Water Quality in Cowpens National Battlefield

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Cowpens National Battlefield in its present form was purchased in the early 1960s. At that time most of the land was farmland. In the 1700s, previous to the battle of Cowpens, the park area was a holding area for cattle. One of the primary reasons that the area served this role was the availability of good water. This water came primarily from the many different springs located in the area. The land around the springs during the 1700s was primarily open deciduous forest. The forest was open enough to allow the grass to grow, but closed enough to provide good cover for an army. This place with its abundance of food for animals, water, and cover made it an ideal place to spend the night.

The 841 acres that encompasses the present park is surrounded by roads. These roads effectively isolate the battlefield from the areas outside the park. Because the springs were included in the park they all flow from the park center toward the outside of the park. This means that anything found in water came from the park.

One of the primary goals of this study was to determine the water quality that leaves the park. This year long study was designed to sample the water through the year and to determine the different inorganic and biological components of the water through the year. In a previous study, the location of the springs had already been done. During that study we found over 90 different locations where there were active springs or evidence of spring activity. We determined the location of springs by first following streambeds to a point where the water flow disappeared. We then dug a small hole about 12 inches deep and if it filled with water within an hour we considered that point to be a spring location. In several areas, many springs were found, in other areas only one or two springs. An area with many springs was found near the old Scruggs House. It is very obvious that this is a very wet area because of the abundance of river cane in the area. An area where only one spring was located was near the Park Headquarters. The small stream feed by the spring at the Park Headquarters had water the day we did the spring location but has not had water since. One of the major problems encountered with this study was the fact that it was proposed and financed during an extremely dry period. Many of the streams dried up during the grant year. In fact one-half of the target streams had extremely low or no flow during 6 months of this study. In several cases we could get enough water for chemical and fecal coliform analysis but there was not enough water to get an adequate sample for other analysis such as total suspended solids.

Membrane Filter Method for the Detection of Fecal Coliforms

The membrane filter method for the detection of fecal coliforms is outline in Standard Method for the analysis of Water and Wastewater Method 9222D. In this procedure water samples are filtered through a membrane filter to separate the bacteria from the water sample.

Material and Methods

General Statement: Water samples were collected every other week from February 2000 until March 2001. The sites for collection were the eight different points where water existed Cowpen National Battlefield. Four of these sites (sites 1,2,3,4) were located on the Highway 11 side of the park, site 5 Zekial Creek is located near the New Pleasant Baptist Church and 3 of the sites (sites 6, 7, and 8) were on the Highway 110 side of the park.(See map Appendix A)

The samples for fecal coliform analysis were collected using 250 milliliter sterile glass bottles. All other samples were collected using 1 liter non-sterile glass bottles. After collection, all samples were stored on ice until they were analyzed.

Fecal Coliform Analysis: The following procedure for fecal coliform analysis is outlined in Standard Methods for the Analysis of Water and Wastewater Method 9222D.

Preparation of phosphate buffer: The phosphate buffer was prepared using the following solutions. The stock buffer solution contains 34.0 grams per liter of KH_2P0_4 with a final pH 7.2. The pH is adjusted with 1 M NaOH . From the stock solution Add 1.25 milliliters to a 1 liter volumetric flask and 5 milliliters of magnesium chloride stock solution. The magnesium chloride stock solution contains 81.8 grams of $MgCl_2 \cdot 6H_2O$ per liter of deionized water. Bring the volumetric flask up to volume and sterilized at 15 psi at 121 ˚C for 15 minutes. Allowed the solution to cool in a dark cabinet.

Preparation of mFC media; The mFC Agar (BBL) was prepared by adding 5.2 grams of the mFC powder to 100 milliliters of deionized water. To this suspension add 0.1g of Rosolic acid which has been dissolved in 1 ml of 0.2N NaOH. Heat the suspension to boiling, boil for 1-2 minutes to dissolve the agar. Cool to 45C and dispense into 50x9 mm sterile petri dishes. Added about 5 mls. of the solution to each petri dish. Allow the dishes to cool until solid and store in the refrigerator.

Preparation of Lauryl Sulfate Broth (BBL): Lauryl sulfate broth (LSB) is the primary medium for the presumptive test for the coliform group. It is prepared by adding 35.6 grams of the LSB to l liter of deionized water and mix. The final pH should be 6.9±0.2. Dispense the broth into fermentation tubes containing Durham tubes. Autoclave the tubes for 15 minutes at 121 ˚C.

Preparation of EC Broth (BBL); EC Broth is the medium for confirmation of E. coli. This broth is prepared by adding 37.0 gram of powder to l liter of deionized water and mix until the powder is dissolved. Dispense the broth into fermentation tubes each containing a Durham tube. Autoclave the tubes for 15 minutes at 121 ˚C.
Sample Analysis The following information is a summary of the procedure used to analyze each sample. The sterile filtration units were unwrapped and placed in the UV sterilization box for 5 minutes. After sterilizing the units remove each one from the UV box using sterile forceps. The forceps were sterilized by immersing in ethanol and then flaming. Place a sterile 0.45 micron membrane filter on the porous filter base and then place the funnel into position of the filtration manifold. Add to each one of the funnels either 10, 50, or 100 milliliters of sample and apply a vacuum. While vacuum is being applied, rinse the filter twice using 25 mL of sterile phosphate buffer. After the sample has been filtered, turnoff the vacuum and remove funnel. Using sterile forceps, remove the filter and place it on the surface of mFC agar. The plates and their filter are then place in whirlpak bags, closed tightly and place in a 45±0.2 ˚C waterbath. These will be incubated for 24±2 hours. The filtration funnels were sterilized between samples by putting them in the UV Sterilization box for 3 minutes.
At the end of the waterbath incubation period the number of colonies on the plates were counted. A sub-set of the colonies were selected, then using an inoculation needle a small portion of each selected colony was transferred to Lauryl Sulfate Broth. The colonies selected represented about 10% of the total population on each plate. Colonies that appear different were selected as well as those blue colonies that indicate E. coli. The LSB tubes were then incubated for 24 hours at 35±0.2 ˚C. Those tubes that produced gas in LSB were considered to contain organisms from the coliform group. Using a sterile inoculation loop a subsample of the positive tubes were transferred to EC Broth and incubated at 45±0.2 ˚C for 24 hours. If gas was again produced this was considered to be positive for E. coli.
The results are reported in concentration of organisms per 100 milliliter of sample.
In the results table there are several sample sites where there was not enough water or no water in the streambed. These are "0" in the data box. The period represented in this report had been an abnormally dry year. This site did not have a weather station but the data from the Greenville/Spartanburg Airport report a rainfall deficit of over 13 inches.

Materials and Methods for Inorganic analysis

General statement: All glassware used was analytically washed. Standard solutions were made with deionized, distilled water (DDI water) in Class A volumetric glassware, using reagent grade chemicals. All salts for making standards were dried 20-24 hours at 110 ˚C. Samples not immediately analyzed were stored in a dark refrigerator (4 ˚C) and were allowed to reach room temperature before being analyzed. In some cases, other precautions were taken and those are noted below. Samples were collected in 1-L Nalgene bottles. For metals analysis, the bottles were acid washed by rinsing with warm 1:2 concentrated HCl:DDI water and rinsed with copious amounts of DDI water before obtaining samples.

Chloride Analysis. Samples were analyzed for chloride (Cl^-) using a VWR chloride ion–selective electrode (Cat. No. 34105-102) and a low level measurement technique. To make a calibration curve of Cl^- standards, 100.0 mL of water was pipetted into a beaker

and stirred with a Teflon-coated magnetic stir bar. To this was added 1.00 mL of 1.0 M $NaNO_3$ as an ionic strength adjustor (ISA). Increments (0.1-2.0 mL) of 10^{-3} M NaCl were added from a buret and the millivolt display from the electrode meter was recorded. Samples were measured by pipetting 100.0 mL aliquots, adding 1.00 mL of ISA, and stirring with a Teflon-coated magnetic stir bar. Each measurement was repeated twice by removing the electrode from the standard or sample, rinsing the electrode with DDI water, blotting the electrode dry, then resubmersing the electrode in the solution. The two electrode readings were averaged.

Ammonia Analysis. Samples were analyzed for ammonia (NH_3) with a Corning ion–selective electrode (Cat. No. 476130). To prepare the electrode, the tip was soaked in pH 7.0 buffer for at least 6 hours, then rinsed with DDI water and blotted dry. Fifteen drops of Ammonia Filler Solution (Cat. No.477394) were placed in the membrane module, the module was screwed onto the electrode body, and the tip of the module was soaked in pH 4.0 buffer for at least 30 minutes before use. Using either NH_4Cl or NH_4Br, standards were made (10^{-3}, 10^{-4}, and 10^{-5} M NH_4^+). A 100.0 mL aliquot of standard was pipetted into a beaker containing a Teflon-coated stir bar, then 1.00 mL of 10 M NaOH was added, and the tip of the electrode was placed in the solution. After the first stable reading, the electrode was removed, rinsed with DDI water, blotted dry, and returned to the solution for a second reading. If samples were analyzed immediately after they were obtained, 100.0 mL of sample was placed in a beaker with a Teflon-coated stir bar, then 1.00 mL of 10 M NaOH was added. Two readings were taken and averaged. If samples were not analyzed immediately, 2 mL of concentrated H_2SO_4 were added to 1 L of sample and the solutions were stored in a dark refrigerator (4 ˚C) until analyzed (1–2 days).

