

Cumberland Piedmont Network Water Quality Report

April 2005

Guilford Courthouse National Military Park

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Introduction

Fiscal-Year 2003, a water quality monitoring effort began in the Cumberland Piedmont Network (CUPN). For all intents and purposes, park managers and program directors can think of this work as a water quality inventory, as for many parks in the CUPN, little, if anything, was known regarding water quality. This two-year period also served as a proving-ground for water quality monitoring protocols and logistics. The report that follows is a park-specific document that describes the monitoring sites, parameters tested, results in graphic form, a brief interpretation of the results, and recommendations of parameters to be measured for the long-term.

Sampling sites were chosen following site visits by the Mammoth Cave National Park (MACA) hydrogeologist Joe Meiman, and with consultation with park staff. Some sites were chosen to coincide with past inventories and monitoring efforts. In most cases sites were chosen at the downstream end of a watershed to serve as an integrator of the basin, and should yield characteristics and contributions from the entire watershed.

The NPS Water Resources Division (WRD) requires each Network water quality program to monitor four core field parameters – water temperature, pH, specific conductance, and dissolved oxygen. Any additional parameters of park interest will be considered through the CUPN Vital Signs selection process. As little was known about water quality in most CUPN parks – exceptions being MACA, Little River Canyon National Preserve (LIRI) and Cumberland Gap National Historical Park (CUGA) – a wide net of water quality parameters was cast during the first two years. Furthermore, as much was known about the water quality of these three parks, they were placed near the end of the park rotation allowing full inventories of parks with little data. In addition to the four core parameters, acid neutralizing capacity (ANC) and fecal coliform tests were performed in the field. Samples were taken and analyzed for a variety of ions and constituents at the MACA Water Quality Laboratory and the WATERS Laboratory (a joint venture between MACA and Western Kentucky University WKU). The MACA laboratory moved to the WKU campus in July 2004.

The CUPN Science and Technical Committee (STC) recently reviewed field and laboratory quality and has made their recommendations to the CUPN Board of Directors. Data quality was reviewed based upon the Relative Percent Difference (RPD) between a field sample and its duplicate. In general the STC found the RPD values of the core four parameters to be of acceptable quality (less than 10% duplicate pairs lying outside a +/- 10% RPD tolerance level), although the fecal coliform and ANC tests need attention. Specifically, ANC results were of poor quality below 10 mg/l as CaCO_3 and fecal coliform results were generally poor throughout its entire range. The STC has been tasked with developing new protocols for ANC and fecal coliform.

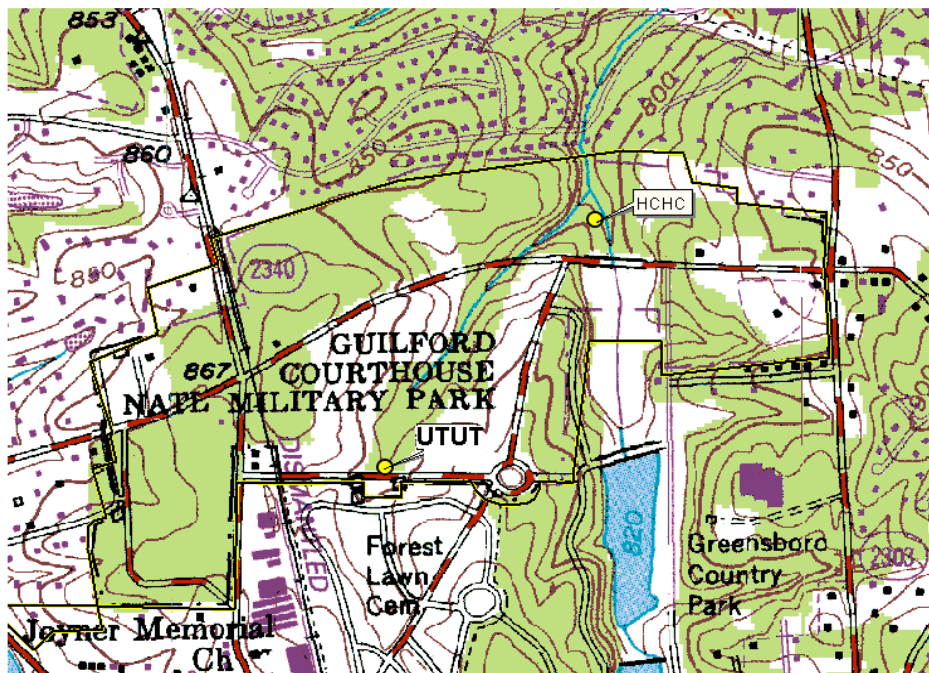
In addition, the STC reviewed RPD values from laboratory analysis. Overall, eleven of the seventeen lab parameters had greater than 10% of duplicate pairs falling outside a +/- 20% RPD tolerance level. Although data generated from the lab are of questionable quality in certain parameters, they are still of use in a basic inventory of water quality for

the park. It should be noted that RPD is a composite error that includes all possible error sources from sampling, transportation, preservation, and analysis. These data also represent both approved and non-standard methods and RPD values tend to be generally higher (poorer quality) for non-standard methods. Although the data that follow of questionable quality, they are still of use in a basic inventory of water quality for the park.

Sampling Sites

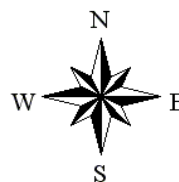
Below is a map of water quality sampling sites at GUCO. During each quarterly sampling round each site was visited and an additional Quality Assurance-Quality Control sample was extracted. Monthly sampling commenced in April 2004 and continued until January 2005, for a total of four sampling events. Additional field parameters were taken during one round as laboratory samples were mis-shipped, necessitating a repeat sampling.

GUCO, Water Quality Monitoring Sites



0.3 0 0.3 0.6 Miles

- Water Quality Site
- Boundary



Description of Sampling Sites

Hunting Creek (HCHC): Samples may be taken at the culvert that takes Hunting Creek beneath the park's tour loop road. This site is just downstream from where the creek enters the park. Access is easy and safe in all conditions.



Spring (UTUT): The unnamed spring that perennially discharges in the park as an unnamed tributary of Hunting Creek adjacent to the Forest Lawn Cemetery can be accessed from the tour loop road. Access is easy and safe in all conditions.



Parameters for Water Quality Inventory

Field Measures

The following text is adapted from the USGS Techniques of Water-Resources Investigations Book 9, Chapters A1-A9 (2001). All equipment specifications and calibration procedures are outlined in this document.

Temperature: Measurements of water and air temperatures at the field site are essential for water-data collection. Determinations of dissolved-oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties rely on accurate temperature measurements. Accurate water- and air-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by human activities. A thermistor thermometer is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity. An electrical signal processor (meter) converts changes in resistance to a readout calibrated in temperature units. Thermistors commonly are incorporated in instruments used for surface-water and groundwater measurements.

Specific Conductance: Electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. Basically, Specific Conductance (SPC) is a quick and reliable estimation of the dissolved solids in the water. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity. A dip-cell electrode sensor was used.

pH: The pH of an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions. Water pH is a useful index of the status of equilibrium reactions in which water participates. The pH of water directly affects physiological functions of plants and animals, and it is, therefore, an important indicator of the health of a water system. The electrometric measurement method uses a hydrogen ion electrode.

Dissolved oxygen: Accurate data on concentrations of dissolved oxygen (DO) in water are essential for documenting changes to the environment caused by natural phenomena and human activities. Sources of DO in water include atmospheric reaeration and photosynthetic activities of aquatic plants. Many chemical and biological reactions in ground water and surface water depend directly or indirectly on the amount of oxygen present. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms. The most commonly used field method for measuring DO in water is the amperometric method, in which DO concentration is determined with a temperature-compensating instrument or meter that works with a polarographic membrane-type sensor.

