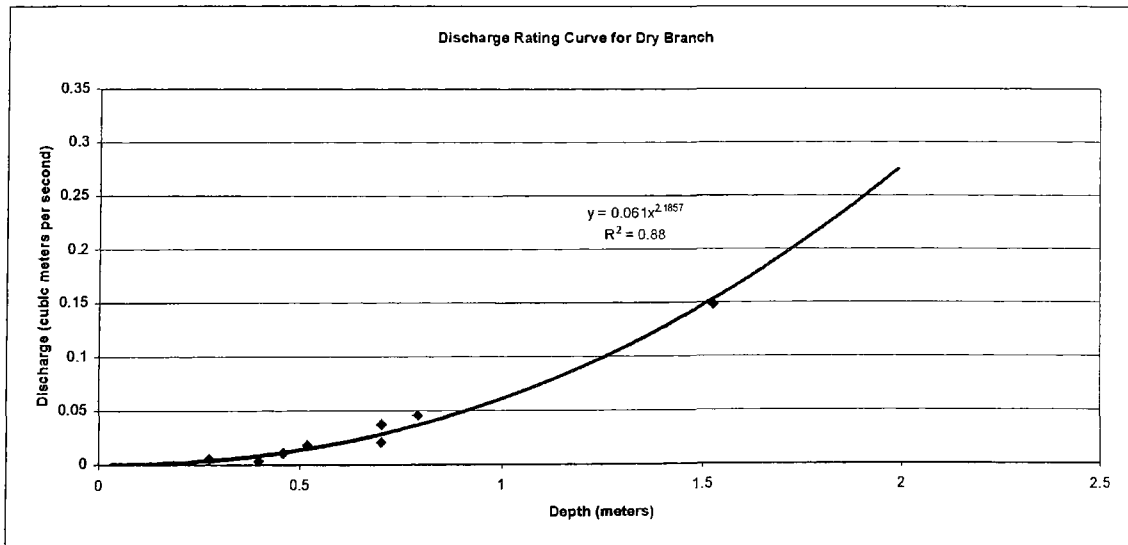


Figure 25 Discharge rating curve for Dry Branch

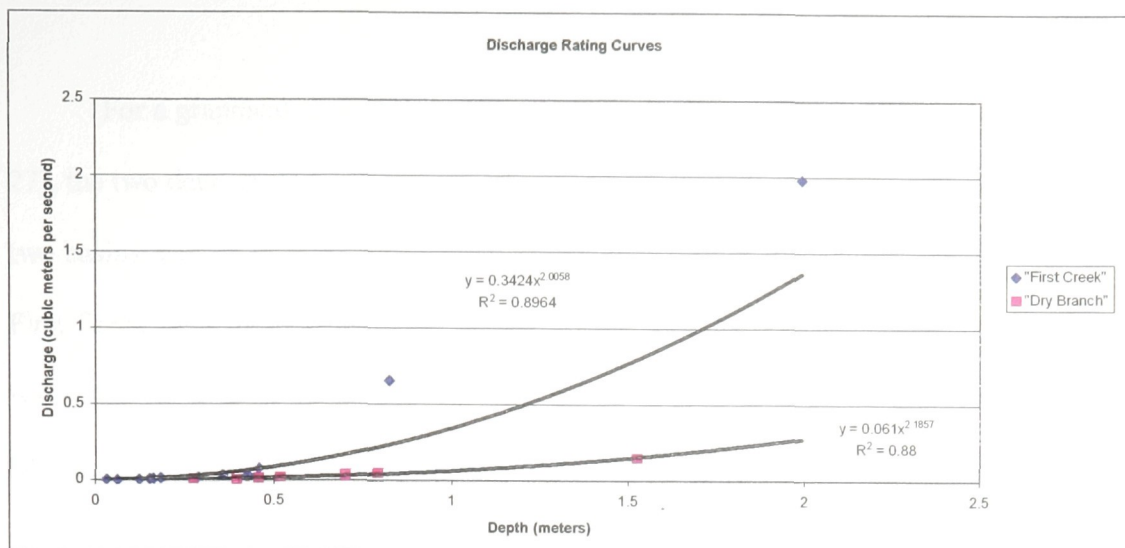


Figure 26 Discharge rating curves for First Creek and Dry Branch compared

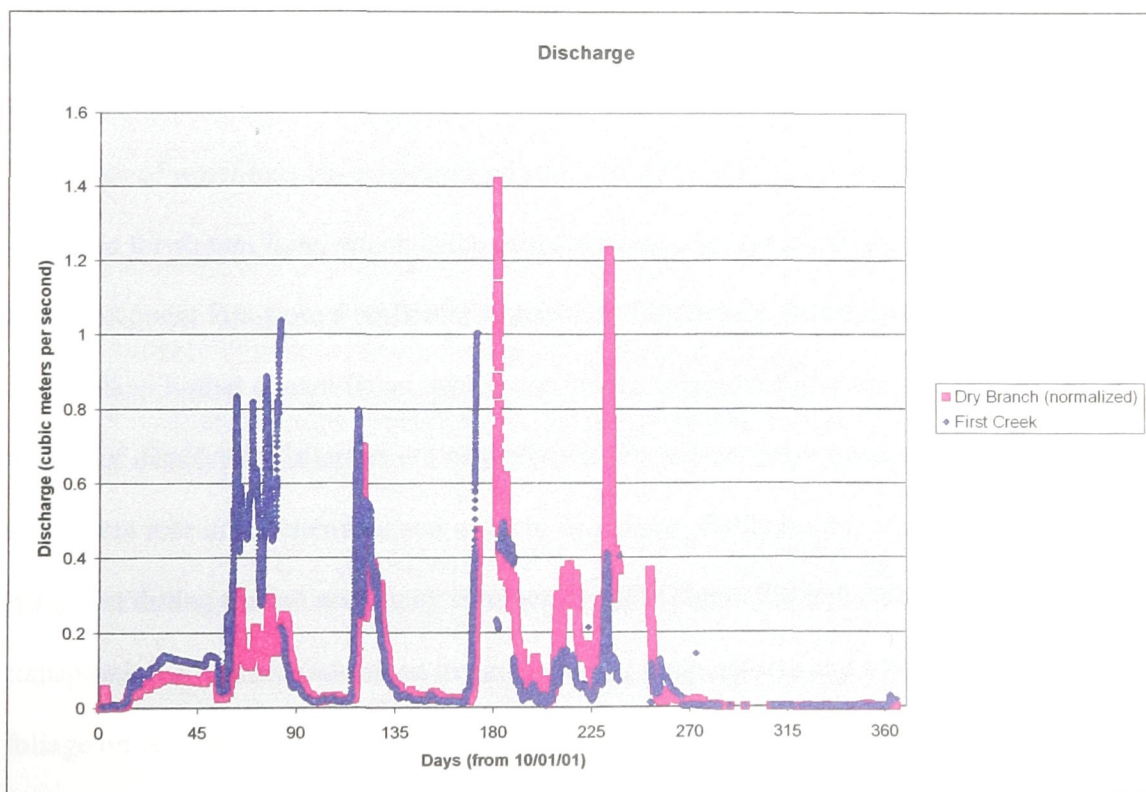


Figure 27 Discharge for the two study basins (since the two basins are not identical in size, for comparison purposes, the discharged data for Dry Branch were normalized)

For a graphical comparison of the discharge between these two basins (Figure 27), the two data sets need to be adjusted (normalized) so that the actual trends within the two basins may be accurately compared. Since the Dry Branch basin is larger than the First Creek basin and discharge is related to basin size, the Dry Branch discharge data was normalized in Figure 27 by adjusting all data points down by the equivalent amount (the percent that the Dry Branch basin is larger than the First Creek basin- or four percent smaller).

### **Evapotranspiration**

Likens and Bormann (1995) found that evapotranspiration significantly regulates and balances chemical and nutrient loss within a basin. This control is due to higher quantities of water loss via evapotranspiration that can result in a lower quantity of water available for stream flow, which is the primary avenue for chemical and nutrient transport and subsequent loss from a particular watershed. Conversely, low evapotranspiration levels allow higher stream flows, which can in turn transport larger amounts of nutrients and other dissolved substances out of the basin. Therefore, evapotranspiration plays a significant role in geochemical and nutrient dynamics. Furthermore, where evaporation is highest during the hot and sunny summer months (Figure 28) coincides with when transpiration is highest (attributed in part to higher temperatures and a full compliment of foliage on vegetation). Although the Mammoth Cave region does not experience a dramatic seasonal trend in precipitation, the available water within a basin may be more prominently pronounced due to the very seasonal nature of evapotranspiration.

As stated earlier, evapotranspiration is a dominant component of the hydrologic cycle. However, evapotranspiration is difficult to accurately measure. For this study, total evapotranspiration was estimated by subtracting the total annual stream discharge (the only other significant output) from the total annual precipitation (input). To partition evapotranspiration, the author placed an evaporation pan at the Mammoth Cave weather station. The placement of a pressure transducer and a datalogger would enable the evaporation component to be subtracted from the evapotranspiration sum, thereby leaving only the estimated transpiration total. However, Mammoth Cave National Park staff had problems with the transducer and datalogger that was planned to be deployed; therefore, it was never used. The author recorded evaporation from this pan manually. The infrequent nature of the site visits prevented obtaining enough usable data to make accurate determinations for evaporation for the different months and seasons throughout the year. Therefore, the author calculated an evaporation formula (Figure 29) using evaporation data from nearby Nolin River Lake (near the First Creek project site). However, not having equivalent transpiration values for this same time period makes the use of any evapotranspiration values for any increment less than an annual total unattainable.

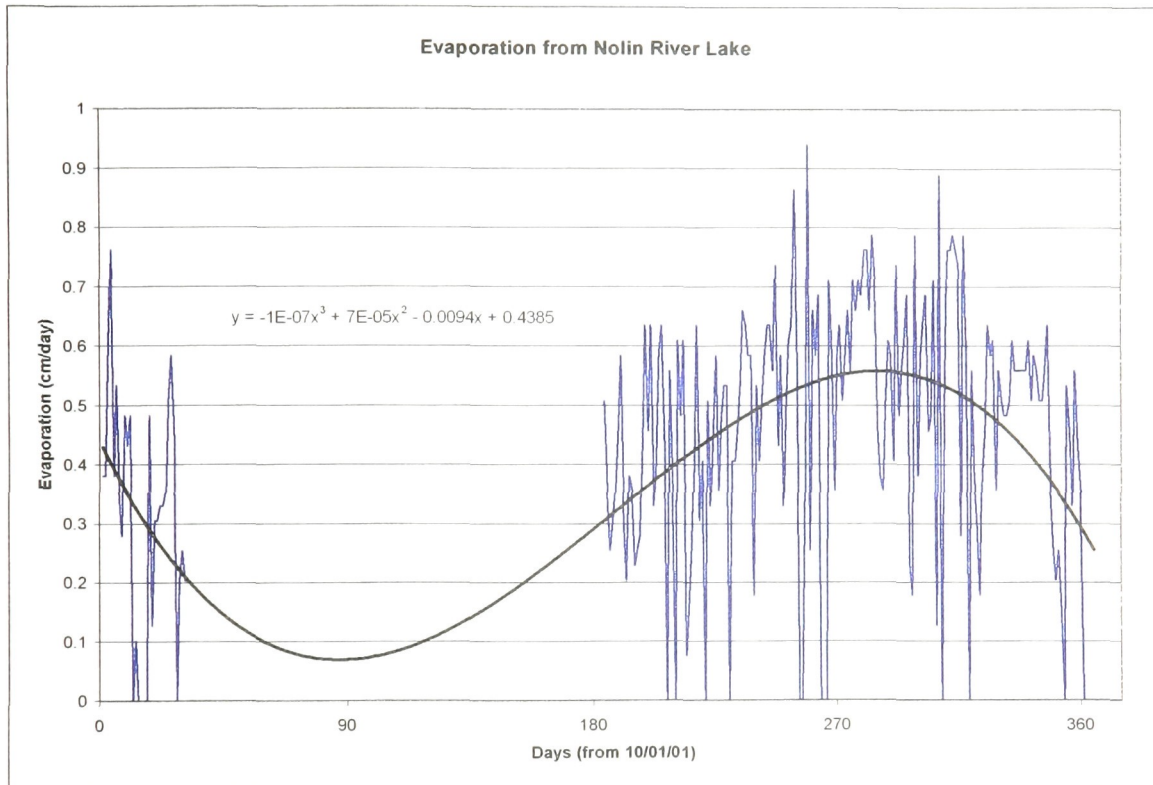


Figure 28 Evaporation from Nolin River Lake (measured by the U.S. Army Corps of Engineers)

The evaporation pan that was deployed at the Mammoth Cave National Park weather station evaporated a total of 1,049mm from a total of 1,323mm of precipitation. Thus, according to these manual readings of this one evaporation pan, the total evaporation for the study period was 79 percent of the precipitation total. Evaporation values obtained from evaporation pans typically overestimate the actual evaporation

experienced within a natural forest system; therefore correction factors are often employed.

Usually, a more reliable estimate for the actual evapotranspiration may be obtained using mass balance calculations (Table 19).

Table 19 Evapotranspiration output for the Dry Branch and First Creek basins

	Precipitation (input)	Stream Discharge (output)	Evapotranspiration (output)
Dry Branch	9,628,100 m <sup>3</sup>	3,487,406 m <sup>3</sup>	6,140,694 m <sup>3</sup>
First Creek	9,212,343 m <sup>3</sup>	3,344,448 m <sup>3</sup>	5,867,895 m <sup>3</sup>

Therefore using streamflow calculations, evapotranspiration for the First Creek and Dry Branch basins during the study period were equal to 64 percent of the total precipitation input.

Thornthwaite (1948) found that his evaporation calculations from evaporation pans and obtained from mass balance calculations differed by 23 percent. In this study, the difference between the calculated combined evaporation and transpiration values obtained from mass balance calculations and the evaporation values obtained from the evaporation pan is 19 percent. Using the evaporation values from Nolin River Reservoir, the estimate evaporation is 63 percent of the total precipitation. However, this value only includes evaporation from April through October. Although evaporation during the months November through March is significantly less, the inclusion of these months



would likely reduce the annual evaporation estimate to some value less than the stated 63 percent. It is also important to note that the Nolin River Reservoir estimate and the evaporation pan estimate are for evaporation only. Transpiration values are only included in the mass balance approach. For to this reason and due to the fact that the mass balance approach is generally more reliable, the estimated evapotranspiration annual total of 64 percent of the total precipitation will be used for the remainder of this study.

### **Water Temperature**

Stream temperature was recorded upon each site visit (Table 20 and Figure 29) as well as every ten minutes via the datalogger.

The water temperature data (Figure 29) shows a noticeable seasonal relationship and a difference in basins. Water temperature values within First Creek were slightly, but consistently, lower during the fall and winter compared with water temperature values for Dry Branch during this same time period. Stream temperature values within both basins during spring were nearly identical. There was a distinctive difference between the water temperature values within the two basins in the summer months. The difference in the water temperatures within these two basins is believed to be the result of the greater concentration of subsurface flow within Dry Branch, attributable to its higher quantity of karst. Water flowing in subsurface karst conduits would be moderated compared to its surface counterparts. Subsurface water would likely get less cool in the winter and less warm in the summer. This trend would be more noticeable in the summer, due to the

Table 20 Temperature values obtained from *in situ* field collection (10/01/01 – 09/30/02)

Month	Temperature					
	By Month		Season		Annual	
	First Creek	Dry Branch	First Creek	Dry Branch	First Creek	Dry Branch
October	Mean = 15.2 sd = min. = 11.7 max. = 18.7 N = 2	Mean = 14.8 sd = min. = 13.9 max. = 15.7 N = 2	<b>Fall</b> Mean = 11.6 sd = 4.0291 Error = 1.6449 95% = 4.2283 99% = 6.6324 min. = 7.1 max. = 18.7 N = 6	<b>Fall</b> Mean = 12.2 sd = 2.1173 Error = 0.7486 95% = 1.7701 99% = 2.6198 min. = 8.6 max. = 15.7 N = 8	Mean = 17.8 sd = 8.4586 Error = 1.4953 95% = 3.0497 99% = 4.1034 min. = 2.1 max. = 31.7 N = 32	Mean = 15.1 sd = 4.6492 Error = 0.7973 95% = 1.6222 99% = 2.1795 min. = 3.9 max. = 22.3 N = 34
November	Mean = 11.5 sd = min. = 10.0 max. = 12.9 N = 2	Mean = 12.3 sd = min. = 11.7 max. = 12.8 N = 2				
December	Mean = 8.1 sd = min. = 7.1 max. = 9.1 N = 2	Mean = 10.8 sd = 1.5840 min. = 8.6 max. = 12.0 N = 4				
January	Mean = 4.9 sd = min. = 4.9 max. = 4.9 N = 1	Mean = 8.9 sd = min. = 8.9 max. = 8.9 N = 1	<b>Winter</b> Mean = 8.8 sd = 3.8628 Error = 1.3657 95% = 3.2295 99% = 4.7797 min. = 2.1 max. = 12.9 N = 8	<b>Winter</b> Mean = 9.2 sd = 2.5583 Error = 0.9669 95% = 2.3661 99% = 3.5851 min. = 3.9 max. = 11.5 N = 7		
February	Mean = 9.5 sd = 2.9513 min. = 7.6 max. = 12.9 N = 3	Mean = 9.4 sd = min. = 8.5 max. = 10.3 N = 2				
March	Mean = 9.2 sd = 4.8176 min. = 2.1 max. = 12.7 N = 4	Mean = 9.2 sd = 3.5341 min. = 3.9 max. = 11.5 N = 4	<b>Spring</b> Mean = 23.1 sd = 6.0429 Error = 2.1365 95% = 5.0521 99% = 7.4773 min. = 14.8 max. = 30.2 N = 8	<b>Spring</b> Mean = 18.3 sd = 3.2360 Error = 1.1441 95% = 2.7054 99% = 4.0041 min. = 13.4 max. = 22.3 N = 8		
April	Mean = 14.8 sd = min. = 14.8 max. = 14.8 N = 1	Mean = 14.8 sd = min. = 14.8 max. = 14.8 N = 1				
May	Mean = 17.3 sd = min. = 15.1 max. = 19.4 N = 2	Mean = 15.0 sd = min. = 13.4 max. = 16.6 N = 2				
June	Mean = 27.2 sd = 2.5803 min. = 23.7 max. = 30.2 N = 5	Mean = 20.2 sd = 1.9591 min. = 18.0 max. = 22.3 N = 5	<b>Summer</b> Mean = 24.5 sd = 4.9248 Error = 1.5573 95% = 3.5230 99% = 5.0616 min. = 17.7 max. = 31.7 N = 10	<b>Summer</b> Mean = 18.7 sd = 1.8922 Error = 0.5705 95% = 1.2712 99% = 1.8083 min. = 16.2 max. = 22.1 N = 11		
July	Mean = 27.8 sd = min. = 27.0 max. = 28.6 N = 2	Mean = 18.9 sd = min. = 17.8 max. = 19.9 N = 2				
August	Mean = 27.9 sd = min. = 24.9 max. = 30.9 N = 2	Mean = 18.3 sd = min. = 17.0 max. = 19.5 N = 2				
September	Mean = 22.3 sd = 4.9834 min. = 17.7 max. = 31.7 N = 6	Mean = 18.7 sd = 2.2373 min. = 16.2 max. = 22.1 N = 7				