Nitrate Analysis. Samples were analyzed for nitrate (NO_3^-) with an Orion Nitrate Ion–selective Electrode (Model 93-07). The electrode was prepared by soaking a nitrate module in 10^{-3} M $NaNO_3$ for one hour before use. A reference electrode (Orion model 90-02) was filled with Orion Cat. No. 900002 for the inner chamber and 0.04 M $(NH_4)_2SO_4$ in the outer chamber, 20-30 minutes before use. A standard curve was made by pipetting 50.00 mL of DDI water, adding a Teflon-coated magnetic stir bar, adding 50.00 mL of nitrate interference suppressor solution (Orion Cat. No. 930710), 1.00 mL of 0.40 M $(NH_4)_2SO_4$ (as an ionic strength adjustor), and increments of 10^{-3} M $NaNO_3$. Samples were analyzed by mixing 50.00 mL of stream water, 50.00 mL of nitrate interference suppressor solution, a Teflon-coated stir bar, and 1.00 mL of 0.40 M $(NH_4)_2SO_4$. After a stable reading, electrodes were removed from the solution, rinsed with DDI water, blotted dry, and returned to the solution for a second reading.

Nitrite Analysis. Samples were analyzed for nitrite (NO_2^-) with an Orion Nitrite Ion-selective Electrode (Model 93-46). The electrode was prepared by soaking for 1 hour in 20 mL of 10^{-3} M $NaNO_2$ that also contained 10 mL of nitrite interference suppressor solution (NISS, Orion Cat. No. 934610). A reference electrode (Orion Model 90-01) was filled with Orion Cat. No. 900046 at least 20 minutes before analysis. The electrode was calibrated by stirring 50.00 mL of DDI water and 50.00 mL of NISS while adding increments of 10^{-3} M $NaNO_2$. Samples were analyzed by mixing 50.00 mL of stream

water with 50.00 mL of NISS while stirring with a Teflon-coated stir bar. After a stable reading, electrodes were removed from the solution, rinsed with DDI water, blotted dry, and returned to the solution for a second reading.

Sulfate Analysis. Samples analyzed for sulfate (SO_4^{2-}) were immediately filtered through glass fiber filters (Pall Corporation, Gelman Labs, Type A/E 47 mm, nominal pore size 1 µm) upon returning to the lab. Samples (500.0 mL) were made acidic with 1:1 HCl until a pH of 2 or less. The solutions were heated to boiling, then 5 mL of $BaCl_2$ (100 g/L) was slowly added. The mixture was kept warm for 2-20 hours. The volume of the solution was reduced until ~100 mL and the remaining liquid was filtered through Whatman 40 ashless filter paper. The filtrant was washed until the filtrate showed no precipitate formation when mixed with a dilute solution of $AgNO_3$. The filter paper and filtrants were placed into preweighed ceramic crucibles, partially covered with a ceramic lid to allow air to enter the crucible, and placed in an 800 ˚C muffle furnace for 1 hour. After removing from the oven, the crucibles were allowed to stand for 3–4 minutes, then cooled overnight in a desiccator before reweighing.

Metals Analysis. Samples were analyzed for sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), and manganese (Mn) by atomic absorption (AA) spectroscopy (Perkin Elmer 3100 Atomic Absorption Spectrometer). Multielement hollow cathode lamps were used for Na and K (Fisher Scientific 14-386-103S), Ca and Mg (Fisher Scientific 14-386-102R), and Fe and Mn (VWR Scientific 58143-340). Samples were analyzed by the standard addition method. Commercially available stock solutions of each metal (1000 ppm) were diluted such that one solution (solution **M1**) contained 4.992 ppm Na, 4.992 ppm K, and 2.496 ppm Mg and a second solution (solution **M2**) contained 49.96 ppm Fe, 24.98 ppm Mn, and 24.98 ppm Ca. The samples were filtered through glass fiber filters (Pall Corporation, Gelman Labs, Type A/E 47 mm, nominal pore size 1 µm) upon returning to the lab and 800 mL of each sample were mixed with concentrated HNO_3 until the pH was less than 2 (typically ~0.5 mL of HNO_3). Samples were stored overnight, then allowed to warm to room temperature before placing 25.00 mL aliquots of each water sample in 4, 100 mL volumetric flasks and 25.00 mL aliquots in 4, 50 mL flasks. The samples in the 100 mL flasks were spiked with 0, 2.00, 4.00, or 6.00 mL of solution **M1**, then diluted to 100.00 mL. The samples in the 50 mL flasks were spiked with 0, 0.25, 1.00, and 1.50 mL of solution **M2** and an appropriate amount of water so that each flask contained a total volume of 26.50 mL. Each element was analyzed under an appropriate wavelength (Table 1) with a 5 s integration time.

Table 1. Wavelengths used for metals analysis

Element	Wavelength (nm)
Na	589
K	766
Mg	285
Ca	423
Fe	249
Mn	279

Carbonate/Bicarbonate Analysis. Samples were analyzed for carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) by titrating with 0.02 M HCl. A pH electrode (Orion ROSS pH electrode 81-02) and automatic temperature compensation probe (Orion ATC-Probe 917005) were calibrated with pH 7 and pH 4 buffers. Aliquots (100.0 mL) of stream water were placed in beakers and titrated until the pH was between 4.3 and 4.7. Titrant was carefully added until the pH was lowered by 0.3 pH units. Since all streams had a pH lower than 8.3, the assumption can be made that the total alkalinity is due to carbonate and not bicarbonate or hydroxide. Thus, only calculations for carbonate were performed, as bicarbonate concentrations were virtually insignificant compared to carbonate.

Temperature, dissolved oxygen, and conductivity. Streams were analyzed for temperature, dissolved oxygen (D. O.), and conductivity at the time of sample collection using a battery operated YSI-85 Oxygen, Conductivity, Salinity, and Temperature Probe. The probe was placed in the flowing stream water and allowed to equilibrate for several minutes before the readings on the electronic display were taken. Units for temperature were degrees Celsius (˚C); for DO, ppm O_2; for conductivity, microsiemans (µS). The meter was allowed to warm up at least 30-45 minutes before the first measurement was taken.

pH. Near the end of the study, it became possible to obtain accurate pH measurements on-site at the time samples were taken. A Hanna Instruments HI 8314 membrane pH Meter and HI 1230 probe were used to obtain the pH of the streams. The probe was soaked in water or a pH 7 buffer for at least an hour before calibration. A two point calibration method was used in which the probe was placed in a pH 7 and pH 4 buffer. While traveling to the sites and between sites, the tip of the probe was kept in DDI water. To make a measurement, the probe was placed in the stream water for several minutes before a stable reading was confirmed.

Phosphate Analysis. Samples collected for total phosphate (PO_4^{3-}) were mixed with 3–4 drops of concentrated sulfuric acid before analysis[1]. Aliquots (50 mL) of phosphate standards (KH_2PO_4) and stream samples were placed in Erlenmeyer flasks with 1 mL of 5.5 M sulfuric acid and 0.4 g ammonium persulfate. The solutions were autoclaved at 121 ˚C for 30 minutes, allowed to cool to room temperature, then one drop of phenolphthalein indicator was added. The solutions were made slightly basic with 6 N NaOH (until phenolphthalein indicator turned faint pink), then 8 mL of a solution containing 2.5 M H_2SO_4, $4.1 \cdot 10^{-4}$ M potassium antimony tartrate ($K(SbO)C_4H_4O_6 \cdot {}^1/_2H_2O$), $5.15 \cdot 10^{-3}$ M ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), and 2.13 M ascorbic acid ($C_6H_8O_6$). After 10 minutes, a blue color developed and the solutions were analyzed at 880 nm with a Hach DR/4000 spectrophotometer.

Total Organic Carbon. Samples collected for non-purgeable organic carbon (NPOC) were mixed with 0.5 mL of phosphoric acid before analysis[2]. Samples were placed in an autosampler of a Shimadzu TOC 5050–A and were analyzed after calibration of the

[1] Samples were collected in 100 mL Nalgene bottles.
[2] Samples were collected in 100 mL Nalgene bottles.

instrument. A portion of the sample was injected into a heated chamber in which all carbon is oxidized to carbon dioxide (CO_2). The amount of CO_2 is quantified by measuring in an infrared beam.

Results and Discussion for Chemical and Microbial Analysis

The chemical results of the study are presented below in both table- and graph-form.

Chloride. Samples were analyzed for chloride four times during the study. Early in the study, each site had flowing water, but as the year-long study progressed, some of the streams dried up. All levels of chloride were low, in the part per million range, and there does not seem to be a trend to the data with respect to time of year.