ANC: is the acid-neutralizing capacity of solutes plus particulates in an unfiltered water sample, reported in mg/l as CaCO_3 . ANC is equivalent to alkalinity for samples without titratable particulate matter. ANC is basically a measure of buffering capacity – the ability of water to buffer the effects of acid. Waters of low ANC are more susceptible to decreased pH by acid precipitation.

Fecal coliform bacteria: Fecal indicator bacteria are used to assess the quality of water because they are not typically disease-causing, but are correlated to the presence of several waterborne disease-causing organisms (pathogens). The concentration of indicator bacteria (the term "indicator bacteria" is used synonymously with fecal indicator bacteria in this section) is a measure of water safety for body-contact recreation or for consumption. The most widely used indicator bacteria are of the total coliform, fecal coliform, enterococci, and fecal streptococci groups, and *E. coli*. Standard Method 9222D, membrane filtration for fecal coliform was used.

Discharge: The anchor of all water quality data. Discharge data are used to compute the mass flux, or loading, of a particular constituent. Mass flux yields valuable insight as to the mode of contaminant entrainment and transport through the watershed.

Laboratory Measures

Anions: A suite of anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate) was analyzed. Sources of anions are varied – from natural and anthropogenic contribution. Anions such as chloride and bromide are common to oil field brines, and nitrite, nitrate, and phosphate are considered nutrients, and are commonly products of animal wastes. Standard Method 300.1 (ion chromatograph) was used.

Cations: A suite of cations (sodium, potassium, magnesium, and calcium) were analyzed on the ion chromatograph, an unapproved method. Note that all data presented below were a product of the ion chromatograph. Any future cation analysis will be analyzed on a flame atomic adsorption spectrometer using Standard Method 3113. The cation sodium is paired with chloride and may indicate brine contamination. Potassium, magnesium and calcium are usually contributed to the dissolution of rock, although the former ion can be agriculturally derived as well.

Total Organic Carbon: TOC is a measure of organic carbon in water, including various constituents in various oxidation states. This is a direct and easy measure of organic carbon, including components of biological and chemical oxygen demand. Standard Method 5310 B was used.

Total Suspended Solids: While turbidity measures are a quick and simple estimation of suspended solid loads, it cannot be directly correlated to TSS, which is a true measure of suspended solids due to particle size and color characteristics. Standard Method 2540 E was used.

Chlorophyll-a: Since chlorophyll-containing organisms are the first step in most food chains, the health and /or abundance of these primary producers will have cascading effects to all higher organisms. Therefore, the determination of chlorophyll concentration is one of the key indices in monitoring the health of any natural system. EPA Method 445.0 was used.

Turbidity: Turbidity measures the scattering effect that suspended solids have on light: the higher the intensity of scattered light, the higher the turbidity. Primary contributors to turbidity include clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton, and microscopic organisms. The measurement is qualitative and cannot be correlated directly as micrograms per liter of suspended solids. Measurements were made in the laboratory with a nephelometer using Standard Method 214 A.

Atrazine: Atrazine, a triazine-class herbicide, represents the most common and durable pesticides used in the United States. They are commonly found after peak applications periods (spring), closely associated with storm pulses (attached to fine particulate matter), and have been found persisting in the water column for six months. The USEPA-approved immuno-assay screening technique was used for this analysis.

Stream Designated Uses

As discussed below, each water body sampled within the CUPN has either been assigned a designated use by the state, or, by using the same ranking criteria, by this author. The USEPA, besides mandating these rankings, also directed the states to develop water quality standards for each designated use. We can use these water quality standards as a minimum to track water quality trends in CUPN parks. By adapting the state standards, we can also track park water quality trends within the states, regions, or watersheds. For more information on North Carolina water quality standards, please see:

North Carolina: Subchapter 2B – Surface Water and Wetland Standards, 15A NCAC 02B .0100 - .0510.

The table below shows that none of the park’s two sites are officially listed – a state is not required to list designated uses for all waters. The author, using the same criteria used by the state process, “listed” designated uses for each site for purposes of water quality comparison.

<i>Park</i>	<i>Code</i>	<i>Site</i>	<i>State</i>	<i>Designated Use</i>
GUCO	HCHC	Hunting Creek	NC	Class WS-IV
GUCO	UTUT	Unnamed tributary	NC	Class WS-IV

Class WS-IV includes waters that may be protected as water supplies and are within moderately to well-developed watersheds. At a minimum, these waters must support aquatic life.

Most of the water quality parameters included in this inventory are not found in the state water quality standards. This is not to say they are unimportant to park management (a suggested list of parameters for long-term monitoring will conclude this report). If a state designated use water quality exists, it will be mentioned in the data interpretation below.

Results and Interpretation

The following graphs are a composite of four quarterly rounds of sampling at GUCO. With only four data points per site, it was not possible to create box-plots (a easy graphic way to show basic statistics), water quality data are displayed as simple scatter plots.

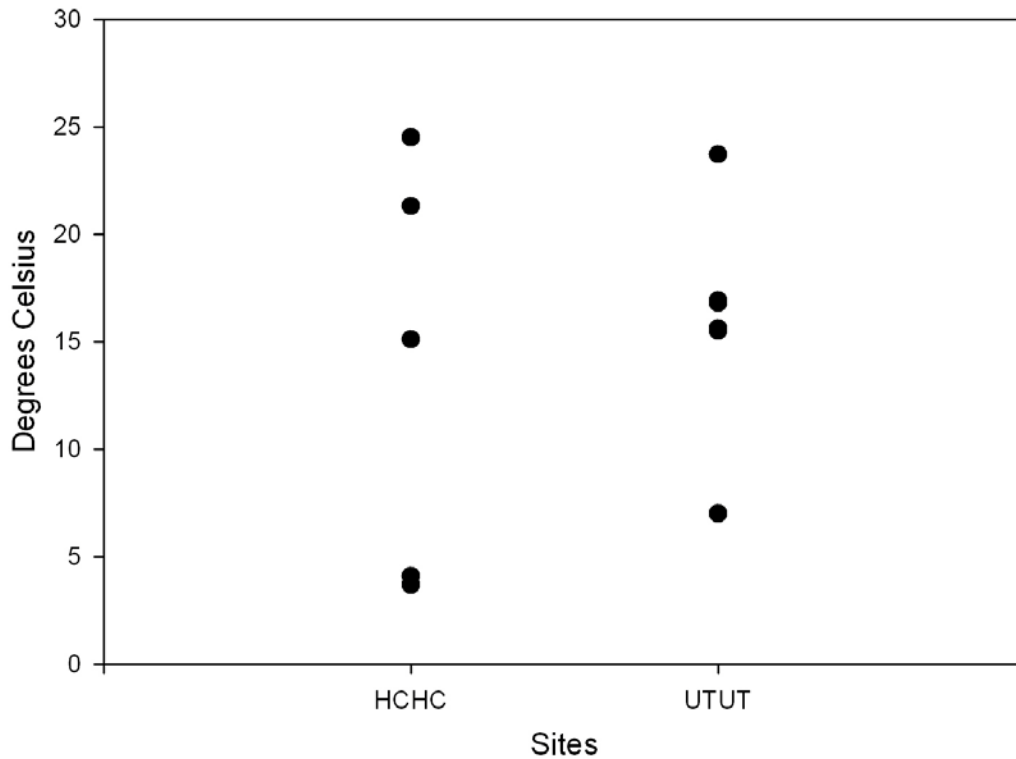
In addition to state water quality standards (where applicable), laboratory “Practical Quantitation Limits” (PQL) will be denoted. The PQL is five times the “Minimum Detection Limit” set by the laboratory. The PQL can be used as a means of determining if a particular parameter is worth monitoring in the future. For example, if samples continually come in well under the PQL value, and there is no known reason to continue that analyte, it would be a candidate to discontinue. The laboratory used the ion chromatograph (unapproved method) for all cation analysis below and did not provide PQL limits. For the cations of calcium, potassium, magnesium, and sodium, PQLs for the flame atomic adsorption method were used. There is also no PQL provided for Chlorophyll-a analysis.