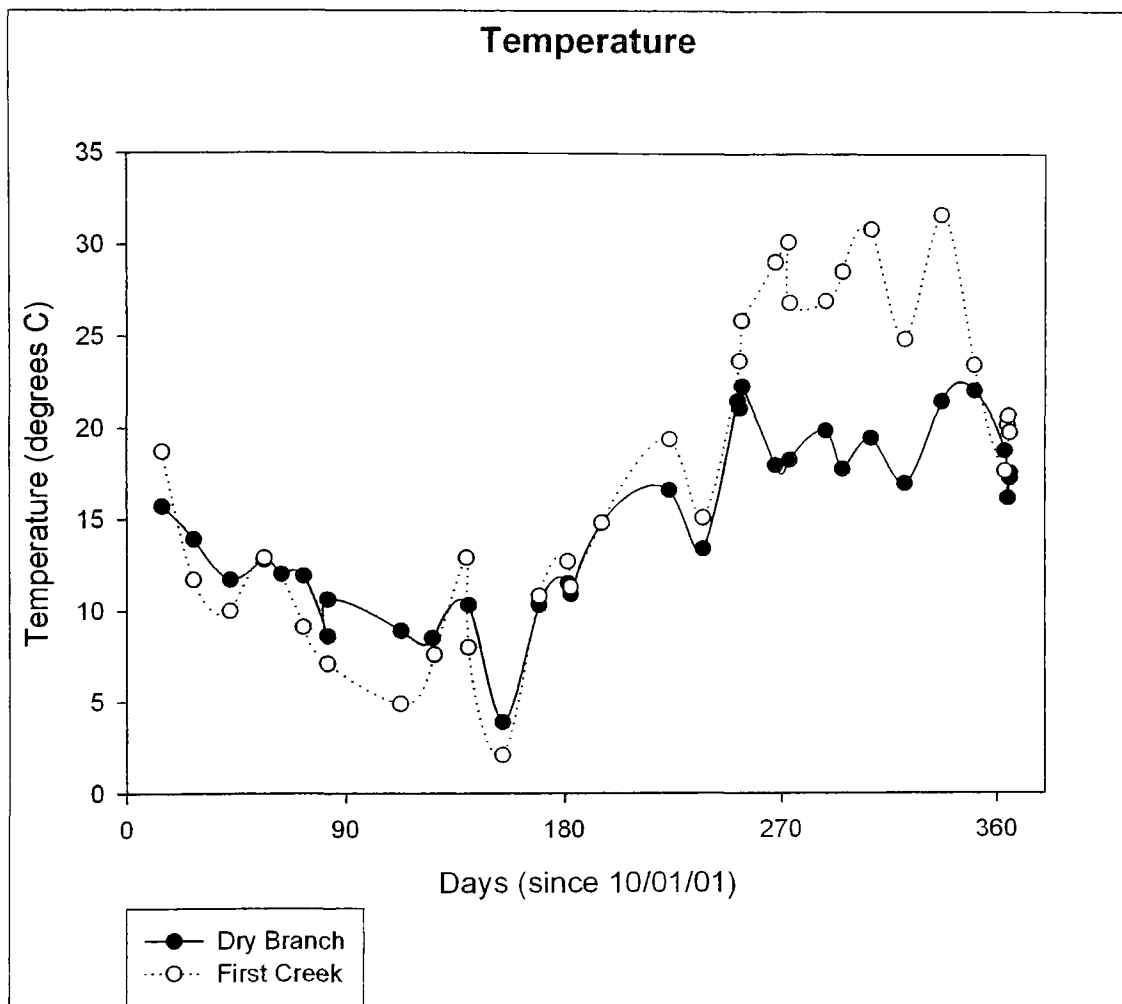


Figure 29 Stream temperature values obtained from in-person field collection

greater difference between summer daytime high temperatures and typical subsurface temperatures. This temperature difference has a moderating/buffering effect upon streams flowing through karst versus streams dominated by surface drainage. The presence of First Creek Lake within the First Creek basin may have affected the observed water temperature values because of the increased surface area thereby lowering water temperatures in the winter and increasing them in the summer.

As one would expect, water temperatures were higher in summer and lower in winter. Water temperatures in the spring were generally higher than in the fall. These differences are believed to be the result of air temperature changes due to solar radiation. Water temperatures were unseasonably warm in June within Dry Branch. The month of June contained the highest water temperatures within Dry Branch, while the peak for First Creek was in August. January contained the lowest water temperatures for both basins. Overall, First Creek experienced higher temperatures than Dry Branch in summer, but was slight cooler in fall and winter. These differences are believed to be caused by the moderating effect of the presence of karst.

### **Specific Conductance**

Specific conductance was generally higher within the basin containing the greater concentration of carbonate rock (Dry Branch). The relationship between the two basins (Figure 31) remains fairly consistent, with only a little seasonal effect. There is a slight increase within the Dry Branch basin within the summer months, compared with the First Creek basin (Table 21). This summer increase may be caused by the lower water volumes and slower water velocities within the summer months. Slow and near stagnant water in contact with soluble rocks provides a greater opportunity for the water to become further saturated. Conversely, a stream during a storm event is dominated just as much, or more, by direct and fast surface runoff that may or may not have been in contact with carbonate rock; therefore its opportunity to dissolve carbonate rocks is reduced, compared with low velocity and low volume groundwater moving slowly across a carbonate rock interface. Since specific conductance is a measure of the total amount of

dissolved matter in solution, one would expect slightly elevated specific conductance during summer low-flow conditions.

There was a noticeable elevated spike in specific conductance for both basins as the very end of the sampling period (Figure 30). This spike occurred during a storm event that occurred at the end of the sampling period. Although it may seem contrary to the above statements of having higher specific conductance values during low-flow conditions, this elevated spike in specific conductance during a storm event in late autumn may have been caused by the flushing of karst water that had been sitting in groundwater storage. It was the first big storm/flushing event following the summer low flow conditions. During this storm event, four separate *in situ* datapoints were obtained for each basin within only a few hours of each other, thereby explaining why the last four specific conductance datapoints are almost stacked on top of one another. These four datapoints in quick succession were obtained during different phases of the storm pulse. The first was at the initial stages of the storm pulse. The second and third reading was near the maximum height of the storm pulse, and the last datapoint was obtained after the water began to subside.

Table 21 Specific conductance values obtained from *in situ* field collection  
(10/01/2001 – 09/30/2002)

Month	Specific Conductance (SpC)					
	By Month		Season		Annual	
	First Creek	Dry Branch	First Creek	Dry Branch	First Creek	Dry Branch
October	Mean = 176.7 sd = min. = 172.6 max. = 180.7 N = 2	Mean = 278.0 sd = min. = 237.0 max. = 319.0 N = 2	<b>Fall</b> Mean = 191.9 sd = 46.3968 Error = 17.5364 95% = 42.9108 99% = 65.0194 min. = 118.9 max. = 250.0 N = 7	<b>Fall</b> Mean = 260.6 sd = 52.5898 Error = 18.5933 95% = 43.9671 99% = 65.0727 min. = 170.9 max. = 334.0 N = 8	Mean = 184.9 sd = 59.5305 Error = 10.3629 95% = 21.1090 99% = 28.3808 min. = 81.5 max. = 386.0 N = 33	Mean = 322.4 sd = 122.1099 Error = 20.9417 95% = 42.6070 99% = 57.2436 min. = 124.6 max. = 683.0 N = 34
November	Mean = 208.3 sd = min. = 166.6 max. = 250.0 N = 2	Mean = 252.5 sd = min. = 170.9 max. = 334.0 N = 2				
December	Mean = 191.1 sd = min. = 118.9 max. = 244.3 N = 3	Mean = 256.0 sd = 24.9933 min. = 220.0 max. = 267.0 N = 4				
January	Mean = 159.9 sd = min. = 159.9 max. = 159.9 N = 1	Mean = 295.0 sd = min. = 295.0 max. = 295.0 N = 1	<b>Winter</b> Mean = 154.1 sd = 17.0132 Error = 6.0151 95% = 14.2237 99% = 21.0515 min. = 128.5 max. = 182.7 N = 8	<b>Winter</b> Mean = 252.6 sd = 66.4377 Error = 25.1111 95% = 61.4458 99% = 93.1042 min. = 145.4 max. = 361.0 N = 7		
February	Mean = 160.3 sd = min. = 156.5 max. = 162.5 N = 3	Mean = 251.0 sd = min. = 248.0 max. = 254.0 N = 2				
March	Mean = 148.0 sd = 23.8525 min. = 128.5 max. = 182.7 N = 4	Mean = 242.9 sd = 89.9679 min. = 145.4 max. = 361.0 N = 4				
April	Mean = 81.5 sd = min. = 81.5 max. = 81.5 N = 1	Mean = 124.6 sd = min. = 124.6 max. = 124.6 N = 1	<b>Spring</b> Mean = 188.2 sd = 66.1971 Error = 23.4042 95% = 55.3434 99% = 81.9098 min. = 81.5 max. = 271.0 N = 8	<b>Spring</b> Mean = 284.8 sd = 92.9296 Error = 32.8556 95% = 77.6928 99% = 114.9876 min. = 124.6 max. = 400.0 N = 8		
May	Mean = 158.3 sd = min. = 145.9 max. = 170.6 N = 2	Mean = 221.3 sd = min. = 176.6 max. = 266.0 N = 2				
June	Mean = 221.5 sd = 53.9583 min. = 148.5 max. = 271.0 N = 5	Mean = 342.2 sd = 39.5373 min. = 296.0 max. = 400.0 N = 5				
July	Mean = 170.1 sd = min. = 160.8 max. = 179.4 N = 2	Mean = 395.5 sd = min. = 386.0 max. = 405.0 N = 2	<b>Summer</b> Mean = 202.1 sd = 79.4337 Error = 25.1191 95% = 56.8247 99% = 81.6405 min. = 115.8 max. = 386.0 N = 10	<b>Summer</b> Mean = 439.1 sd = 126.5049 Error = 38.1427 95% = 84.9890 99% = 120.8953 min. = 319.0 max. = 683.0 N = 11		
August	Mean = 205.0 sd = min. = 167.0 max. = 243.0 N = 2	Mean = 324.0 sd = min. = 319.0 max. = 329.0 N = 2				
September	Mean = 211.9 sd = 101.0834 min. = 115.8 max. = 386.0 N = 6	Mean = 484.4 sd = 138.5182 min. = 340.0 max. = 683.0 N = 7				

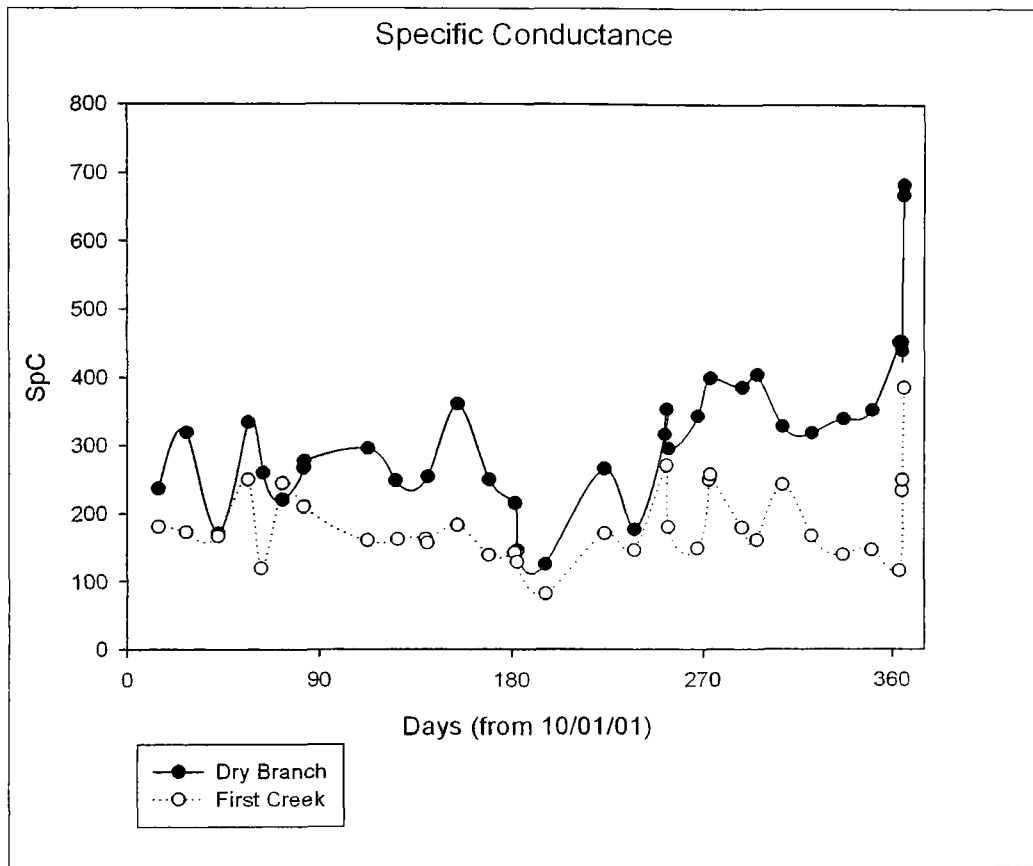


Figure 30 Specific conductance for both Dry Branch and First Creek

For both First Creek and Dry Branch, specific conductance was higher in summer and lower in winter. Specific conductance was higher in the spring than fall for Dry Branch but for First Creek it was higher in the fall than in the spring. The highest specific conductance values for First Creek occurred in June, while for Dry Branch it was in September. The lowest specific conductance values were in April for both basins. Specific conductance in the spring was highly variable for both basins. This variability in the spring is believed to be caused by the sporadic rainfall events that occurred simultaneously. Although specific conductance within Dry Branch was consistently higher in Dry Branch than in First Creek, the annual pattern within the two basins

remained generally the same. There may possibly be a little more of a flattened nature in First Creek in the winter compared to Dry Branch however the opposite may be true in the summer. The higher specific conductance values within Dry Branch may be attributed to the fairly consistent precipitation in the winter in the strictly surface waters of First Creek that reflect the specific conductance of rainwater, while in Dry Branch, during low rainfall periods, the higher specific conductance represents water with a higher ionic strength as a result of the dissolution of carbonate rocks.

### **Dissolved Stream Chemistry**

#### **Hydrogen**

The annual  $H^+$  ion total for the First Creek basin was 0.515 grams. This value converts to  $7.81 \times 10^{-7}$  kg/ha. In the Dry Branch basin the annual  $H^+$  ion total was 0.279 grams ( $4.04 \times 10^{-7}$  kg/ha). While these values are low in comparison to many of the other ions monitored as part of this study (e.g.  $Ca^{2+}$  at 114.09 kg/Ha,  $Na^+$  at 6.01 kg/Ha, or even  $Br^-$  at 0.56 kg/Ha), the  $H^+$  ion may at times play an important hydrogeochemical role.

The highest recorded pH values for Dry Branch occurred in the winter, while the highest recorded pH values for First Creek was in spring (Table 22). The lowest recorded pH values were recorded in the summer for both Dry Branch and First Creek. In general, pH values were highly variable during the winter; however for both basins the highest average pH value of any single month occurred in the winter (Figure 31). The lowest pH average value for any single month was in September for Dry Branch and in March for



First Creek. It is believed that these changes and patterns are largely influenced by rainfall/precipitation events. Overall, pH values are slightly higher in First Creek than those recorded in Dry Branch, but the difference is slight. The most noticeable differences occurred in late winter, where Dry Branch appears graphically to be higher and flatter and not so peaked (trough) as the graph for First Creek. This affect is believed to be the result of the buffering affect of karst, which is more prevalent within the Dry Branch basin.

Table 22 pH values obtained from *in situ* field collection (10/01/2001 – 09/30/2002)

Month	pH					
	By Month		Season		Annual	
	First Creek	Dry Branch	First Creek	Dry Branch	First Creek	Dry Branch
October	Mean = 6.86 sd = min. = 6.60 max. = 7.11 N = 2	Mean = 6.96 sd = min. = 6.90 max. = 7.01 N = 2	<b>Fall</b> Mean = 6.88 sd = 0.2020 Error = 0.0764 95% = 0.1868 99% = 0.2831 min. = 6.60 max. = 7.11 N = 7	<b>Fall</b> Mean = 7.09 sd = 0.1808 Error = 0.0639 95% = 0.1511 99% = 0.2237 min. = 6.90 max. = 7.39 N = 8		
November	Mean = 6.95 sd = min. = 6.95 max. = 6.95 N = 1	Mean = 7.20 sd = min. = 7.00 max. = 7.39 N = 2				
December	Mean = 6.85 sd = 0.2255 min. = 6.62 max. = 7.07 N = 3	Mean = 7.11 sd = 0.1706 min. = 6.91 max. = 7.16 N = 4				
January	Mean = 7.66 sd = min. = 7.66 max. = 7.66 N = 1	Mean = 7.72 sd = min. = 7.72 max. = 7.72 N = 1	<b>Winter</b> Mean = 6.92 sd = 0.4536 Error = 0.2028 95% = 0.5632 99% = 0.9337 min. = 6.55 max. = 7.66 N = 5	<b>Winter</b> Mean = 7.15 sd = 0.3246 Error = 0.1452 95% = 0.4030 99% = 0.6682 min. = 6.90 max. = 7.72 N = 5		
February	Mean = 7.02 sd = min. = 7.02 max. = 7.02 N = 1	Mean = 7.07 sd = min. = 7.07 max. = 7.07 N = 1				
March	Mean = 6.63 sd = 0.0971 min. = 6.55 max. = 6.74 N = 3	Mean = 6.99 sd = 0.0819 min. = 6.90 max. = 7.06 N = 3				
April	Mean = 6.85 sd = min. = 6.85 max. = 6.85 N = 1	Mean = 7.27 sd = min. = 7.27 max. = 7.27 N = 1	<b>Spring</b> Mean = 7.14 sd = 0.2107 Error = 0.0796 95% = 0.1949 99% = 0.2953 min. = 6.85 max. = 7.38 N = 7	<b>Spring</b> Mean = 7.15 sd = 0.3070 Error = 0.1160 95% = 0.2840 99% = 0.4303 min. = 6.72 max. = 7.58 N = 7	Mean = 6.93 sd = 0.3448 Error = 0.0640 95% = 0.1312 99% = 0.1770 min. = 6.21 max. = 7.66 N = 29	Mean = 7.08 sd = 0.2862 Error = 0.0514 95% = 0.1050 99% = 0.1448 min. = 6.60 max. = 7.72 N = 31
May	Mean = 7.15 sd = min. = 6.91 max. = 7.38 N = 2	Mean = 7.30 sd = min. = 7.01 max. = 7.58 N = 2				
June	Mean = 7.20 sd = 0.1370 min. = 7.05 max. = 7.35 N = 4	Mean = 7.05 sd = 0.3187 min. = 6.72 max. = 7.39 N = 4				
July	Mean = 7.02 sd = min. = 6.94 max. = 7.09 N = 2	Mean = 6.96 sd = min. = 6.82 max. = 7.10 N = 2	<b>Summer</b> Mean = 6.84 sd = 0.4218 Error = 0.1334 95% = 0.3017 99% = 0.4335 min. = 6.21 max. = 7.50 N = 10	<b>Summer</b> Mean = 7.00 sd = 0.3321 Error = 0.1001 95% = 0.2231 99% = 0.3173 min. = 6.60 max. = 7.60 N = 11		
August	Mean = 7.10 sd = min. = 7.01 max. = 7.19 N = 2	Mean = 7.41 sd = min. = 7.21 max. = 7.60 N = 2				
September	Mean = 6.70 sd = 0.5002 min. = 6.21 max. = 7.50 N = 6	Mean = 6.89 sd = 0.3087 min. = 6.60 max. = 7.39 N = 7				