Table 2. Summary of chloride concentration in Cowpens streams.
All values are reported in ppm Cl.

Site	Feb-00	Mar-00	Aug-00	Jan-01
1	6.22	3.41	no sample	3.85
2	3.62	3.22	1.85	2.99
3	3.62	4.03	2.58	3.45
4	6.69	3.46	no sample	no sample
5	4.08	2.90	3.65	2.93
6	4.85	3.96	2.05	no sample
7	5.47	3.55	no sample	no sample
8	5.63	5.33	7.78	4.48

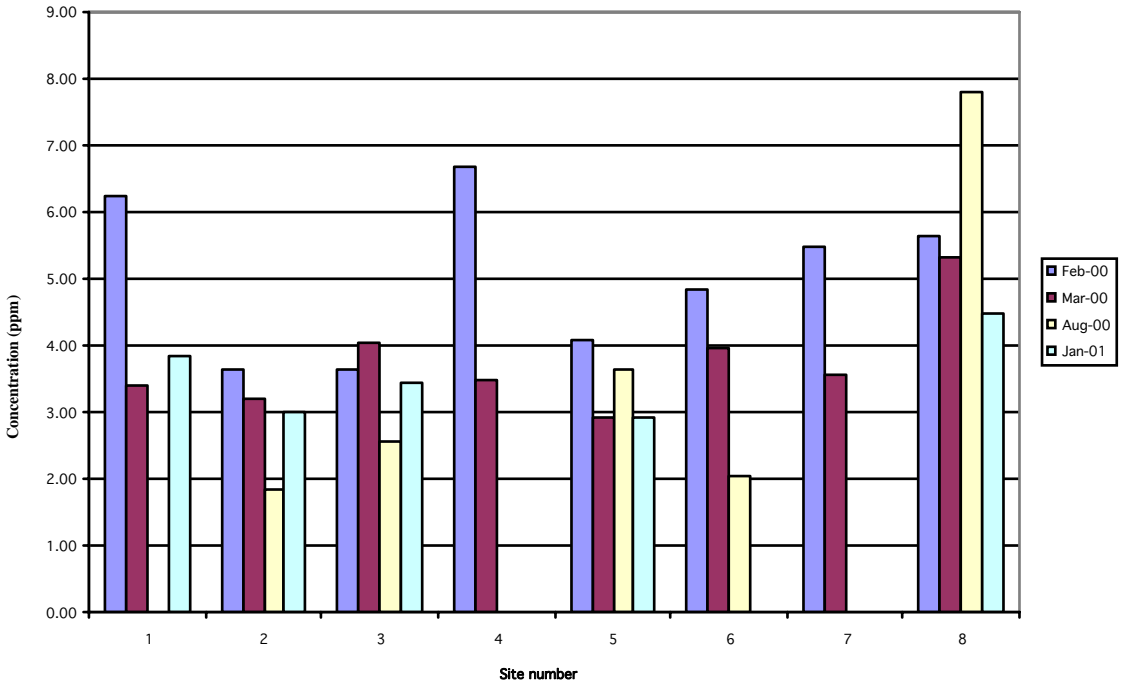

Figure 1. Concentration of chloride ion at sites 1-8 over the year-long study.

Ammonia. Samples were analyzed for ammonia (NH_3) four times throughout the study. In all cases, the concentration was quite low, at sub-part per million levels. During the year some streams dried out and thus had no water (indicated with "no sample" in the table), but at other points during the year, levels were below the detection limit of 0.17 ppm (indicated with "<0.17" in the table). While there is no clear trend to the data, it does appear that levels of ammonia were higher in May and August than in July or March.

Table 3. Summary of ammonia concentration in Cowpens streams.
Units are in ppm NH_3

Site	May-00	Jul-00	Aug-00	Mar-01
1	0.28	<0.17	no sample	0.28
2	0.30	<0.17	0.31	<0.17
3	0.55	0.18	0.53	<0.17
4	0.74	no sample	no sample	<0.17
5	0.46	<0.17	0.47	<0.17
6	0.19	<0.17	0.43	<0.17
7	0.31	no sample	no sample	<0.17
8	<0.17	<0.17	0.18	<0.17

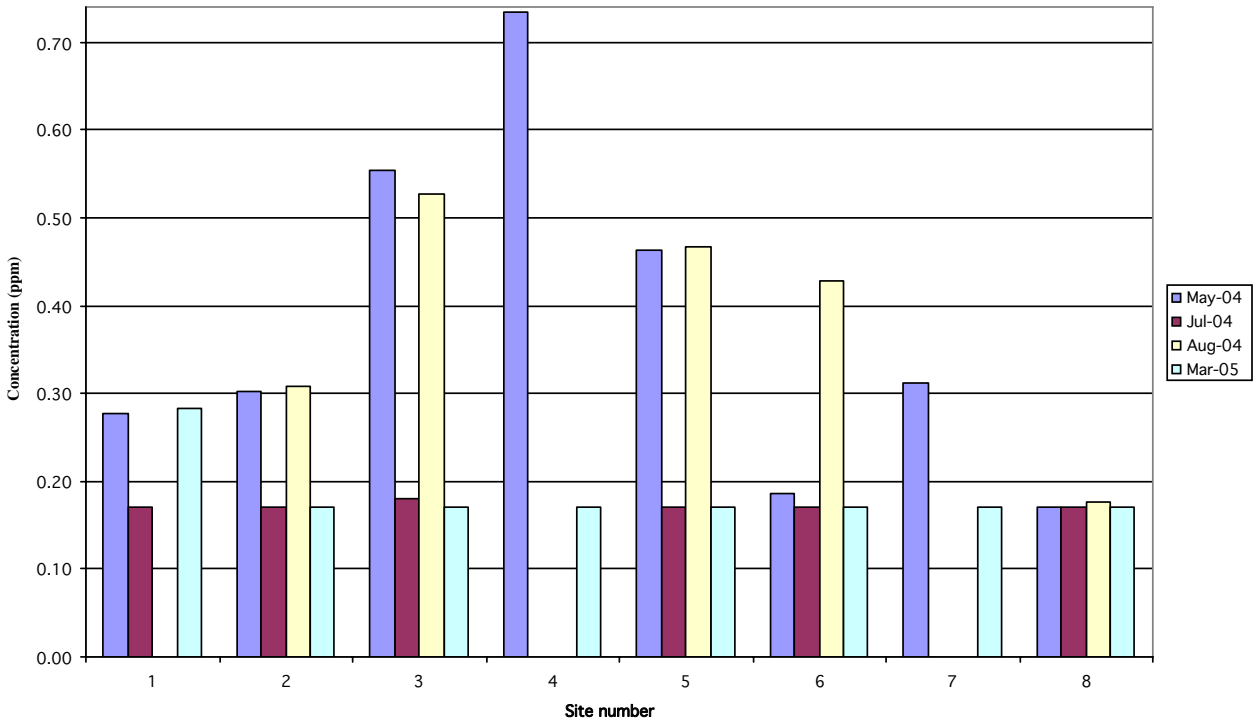

Figure 2. Concentration of ammonia (NH_3) in sites 1-8 for the year-long study.

Nitrate. Samples were analyzed for nitrate (NO_3^-), three times during the year. Although many of the streams did not have water in them when sampling occurred, none of the nitrate levels were below the detection limit of the analysis. Because of the lack of water in streams, an apparent trend to the data is not observable.

Table 4. Summary of nitrate concentration in Cowpens streams.			
Concentrations are in ppm NO_3^-			
Site	Jun-00	Oct-00	Feb-01
1	no sample	no sample	0.31
2	0.53	2.51	2.97
3	1.93	3.57	3.50
4	no sample	no sample	no sample
5	1.28	1.02	1.08
6	0.45	no sample	no sample
7	no sample	no sample	no sample
8	4.00	2.95	0.23