Field Parameters

Water Temperature

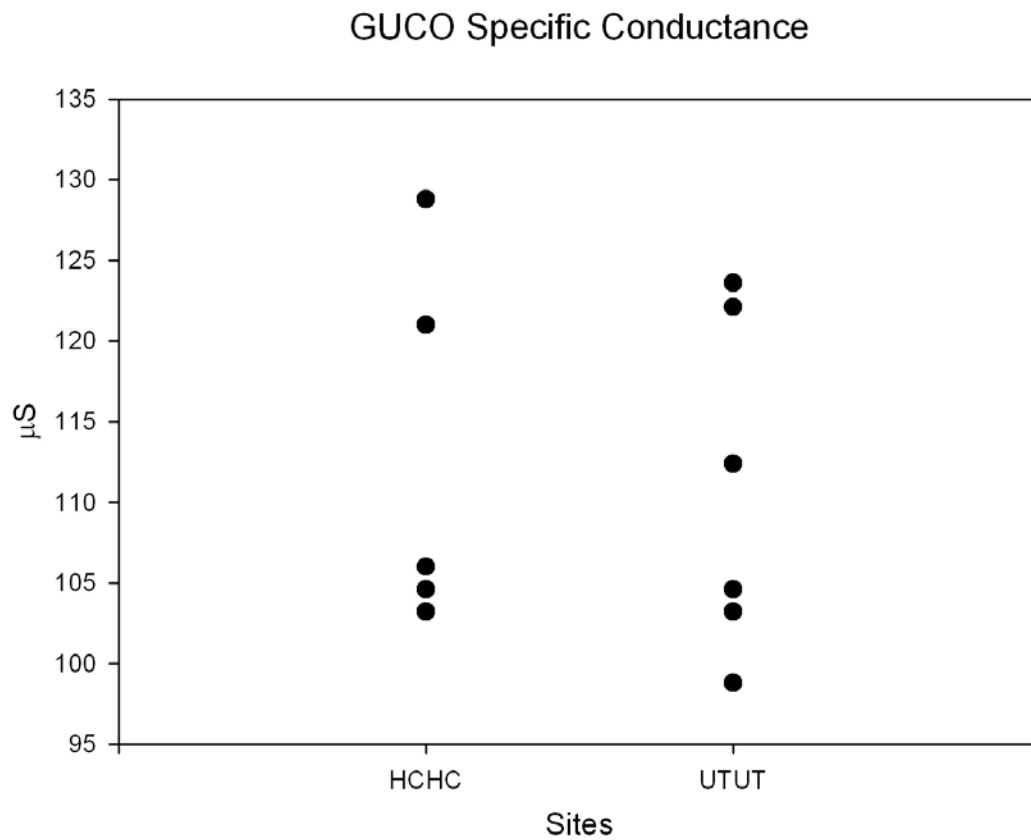
Water temperatures at GUCO are considered to be within range to support native aquatic life. The slightly compressed temperature range at the Unnamed tributary (UTUT) is a function of longer retention times of groundwater recharging the spring. North Carolina designated use standards for WS-IV waters state that temperature cannot exceed natural conditions by more than 2.8°C. Although it will take time to establish “natural conditions” for these waters, there is no reason to believe that temperature is an issue with respect to compliance.

GUCO Water Temperature



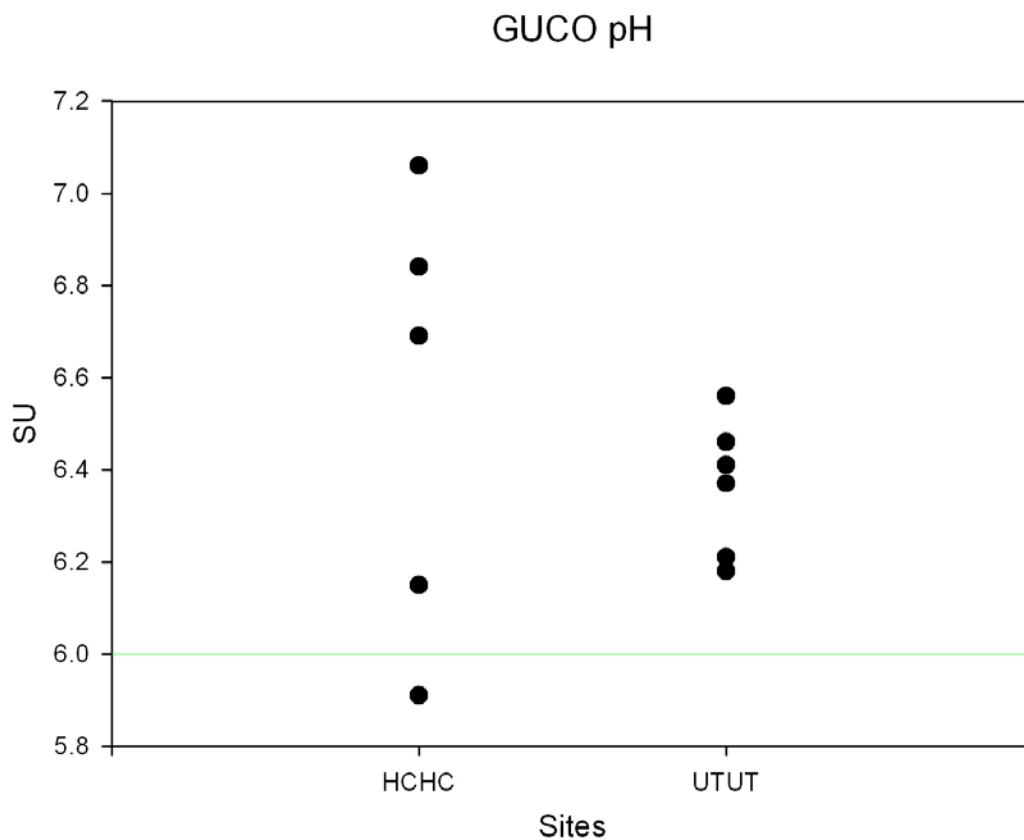
Specific Conductance

The distribution of specific conductance (SPC) at GUCO, like anywhere, is a function of the amount of dissolved ions in the water. These two sites contain a moderate amount of dissolved ions – some parks (CARL) have SPC values an order of magnitude lower than found here, while others (STRI) may exceed 400 μS . There are no state standards for SPC.