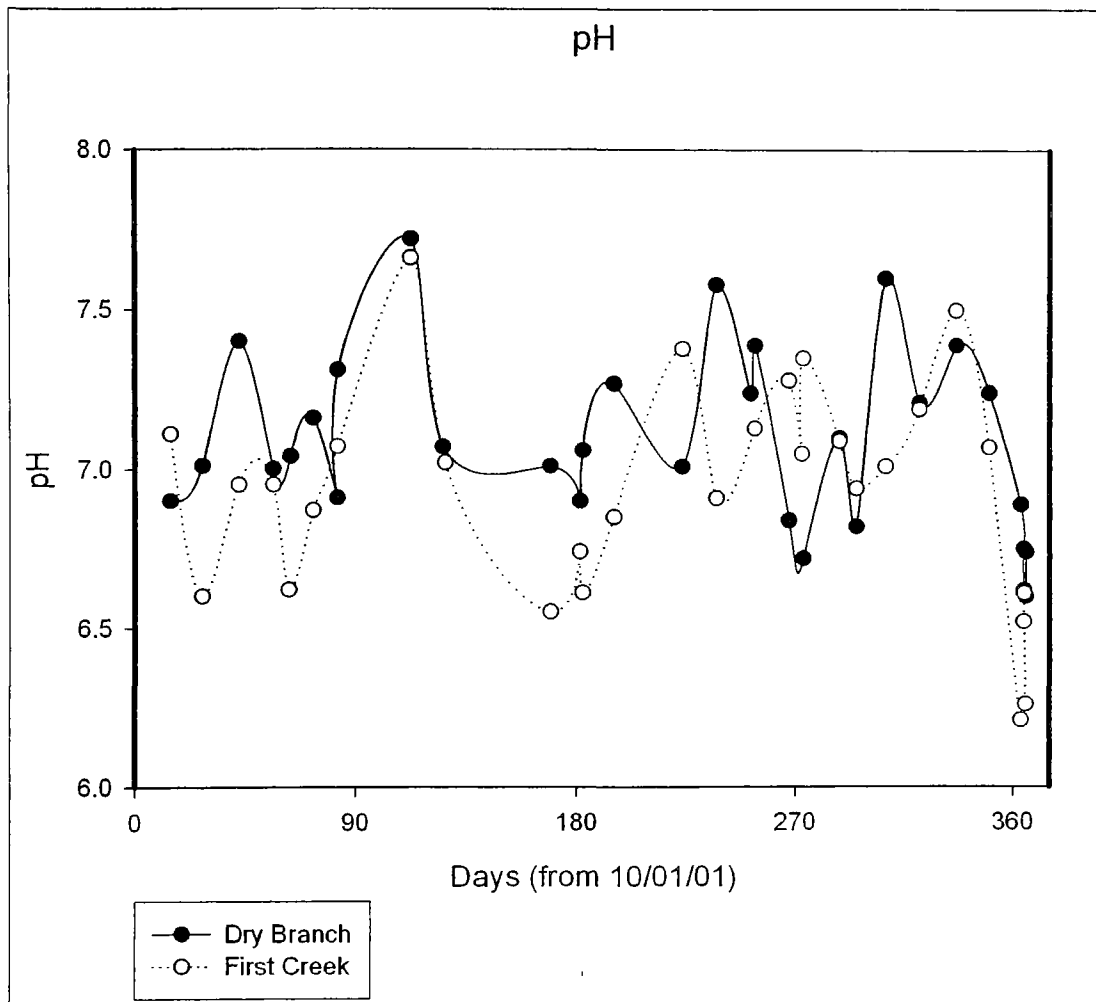


Figure 31 Stream pH values obtained from *in situ* field collection

### Dissolved Oxygen

Dissolved oxygen is an important parameter for aquatic biology, and the differences and similarities in dissolved oxygen between karst and non-karst basins warrant its discussion. Dissolved oxygen values for the two basins (Table 23 and Figure 32) were highly variable throughout the year, but were similar enough to each other to

Table 23 Dissolved oxygen values obtained from in situ field collection (10/01/2001 – 09/30/2002)

Month	Dissolved Oxygen (DO)					
	By Month		Season		Annual	
	First Creek	Dry Branch	First Creek	Dry Branch	First Creek	Dry Branch
October	Mean = 5.10 sd = min. = 5.10 max. = 5.10 N = 1	Mean = 5.90 sd = min. = 5.90 max. = 5.90 N = 1	<b>Fall</b> Mean = 6.0833 sd. = 0.8694 Error = 0.5019 95% = 2.1552 99% = 4.9094 min. = 5.10 max. = 6.75 N = 3	<b>Fall</b> Mean = 6.68 sd = 0.7018 Error = 0.3509 95% = 1.1165 99% = 2.0461 min. = 5.90 max = 7.32 N = 4	Mean = 7.115 sd = 1.7661 Error = 0.5098 95% = 1.1221 99% = 1.5835 min. = 4.78 max. = 11.04 N = 12	Mean = 7.6146 sd = 1.8391 Error = 0.5101 95% = 1.1114 99% = 1.5582 min. = 5.9 max. = 11.51 N = 13
November	Mean = 6.75 sd = min. = 6.75 max. = 6.75 N = 1	Mean = 6.27 sd = min. = 6.27 max. = 6.27 N = 1				
December	Mean = 6.40 sd = min = 6.40 max. = 6.40 N = 1	Mean = 7.27 sd = min. = 7.22 max. = 7.32 N = 2				
January	Mean = 11.04 sd = min. = 11.04 max. = 11.04 N = 1	Mean = 11.51 sd = min. = 11.51 max. = 11.51 N = 1	<b>Winter</b> Mean = 9.375 sd = Error = 95% = 99% = min. = 7.71 max. = 11.04 N = 2	<b>Winter</b> Mean = 9.27 sd = Error = 95% = 99% = min. = 7.03 max. = 11.51 N = 2		
February	Mean = sd = min. = max. = N = 0	Mean = sd = min. = max. = N = 0				
March	Mean = 7.71 sd = min. = 7.71 max. = 7.71 N = 1	Mean = 7.03 sd = min. = 7.03 max. = 7.03 N = 1				
April	Mean = sd = min. = max. = N = 0	Mean = sd = min. = max. = N = 0	<b>Spring</b> Mean = 8.99 sd = Error = 95% = 99% = min. = 8.99 max. = 8.99 N = 1	<b>Spring</b> Mean = 9.16 sd = Error = 95% = 99% = min. = 9.16 max. = 9.16 N = 1		
May	Mean = 8.99 sd = min. = 8.99 max. = 8.99 N = 1	Mean = 91.6 sd = min. = 91.6 max. = 91.6 N = 1				
June	Mean = sd = min. = max. = N = 0	Mean = sd = min. = max. = N = 0				
July	Mean = sd = min. = max. = N = 0	Mean = sd = min. = max. = N = 0	<b>Summer</b> Mean = 6.565 sd = 1.3049 Error = 0.527 95% = 1.3694 99% = 2.1480 min. = 4.78 max. = 8.61 N = 6	<b>Summer</b> Mean = 7.43 sd = 1.8701 Error = 0.7635 95% = 1.9626 99% = 3.0785 min. = 5.99 max. = 10.72 N = 6		
August	Mean = 6.065 sd = min. = 4.78 max. = 7.35 N = 2	Mean = 8.66 sd = min. = 6.60 max. = 10.72 N = 2				
September	Mean = 6.815 sd = 1.2195 min. = 5.99 max. = 8.61 N = 4	Mean = 7.67 sd = 2.2062 min. = 6.24 max. = 10.96 N = 4				

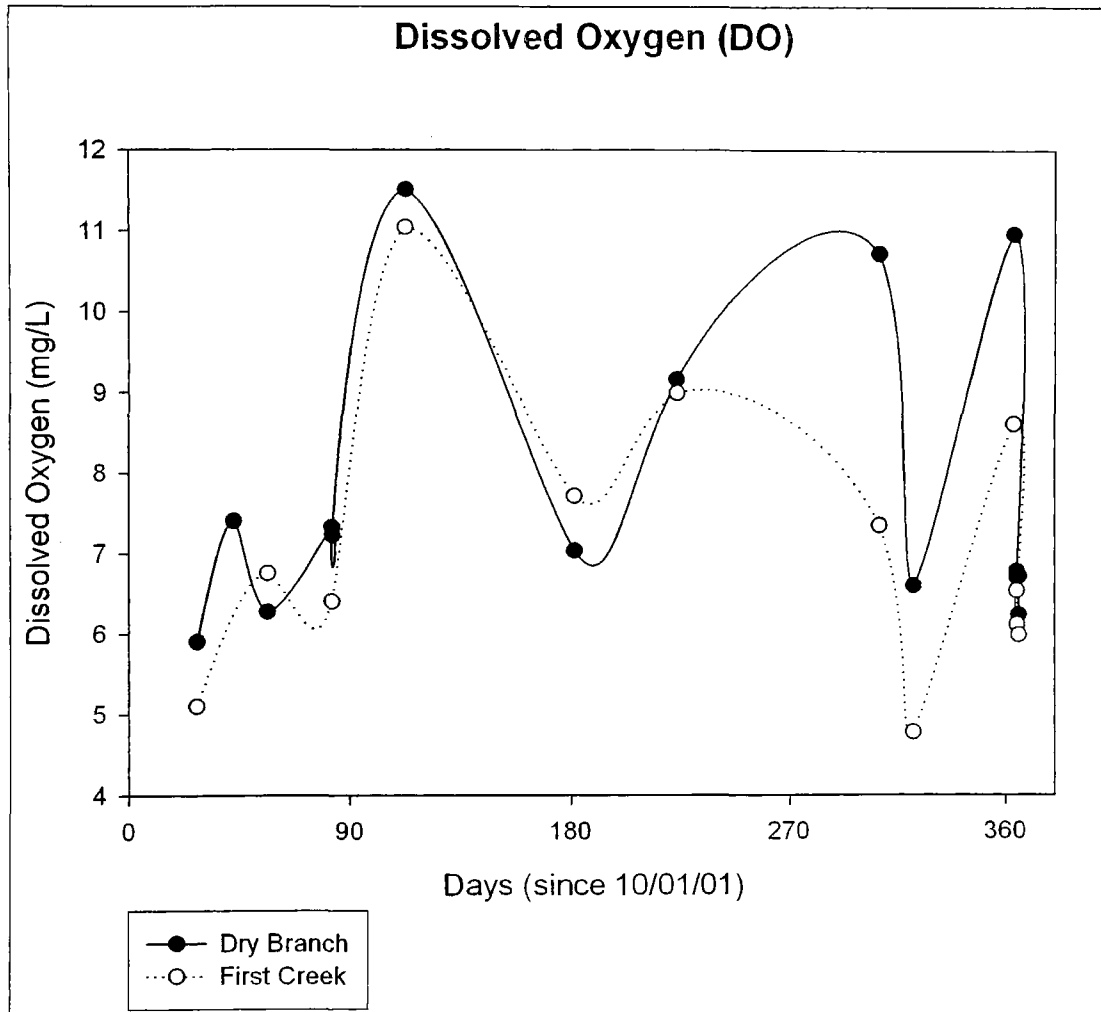


Figure 32 Dissolved oxygen values obtained from *in situ* field collection

conclude that if the presence of carbonate karst had any effect upon dissolved oxygen, it was too subtle to observe.

### Calcium

Calcium shows similar trends within the two basins, except for the higher concentrations within the Dry Branch basin (Figure 33). The cause of this difference is

believed to be the higher quantity of exposed carbonate rocks within the Dry Branch basin.

There does not appear to be a noticeable seasonal trend, beyond a higher range of variability during the summer.

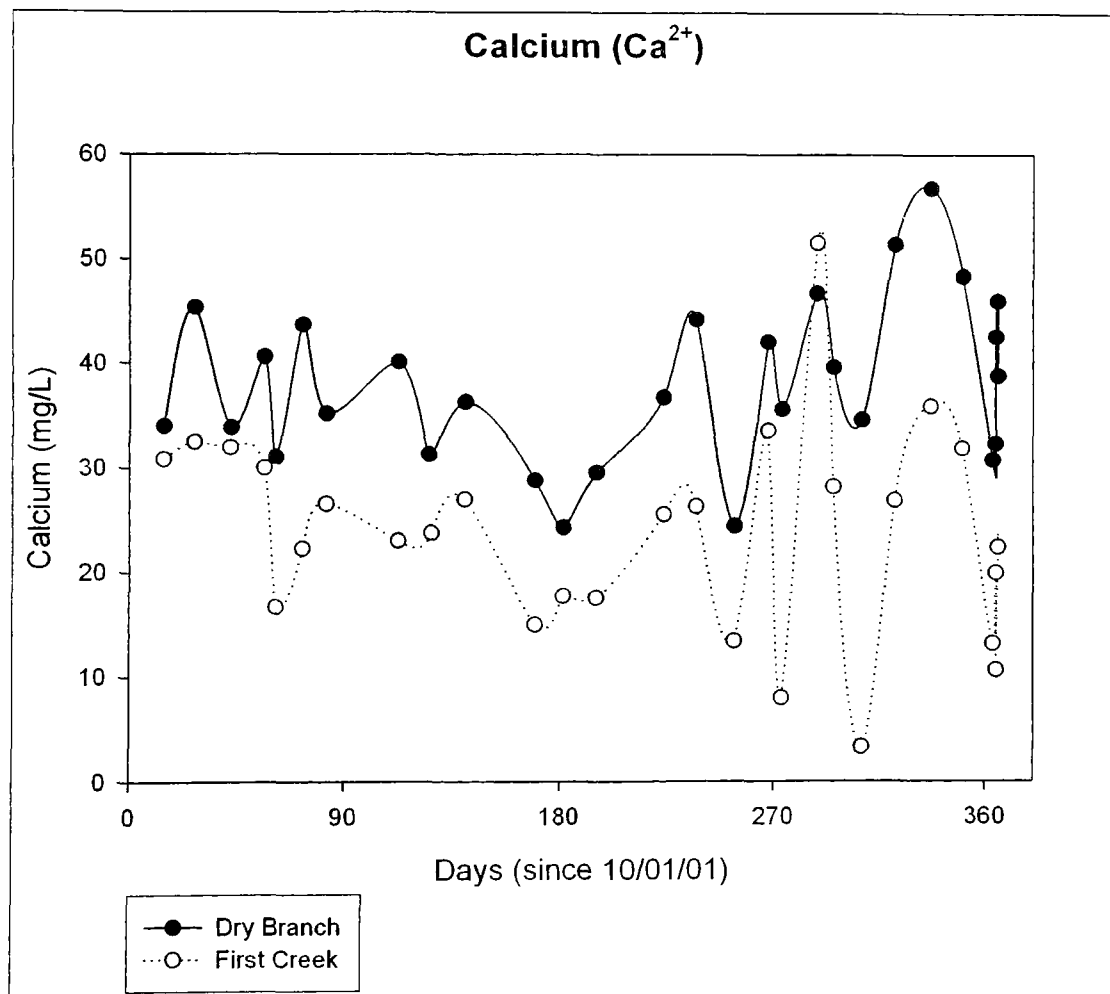


Figure 33 Calcium ion concentrations from First Creek and Dry Branch

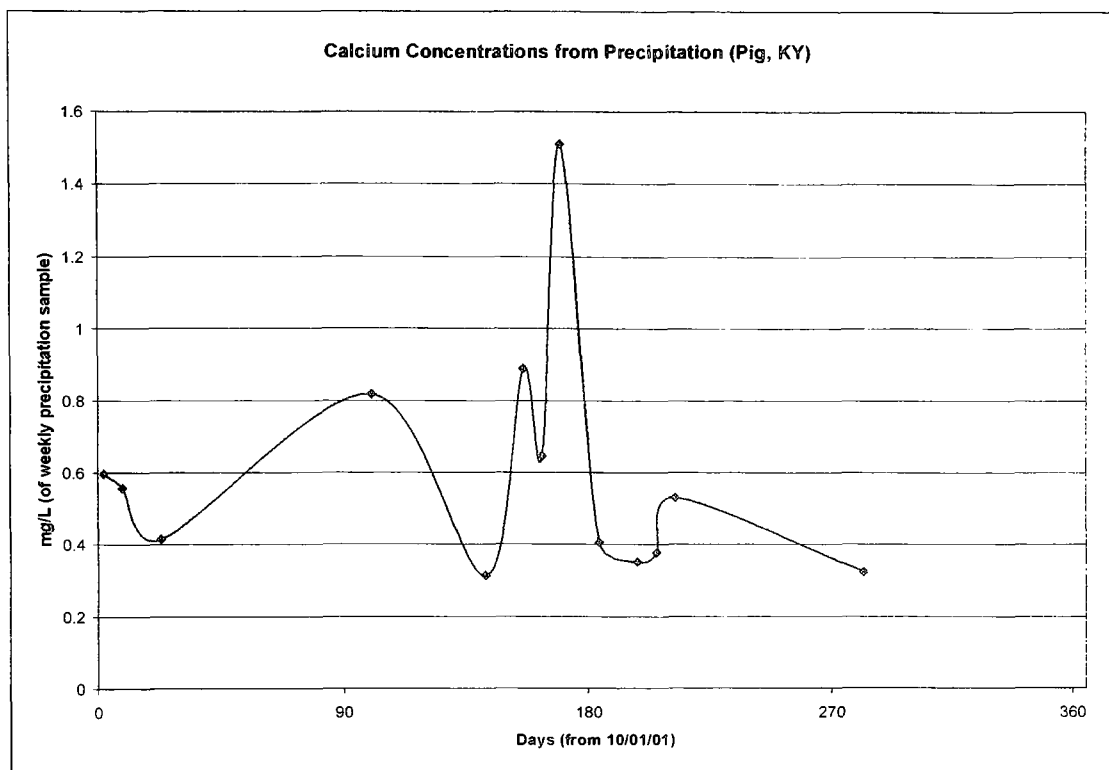


Figure 34 Calcium concentrations from precipitation at Fig, Kentucky

### Magnesium

The magnesium concentrations trends for the two basins are nearly identical, except for generally higher values for the Dry Branch basin (Figure 35). The explanation may be the higher quantity of exposed carbonate rocks within the Dry Branch basin, the primary source of both calcium and magnesium in this setting. An interesting trend is that the differences between the magnesium concentrations within the two basins appear to be more pronounced in the peaks rather than the troughs. These may be affected by storm events versus the more common base-flow conditions.

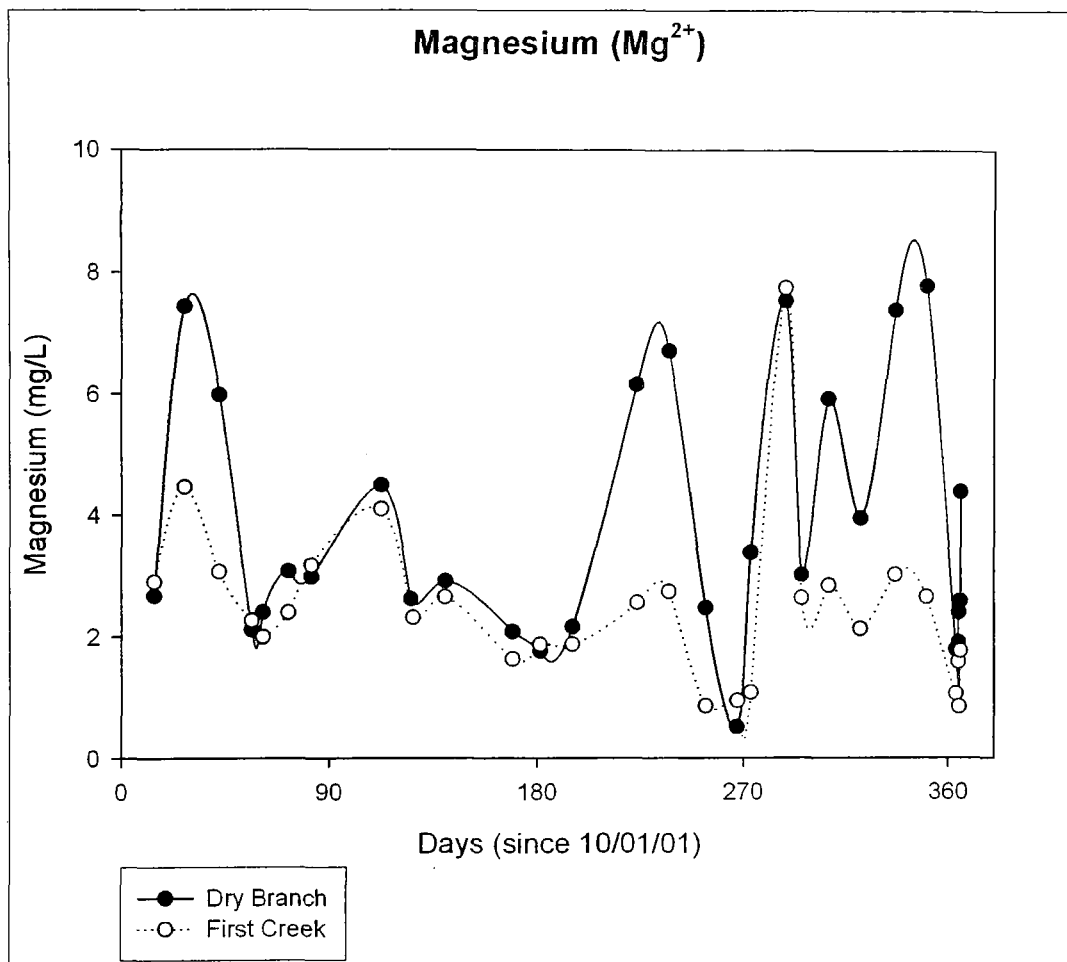


Figure 35 Magnesium ion concentrations from First Creek and Dry Branch

#### Bicarbonate

For the purposes of this study, the concentration of bicarbonate is assumed to be equal to alkalinity. The alkalinity values for Dry Branch were consistently higher than those within First Creek (Figure 36). The general pattern remained the same, with fall and summer highs and late winter/early spring lows. The alkalinity values are probably the result of carbonate dissolution. The winter/spring lows may be attributed to the increased rainfall and discharge during this period. It is believed that the high discharge