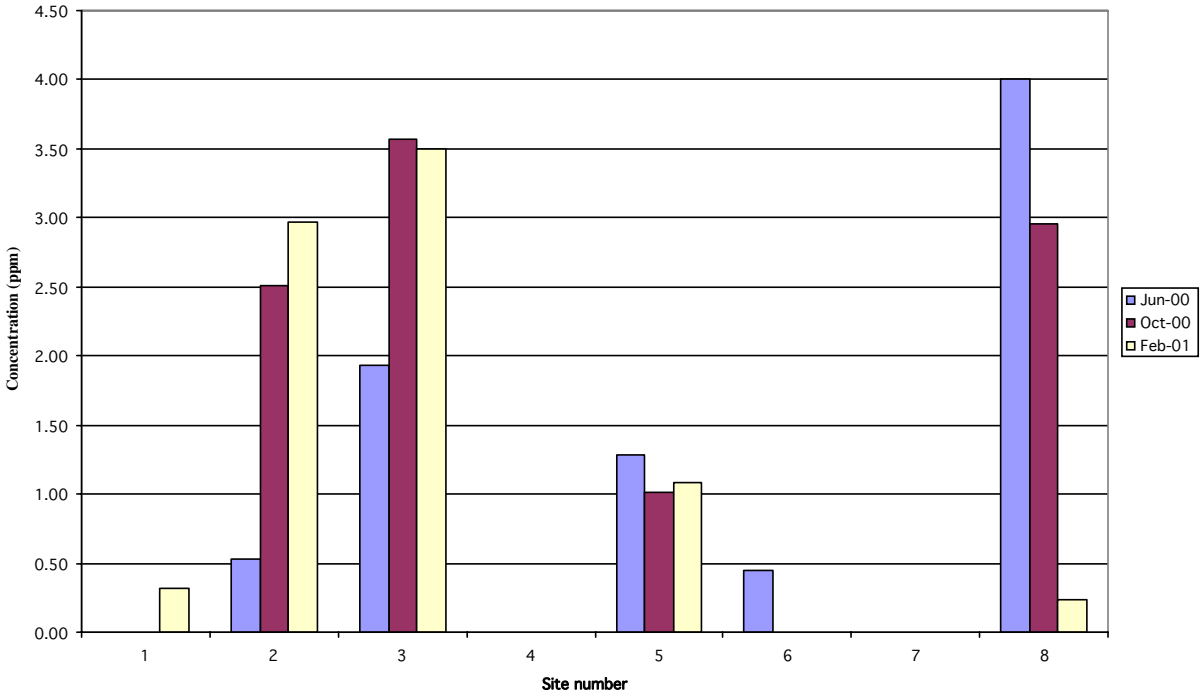

Figure 3. Concentration of nitrate (NO_3^-) in sites 1-8 for the year-long study.

Nitrite. Samples were analyzed for nitrite (NO_2^-) three times throughout the year. Since the samples were taken at the same time as the nitrite analyses, there are considerable "gaps" where the streams were dried up. Nitrite was present in much lower concentrations, and in most cases was below a detection limit of 0.046 ppm NO_2^-. Only in the last analysis period, February 2001, did the levels climb high enough to measure nitrite levels.

Table 5. Summary of nitrite concentration in Cowpens streams.			
Concentrations are in ppm NO_2^-			
Site	Jun-00	Oct-00	Feb-01
1	no sample	no sample	0.15
2	<0.046	<0.046	0.12
3	<0.046	<0.046	0.13
4	no sample	no sample	no sample
5	<0.046	<0.046	0.10
6	<0.046	no sample	no sample
7	no sample	no sample	no sample
8	<0.046	<0.046	0.16

Sulfate. Samples were analyzed for sulfate (SO_4^{2-}) four times throughout the year. Again, many streams were dried up and no sample was available. In cases where water was available for analysis, concentrations of sulfate ion were low, in the parts per million range or lower. There is no clear trend to the data, but on average, the analyses in February showed a slight increase in sulfate levels compared to the rest of the year. One note about the October 2000 sample period: the samples for sites 3 and 5 were improperly carried out and thus, though samples were available, the data for those trials was discarded.

Table 6. Summary of sulfate concentration in Cowpens streams.				
Units are in ppm SO_4^{2-}				
Site	**25-Apr-00**	**6-Jun-00**	**7-Oct-00**	**3-Feb-01**
1	3.0	1.9	no sample	5.5
2	6.1	2.4	0.4	4.5
3	0.6	0.7	?	0.2
4	0.5	no sample	no sample	no sample
5	0.1	0.4	?	1.5
6	0.5	0.7	no sample	no sample
7	1.4	no sample	no sample	no sample
8	1.5	1.4	1.4	2.0

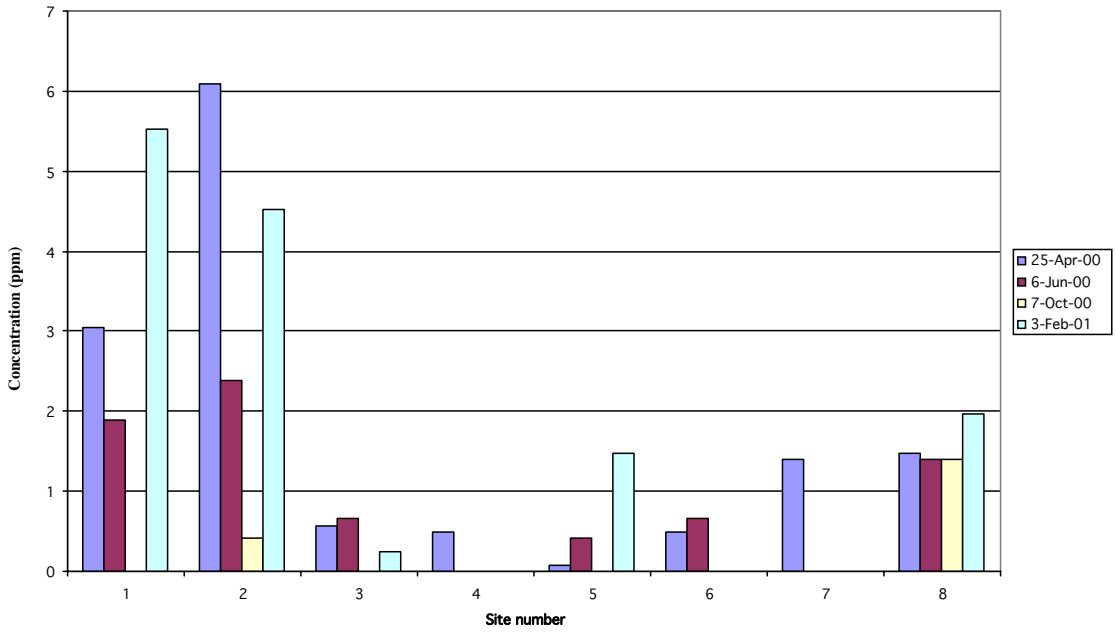

Figure 4. Concentration of sulfate (SO_4^{2-}) in sites 1-8 for the year-long study.

Metals. Samples were analyzed for sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), and manganese (Mn) four times throughout the study. Only in the first sample period was water available in all of the streams. In most cases, only sodium, potassium, magnesium, and calcium were present at detectable levels. Routinely, iron and manganese were at such low concentrations, that they fell below a detection limit of 0.010 ppm. (In the table, XX represents samples with iron concentrations below 0.010 ppm Fe, and X represents samples with manganese concentration below 0.010 ppm Mn.)

Table 7. Summary of metal concentrations in Cowpens streams.

Unites are in ppm

Mar-00								
Metal	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Na	1.765	3.667	2.518	2.430	3.054	3.263	1.381	3.771
K	0.733	1.865	1.333	0.761	1.869	1.597	1.293	1.617
Mg	0.528	0.893	0.468	0.516	0.781	0.909	1.121	1.069
Ca	1.289	3.186	0.887	1.367	3.165	2.628	3.021	3.571
Fe	XX	0.015	XX	0.028	0.040	0.054	XX	0.029
Mn	X	X	X	X	X	0.011	X	X
Jun-00								
Metal	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Na	3.086	2.454	2.534	No sample	2.910	5.128	No sample	4.247
K	0.488	1.958	1.157		1.597	2.026		1.918
Mg	0.452	0.753	0.428		0.677	0.709		0.929
Ca	0.685	1.200	0.794		1.440	1.378		1.907
Fe	0.025	0.022	XX		0.033	0.056		0.029
Mn	X	X	X		X	0.039		X
Sep-00								
Metal	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Na	No sample	12.026	1.910	No sample	1.873	No sample	No sample	3.175
K		5.128	1.789		3.743			5.396
Mg		0.737	0.392		0.745			0.825
Ca		1.359	0.474		0.992			1.430
Fe		XX	XX		XX			XX
Mn		X	X		X			X
Jan-01								
Metal	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Na	No sample	1.821	2.274	No sample	2.010	No sample	No sample	4.632
K		0.885	1.205		1.525			2.486
Mg		0.933	0.516		0.793			1.053
Ca		2.231	0.627		1.634			2.065
Fe		XX	XX		XX			XX
Mn		X	X		X			X