pH

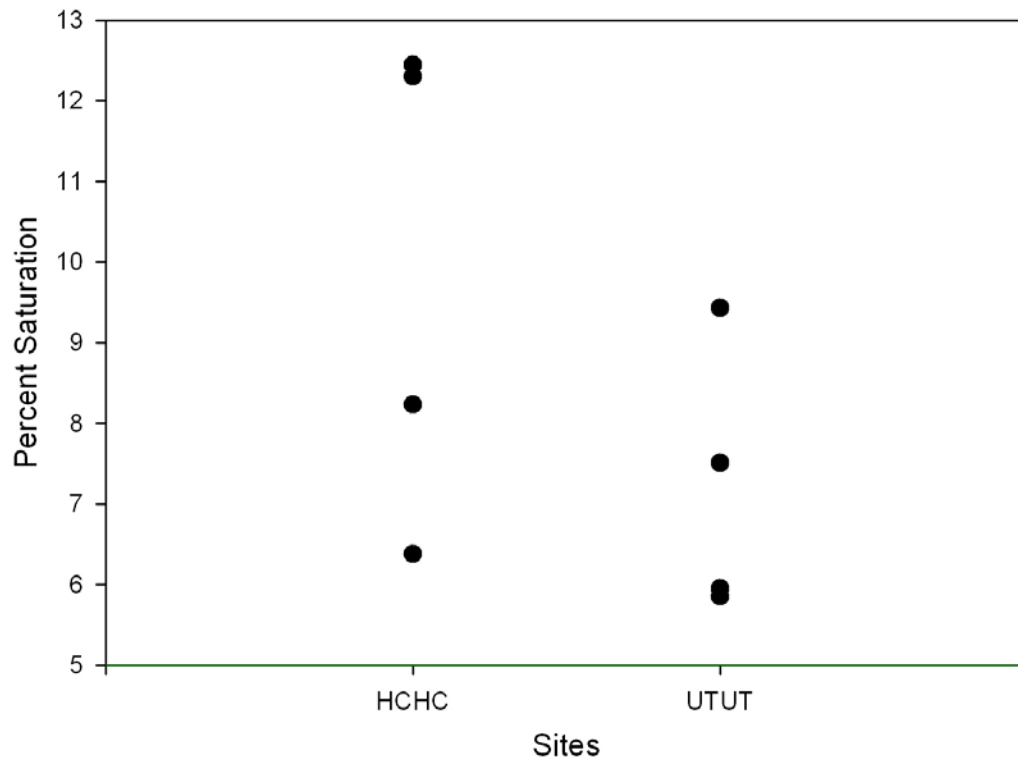
Waters of GUCO are slightly to moderately acidic. State standard for freshwater pH is between 6.0 and 9.0 SU. Hunting Creek shows a wider range of pH, and one sample exceeded the lower limit. The samples of the Unnamed tributary display a tighter range and approach this limit. As these streams are recharged in a buffering-limited environment, this low pH is most likely natural.



Dissolved Oxygen

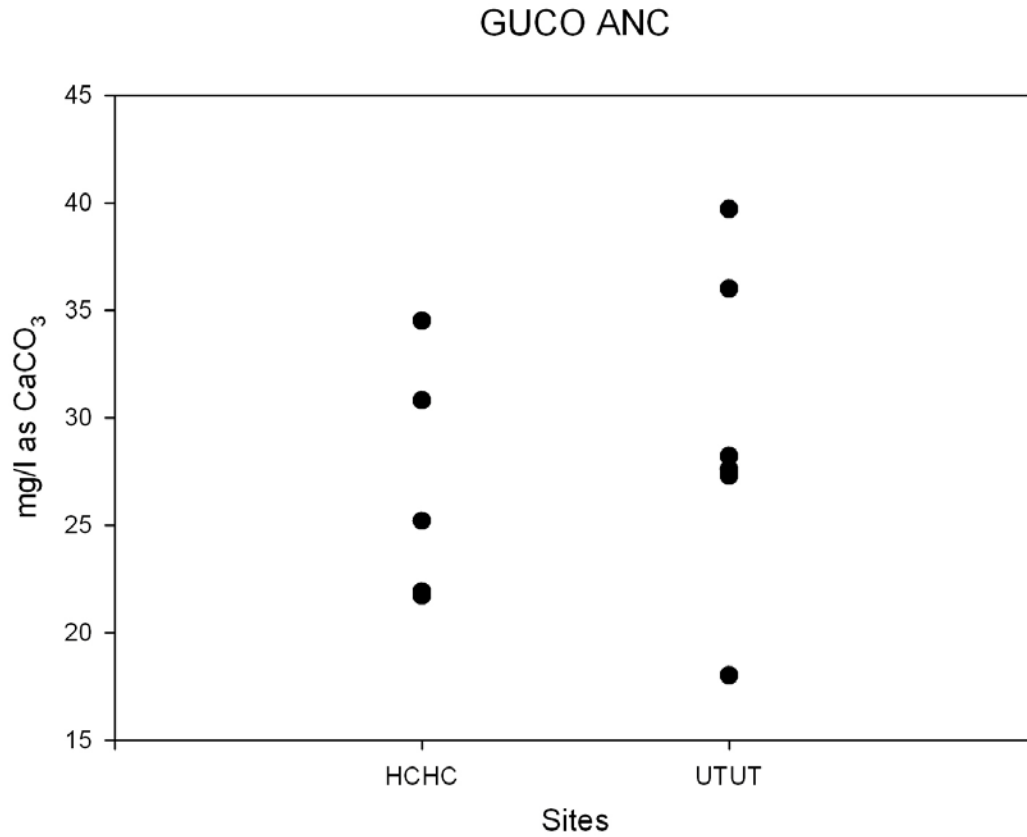
Dissolved oxygen, in all samples, was above the state limit of 5.0 mg/l. There were a few readings at the Unnamed tributary (UTUT) and one at Hunting Creek (HCHC) that approach this limit. It should be noted that due to a malfunction of the DO sensor, no reading were taken during the July round. Typically the lowest dissolved oxygen levels occur in the warmer months as warm water cannot hold as much oxygen as cold water.

GUCO Dissolved Oxygen



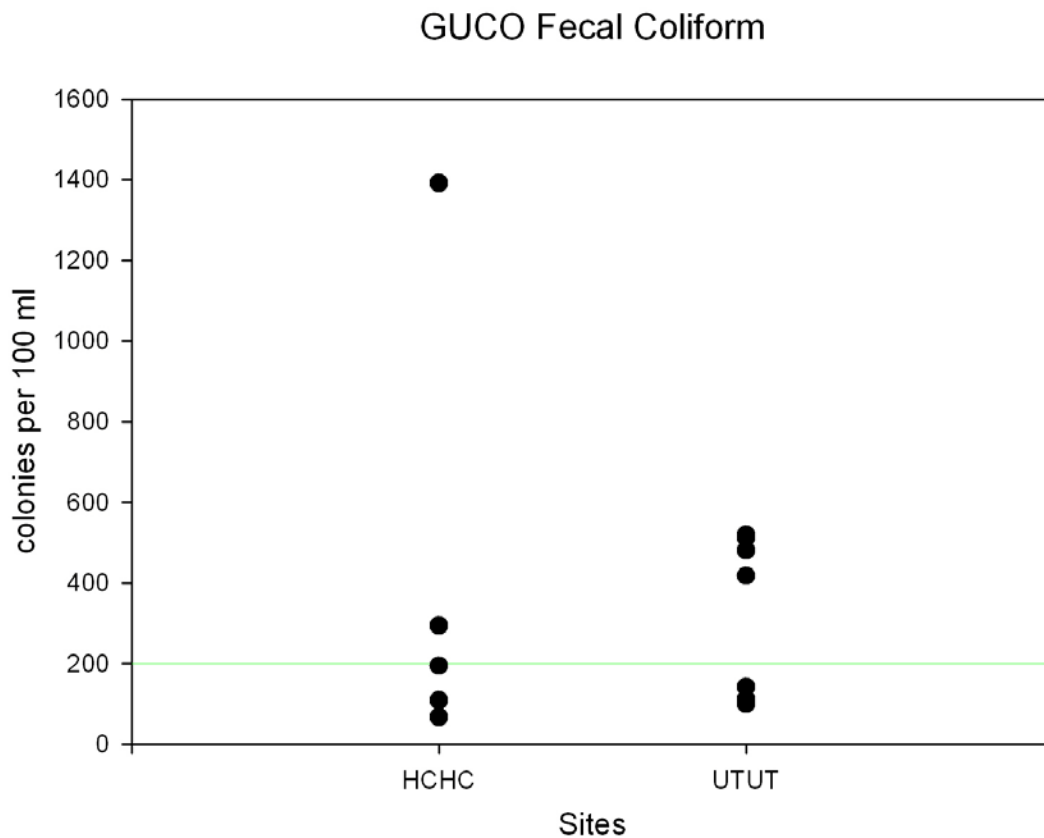
Acid Neutralizing Capacity

Acid neutralizing capacity (ANC) of GUCO waters is fairly low to very low, indicating a lack of contact with carbonate strata or other sources of the bicarbonate ion. Low ANC levels make waters more susceptible to acid precipitation as there are limited amounts of bicarbonates available to counter additional acids.