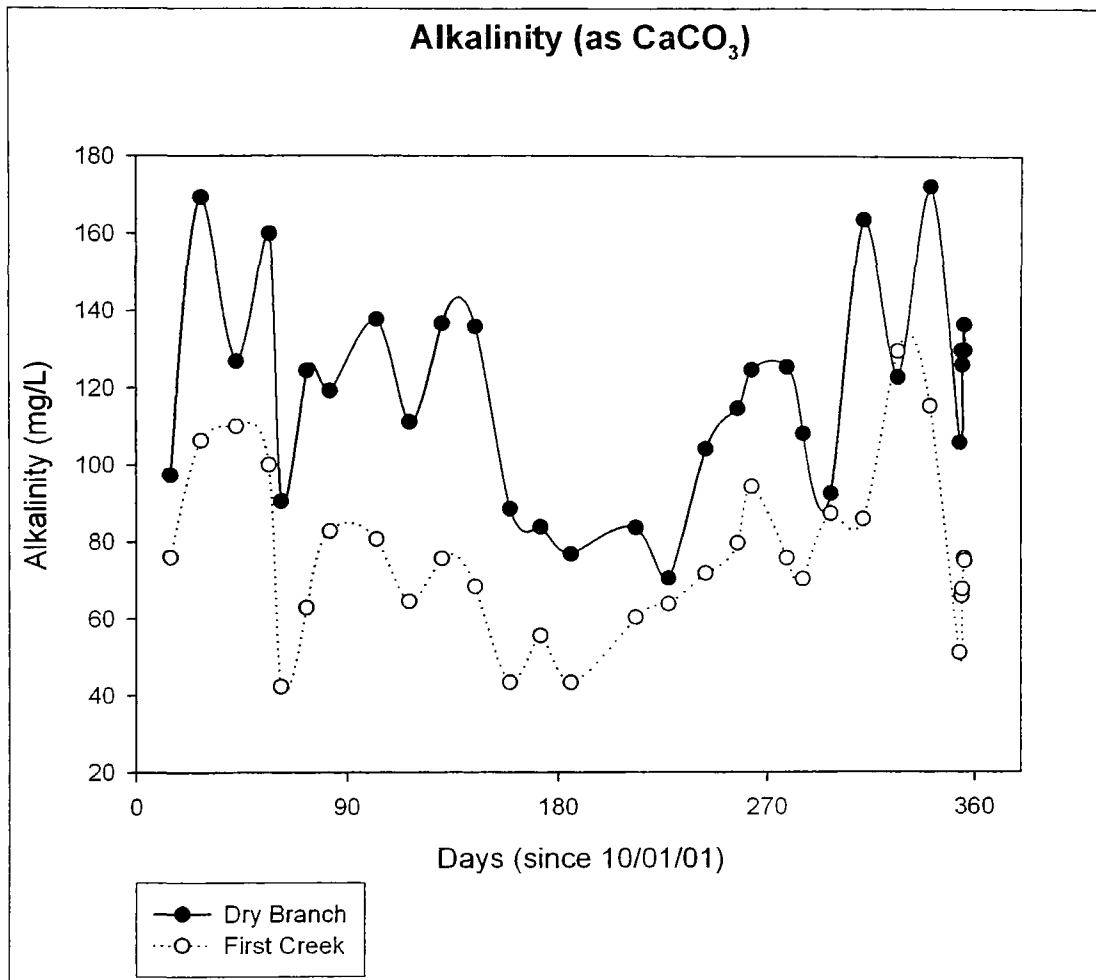


Figure 36 Alkalinity from First Creek and Dry Branch

values contain a higher percentage of overland flow with short residence times, thus lowering the relative concentration of dissolved carbonate species such as bicarbonate. During lower base-flow conditions, the relative concentration of carbonate dissolution would be higher.

The atmospheric monitoring station located in Pig, Kentucky was not equipped to record alkalinity of the precipitation. Therefore, direct comparisons cannot be made.

The Pig Station did record precipitation acidity (Figure 37). The study of the precipitation acidity data did not indicate a seasonal trend as significant as that of alkalinity of the streamwater, presumably due to the lack of contact with carbonate rocks.

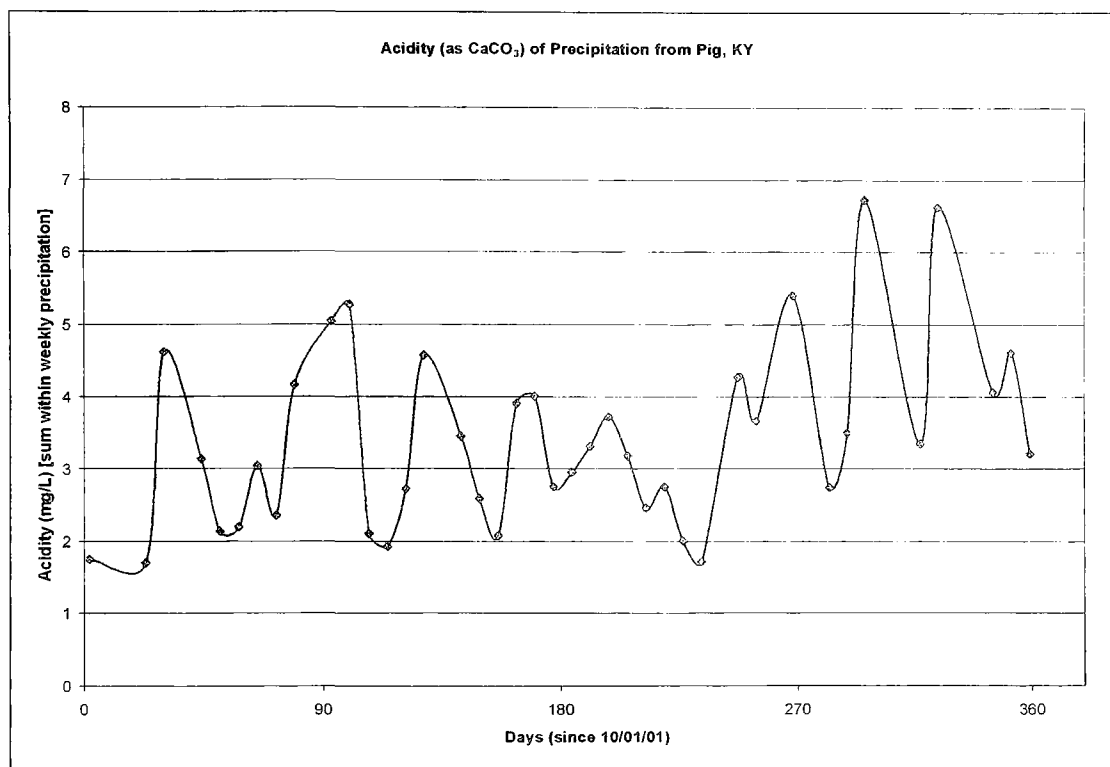


Figure 37 Acidity of precipitation from Pig, Kentucky

### Sodium

The fairly sporadic concentrations of sodium within both the First Creek and Dry Branch basins generally match each other. The main exception was that the sodium concentration within Dry Branch was consistently higher than the corresponding sodium concentrations within First Creek (Figure 38). These trends and the nature of sodium within natural waters leads me to the assumption that the dominate source of sodium

within these two basins is the product of weathering of non-carbonate bedrock such as shale or sandstone (Hem, 1989). Anthropomorphic sources, such as road salt used in the winter for de-icing or during certain oil well operations (Hem, 1989), may also be an occasional factor within the Dry Branch basin, but the author does not believe that they were a significant factor during this study, because most of the observed peaks and troughs, to varying degrees, occurred within both basins simultaneously. Since there are no significant roads or human habitation within the First Creek basin, one would not expect anthropomorphic perturbations that may occur within Dry Branch to be represented within the First Creek basin, unless the perturbations were from the atmosphere. The atmosphere generally is not a significant source of sodium (Hem, 1989).

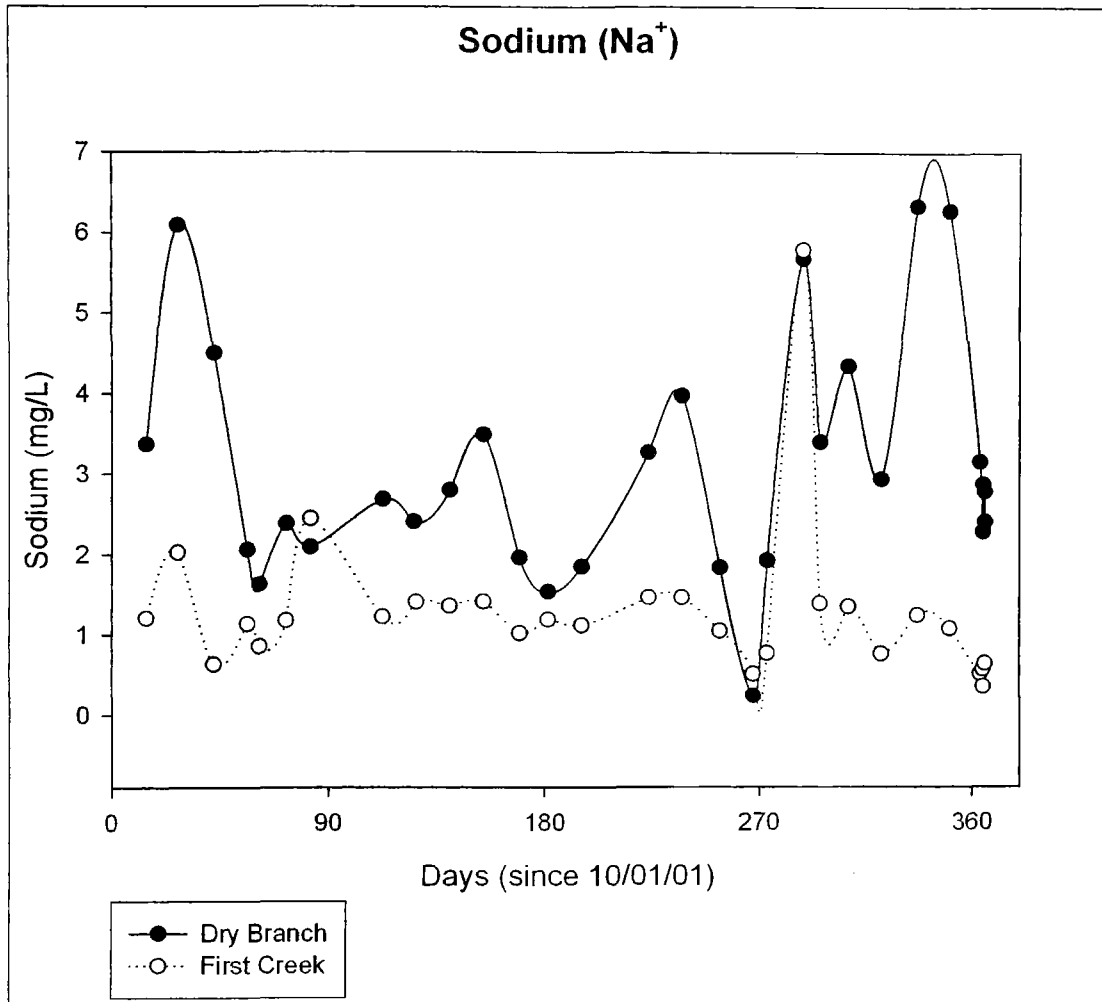


Figure 38 Sodium ion concentrations from First Creek and Dry Branch

### Potassium

Potassium concentrations within the First Creek and Dry Branch basins appear to behave in many of the same ways as do the sodium concentrations. However, there appears to be a difference in the seasonal trend (Figure 39). Unlike the trend in sodium concentrations for the First Creek and Dry Branch basins, which shows a slight increase during the spring and summer months, graphically the trend for potassium appears to experience a trough, a seasonal low, in winter.

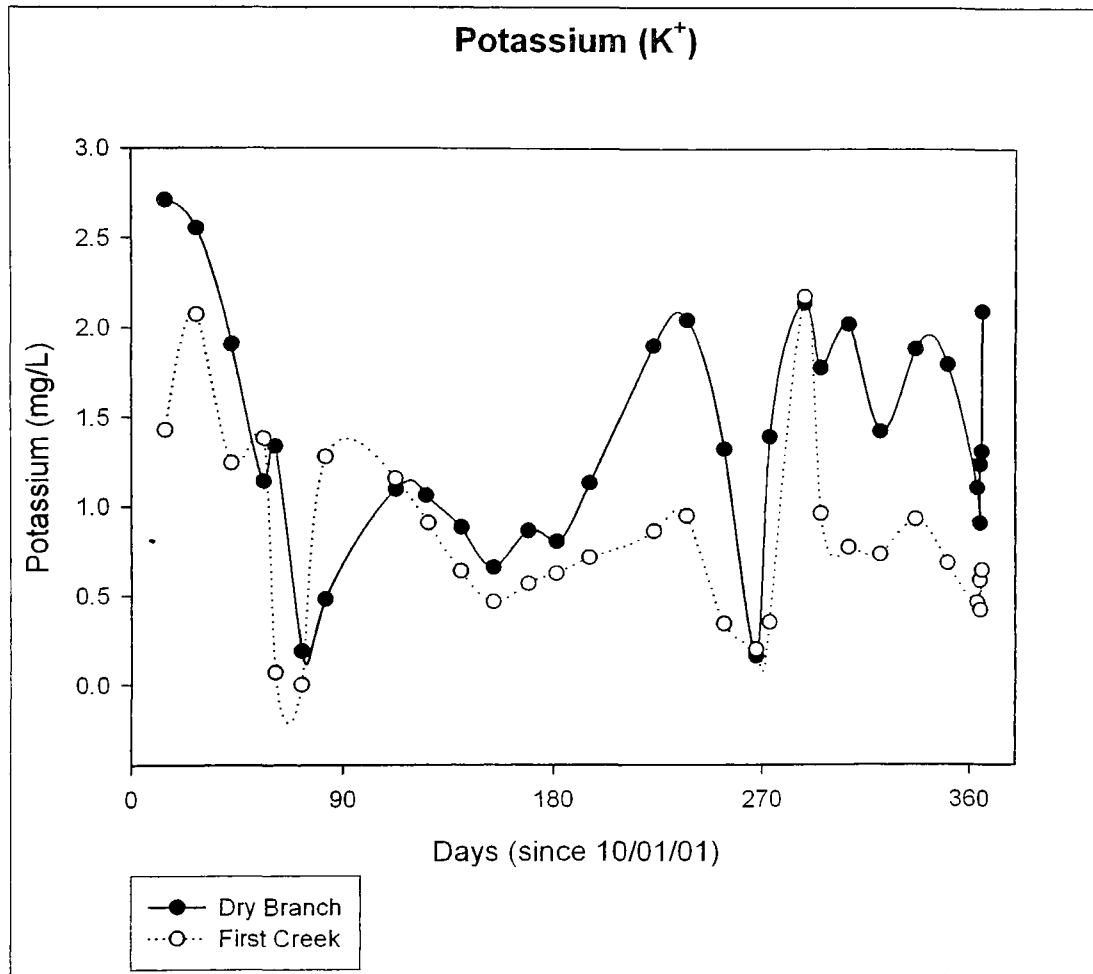


Figure 39 Potassium ion concentrations from First Creek and Dry Branch

Potassium concentrations in the two basins are similar, except for a slight depression of potassium concentrations in the First Creek Basin during the spring and summer. However, this trend is not consistent, whereas the trough and spike in late spring and early summer are nearly identical. I infer that the primary sources of potassium within the First Creek and Dry Branch basins are a combination of the atmosphere and the weathering of surface bedrock such as shale and sandstone.

## Chloride

Chloride concentrations follow similar patterns within both the First Creek and Dry Branch basins; however, concentrations are consistently higher within Dry Branch (Figure 40). The reason for this difference is possibly the result of weathering byproducts of a geological formation (such as a sandstone) containing more chlorine within Dry Branch basin than in the First Creek basin. Since chloride is not readily adsorbed and often not reactive with other chemicals and compounds (Hem, 1989), it would therefore suggest that the differences are either due to geological differences within the two basins or different atmospheric deposition characteristics.

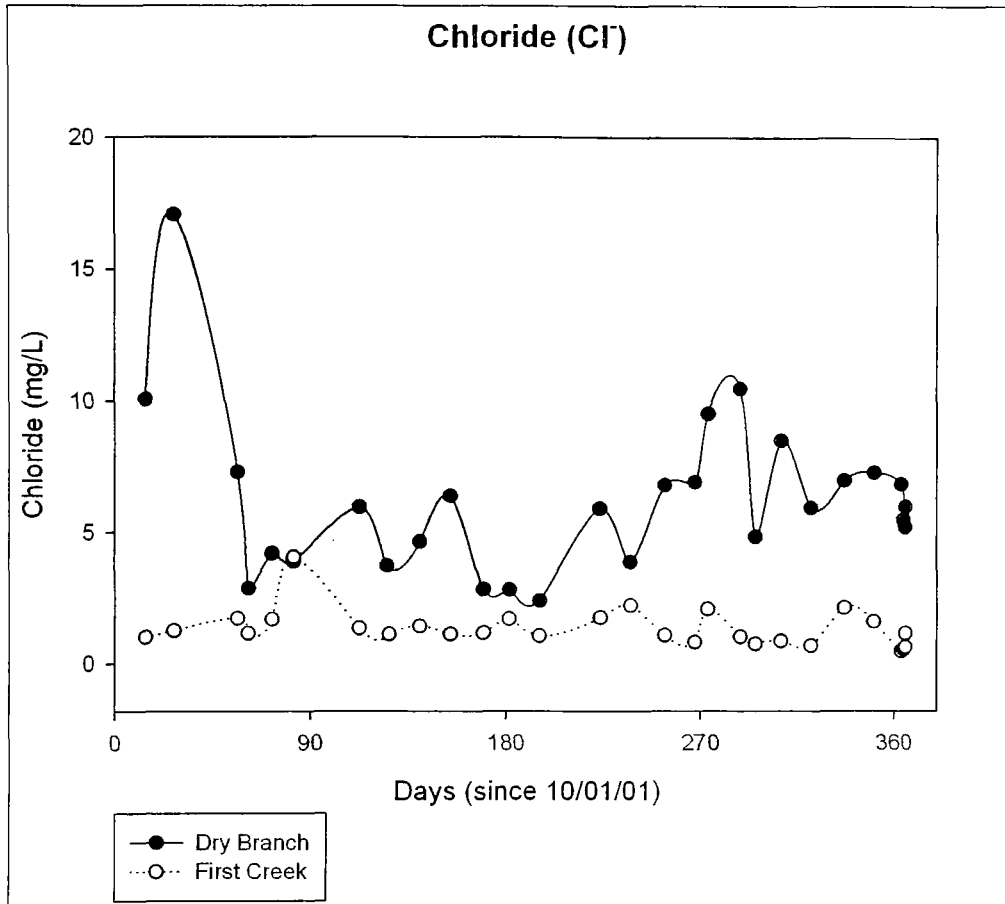


Figure 40 Chloride ion concentrations in First Creek and Dry Branch

Anthropomorphic causes, such as the winter application of salt on roadways for de-icing, are also a potential source of chloride in stream water as are brines and other associated products from oil well operations. Comparison with chloride concentrations found in rainwater from the nearby atmospheric monitoring station in Pig, Kentucky (Figure 41) indicates that the noticeable spike in chloride concentrations found in Dry Branch on approximately day 20 is derived from an atmospheric source. The cause of this spike may have been a localized storm that did not significantly affect the First Creek

basin. There appeared to be no other clearly observed correlation between the stream water concentrations and the concentrations recorded from precipitation.