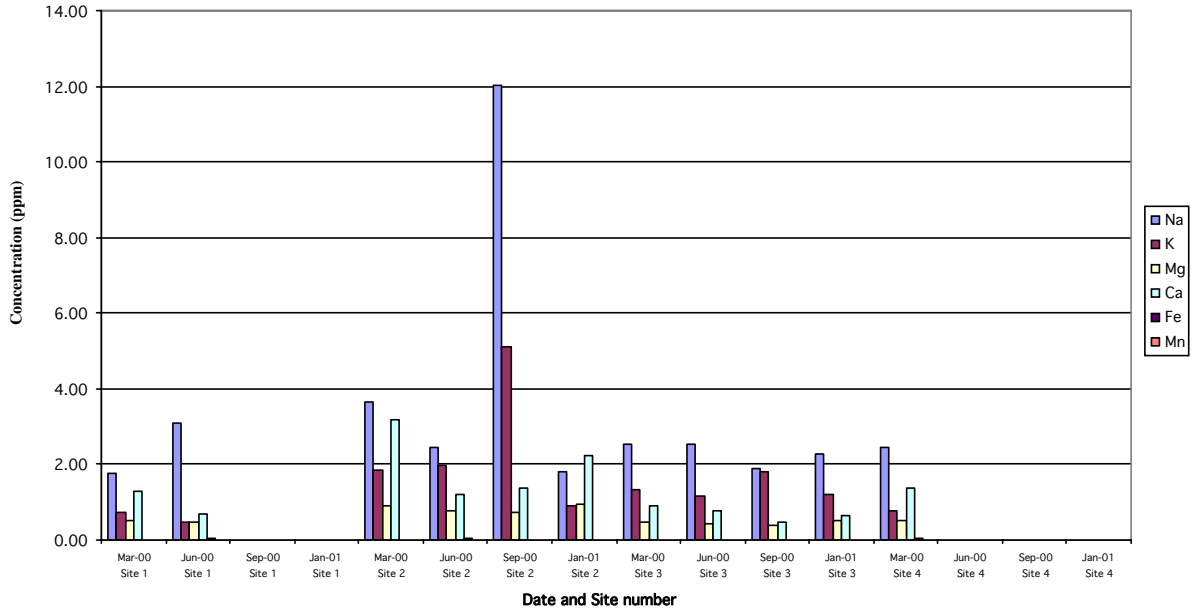

Figure 5. Concentrations of sodium, potassium, magnesium, calcium, iron, and manganese in sites 1-4 for the year-long study.

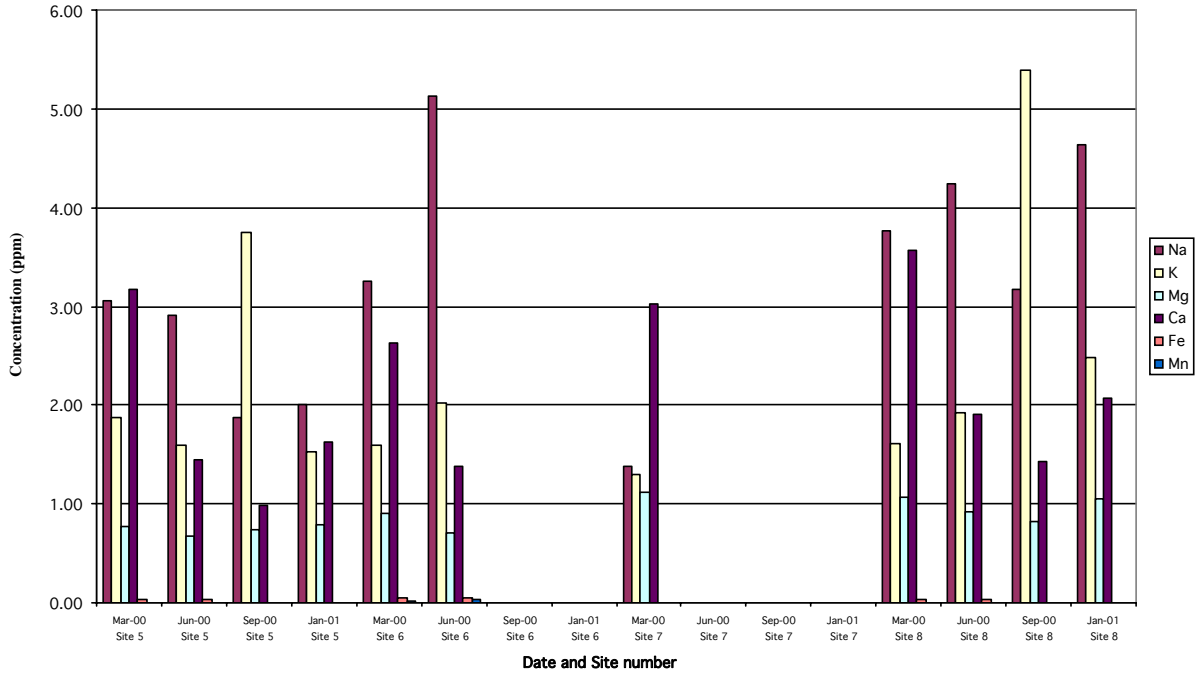

Figure 6. Concentration of sodium, potassium, magnesium, calcium, iron, and manganese in sites 5-8 for the year-long study.

Sodium. Except for a spike in sodium concentration in September 2000 at site 2, all concentrations were roughly in the same range, 2-4 ppm Na. Since the values are so close together, it is dangerous to subscribe definitive seasonal trends to this data, but it was seen that in streams that dried up, sodium levels increased before the dry months. Otherwise, sodium levels remained relatively constant during the year, though levels dropped a bit in September (excluding Site 2 which had a significant increase).

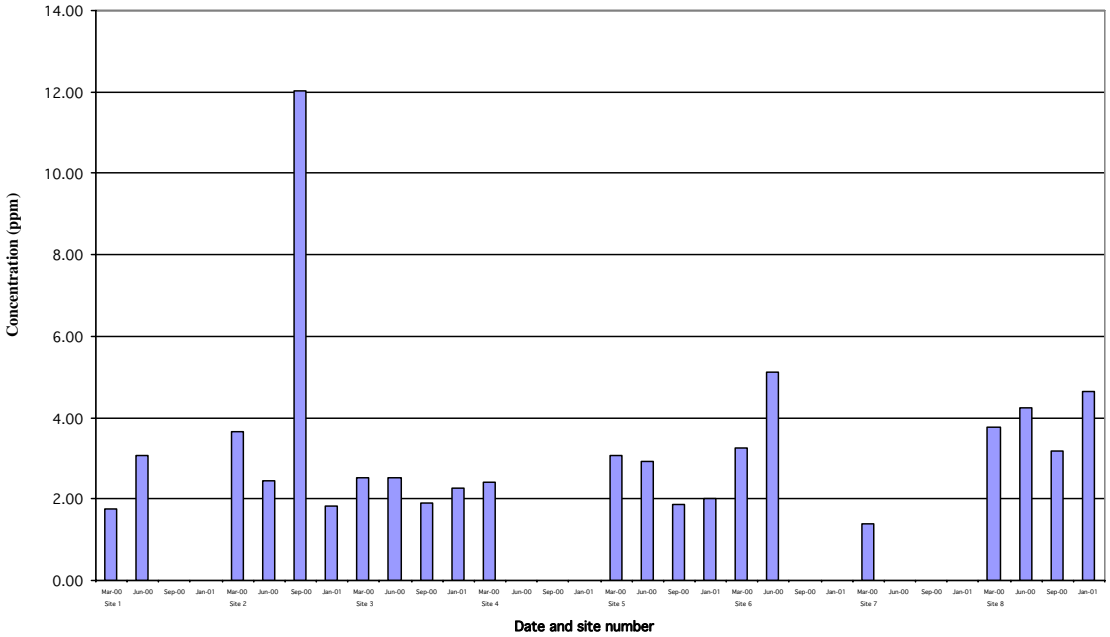

Figure 7. Concentration of sodium ion in sites 1-8 for the year-long study.

Potassium. While sodium levels generally dropped in September, the opposite happened for potassium. In all cases where sites had water, the September concentrations were the highest. The rest of the year showed relatively little change in concentration.

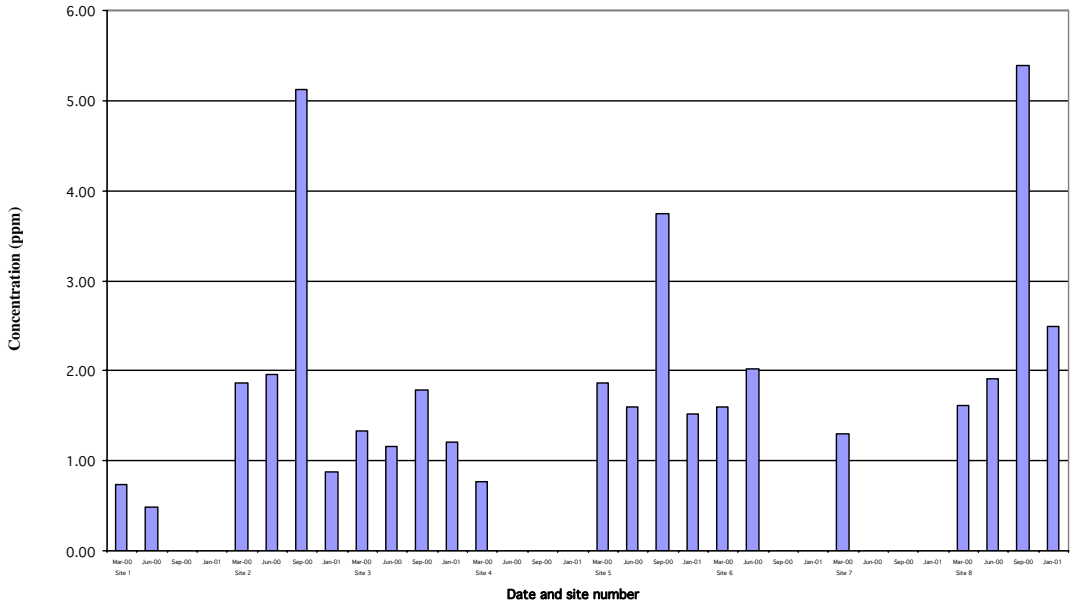

Figure 8. Concentration of potassium in sites 1-8 for the year-long study.