Fecal Coliform

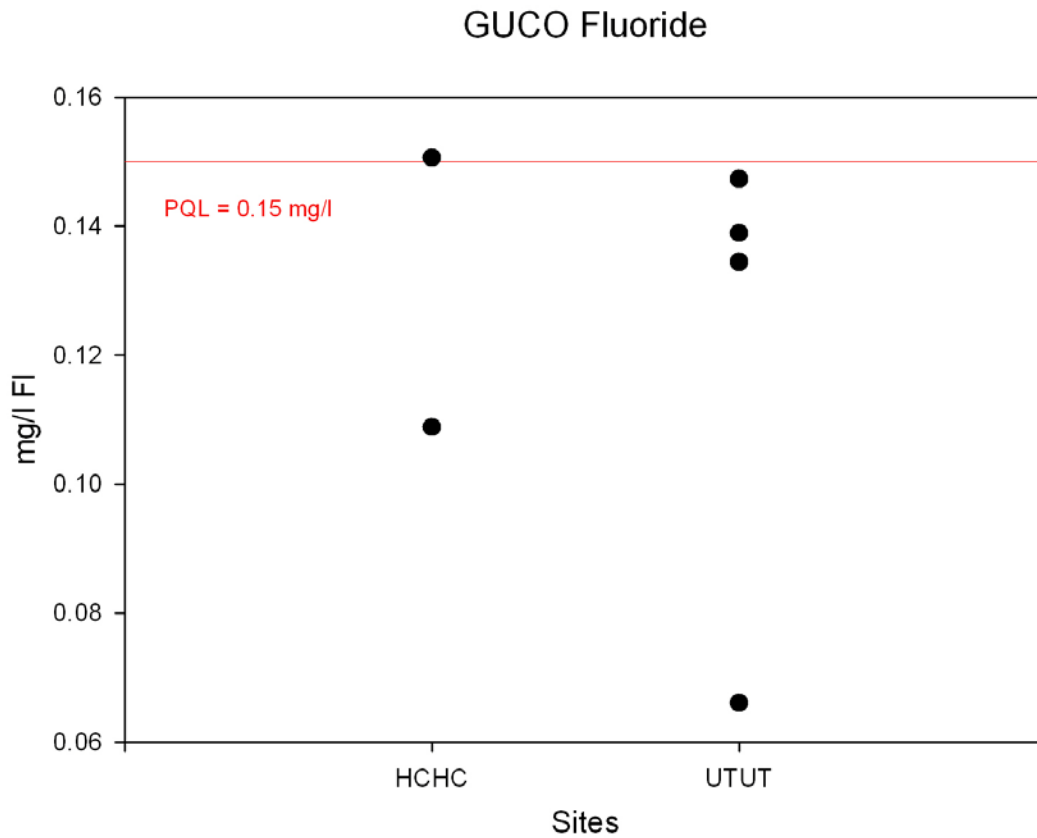
Fecal coliform levels at GUCO are among the highest within the CUPN. Hunting Creek is fed by a series of lakes in Greensboro County Park. This lake has been commonly observed to be home to scores of ducks and geese and may be prime contributors to the bacterial load. The highest level was found in the July sample. Also it is obvious that the watersheds upstream of the park is highly developed, mostly residential and light commercial, may contribute. There is no apparent correlation between flow and fecal coliform. In any case, the fecal coliform standards for WS-II and HQW is 200 colonies per 100 ml, based on a geometric mean of a series of 5 samples taken within a 30 day period.



Laboratory Measures

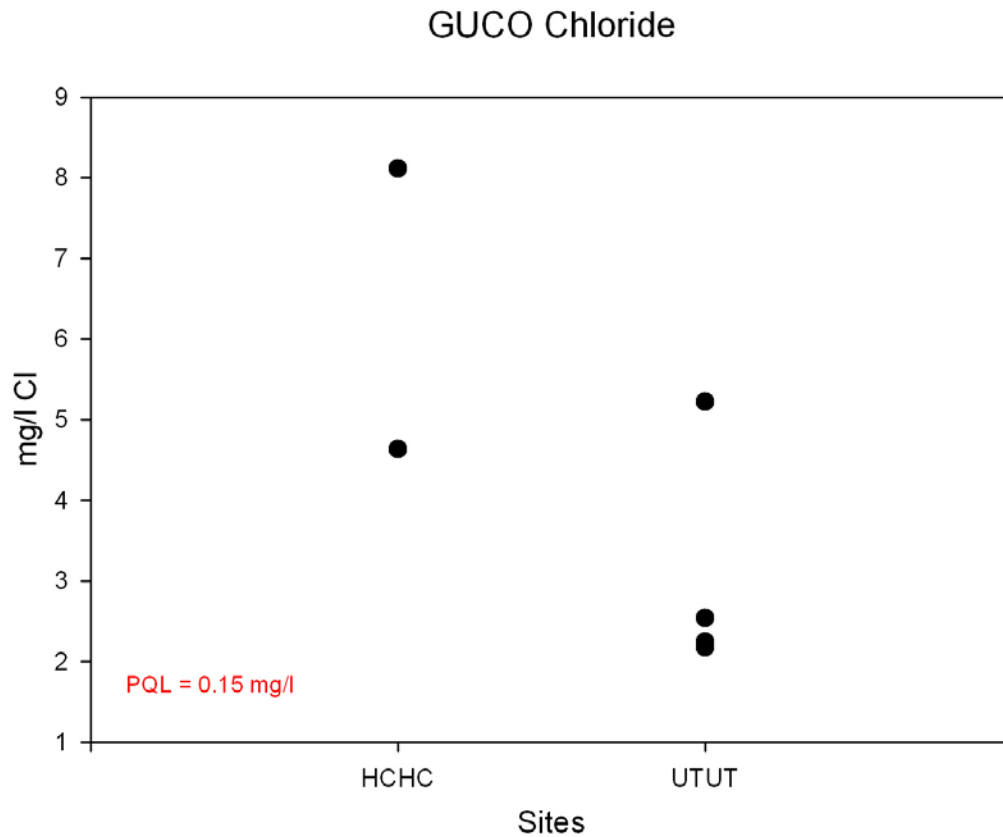
Fluoride

Fluoride concentrations of GUCO waters are very low; so low that all samples registered lower than or at the PQL of 0.15 mg/l. The state standard is 1.8 mg/l, over an order of magnitude higher than the PQL.