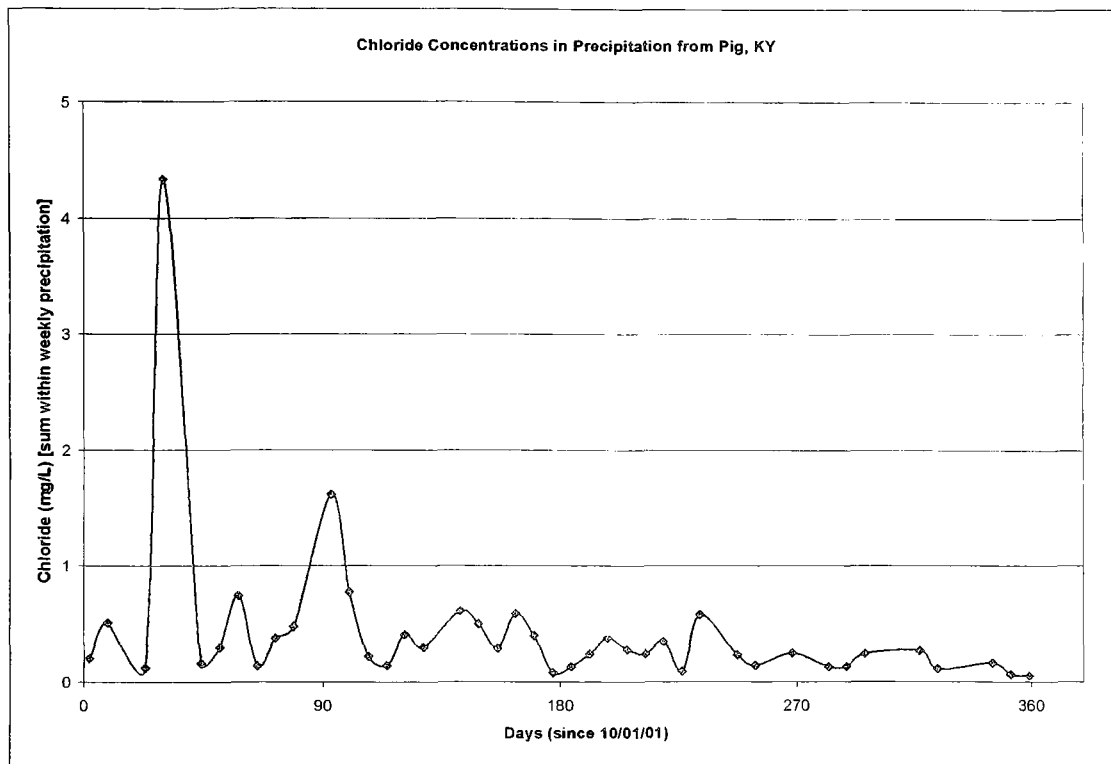


Figure 41 Chloride concentrations from precipitation from Pig, Kentucky

## Lithium

Dry Branch experienced more dynamic lithium concentrations than First Creek (Figure 42). Dry Branch was the only site that experienced two dramatic peaks (relative to the majority of the values throughout the year), one in early fall and the other in early spring. Besides these two noticeable dramatic peaks, there were five other peaks: both basins experienced a moderate peak in early summer, the Dry Branch basin had another



moderate peak in late summer, while First Creek's other moderate peaks (in early spring and early fall) corresponded with both of Dry Branch's large peaks. The lithium peak in Dry Branch in late summer was the only peak that was not represented at all in the First Creek basin. It is important to note that while graphically these peaks are dramatic; they still represent small quantities of lithium concentrations.

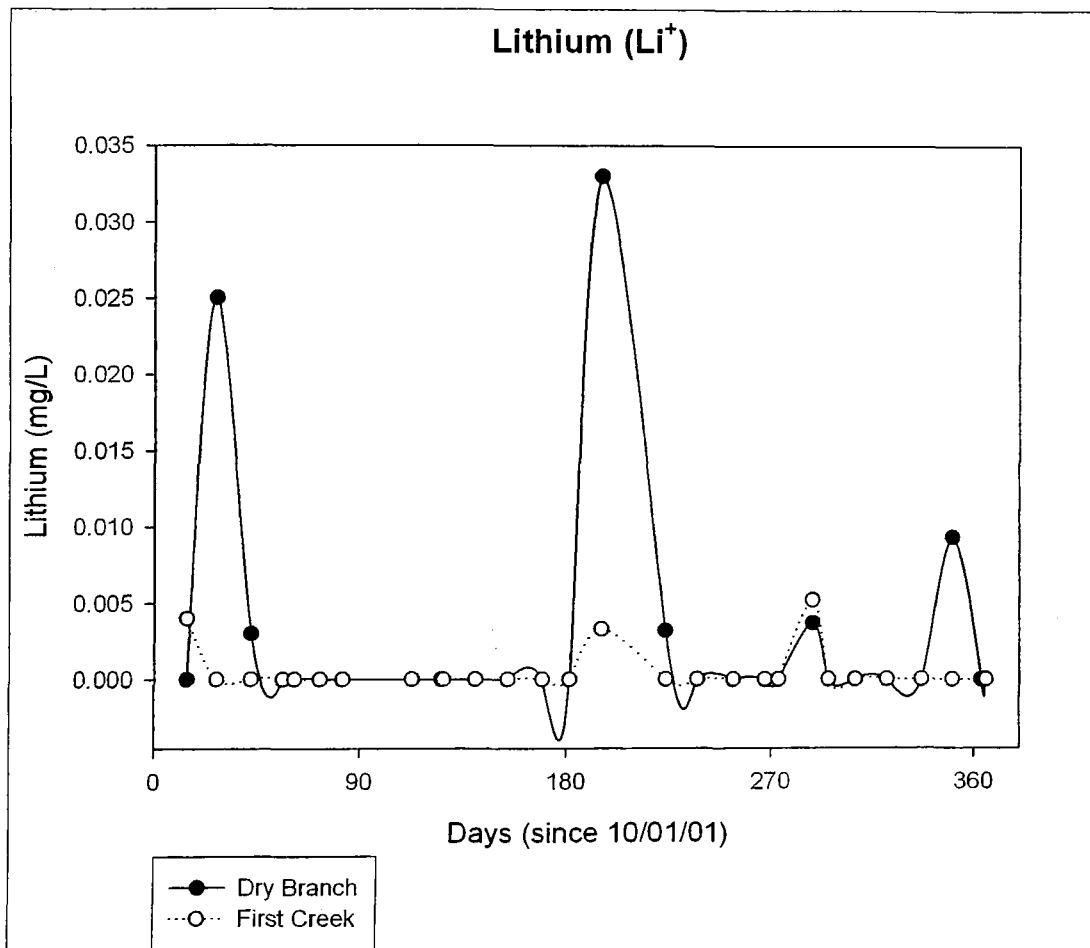


Figure 42 Lithium ion concentrations within Dry Branch and First Creek

Shales are known to contain a moderate amount of lithium (Horn and Adams, 1966). The Dry Branch basin contains more shale than does First Creek. Therefore the source of the lithium for these two basins may be the various shales. However, the

several peaks separated by zero lithium concentrations do not appear to be consistent with typical weathering patterns. It is notable that bromide concentrations experienced a similar pattern; however not all the bromide peaks corresponded with the lithium peaks. It is important to remember that although the lithium spikes depicted in Figure 42 are quite noticeable they still represent very small concentrations.

### Bromide

Due to the nearly identical trends and concentration levels between the two basins (Figure 43), it is assumed that the bromide source is precipitation. However, since the nearby atmospheric monitoring station located in Pig, Kentucky was not set up to record bromide concentrations, I was unable to confirm this assumption. An atmospheric source appears consistent with other studies (Hem, 1989). The two spikes in the graph, above a zero background level, occurred in mid-winter and late summer.

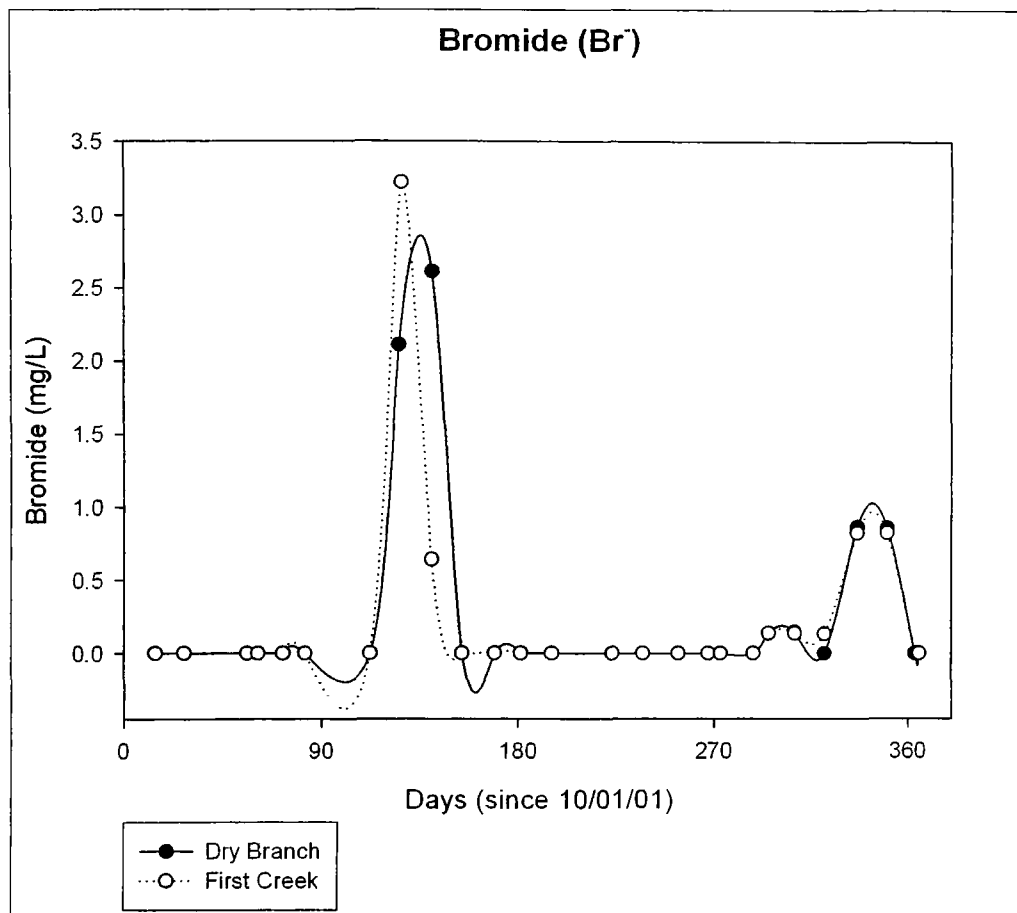


Figure 43 Bromide ion concentrations within Dry Branch and First Creek

### Fluoride

Although the fluoride concentrations from the two basins (Figure 44) are low, the primary seasonal trend demonstrated on the graph indicates a slight increase in fluoride concentrations during the summer months.

Hem (1989) indicates that sedimentary rocks are a primary source of dissolved fluoride in streams. However, since the geology of the two basins is different and presumably the atmospheric inputs similar, everything else being equal, it is logical to

conclude that if the fluoride concentrations in the two basins are similar, they would be due to atmospheric inputs. The atmospheric monitoring station located in Pig, Kentucky was not set up to record fluoride concentrations during this time period; therefore I am unable to confirm this assumption. However, nothing was found in the literature to conclude that the atmosphere can be a greater source of fluoride than the weathering of bedrock; therefore, I conclude that the primary source of fluoride ions within Dry Branch and First Creek is from bedrock weathering and that the differences in geology between the two basins are insignificant with respect to being a source for fluoride.

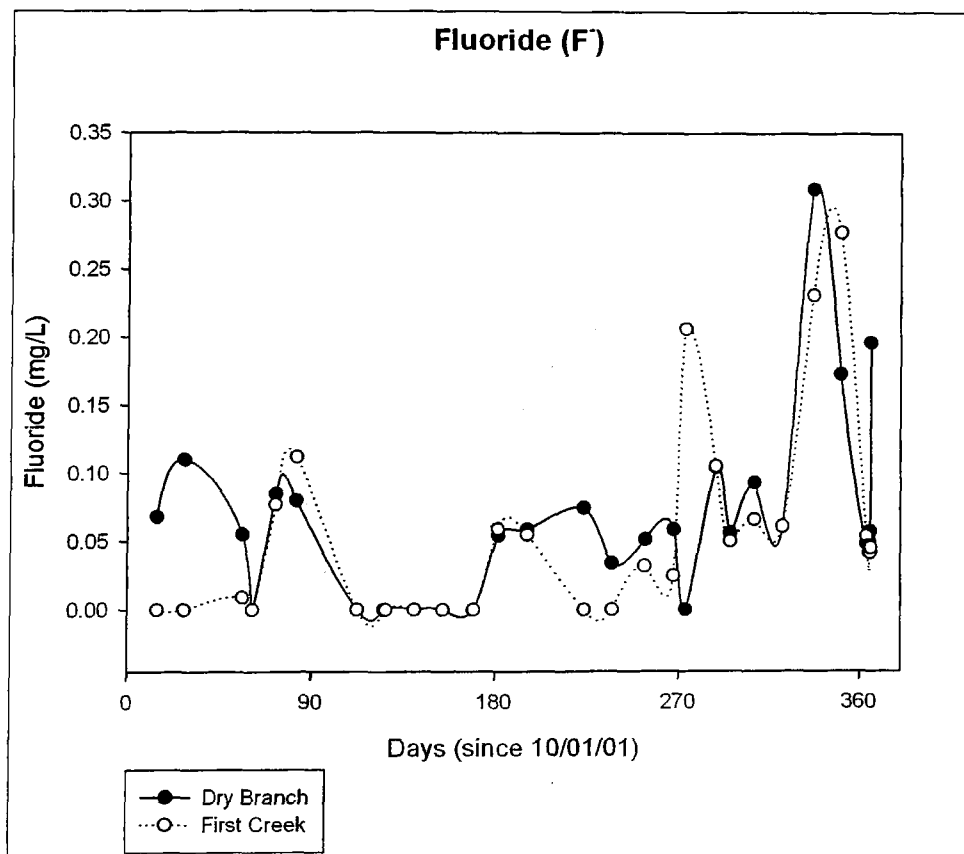


Figure 44 Fluoride ion concentrations within Dry Branch and First Creek

## Sulfate

Likens and Bormann (1995) found that sulfate concentrations reached their annual low in late winter within the Hubbard Brook basin in New England. However, these trends are nearly opposite from the observed values within both the First Creek and Dry Branch basins. Late fall and early winter was the annual peak for sulfate for both the Dry Branch and First Creek basins (Figure 45). Sulfate concentrations within Dry Branch experienced many peaks and troughs, but generally remained fairly consistent throughout the year (at approximately 12 mg/L).

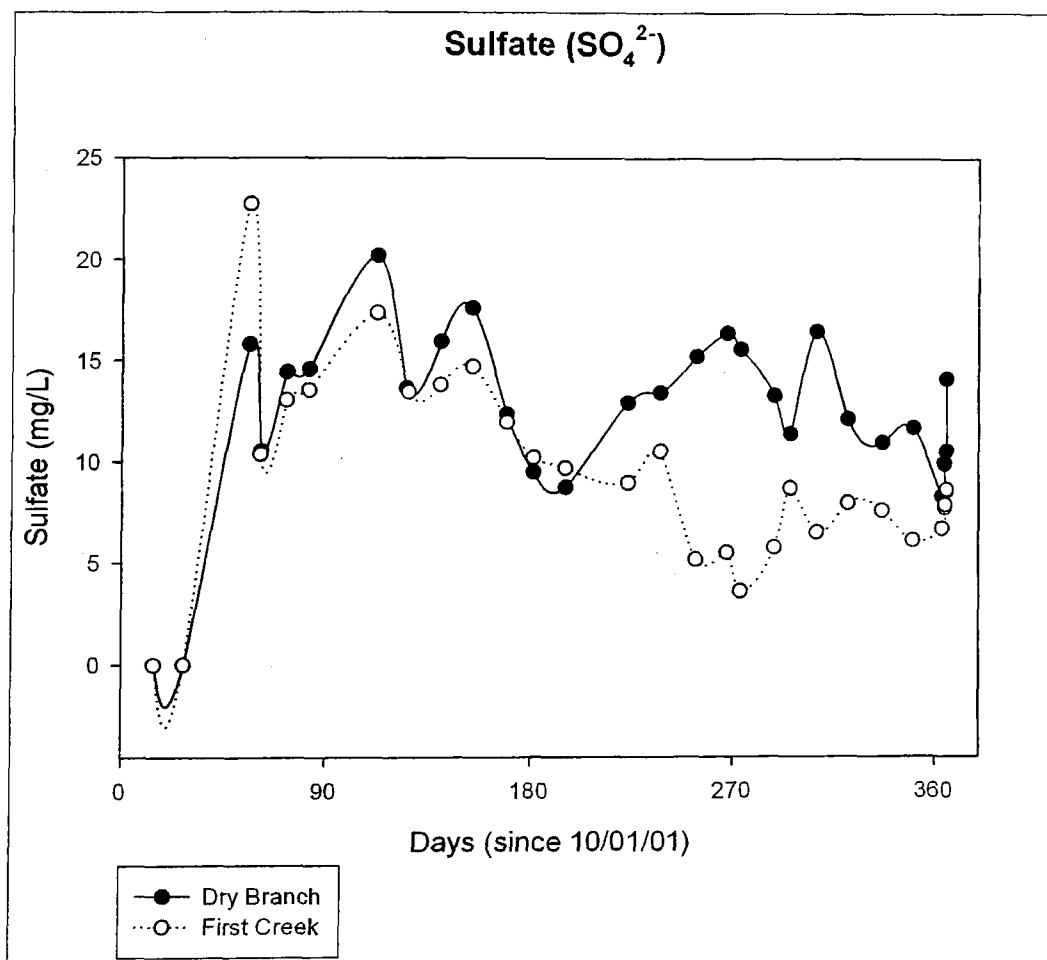


Figure 45 Sulfate ion concentrations from Dry Branch and First Creek

Sulfate concentrations for the First Creek basin matched closely the trends observed in the Dry Branch basin during the fall and winter, but declined and showed different individual trends throughout most of the spring and summer. The timing of these differences corresponds well with the timing of the basin's biologic activities. If these differences are the result of biologic processes, then karst's influences on sulfate would be similar to its influence upon both nitrate and phosphate- all three being important biologic nutrients.

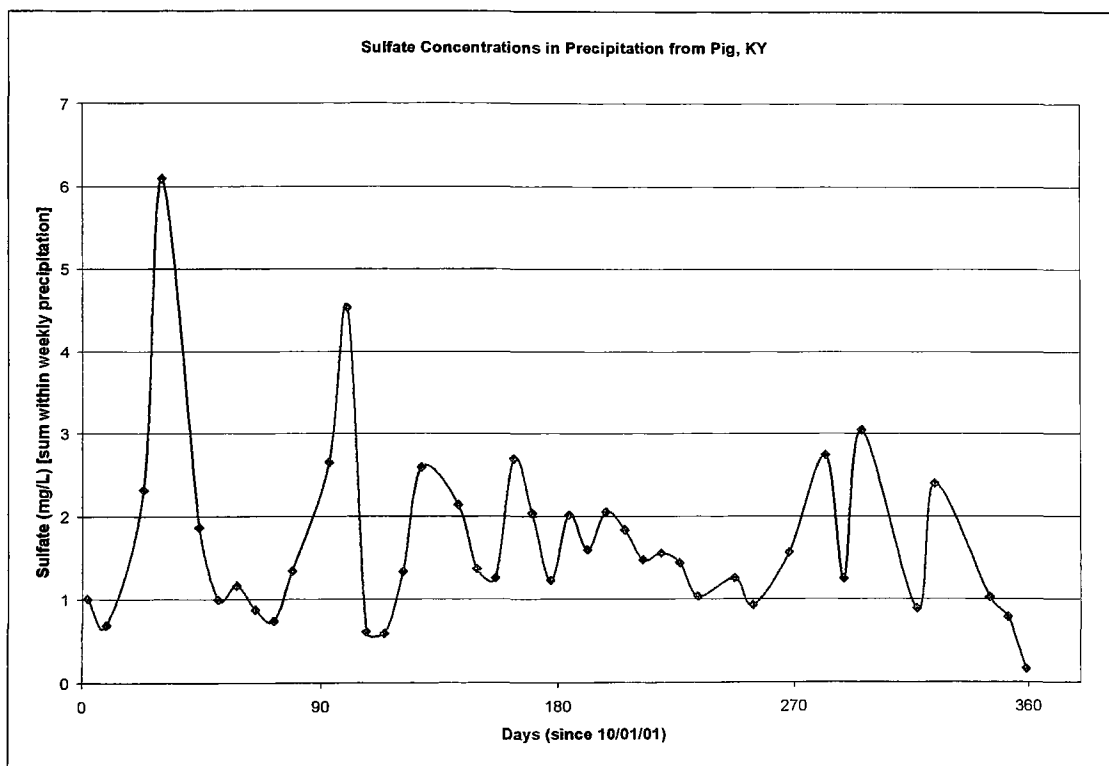


Figure 46 Sulfate ion concentrations from precipitation at Pig, Kentucky

While the presence and/or absence of karst within a basin may affect the relative concentration of dissolved sulfate concentration within streams, the sulfate concentrations

within precipitation (Figure 46) indicates that atmospheric sources highly affect and/or drive the general patterns of sulfate input into the two study basins.