Magnesium and Calcium. Again, concentrations were fairly consistent throughout the year, with only small variations occurring. A trend was visible in both of these ions: March started out as the highest concentration, then as water levels decreased, magnesium and calcium ion concentrations also decreased, then in January, levels of these ions increased again. The trend is consistent with both ions and this is likely since they have very similar reaction chemistries, ionic charges, and solubilities.

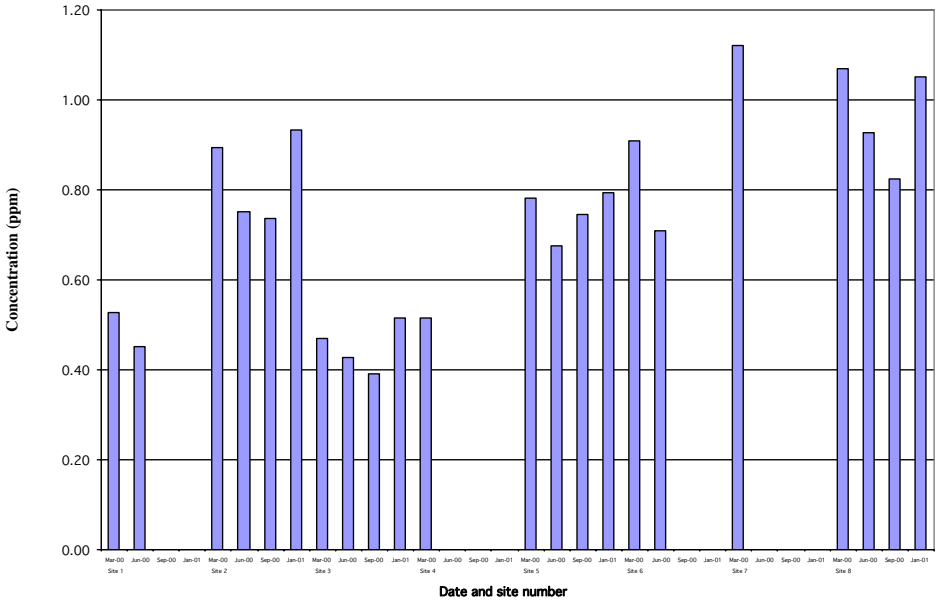

Figure 9. Concentration of magnesium in sites 1-8 for the year-long study.

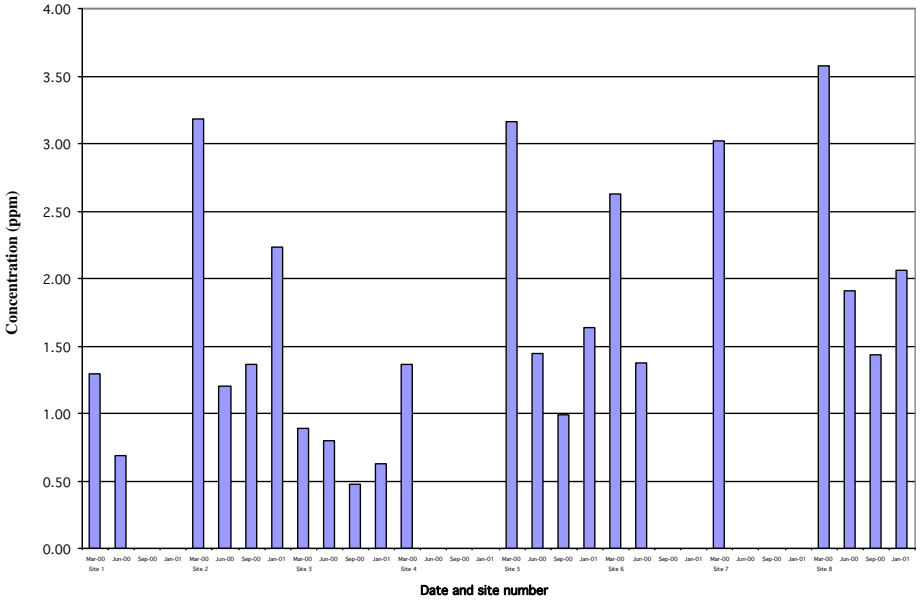

Figure 10. Concentration of calcium in sites 1-8 for the year-long study.

Iron and Manganese. Due to the very low concentrations of these ions, general trends could not be determined. Only site 6 had any measurable quantity of manganese, and this stream dried out after the June sampling. Iron was slightly more concentrated in some sites through the June sampling, but appreciable levels of iron could not be determined after September.

Carbonate/bicarbonate. Samples were analyzed for carbonate/bicarbonate (CO_3^{2-}/HCO_3^-) four times throughout the study. These two ions are very closely related and bicarbonate is a slightly acidified form of carbonate. Thus, the presence of these ions is closely related to the level of acidity in the water. For all of the samples taken, measurements indicated that the pH (acidity level) was too low for bicarbonate to be present (from acid dissociation constants, there will be approximately a 10^4 difference in concentration of equilibrated carbonate/bicarbonate systems). From the resulting analysis, all concentrations are given in part per million carbonate, as bicarbonate concentrations would be several orders of magnitude lower than this.

Table 8. Summary of carbonate concentration in Cowpens streams.

Units are in ppm CO_3^{2-}

Site	Apr-00	Jul-00	Nov-00	Mar-01
1	1.9	0.39	no sample	3.4
2	7.3	12.7	6.7	6.8
3	4.8	7.6	3.7	7.4
4	3.6	no sample	no sample	4.3
5	9.9	7.7	9.5	5.7
6	11.6	13	no sample	9.7
7	6.9	no sample	no sample	4.4
8	12.8	6.2	5.7	8.7

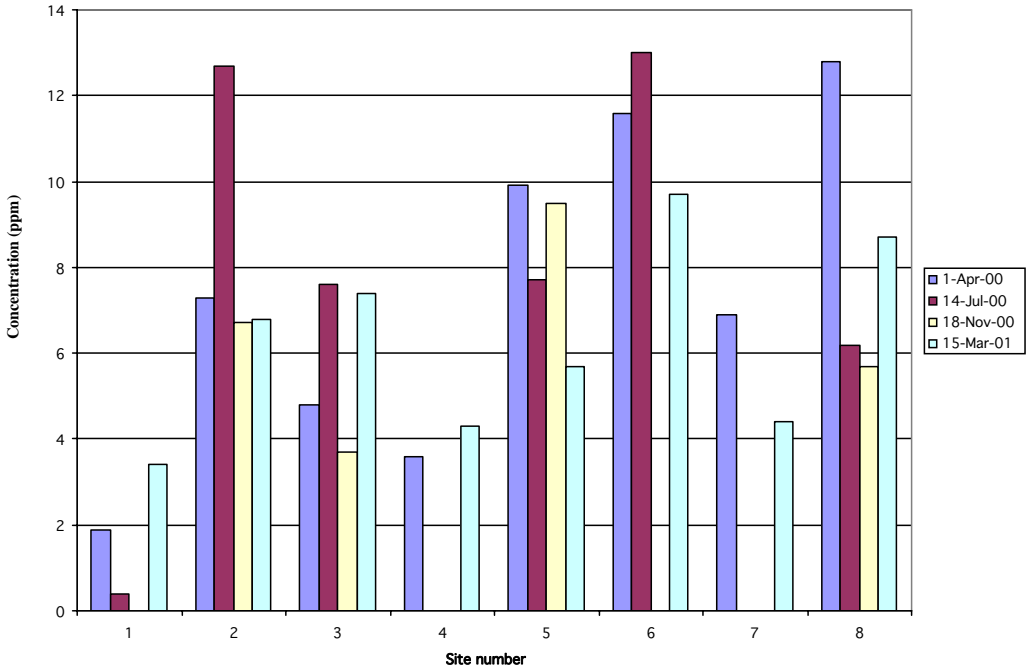

Figure 11. Concentration of carbonate (CO_3^{2-}) in sites 1-8 for the year-long study.