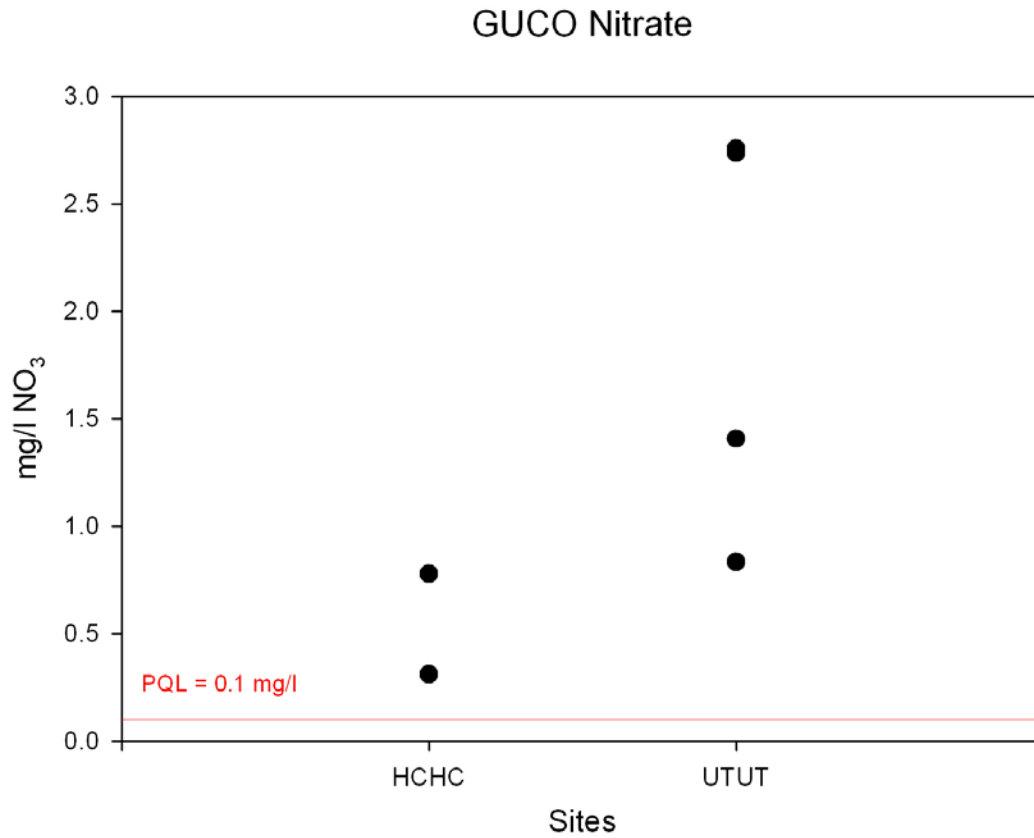
Chloride

While all samples were above the PQL of 0.15 mg/l, no samples exceeded the state standard for chloride, set at 250 mg/l. Chloride is found as natural background ion, a leftover of evaporation and evapotranspiration processes. These levels are within what are expected as natural concentrations.



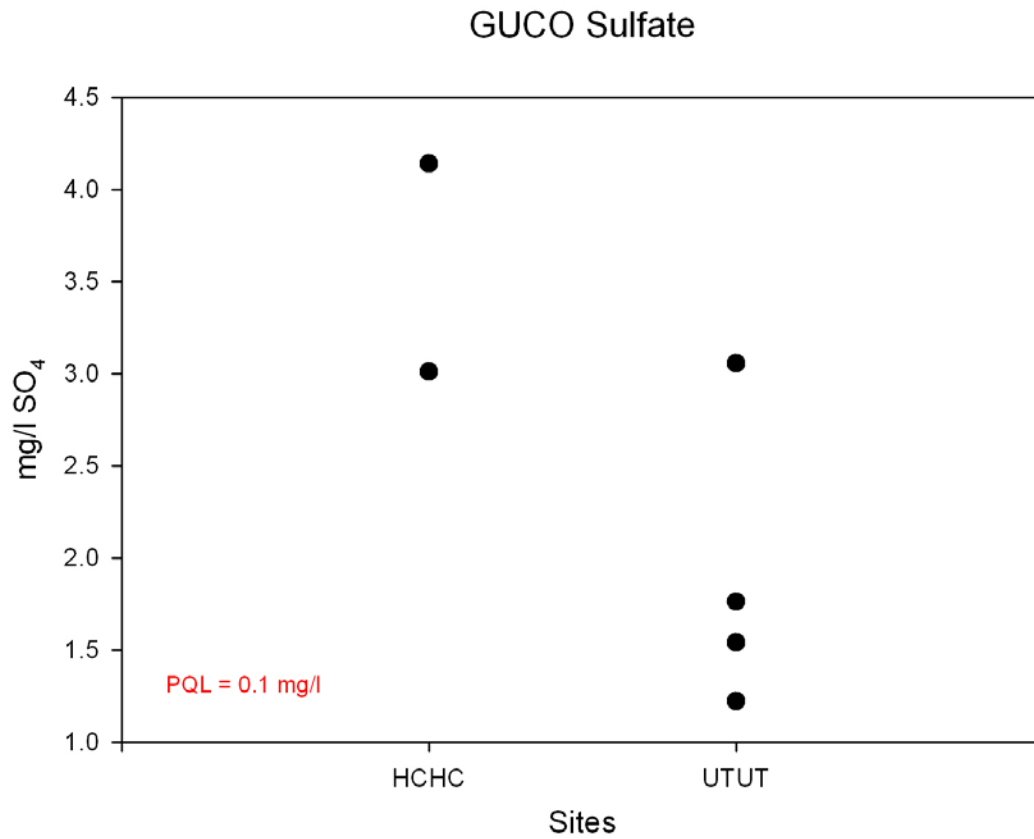
Nitrate

Nitrate levels at GUCO are low to very low. The state standard is 10 mg/l as N-NO₃, or 45 mg/l as NO₃ as graphed below – ten to over one hundred times higher than found at the two sites.



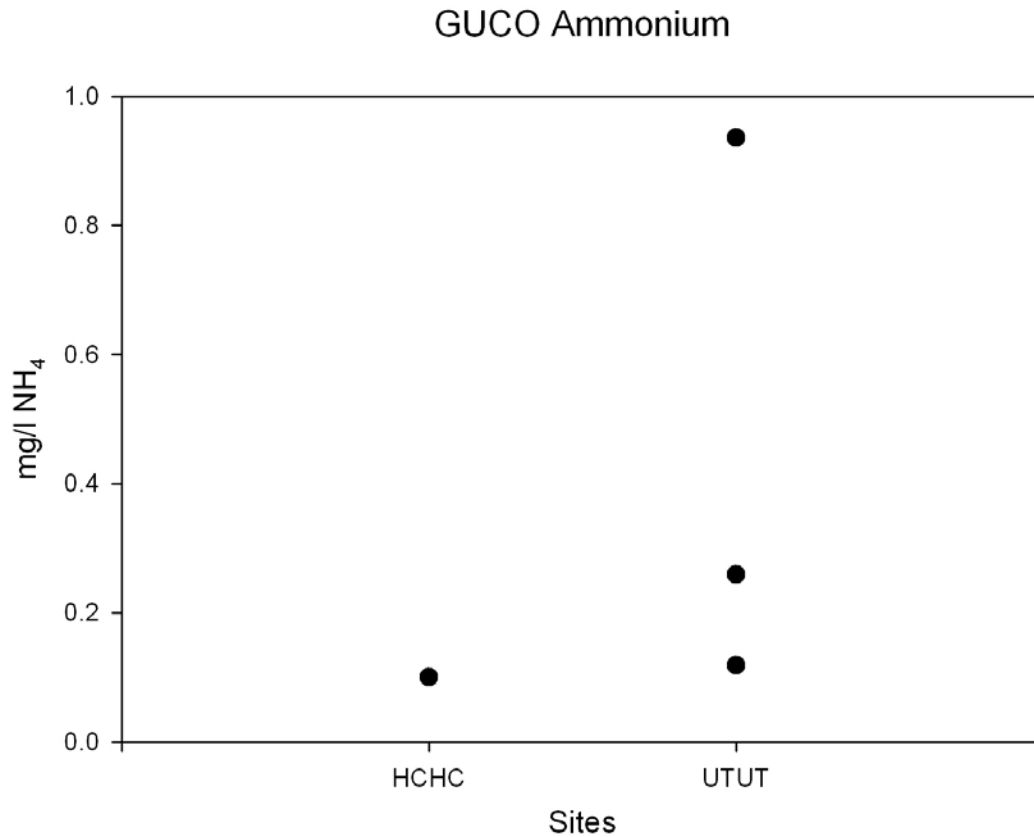
Sulfate

Waters of GUCO have low sulfate concentrations. For comparison, the state standard is 250 mg/l.