### Phosphate

With the exception of small detections in the Dry Branch basin within the fall, phosphate concentrations within both basins were zero (Figure 47). The spikes (still very low concentrations) in phosphate within the Dry Branch basin for the fall are either the result of natural processes or due to anthropomorphic sources. Since phosphorus is a minor but widespread constituent of several rock types within these basins (and therefore a byproduct of weathering) and is an important but limited nutrient for plant growth, the absence of phosphate in both basins through most of the year may be explained by biologic retention and utilization within the basins. Natural causes of the fall spikes could be perhaps due to the bypassing of the surface vegetation by the filling and routing of early season water through subsurface karst conduits (also discussed under the nitrate section). There is a small population of people living within the Dry Branch basin. Although human sewage can be a source of phosphorus (Hem, 1989), if it were the source of the phosphate concentration observed within Dry Branch during the autumn, it is logical to conclude that this sewage leakage would occur throughout the year. Comparison with other non-populated karst basins in the region would be helpful in deciphering the observed phosphate concentrations in the Dry Branch basin. Since there were only two detected phosphate values, and that these two values still represents very low concentrations, there is possibility that these two points are in error.

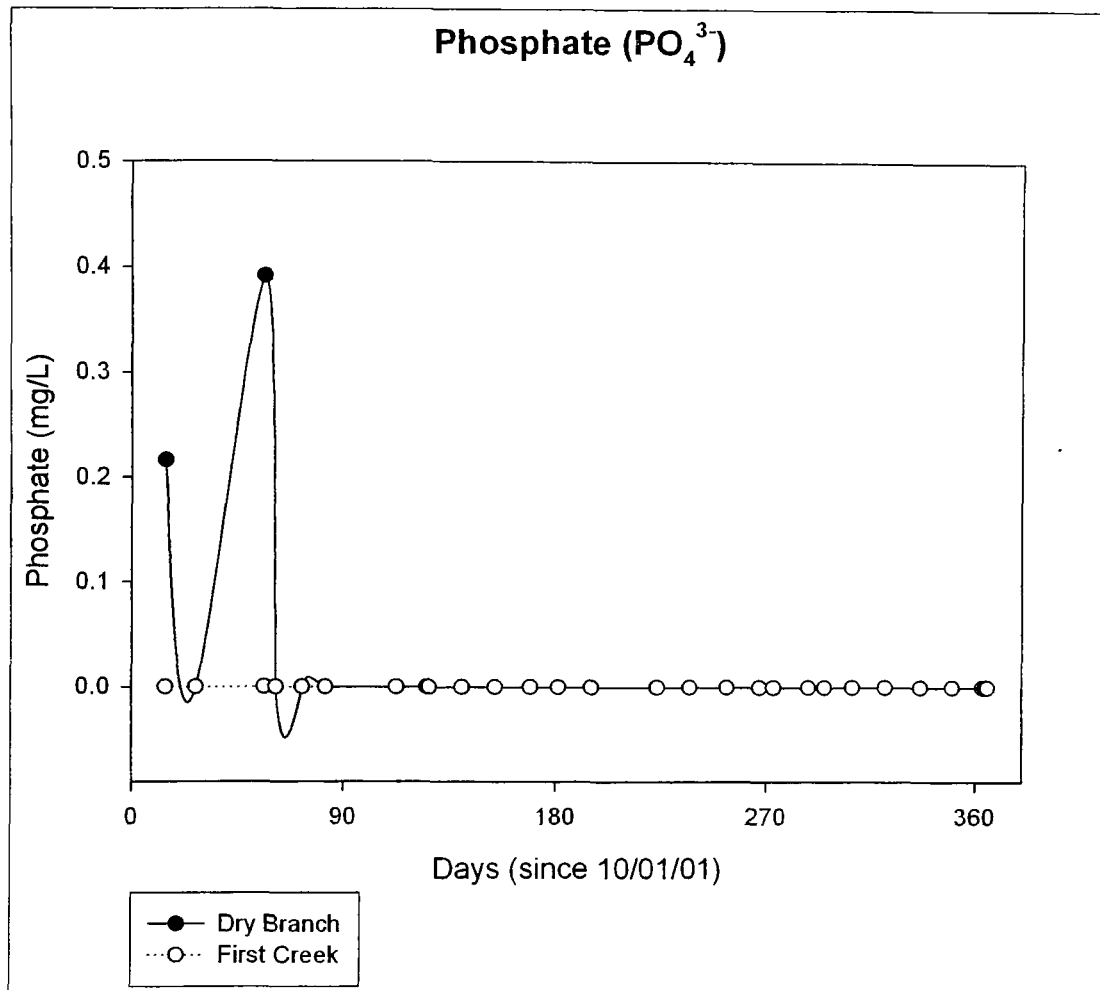


Figure 47 Phosphate ion concentrations from First Creek and Dry Branch

### Ammonium

With two exceptions, the ammonium concentrations within the First Creek and Dry Branch basins are similar (Figure 48), leading the author to assume that the dominant source is atmospheric deposition. There does appear to be a slight increase in ammonium concentrations in the spring and summer. There are two noticeable spikes in the ammonium concentrations in the First Creek basin, one occurring in early fall and



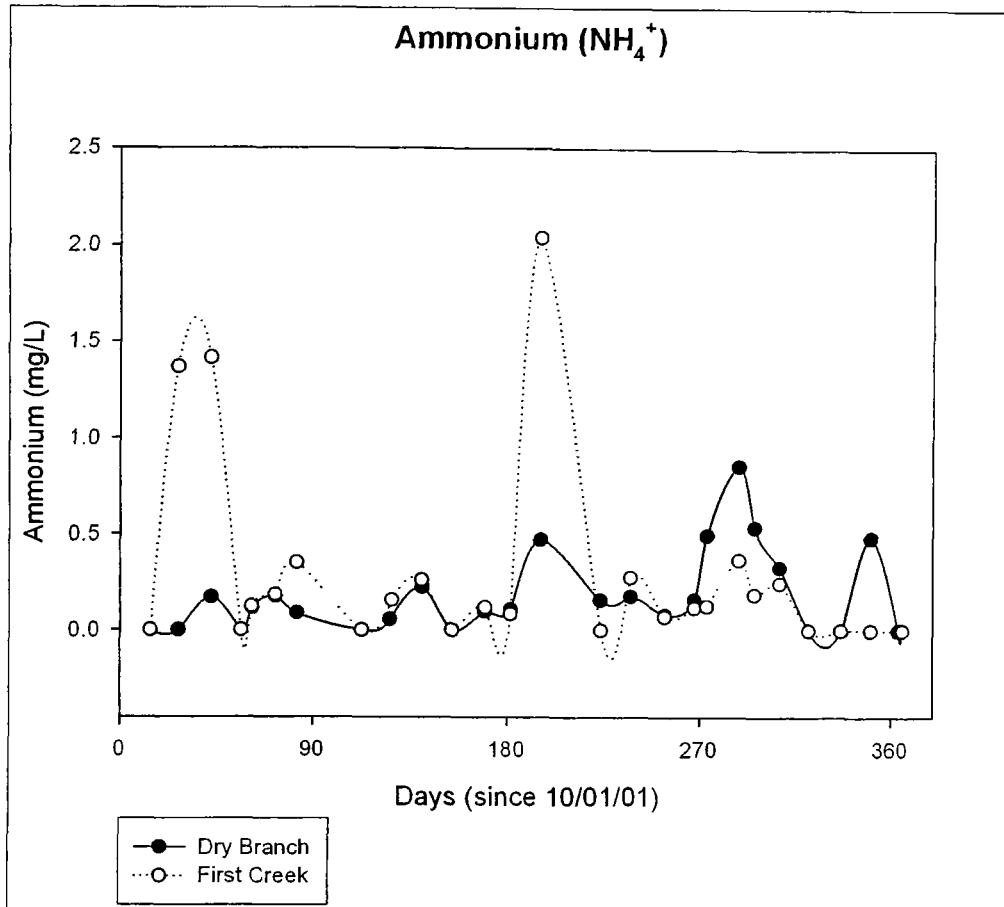


Figure 48 Ammonium ion concentrations from First Creek and Dry Branch

the other in early spring. It is possible that these spikes were the result of an unnatural pollution event that occurred in the First Creek basin; however the nature and source of this potential pollution event is unknown.

The atmosphere is a typical source of ammonium, often as a result of human-induced pollution or disturbances (Hem, 1989). Atmospheric sources often enter watersheds via precipitation (Figure 49). Other potential anthropomorphic sources of ammonium include artificial fertilizers from home, yards and gardens.

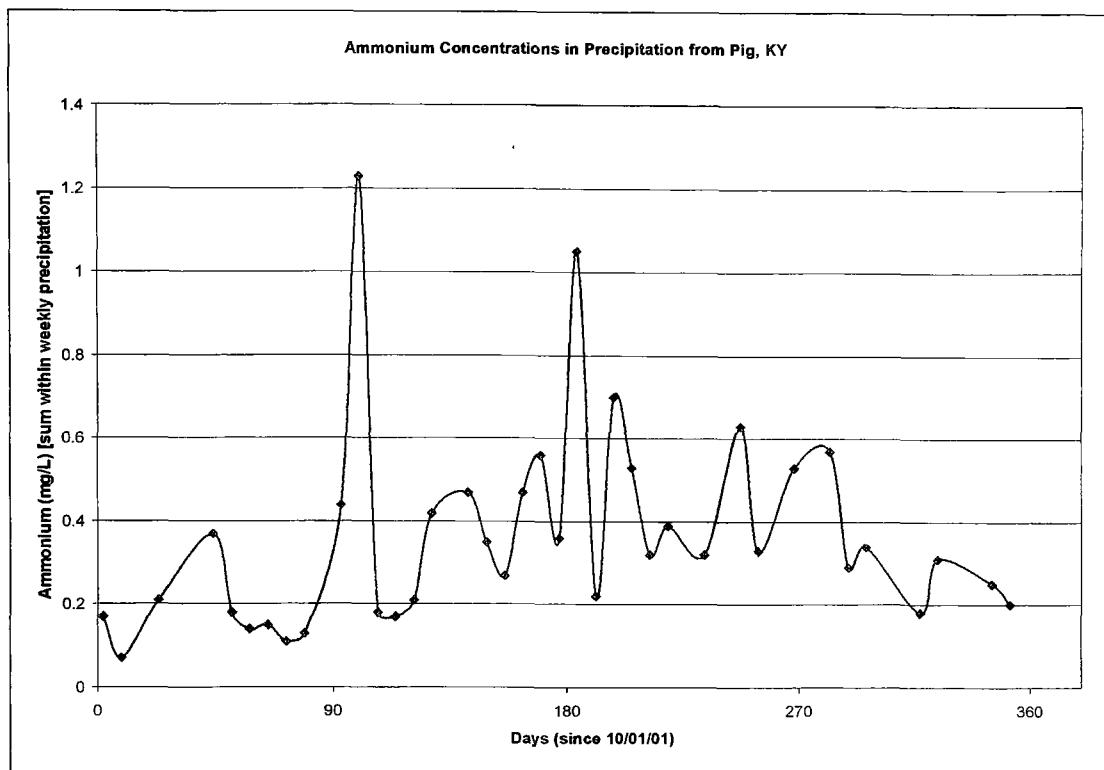


Figure 49 Ammonium ion concentrations within precipitation at Pig, Kentucky

Atmospheric sources may explain the similar trends observed throughout the year, but it does not adequately explain both peaks in the First Creek ammonium concentrations. The noticeable ammonium spike that occurred within the precipitation near day 180 corresponds well with the noticeable ammonium concentration spike within the First Creek water samples. However the even higher spike in ammonium concentration within precipitation that occurred near day 90 is nearly unnoticeable within either the First Creek or Dry Branch water samples. In addition, the noticeable water chemistry spike in ammonium that occurred at the very start of the sampling period (approximately day ten) does not correlate well with an atmospheric source, as indicated from the precipitation samples obtained from Pig, Kentucky. It is interesting to note that

timing of the spikes and troughs within the ammonium stream chemistry data matched very well. It is also important to note that although the First Creek spikes in Figure 48 appear dramatic relative to the rest of the data, the concentrations that these spikes represent are still relatively low concentrations and the spikes may be nothing more than random fluctuations.

### Nitrite

Nitrite concentrations within Dry Branch basin were zero through the period of the study. During most of this period the nitrite concentrations were zero for the First Creek basin as well. However, during the summer there were three noticeable spikes of nitrite concentrations (Figure 50) that do not correspond well with any other measured parameter or observed trend. The presence of nitrite in streams is often associated with wastewater or pollution sources. However, the First Creek basin is entirely within the boundaries of Mammoth Cave National Park and is undeveloped and has no human occupation. Therefore, the causes or sources of these summer spikes are unknown. The presence of the summer spikes of nitrite within First Creek may be due to redox processes caused by microbiologic activity within First Creek Lake, located directly upstream of the sampling site. It is important to note that while these summer spikes are noticeable compared with the rest of the dataset, the concentrations represented are considered low.

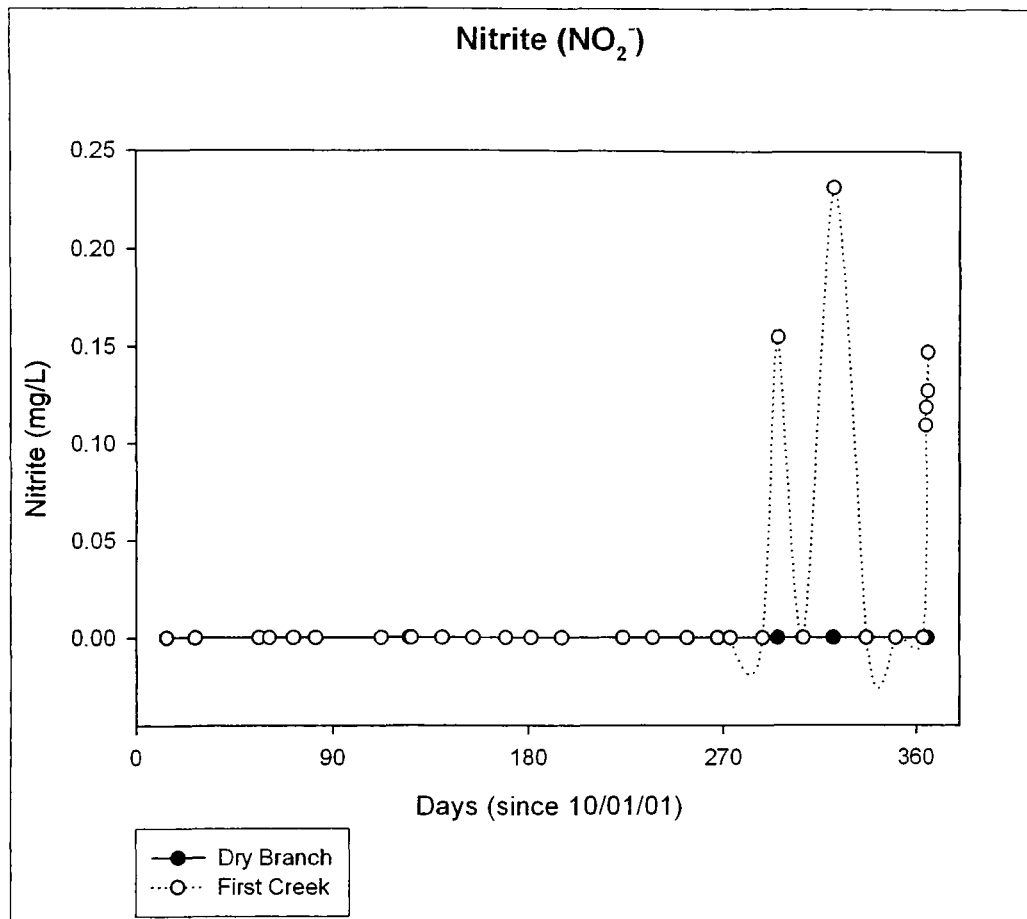


Figure 50 Nitrite ion concentrations from First Creek and Dry Branch

## Nitrate

The nitrate concentrations within the First Creek and Dry Branch basins showed some interesting trends (Figure 51). With the exception of one storm event in later summer, winter was the only time that concentrations within the two basins were similar. Throughout the rest of the year, nitrate concentrations were consistently higher in the Dry Branch basin. The higher values within Dry Branch may be the result of the individual

geologic characteristics of the basin, or it may be due to the presence of a few homesites, oil wells and roads within the basin thereby increasing the potential for anthropomorphic

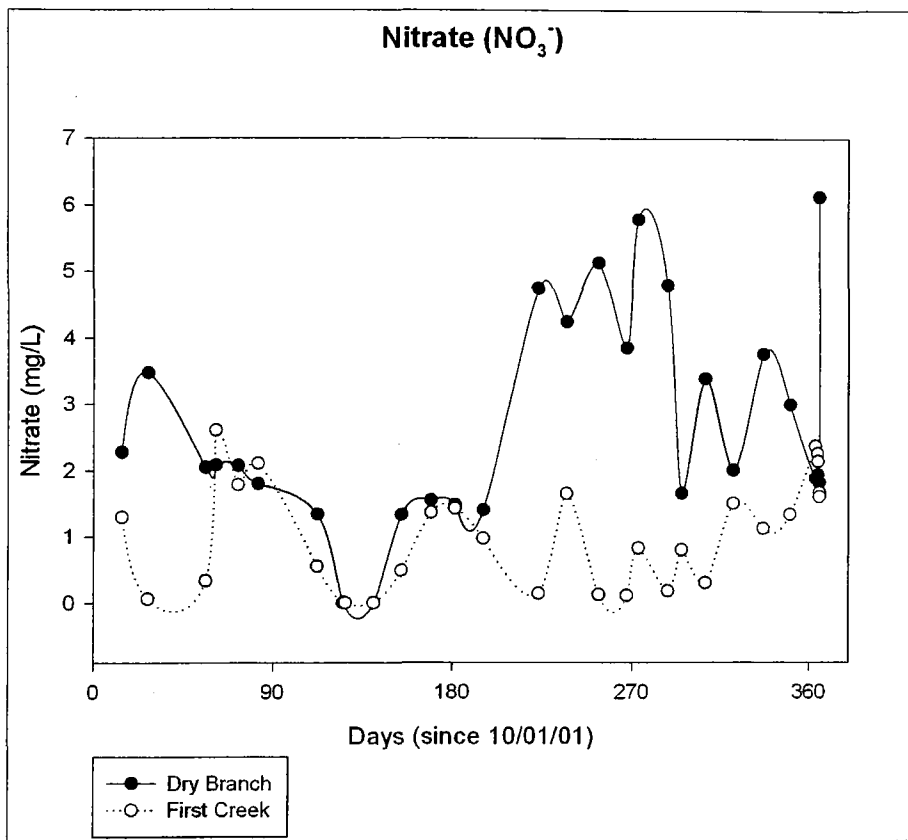


Figure 51 Nitrate ion concentrations from First Creek and Dry Branch

sources of nitrate. Although the values of nitrate are higher in the Dry Branch basin, the general trend in concentrations within the two basins was similar during the spring and summer. However, during the fall the Dry Branch basin experienced a nitrate peak while nitrate concentrations within the First Creek basin showed a trough (nearly a record low for the year). Likens and Bormann (1995) and Hutchinson (1957) found nitrate concentrations in New England peaking in the winter when biologic activity decreases

and nitrification processes at their peak. However, the opposite trends appear to be operating within the Dry Branch basin. The higher nitrate concentrations in the spring and summer within the Dry Branch basins may be due to potentially higher nitrate availability for vegetation/biologic processes within the First Creek basin compared with the Dry Branch basin. Since a higher percentage of water within the Dry Branch basin flows through subsurface karst conduits, compared with the First Creek basin, then this water presumably is less available for uptake by surface vegetation. If true, then nitrate ions within this water would be used and stored preferentially within the First Creek basin. Therefore, a higher percentage of nitrate ions within the Dry Branch basin would be flushed out of the basin within the stream while a higher percentage of nitrate ions within the First Creek basin would be retained within biologic reservoirs. If this is the case, then this difference would be negligible within the winter when biologic activities and processes are dormant. This trend was indeed observed within the First Creek and Dry Branch basins. It could also partly explain the reason for the early fall reversal (a peak in the Dry Branch nitrate levels and a trough in the First Creek nitrate levels).