Temperature. Temperature readings were done on-site at the time of sample collection. There was an expected seasonal trend. Water temperatures were as high as 20 ˚C (68 ˚F) in July and August, but dropped below 8 ˚C (46 ˚F) in January and February

Table 9. Summary of water temperatures in Cowpens streams.
Units are in degrees Celsius (˚C)

Site	1	2	3	4	5	6	7	8
18-Feb-00	9.4	8.6	10.1	8.5	8.3	8.1	7.7	8.9
10-Mar-00	13.4	12.5	13.7	13.1	13.1	12.9	12.4	14
31-Mar-00	13.5	12.9	13.4	12.4	13.1	12.7	12.8	12.9
21-Apr-00	14.9	14.6	15.1	14.4	15.1	14.6	14.4	14.8
12-May-00	16.6	16.1	16.2	16.6	16.7	17.4	16.9	Not taken
2-Jun-00	18.1	17.7	16.8	No sample	17.7	17.7	No sample	17
6-Jun-00	18	17.5	16.7		18.1	17.3		16.9
23-Jun-00	No sample	18.8	17.4		18.9	19.3		17.3
14-Jul-00	21.1	20.5	18.4		21.3	20.5		20.5
5-Aug-00	No sample	20.4	18.4		20.4	20.4		19.6
26-Aug-00		19.6	18		20.5	19.8		19.5
16-Sep-00		16.1	15.9		16.2	No sample		15.2
7-Oct-00		15.7	15.1		16			15.4
27-Oct-00		15.8	16.2		15.6			15.9
18-Nov-00		7.2	10		7.2			9.4
4-Dec-00		8.1	10.3		8.4			9.1
3-Jan-01	7.4	5.7	8.3		5.3			7
3-Feb-01	7.6	6.2	8.2		5.6			7.5
15-Mar-01	11.1	11.3	12	10.7	11.3	10.8	11.1	11.2

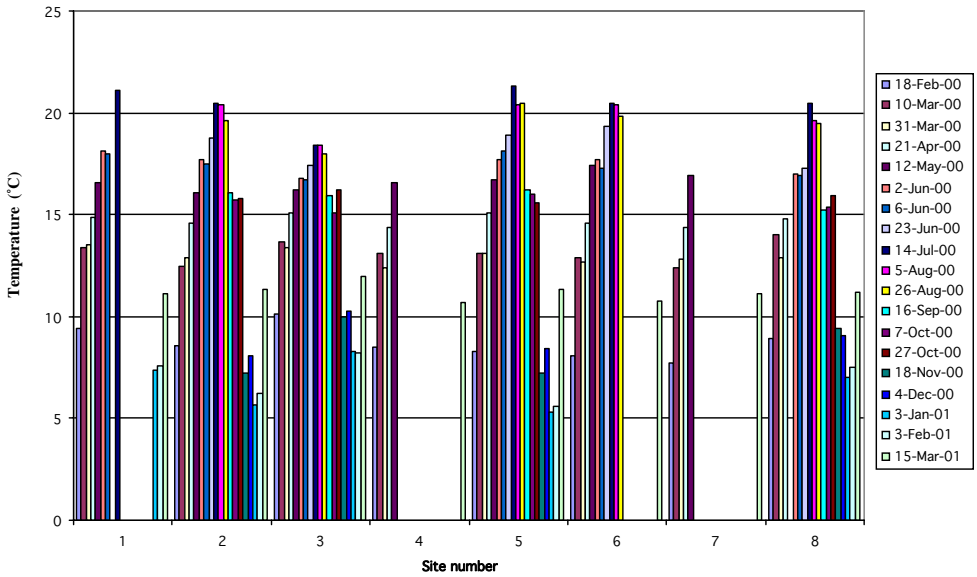

Figure 12. Water temperature in sites 1-8 for the year-long study.

Dissolved oxygen. Dissolved oxygen was measured on-site during sample collection. Though the data were not as consistent as the temperature readings, there is a general trend with seasonal variations. Gases have a lower solubility in warm water than in cooler water, thus summer readings are somewhat lower than those in cooler months. It should be noted, however, that there are competing factors for the content of dissolved oxygen and temperature is not the only variable. Plant life will increase the amount of D. O., while animal life (fish, crustaceans, insects, etc.) will decrease the amount of D. O.

Table 10. Summary of dissolved oxygen concentration in Cowpens streams.

Units are in ppm O_2

Site	1	2	3	4	5	6	7	8
18-Feb-00	5.6	8.4	8.6	4.7	8.8	8.7	7.2	8.6
10-Mar-00	3.62	8.45	8.75	1.45	8.5	7.4	4.55	7.98
31-Mar-00	4.15	7.55	8.15	1.74	8.05	6.54	5.63	9.28
21-Apr-00	3.85	8.74	Not taken	3.17	8.07	7.46	6.48	6.69
12-May-00	2.4	7.14	7.4	2.61	6.4	3.09	1.42	6.89
2-Jun-00	2.75	4	7.41	No sample	3.9	5.14	No sample	5.72
6-Jun-00	2.78	6.95	7.29		4.67	4.48		6.17
23-Jun-00	No sample	1.77	10.02		9	6.15		7.82
14-Jul-00	3.55	5.3	6.54		4.3	5.45		5.35
5-Aug-00	No sample	7.9	7.17		7.36	6.09		6.67
26-Aug-00		2.98	4.3		4.8	2.83		5.14
16-Sep-00		4.43	4.61		7.2	No sample		4.3
7-Oct-00		5.8	5		5.61			4.27
27-Oct-00		2.31	2.41		5.62			2.77
18-Nov-00		8.71	7.09		10.1			5.79
4-Dec-00		7.37	7.68		7.71			7.86
3-Jan-01	6.37	10.12	9.15		11.52			9.8
3-Feb-01	5.37	9.48	9.05		10.6			8.8
15-Mar-01	7.61	10.96	10.35	8.13	11.34	11.08	9.57	11.22

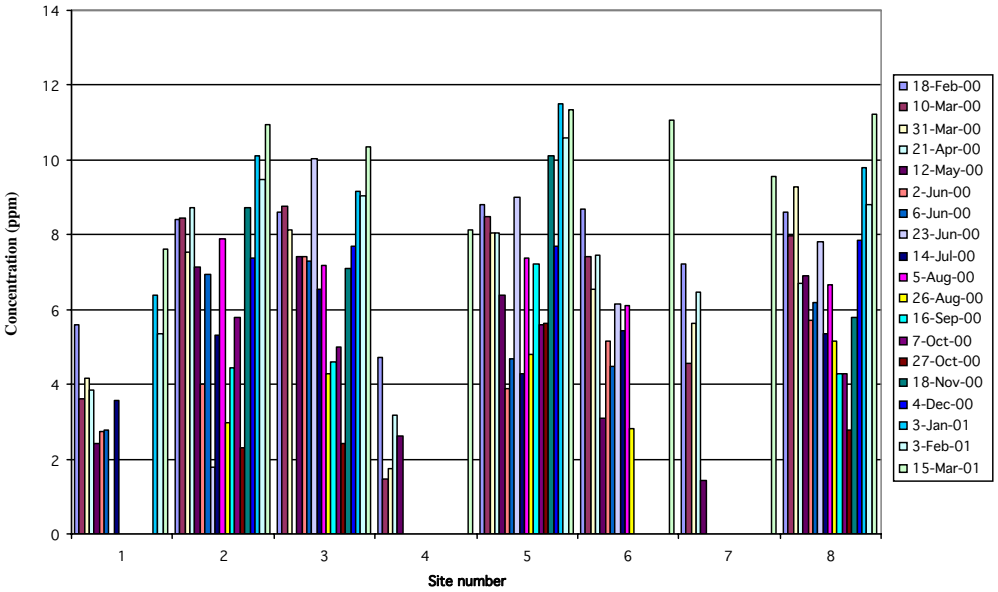

Figure 13. Concentration of dissolved oxygen (O_2) in sites 1-8 for the year-long study.

Conductivity. Conductivity was measured on-site while samples were being collected. Conductivity is a rough measurement of the amount of dissolved ions present in solution; the more ions in solution, the higher the conductivity. The units are microsiemans, a derived unit which includes the reciprocal of resistance. Of the sites that consistently had water in them (2, 3, 5, and 8), they all roughly had the same conductivity, though site 3 was a little lower, on average.

Table 11. Summary of conductivity in Cowpens streams.
Units are in microsiemans (µS)

Site	1	2	3	4	5	6	7	8
18-Feb-00								
10-Mar-00	12.2	29.5	19.8	0.4	25.3	29	26.2	36.4
31-Mar-00	0	14	20	27	32	39	33	47
21-Apr-00	23.5	35.2	23.7	14.3	23.2	41.5	29	45.8
12-May-00	11.4	37	24.3	29.3	33.2	41.6	31.7	45.9
2-Jun-00	23.1	38	23	No sample	32.3	36.5	No sample	41.1
6-Jun-00	23.4	37.4	22.6		31.4	28		37.9
23-Jun-00	No sample	38.4	23.3		31.2	0		39.2
14-Jul-00	41.3	42.2	26.3		36.6	36.1		22.4
5-Aug-00	No sample	36	16.6		39.6	27.9		26
26-Aug-00		41.4	22.3		30.8	56.1		63.4
16-Sep-00		40.6	22.7		26.6	No sample		44.9
7-Oct-00		35.4	23		32			26.7
27-Oct-00		48.2	26.8		35			45.5
18-Nov-00		45.8	24.1		32.8			46.5
4-Dec-00		46	26.9		33.7			44.4
3-Jan-01	46.7	45.4	26.1		34.1			45.5
3-Feb-01	41.1	45.2	25.8		34.2			41.2
15-Mar-01	32	50.2	39.6	50	35.3	44	51.8	41.9