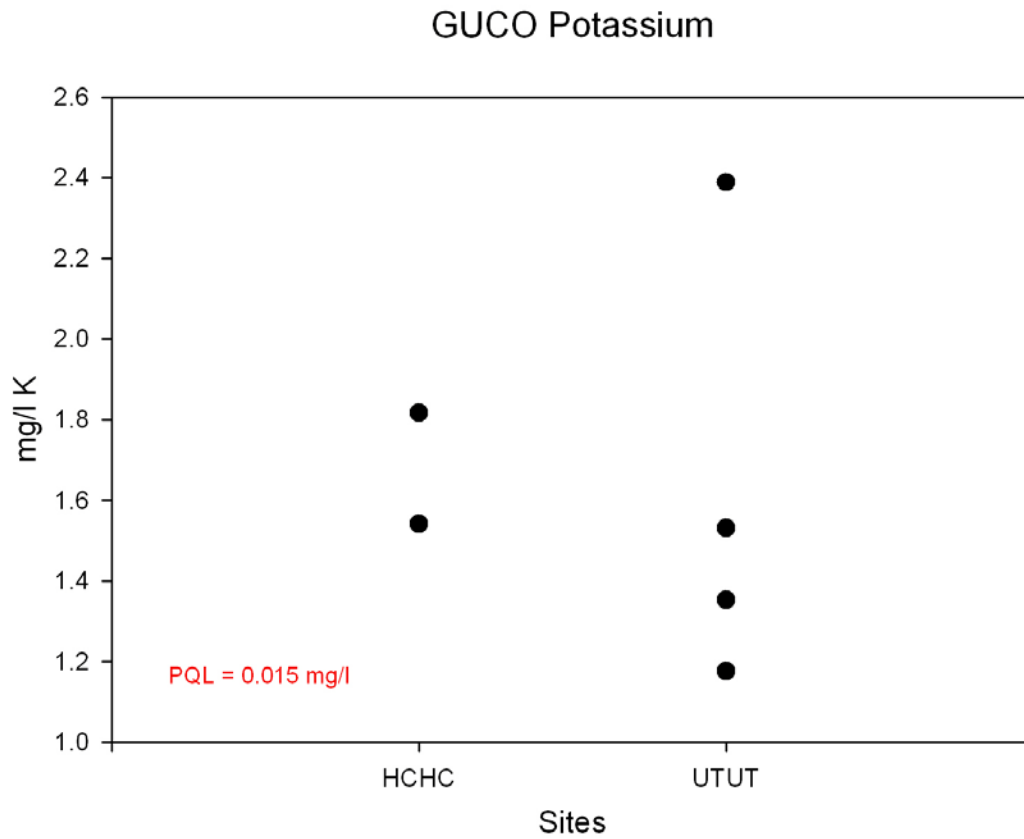
Ammonium

Ammonium levels at all sites are low. It should be noted that the laboratory did not perform ammonium analysis by an approved method. General ammonium reproducibility from the lab is questionable, and these data are presented in this light and not for management actions or decisions. As dissolved oxygen levels indicate moderate to well-aerated stream conditions, there is no reason to believe ammonium values to be of any significant levels.



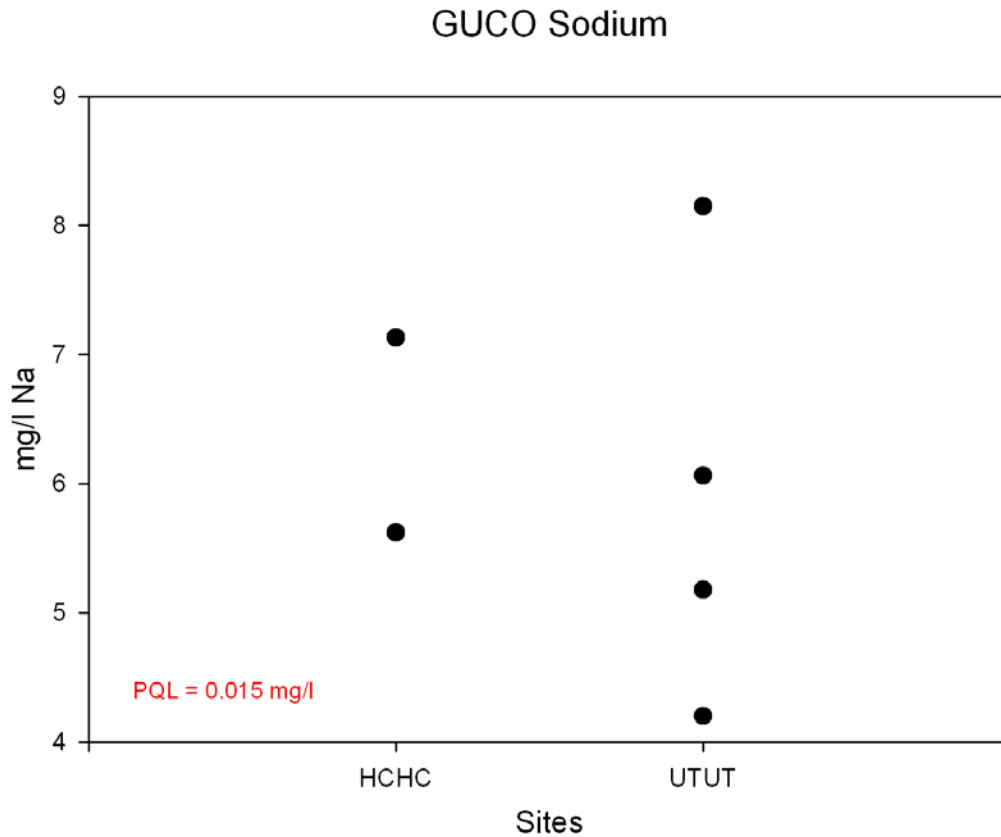
Potassium

Potassium levels of waters monitored at GUCO are consistently low. There are no potassium standards for WS-IV designated uses.