The first fall rains after a summer dry period often bring in an increase in nitrate levels from precipitation (Likens and Bormann, 1995). The nitrate levels within this precipitation (Figure 50) would be quickly adsorbed by the surface vegetation and soils within the First Creek basin (the soils and surface biomass is a large reservoir of nitrogen (Likens and Bormann, 1995). However, these first rains within the Dry Branch basin flush some stored nitrate in the soils, but quickly pass through the dry open subsurface

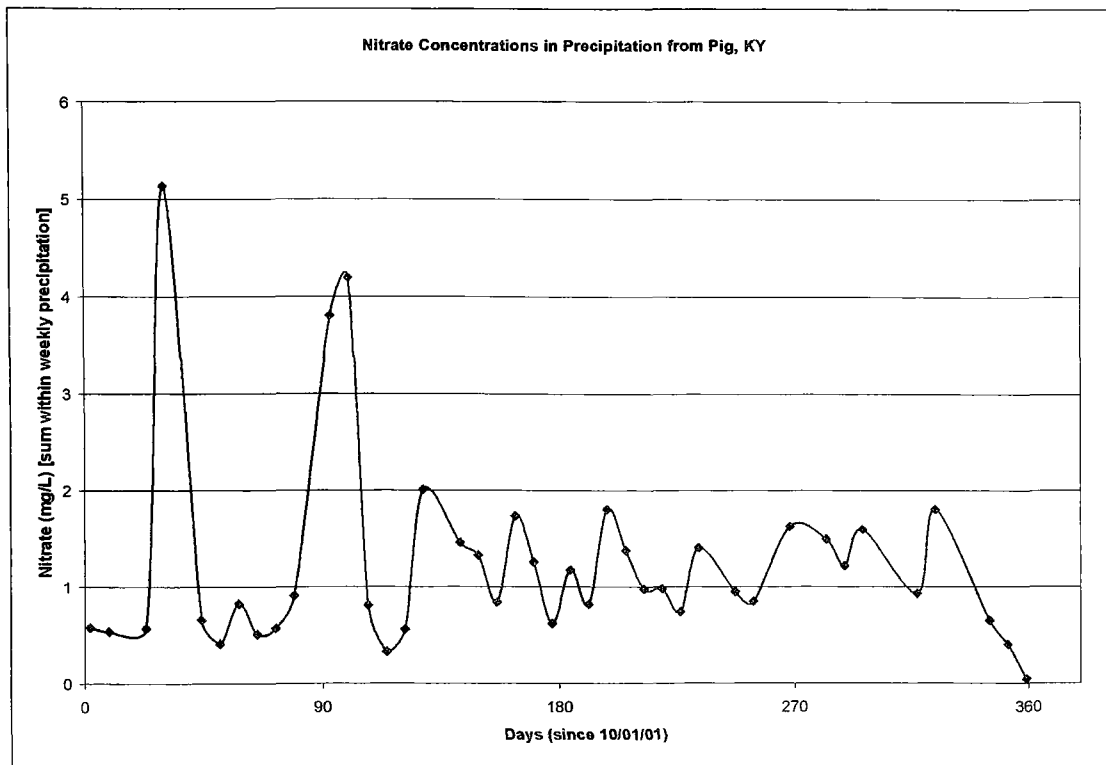


Figure 52 Nitrate concentrations from precipitation from Pig, Kentucky

karst conduits, thus bypassing much of the basin's surface vegetation. Further rains saturate and fill these small karst conduits sufficiently, whereas further precipitation runs off through both surface and subsurface flow route. However, this scenario would only partly explain the observed values.

There does not appear to be any clear and direct relationship between the nitrate concentrations observed in precipitation (Figure 52) to that of nitrate concentrations in either First Creek or Dry Branch (Figure 51).

It is also interesting to note that with the exception of winter, the timing of many of the peaks in nitrate concentrations within Dry Branch corresponds with troughs within First Creek, and vice versa. Since the precipitation inputs do not appear to be driving this pattern, and nitrate levels are often heavily influenced by biologic affects, it leads the author to conclude that these seasonal patterns and variations may be the result of within basin biologic processes. The similarities between the two basins during the winter low point would also support this conclusion, since it coincides with the biologic dormant period.

The increased concentrations of nitrate within Dry Branch during the spring could also be the result of anthropomorphic sources, such as fertilizer run off. Allen and Kramer (1972) demonstrated that there is a significant increase in nitrate concentrations as a result of runoff from forest clearcuts, crops and agricultural lands. However, if anthropomorphic sources were the significant cause of the increased nitrate levels within Dry Branch, it appears more likely that these higher values would be tied to precipitation and storm events, rather than occurring predominately in the spring. Therefore, although currently unknown, the most likely cause is natural biologic or physical processes. In addition, the apparent opposing trend between the two basins (peaks in one basin corresponding with troughs in the other, etc.) is also unknown. However I also conclude that the opposing nature of these peaks and troughs may also be primarily caused by a combination of basin morphology and biologic processes. Biologic processes affecting this trend would likely involve vegetation, soil and aquatic biota within First Creek Lake.



Morphology, such as the presence of karstic subsurface hydrologic pathways, is another potential factor.

In order to better explain the increase in nitrate concentration within Dry Branch, the following potential scenarios are listed and individually discussed:

- Scenario 1- Summer decrease of nitrate within First Creek
  - 1a- Denitrogenization
  - 1b- Nitrogen sink in basin
    - 1b1- First Creek Lake
    - 1b2- Pedosphere/biosphere
  
- Scenario 2- Summer increase of nitrate within Dry Branch
  - 2a- Atmospheric inputs
  - 2b- Localized anthropomorphic inputs
    - 2b1- Oil wells
    - 2b2- Septic systems
    - 2b3- Homes
    - 2b4- Agriculture
    - 2b5- Roads
  - 2c- Biosphere production
  - 2b- Release from basin reservoirs
    - 2b1- Biosphere release
    - 2b2- Bedrock weathering

Scenario 1a, denitrogenization, occurs primarily within anaerobic conditions, such as in some wetland soils or within certain lake bottoms. However, First Creek Lake was so shallow and reduced within the summer that significant anaerobic conditions seem unlikely. Similarly, ammonification (scenario 1b1) within First Creek Lake also seems unlikely, for some of the same reasons, but also due to ammonification converts nitrate into ammonium. Water samples taken both upstream and downstream of First Creek Lake on May 11, 2002 indicated that ammonium concentrations actually went down as a

result of the presence of First Creek Lake (went from 0.1617 mg/L and 2.2019 mg/L upstream of First Creek Lake to 0.0 mg/L downstream of the Lake). Scenario 1b2, biological causes, does at first seem like a likely cause of the summer increase in nitrate concentrations within Dry Branch relative to First Creek. As indicated earlier, Likens and Bormann (1995) and Hutchinson (1957) found nitrate concentrations in New England peaked in the winter when biologic activity decreases and nitrification processes are at their peak. However, the opposite trends appear to be operating within the Dry Branch basin. Water samples taken on May 11, 2002 both upstream and downstream of First Creek Lake indicated that the Lake may have indeed caused a decrease in nitrate concentrations in First Creek. Nitrate concentrations on this date for the two streams entering First Creek Lake were 0.6701 mg/L and 0.9828 mg/L. Nitrate concentration in First Creek downstream of the Lake was 0.1396 mg/L. While nitrate concentrations may have been reduced due to biologic activity within First Creek Lake, this alone cannot explain the elevated nitrate concentrations found in Dry Branch, since on this same date nitrate concentration within Dry Branch was 4.7364 mg/L. It appears that other factors other than the presence of First Creek Lake are the dominant causes of the summer increases in nitrate. Under this scenario, the increased biologic activity within the summer decreases the nitrate concentrations within First Creek; however, since much of Dry Branch is flowing in the subsurface, karst conduits, the nitrate ions within Dry Branch would be less accessible for biologic uptake and flushed out of the basin within the stream. If this was the sole cause of the summer increase in nitrate concentrations, then one would expect a similar trend in the other ions that form essential plant nutrients, such as phosphorus and potassium. There is a similar summer increase within Dry

Branch for these nutrients. However, there is also a similar summer increase in many of the other ions studied as part of this research project, including ions such as sodium which is not often absorbed by vegetation. I therefore conclude that the principal cause must be other than biologic.

Instead of a decrease in nitrate concentrations within First Creek, the second scenario (2) involves an increase in nitrate concentrations within Dry Branch. Scenario 2a involves atmospheric inputs. Looking at precipitation chemistry data from Pig, Kentucky (Figure 50) it does not appear that scenario 2a is a viable cause of the summer increase in nitrate concentrations within Dry Branch. Scenarios 2b1 would necessitate an oil spill or other episodic event. While there have been oil spills within the Dry Branch basin before, there is no indication of spills during the course of this study. In addition, many other ions not commonly associated with oil wells also were observed to have similar summer increases in concentration. Spills from oil wells would likely contribute additional sodium, chloride and sulfide ions (May, 2004). Similarly, if the source of nitrate were from chronic oil well spills, then nitrate concentrations would more likely be linked closely to precipitation, which it is not.

The same precipitation event correlation would also apply to scenario 2b3, 2b4 and 2b5. If the source of nitrate were from septic tanks/leach fields, then the data would likely show an increase in the concentration of phosphate ions, which it does not. Scenario 2b4, agriculture, would also be likely correlated closely with precipitation events, and would likely be confined to nutrients commonly found in fertilizer (such as

phosphate), not the wide variety of ions, such as sodium, potassium, magnesium, calcium, chloride, nitrate and sulfate, which exhibit summer increases in concentration. Scenario 2b5, roads, would more likely be confined to sodium and chloride within the winter months as a road de-icer.

If the source of nitrate was as described by scenario 2c, biosphere production, again, one would expect it to be limited to the various nitrogen species and other ions typically produced by biologic processes, not the wide variety of ions depicted by the data. Similarly, if the nitrate source was as described by scenario 2b1, biological release (such as in a fire or other disturbance to the vegetation), then the trend would likely be confined to the ions typically found in organic matter, not the wide variety of ions depicted by the data. In addition, no major disturbance such as fire occurred within the Dry Branch basin during the course of this study. As indicated earlier, this increase in ion concentration during the summer occurred with the majority of the ions studied as part of this research. The nitrate source must be broad-based as possible, and not limited to single episodic events or to any one ionic reservoir. The nitrate source would likely involve the source of most of the ions in solution.

This leaves the last scenario, 2b2 (bedrock weathering) as the most likely source of nitrate. If an explanation for an increase in weathering within the Dry Branch basin, compared with the First Creek basin, could be found then this scenario would match the data, since all the ions within this observed trend are weathering byproducts. However, the only situation that was observed that would increase the relative weathering within

Dry Branch compared to First Creek is stream discharge. Stream discharge was generally higher in Dry Branch than in First Creek. The increase in discharge within Dry Branch was quite noticeable in the summer, when the flow within First Creek was reduced to a mere trickle. Conversely, summer discharge in Dry Branch remained consistent and steady. Under this situation, the greatly reduced flow within First Creek probably severely hampered its ability to transport high quantities of ions in solution out of the basin in comparison to Dry Branch. Under this scenario, although the slow moving water had prolonged contact with carbonate rocks and therefore probably contained a higher concentration of ions, the highly reduced stream discharge severely limited the ability of the stream to transport ions out of the basin. An extreme example would be a series of isolated stagnant pools of water that may actually be totally saturated with respect to calcium, but without any flow, these ions would not leave the basin.

As discussed in the evaporation section (Part VI- Evaporation), the higher summer flow within Dry Branch is largely a karst phenomena. However, the reason that the summer increase in vegetation growth does not severely suppress the nitrate and other nutrients within Dry Branch may be due to a partial bypassing of surface biologic processes via subsurface karst conduits.

Therefore, it appears as if the dominant nitrate concentration difference during the summer months involved the increased discharge of Dry Branch, compared with First Creek, which in turn allowed Dry Branch to more efficiently transport weathering byproducts out of the basin. While this dominant process was going on within the

summer, biologic processes were also occurring on the surface and within First Creek Lake that also complicated the process. Lastly, the presence of karst appears to have played a role in affecting the process and partly accounting for the observed trends.

#### Trace Metals

Ions of the following metals were also analyzed as part of this study: iron (III), iron (II), copper, nickel, zinc, cobalt, cadmium and manganese. Of these trace metals, only cadmium and manganese were not detected in either basin at least once during the course of this study. Minor quantities of zinc were detected only within First Creek. Minor concentrations of ferric, ferrous, cobalt, and nickel ions were detected within both basins during the course of this study (Figures 53 and 54). Although trace metals were detected within both basins, complications with the lab analysis resulted in all the trace metal data to be determined unreliable. Therefore, figures 53 and 54 are presented for general interest only. Furthermore, I incorporated no trace metal data into any subsequent analysis or discussion.

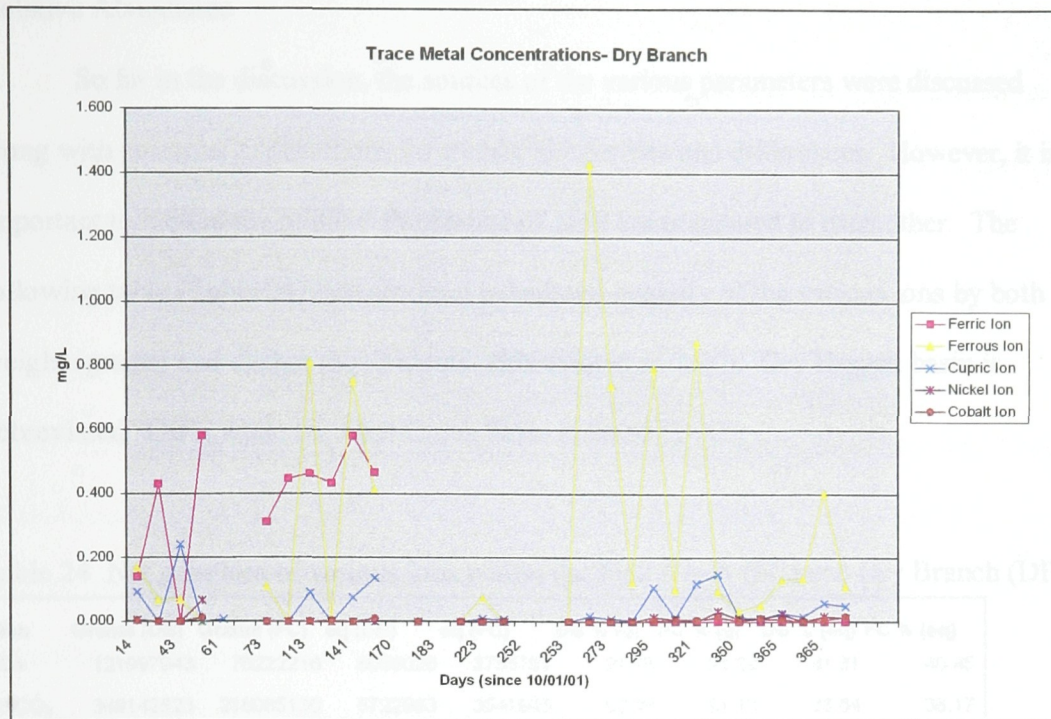


Figure 53 Trace metal concentrations from Dry Branch

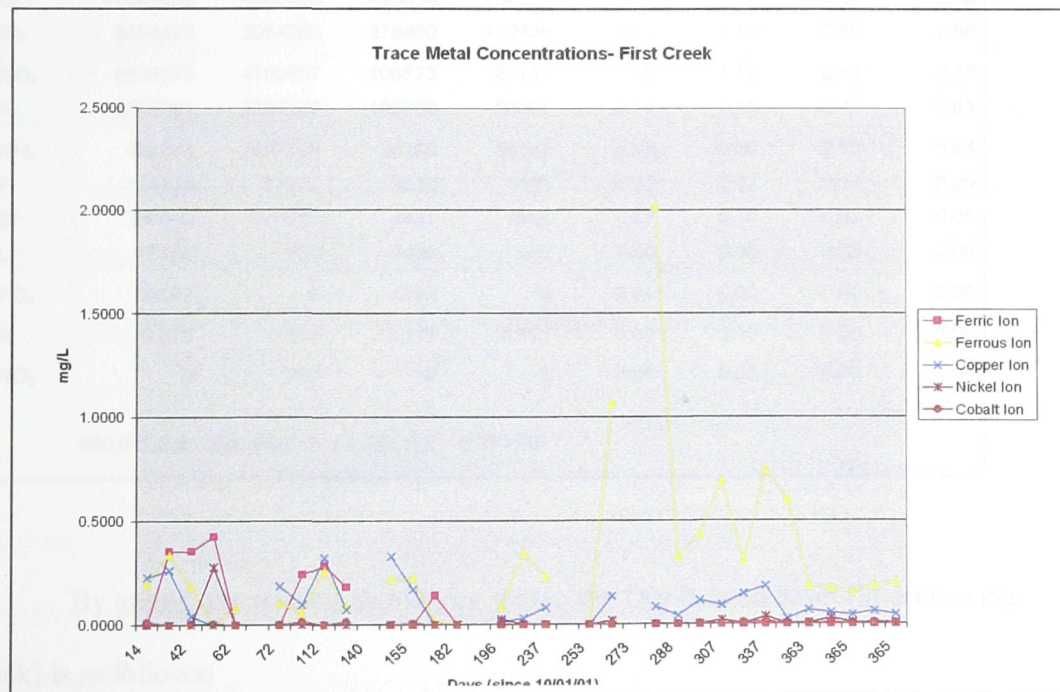


Figure 54 Trace metal concentrations from First Creek

## Relative Abundance

So far in the discussion, the sources of the various parameters were discussed along with potential explanations for trends, similarities and differences. However, it is important to look at the relative abundance of each ion compared to each other. The following table (Table 24) lists the total calculated quantity of the various ions by both weight (grams) and charge (equivalents- abbreviated as “eq”). Dry Branch basin is abbreviated “DB”, while the First Creek basin is listed “FC.”