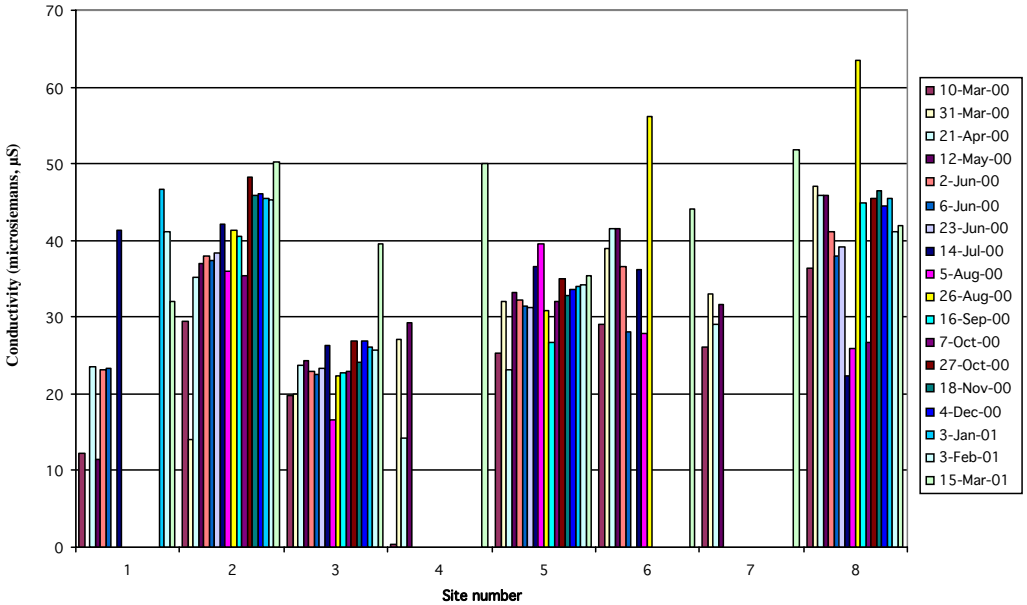

Figure 14. Conductivity of the water in sites 1-8 for the year-long study.

pH. pH was measured on-site while samples were being collected from October 2000 to the end of the analysis period in March 2001. pH is a measure of acidity, with numbers lower than 7 indicating an acidic environment and values greater than 7 indicative of a basic environment. Values of 7 indicate the system is neutral.

The data show that the water at Cowpens is very slightly acidic, and naturally occurring water will typically have slightly acidic values due to dissolved carbon dioxide.

Table 12. Summary of pH in Cowpens streams.

Site	1	2	3	4	5	6	7	8
7-Oct-00	No sample	6.3	6	No sample	6.65	No sample	No sample	5.8
18-Nov-00		6.08	5.6		5.93			5.8
4-Dec-00		5.3	4.9					5.8
3-Jan-01	4.81	6.01	5.8		6.3			5.68
3-Feb-01	5.1	6.38	6.12		6.51			5.05
15-Mar-01	5.01	5.75	5.83	5.6	5.88	5.56	5.58	5.91

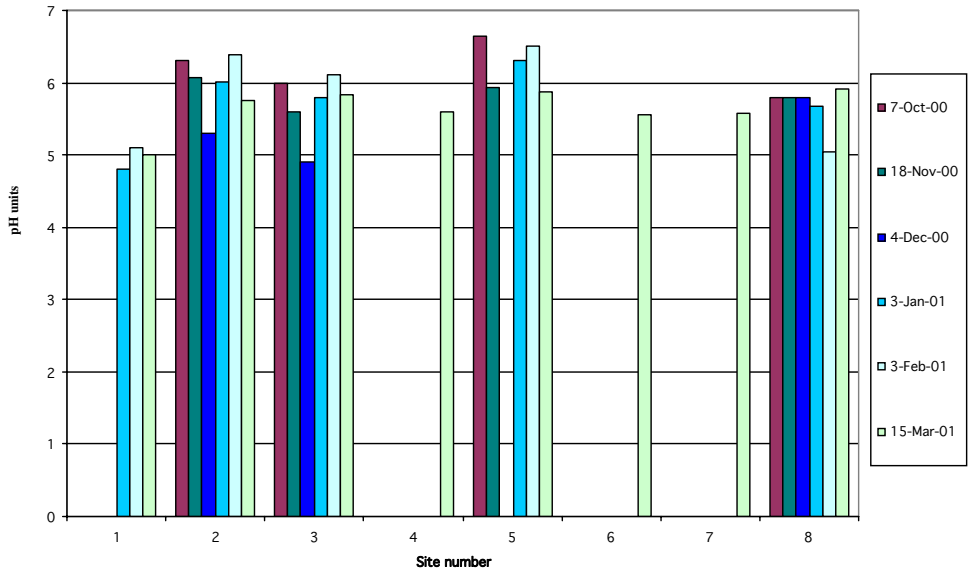

Figure 15. pH levels of sites 1-8 from October 2000 to March 2001. Values below 7 are considered acidic, values above 7 are considered basic, a value of 7 is a neutral solution.

Total organic carbon. Total organic carbon, as non-purgeable organic carbon (NPOC), was measured by instrumentation at the Spartanburg Water Works, R. B. Simms facility in Boiling Springs, SC. Only two samples were taken during the study, thus no clear seasonal trends of the data can be seen. There was a general increase in NPOC levels from May to August.

Table 13. Summary of total organic carbon (as non-purgeable carbon) concentration in Cowpens streams.		
Units are in ppm C		
Site	May-00	Aug-00
1	1.97	no sample
2	1.59	1.64
3	1.02	2.67
4	4.55	no sample
5	1.33	1.51
6	1.53	2.63
7	8.55	no sample
8	1.14	2.33

Phosphate. Phosphates were measured spectrophotometrically by reaction with a molybdenum reagent at the Spartanburg Water Works, R. B. Simms facility in Boiling Springs, SC. Only two samples were taken during the study, thus no clear seasonal trends of the data can be seen. Opposite of the TOC levels, phosphate levels generally decreased from May to August in 2000, though it should be cautioned that the phosphate levels are quite low (considerably less than 1 ppm all cases) and thus even small fluctuations might seem out of proportion.

Table 14. Summary of phosphate concentration in Cowpens streams.		
Units are in ppm PO_4^{3-}		
Site	May-00	Aug-00
1	0.09	no sample
2	0.21	0.12
3	0.18	0.12
4	0.18	no sample
5	0.21	0.18
6	0.43	0.28
7	0.21	no sample
8	0.18	0.18

RESULTS AND DISCUSSION

The results from the E. coli analysis are in Table 15. The results indicate that each one of the streams had a different level of E. coli. Stream #5 carries a much higher level of E. coli than do the other streams. There are several factors that may contribute to this: it drains a larger portion of the park and it is closer to human population because it comes close to the church properties, the park headquarters, and the nature trail. It also receives heavy traffic from the horses that are ridden in the park. There are many places along the stream where horses have crossed and fecal dropping were seen. An antibiotic analysis of the E. coli from this area indicate that they are not similar to isolates from human and cow. In a study of antibiotic resistant profiles of E. coli from different animal sources Harwood et al (2000) found that profiles from different animals were different. In their study the antibiotic resistant profiles were different enough to predict the source of unknown organisms. In a comparison of the antibiotic resistant profile of E. coli isolated from bovine feces and human feces, the Cowpen samples were very different. This suggests that the source is probably not human or cows. There is no evidence that there are cows in the park but the park was used extensively in the past as cattle pastures. Besides horses, there are other animals found in the park such as raccoons, possum, and fox. Raccoons are noted for spending part of their time playing in the water. This habit could be a source of fecal coliforms in that stream. Again all of these plus the low flow of water could contribute to the high numbers of E. coli found in some streams in the park. The violation column in Table 1 represent the percentage of the time that the stream would violate the 200 coliforms/100 milliliters of water standards set by DHEC. Again site # 5 violates this standard 59% of the time which is the highest number of violation for any of the sites.

Conclusions

This study points up the fact that most every stream will have a certain level of fecal coliforms present. In many cases these can be traced to human sources or to domestic animals but in the case of Cowpens National BattleField I suspect that wild animals may contribute some to the fecal coliform load in the streams. I do think that the horse population in the park should be a concern because horses do have fecal coliform in their bowl and there is evidence that they defecate in the streams. The remaining parameters in the study were with out exception very low.

It is my understanding that there is going to be an effort to "burn" some of the area; if this happens it will have a profound effect on the water quality in the streams. There will be an increase in runoff, which will lead to an increase in stream sediments. Accompanying this increase in sediment will be an increase in nitrogen in the stream plus other minerals. If this is done every effort should be made to protect the riparian zone along each of the creeks.

Literature Cited

American Public Health Association. 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. P.9.60-9.61. American Public Health Association. Washington. D.C.

Harwood, V. J., Whitlock, J., and Withington V. 2000. Classification of Antibiotic Resistance Patterns off Indicator Bacteria by Discriminant Analysis: use in predicting the sources of fecal contamination in subtropical Waters. Applied and Environmental Microbiology. 66:3698-3704.

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