Table 24 Net gain/loss of various ions within the First Creek (FC) and Dry Branch (DB)

Ion	Grams (DB)	Grams (FC)	eq (DB)	eq (FC)	DB % (g)	FC % (g)	DB % (eq)	FC % (eq)
Ca	121997943	75222216	6088026	3753791	21.76	21.28	41.31	40.45
HCO <sub>3</sub>	349142823	216085130	5722983	3541965	62.28	61.13	38.84	38.17
Mg	12138329	8720083	998834	717555	2.17	2.47	6.78	7.73
SO <sub>4</sub>	41817525	36576445	870622	761505	7.46	10.35	5.91	8.21
Cl	15069322	4900633	425054	138230	2.69	1.39	2.88	1.49
Na	8654493	3964268	376450	172436	1.54	1.12	2.55	1.86
NO <sub>3</sub>	6608075	4199857	106573	67734	1.18	1.19	0.72	0.73
K	4138791	2287286	105856	58501	0.74	0.65	0.72	0.63
NH <sub>4</sub>	483358	1067198	26796	59162	0.09	0.30	0.18	0.64
F	124104	83977	6532	4420	0.02	0.02	0.04	0.05
Br	386042	370833	4831	4641	0.07	0.10	0.03	0.05
Li	17138	988	2469	142	0.00	0.00	0.02	0.00
PO <sub>4</sub>	34697	0	1096	0	0.01	0.00	0.01	0.00
H	0.279	0.515	0.277	0.511	0.00	0.00	0.00	0.00
NO <sub>2</sub>	0	399	0	9	0.00	0.00	0.00	0.00
	560,612,640	353,479,313	14,736,122	9,280,091				

By grams, the relative abundance within the Dry Branch basin (in decreasing rank) is as follows:

HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Br<sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Li<sup>+</sup>, H<sup>2+</sup>, and NO<sub>2</sub>.



The relative abundance (in descending order) of these ions are slightly different for the First Creek basin (a swap between Mg and Cl; H and NO<sub>2</sub>, as well as PO<sub>4</sub> dropping to the bottom of the list), which is as follows:

HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>-</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Br<sup>-</sup>, F<sup>-</sup>, Li<sup>+</sup>, NO<sub>2</sub><sup>-</sup>, H<sup>+</sup>, and PO<sub>4</sub><sup>3-</sup>.

However, comparing the relative abundance by weight is misleading, since the atomic masses of the ions differ. A more appropriate comparison may be made by looking at equivalents, which factor out ionic mass. The relative abundance by mass (in descending order) of the ions within Dry Branch is as follows:

Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, F<sup>-</sup>, Br<sup>-</sup>, Li<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, H<sup>+</sup> and NO<sub>2</sub><sup>-</sup>.

The relative abundance of these ions is slightly different from the equivalent values for the First Creek basin (the primary differences were in the increase importance of NH<sub>4</sub><sup>+</sup> and the switching of Mg<sup>2+</sup> and SO<sub>4</sub><sup>-</sup>). The relative abundance (in descending order) of the ions within First Creek is as follows:

Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, F<sup>-</sup>, Br<sup>-</sup>, Li<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, H<sup>+</sup> and NO<sub>2</sub><sup>-</sup>.

Another way to look at comparing one basin with the other is by converting the total annual mass flux into output per unit area (in this case kilograms per hectare- kg/ha). The following tables (Table 25 and 26) summarizes the annual mean kg/ha for both the Dry Branch and First Creek basins and compares these values with the similar values observed by Likens and Bormann (1995) for their Hubbard Brook (New Hampshire)

study. The quantity of output was higher within the Dry Branch basin for calcium, magnesium, potassium, sodium, nitrate, chloride, phosphate, bicarbonate, lithium, and fluoride. The only ion that had higher concentrations within First Creek basin, compared with Dry Branch, was ammonium. Bromide, hydrogen, sulfate and nitrite concentrations (by mass per unit area) were nearly the same for both basins. Tri-linear plots would be an additional means of observing many of these same relationships mentioned in the preceding sections, however these relationships were represented well in the preceding time-series charts and tables depicted in this study.

With the possible exception of sulfate, there were very few similarities between mass per unit area of outputs between First Creek and Dry Branch with that of Hubbard Brook in New Hampshire. Therefore, many of the mass balance findings between these two regions are not comparable.

Table 25 Net gain/loss of various ions within the study areas compared to Hubbard Brook, NH [note: the Hubbard Brook data is shown on this table for comparison purposes only, and are not factored in any of the calculations in the rest of the table]

		Hubbard Brook, NH (Likens & Bormann, 1995)- Annual mean kg/ha	Dry Branch, KY Annual mean kg/ha (‘karst’ basin)	First Creek, KY Annual mean kg/ha (‘non-karst’ basin)	Difference Between Karst vs. Non-karst Basins (kg/ha)
Calcium:	Input	2.2	2.5	2.5	
	Output	13.7	177.1	114.1	
	Net	-11.5	-174.6	-111.6	-63.0
Magnesium:	Input	0.6	1.1	1.1	
	Output	3.1	17.6	13.2	
	Net	-2.5	-16.5	-12.1	-4.4
Potassium:	Input	0.9	0.2	0.2	
	Output	1.9	6.0	3.5	
	Net	-1.0	-5.8	-3.3	-2.5
Sodium:	Input	1.6	0.9	0.9	
	Output	7.2	12.6	6.0	
	Net	-5.6	-11.7	-5.1	-6.6
Aluminum:	Input	Trace			
	Output	2.0	Not Analyzed	Not Analyzed	Not Analyzed
	Net	-2.0			
Ammonium:	Input	2.9	3.6	3.6	
	Output	0.3	0.7	1.6	
	Net	2.6	2.9	2.0	0.9
Hydrogen:	Input	0.96	$8.23 \times 10^{-4}$	$8.23 \times 10^{-4}$	
	Output	0.10	$4.23 \times 10^{-7}$	$7.81 \times 10^{-7}$	
	Net	0.86	$8.229 \times 10^{-4}$	$8.225 \times 10^{-4}$	$4.0 \times 10^{-7}$
Sulfate:	Input	38.0	17.3	17.3	
	Output	52.8	60.7	55.5	
	Net	-14.8	-43.4	-38.2	-5.2
Nitrate:	Input	19.0	11.8	11.8	
	Output	16.1	9.6	6.4	
	Net	2.9	2.2	5.4	-3.2
Nitrite:	Input				
	Output	Not Analyzed	0.0	0.0	
	Net				0.0
Chloride:	Input	6.2	4.0	4.0	
	Output	4.6	21.9	7.4	
	Net	1.6	-17.9	-3.4	-14.5
Phosphate:	Input	0.11			
	Output	0.020	0.05	0.00	0.05
	Net	0.09			
Bicarbonate:	Input	Trace			
	Output	7.7	506.7	327.7	-179.0
	Net	-7.7			
Dissolved silica (SiO <sub>2</sub> )	Input	Trace			
	Output	37.7	Not Analyzed	Not Analyzed	Not Analyzed
	Net	-37.7			
Lithium:	Input				
	Output	Not Analyzed	0.02	0.00	0.02
	Net				
Fluoride:	Input				
	Output	Not Analyzed	0.18	0.13	0.05
	Net				
Bromide:	Input				
	Output	Not Analyzed	0.56	0.56	0.00
	Net				
TOTAL:	Input	72.5			
	Output	147.3	813.7	536.1	-277.6
	Net	-74.8			

Table 26 Net gain/loss of various ions within the study areas

Total output difference between karst vs. non-karst ranked by percentages	Ion source/sink of both basins relative to total output compared to input	Ion source/sink of output in karst relative to non-karst basin
Ammonium (+56%)	SINK	More of a SINK in karst vs. non-karst basin
Hydrogen (+48%)	SINK	More of a SINK in karst vs. non-karst
Bromide (0%)	?	Whether the basins are sources or sinks for bromide, it appears as if the presence of karst makes no difference, therefore it is a transmitter
Sulfate (-12%)	Source	More of a source in karst vs. non-karst basin
Magnesium (-27%)	Source	More of a source in karst vs. non-karst basin
Fluoride (-28%)	?, presumed source	If the basins are a SINK for fluoride, then karst is less of a SINK than non-karst. If basins are a Source of fluoride, then karst is more of a source than non-karst
Nitrate (-33%)	SINK	Less of a SINK in karst vs. non-karst basin
Calcium (-36%)	Source	More of a source in karst vs. non-karst basin
Potassium (-43%)	Source	More of a source in karst vs. non-karst basin
Bicarbonate (-51%)	?, presumed source	More of a source in karst vs. non-karst basin
Sodium (-56%)	Source	More of a source in karst vs. non-karst basin
Chloride (-81%)	Source	More of a source in karst vs. non-karst basin
Lithium (-100%)	?	If the basins are a SINK for lithium, then karst is less of a SINK than non-karst. If basins are a Source of lithium, then karst is more of a source than non-karst
Phosphate (-100%)	?, presumed SINK	If presumption correct, Less of a SINK in karst vs. non-karst basin

In summary, both basins acted as a sink for ammonium, hydrogen, nitrate and possibly phosphate ions and a source for calcium, magnesium, potassium, sodium, bicarbonate, chloride and sulfate. It is unknown if the basins are a source or a sink for fluoride, lithium and bromide. For the ions that the basins served as a sink, the karst basin (Dry Branch) acted like more of a sink for ammonium and hydrogen compared to the non-karst basin (First Creek), while the karst basin acted as less of a sink for nitrate

and phosphate. For all the ions that the basins served as a source, the karst basin was more of a source than the non-karst basin.

From the preceding tables, one can see that for both basins there was a net loss (more output from the basin within the stream than inputs to the basin from precipitation) leaving the basins of calcium, magnesium, potassium, sodium, chloride, and sulfate, with the Dry Branch basin consistently experiencing the greatest loss. These losses appear to be the result of weathering processes occurring within the basins. The loss of calcium, bicarbonate and magnesium are the easiest to explain, since the principle products of limestone dissolution are calcium and bicarbonate, with lesser amounts of magnesium. Therefore, clearly calcium, bicarbonate and magnesium would be specifically affected by the quantity of carbonate mineral outcrop within a basin. However, are the increases in weathering rates for potassium, sodium, chloride and sulfate affected by the presence of karst or karst processes or do they only represent weathering of non-karst rocks while the karst remained inert?

There were two constituents that experienced a net gain: ammonium and nitrate. The gain of ammonium was greatest in the Dry Branch basin, while the First Branch basin experienced the greatest gain in nitrate. In tables 25 and 26 there appears to be a net gain to the basins in hydrogen, however this is deceptive. These hydrogen ion concentrations are based upon pH, and indeed free hydrogen ions, as represented by pH, did have greater inputs than outputs. However, these hydrogen ions reacted with the carbonate and other minerals in the basins and formed other compounds, such as

bicarbonate ( $\text{HCO}_3^-$ ). Therefore, the quantity of hydrogen atoms leaving the basins would be much higher than the data would indicate. There was a net loss in both basins for calcium, magnesium, potassium, sodium, sulfate, and chloride.

### **Comparability with Hubbard Brook Findings**

Likens and Bormann (1995) found in their Hubbard Brook study:

- 1) precipitation provides an important source of mineral inputs into the basin;
- 2) forests acted as a filter for atmospheric pollutants, especially H, N, S and P;
- 3) evapotranspiration was relatively constant over a wide range of precipitation and environmental conditions, and served to regulate certain aspects of the hydrologic cycle;
- 4) stream water chemistry was highly predictable, based upon given environmental conditions. Although it was recognized in this study that fixed time series monitoring schedules often do not accurately represent actual conditions for highly variable parameters, it was found that while stream water chemistry did vary with the seasons, the short-term fluctuations were so small that bi-weekly or even monthly sampling was sufficient to characterize the chemistry of that (non-karst) system;
- 5) the output of most individual nutrients can be closely predicted from the annual output of water alone;
- 6) many of the minerals and nutrients within the basin, when comparing the total input (such as from precipitation or the weathering of rocks) into the basin's

streams versus the total dissolved output being removed from the basin by the basin's streams, experienced some form of net gain or loss;

- 7) dissolved species experiencing net losses include Si, Ca, Na, Al, Mg, and K. Net gains were found for C, N, S, P and Cl;
- 8) the input/output budgets for many (non-karst) vegetated watersheds throughout the world show many similar patterns as those of Hubbard Brook.

Comparing these findings for Hubbard Brook with the findings for First Creek and Dry Branch, I found that:

- 1) while precipitation provided an important source of minerals into both Dry Branch and First Creek basins, the annual and seasonal trends appear to be dominated by bedrock weathering, while precipitation inputs acted more as episodic events;
- 2) Dry Branch and First Creek basins acted as a filter for hydrogen, nitrogen and phosphorus, but not for sulfate;
- 3) evapotranspiration did regulate aspects of the hydrologic cycle, however the differences between the evapotranspiration rates were different for the two basins so it affected the hydrologic cycle differently, which in turn affected geochemical cycles;
- 4) I need more than one year data set to make predictions; however, I assume that within the more dynamic karst systems, predictions would be unreliable;
- 5) the outputs of nutrients cannot be predicted from the annual output of water;

- 6) minerals, nutrients and other dissolved inorganic species within the Dry Branch and First Creek basins experienced some form of net gain or loss;
- 7) net losses were indeed found to occur for calcium, magnesium, sodium and potassium, and net gains were found to occur for nitrogen and phosphorus; however, net gains were not found for carbon, sulfate, and chloride.
- 8) while there are some similarities between the annual net gain and loss values and hydrogeochemical cycles and trends between the two study basins and that of Hubbard Brook, there are distinct differences as well.

Overall, the individual ion concentration values obtained from Dry Branch and First Creek do not compare well with those obtained from Hubbard Brook, nor do many of the annual and seasonal trends. Therefore, future research within basins containing karst within the Interior Low Plateau Province of South-central Kentucky may find the Hubbard Brook data set useful; however, it is not comparable.

### **Potential Correlations**

One aspect of this study was to determine if any correlations existed between particular dissolved species with that of more easily obtained parameters. The determination of particular ionic concentrations usually requires costly lab analysis. The determination of ion concentrations also involves a certain degree of time lag between sample collection and lab result. Conversely, many parameters such as temperature, pH, specific conductance, and stage are often easily obtained in real-time while in the field. If it were found that reliable correlations existed between a particular ionic concentration



to that of the more easily obtained field parameters, then a mathematical prediction of the ionic concentration could be made that would aid researchers conducting water chemistry-related projects. However, in this study no reliable correlations were found between any of the measured ionic concentrations with any of the more easily obtained field data.

## PART VII DISCUSSION

The preceding data indicate that there is very little difference between the dissolved components of a stream originating from basins comprising different percentages of carbonate karst. Of more importance is the presence of karst in the basin rather than any specific percentage of exposed carbonate rocks within the basin. This relationship may be explained by the rapid dissolution processes of carbonate rock. Upon contact with carbonate rock, water approaches saturation with respect to calcite. Therefore, further contact with additional carbonate rock has only minimal effect upon the generalized stream chemistry. These systems may operate differently during periods of dramatic storm events. During these storm events, perhaps insoluble particulate erosion plays a significant role in weathering. This aspect of geochemical flux was not considered in this research.

There are two aspects to consider when comparing the effect carbonate karst has upon hydrogeochemical cycling, geochemical and morphological. The geochemical component pertains to effects resulting from the chemical products of carbonate dissolution and how these products alter the geochemical environment. The morphological component pertains to the physical landforms and features that this carbonate dissolution process creates, such as subsurface conduits, surface sinkholes, etc. Each of these components individually or in combination may have an effect upon the environment.

This study reinforced and strengthened the understanding of karst acting as a buffer. There are numerous ways that karst may serve the role of an environmental buffer. Some examples include:

- 1) karst moderates temperature extremes in surface water;
- 2) karst lessens the affect of acid precipitation on stream pH;
- 3) karst moderates discharge (stream flow) during storm pulses;
- 4) karst moderates/lessens a basin's evaporative loss;
- 5) and karst moderates surface erosion and stream/channel incision.

Karst can also influence hydrology and geochemistry in that its presence reduces the following:

- 1) available moisture to surface vegetation and biologic processes;
- 2) available nutrients to surface vegetation and biologic processes.

Furthermore, these hydrological effects continue to affect the stream's geochemistry. Karst may also increase some geochemical species relative to non-karst, such as, the ionic strength content. These effects may be largely geochemical as the result of the presence of carbonate rocks, or they may be due to the physical features of karst (such as the moderation of temperature extremes), or they may be due to a combination of both.

Since karst may impact certain processes, it is in essence acting as a source, while non-karst basins act more as a sink. A sink is defined as a situation in which a higher

quantity of a particular ion enters the non-karst basin than is exiting; therefore, the ion is being added to a reservoir within the non-karst basin. Conversely, in the karst basin, water and nutrients are being retained in the basin to a lesser degree; therefore more readily flushes these materials out of the basin along with other weathering products. Sources are basins that produce and transmit out of the basin more weathering products than inputs that they retain from precipitation.

Other studies have confirmed the validity of the concept of a karst (calcium/magnesium-bicarbonate) water. By this, it is meant that a typical carbonate karst water contains a certain geochemical signature, particularly a certain range of calcium, magnesium and bicarbonate concentrations, as well as a similar range in pH and specific conductance. In the study of the two basins, one dominated by carbonate karst and the other having carbonate karst as only a minor component, it was found that both basins contained "calcium/magnesium-bicarbonate water." It is believed that the presence of calcium/magnesium-bicarbonate water is more a function of the spatial distribution of the karst within the basin than the actual quantity of carbonate karst within the basin. To demonstrate this spatial relationship, the following three scenarios are provided:

- 1) A stream passes over and through a small quantity of carbonate rock high in the basin then runs over non-carbonate bedrock for the remainder of its course through the basin. In this scenario, since carbonate rock is relatively quick to dissolve under normal pH ranges, the water passing through the carbonate bedrock quickly becomes a

“karst water.” However, as the water proceeds down gradient within the basin, there is much mixing with water that fell on and passed through non-carbonate bedrock (the majority of the basin), so that the karst water component becomes diluted to such a degree by the mixing of non-karst waters, that it becomes less and less of a “karst water”. In this situation, the only portion of the basin that would be containing karst hydrogeochemical processes is the portion of the basin containing carbonate karst bedrock.

- 2) Conversely, if the same quantity of carbonate karst is located near the lower reaches of the basin, the majority of water from the basin passes over and through the carbonate karst and quickly becomes a “karst water.” In this situation, the entire surface area of the basin should be classified as a karst basin, because the karst is affecting the water originating from the entire basin, not just the portion falling on the actual carbonate bedrock.
- 3) A basin containing mostly carbonate karst will produce a stream that would be classified as a “karst water.” Due to the quantity of carbonate material, the water will likely contain higher concentrations of calcium and bicarbonate. However, due to the rapidity of carbonate dissolution and the diminishing rate of carbonate mineral dissolution as it approaches saturation, there is little room for a dramatic change in the “karst water” geochemical signature between a basin containing some karst versus one containing an abundance of karst.

This “calcium/magnesium-bicarbonate water” effect may be more relevant for the geochemical effect of karst. However, as stated earlier, besides the chemical aspects, the other categories of hydrogeochemical effects that karst may play within a basin is due to the morphological aspects of the karst. In these situations, everything else being equal, a basin containing mostly carbonate bedrock will likely contain more developed physical karst features, such as sinkholes and underground conduits, etc. In these situations, a basin containing well-developed karst will likely affect the basin’s hydrogeochemical flux much greater than a similar basin contain less developed karst features.

The importance of the spatial distribution of the carbonate rocks is significant for not only the geochemical effects, but the physical as well. It appears as if the geochemical effects, such as the chemical signature of a calcium/magnesium-bicarbonate water may last for a significant distance downstream of the presence of the carbonate rocks. However, the physical effects may be more transitory. For example, a stream flowing in a subsurface karst conduit has been shown to be buffered from the temperature extremes found in equivalent surface water. However, if this karst conduit is located high in a watershed and then the stream flows on the surface the rest of the way, the moderating effects of the karst may have been lost by the time the stream leaves the basin. Conversely, if the karst conduit were present in the location where a surface stream would experience the greatest degree of surface warming, then the temperature buffering effects of the karst stream would have been optimized. Therefore, two basins with identical percentage of karst versus non-karst geology, however spatially arranged

differently, will likely contain different hydrogeochemical relationships and trends. If true, then the hydrogeochemical flux within a karst basin depends on a complex array of climatic, geologic, biologic, topographic, spatial, and temporal factors. These results indicate that with the right mix of these factors, karst can affect the basin's hydrogeochemical flux in a manner that is usually not factored in typical global-scale geochemical budgets and models. Considering the quantity of surface and near surface carbonate bedrock in certain locations, regions and globally, such karst effects may need to be factored in these models in order to be a more accurate representation of processes occurring in the real world.

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*“The efforts of many researchers have already cast much darkness on the subject; and is likely that, if they continue, we will soon know nothing about it at all.”*

Mark Twain