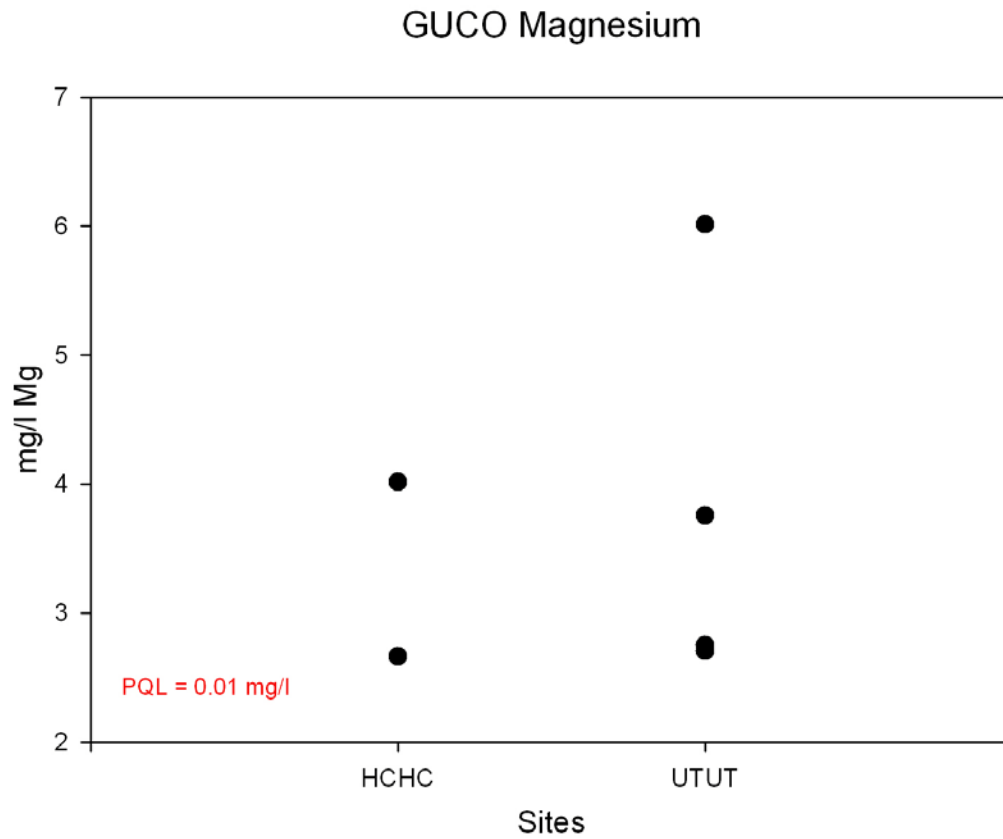
Sodium

The occurrence of sodium approximates that of chloride. These two ions are commonly found in all freshwaters of the world and are primary products of oceanic evaporation of seawater – that is a small amount of NaCl is evaporated along with H₂O and precipitated across the land. This is not the only source of sodium or chloride, as many human-related land uses also liberate these ions. In any case, sodium levels are within normal ranges for waters of GUCO, and there is no sodium standard for WS-IIV.



Magnesium

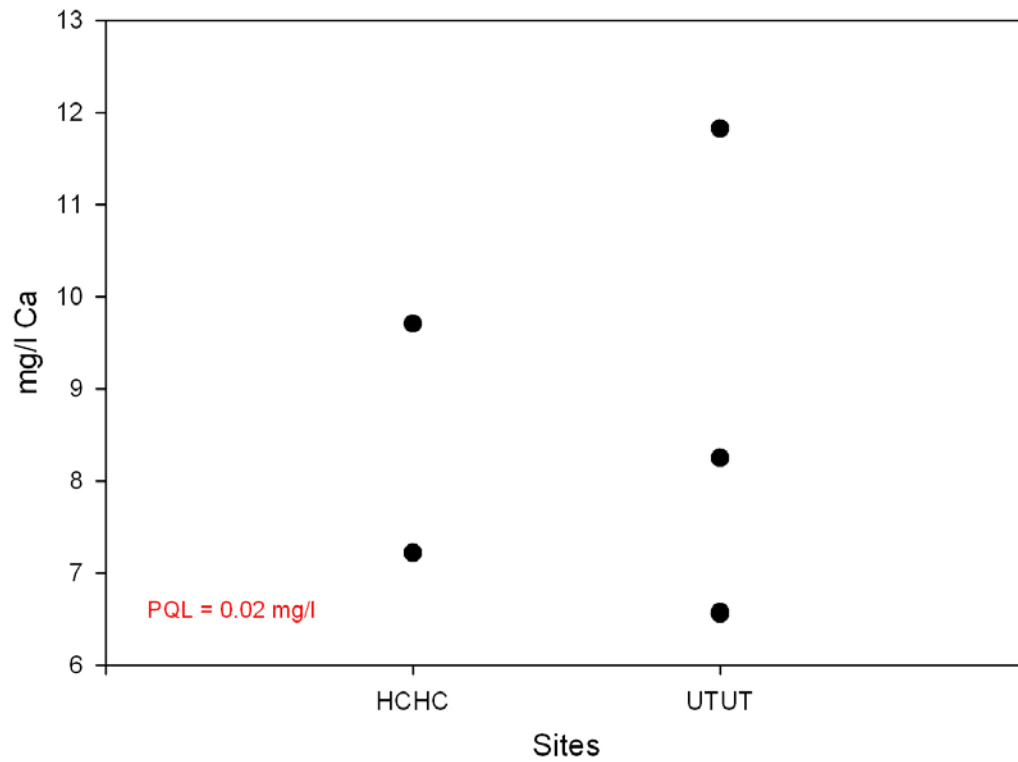
Magnesium levels at GUCO are fairly low. There are no magnesium standards for WS-IV waters.



Calcium

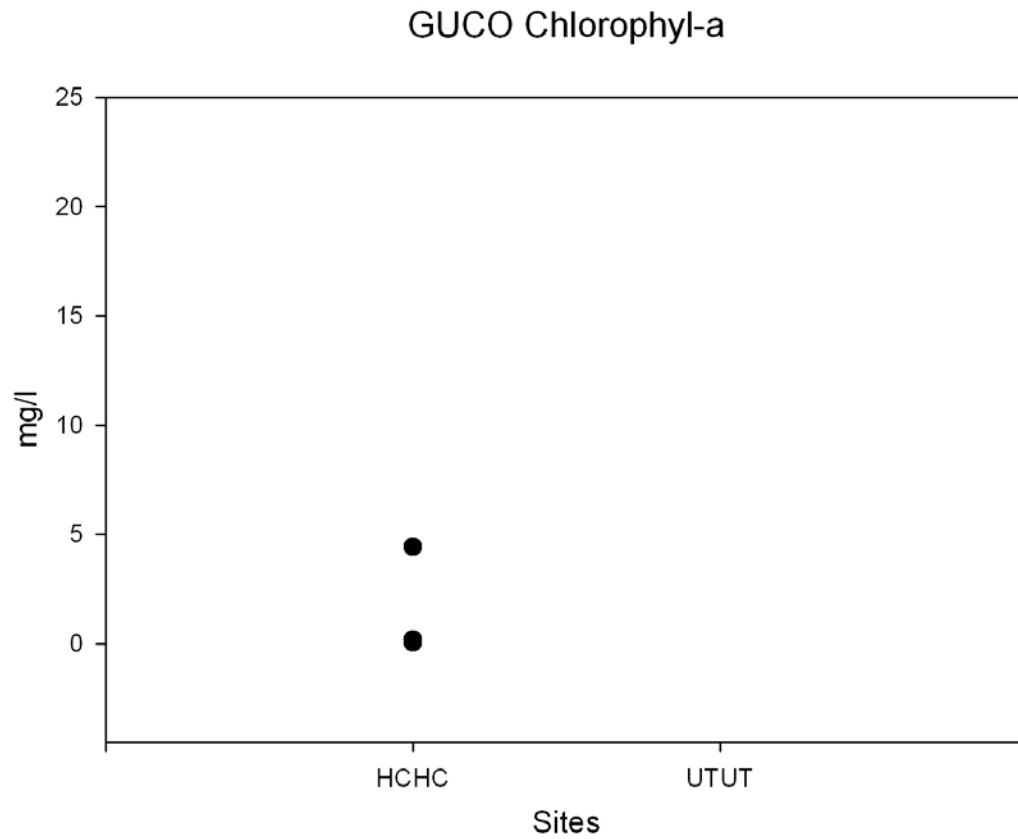
Relative concentrations of the calcium ion mirror that of magnesium, and are fairly low. Both divalent cations, calcium and magnesium are often found replacing one another in mineral crystalline matrices. There is no state standard for calcium.

GUCO Calcium



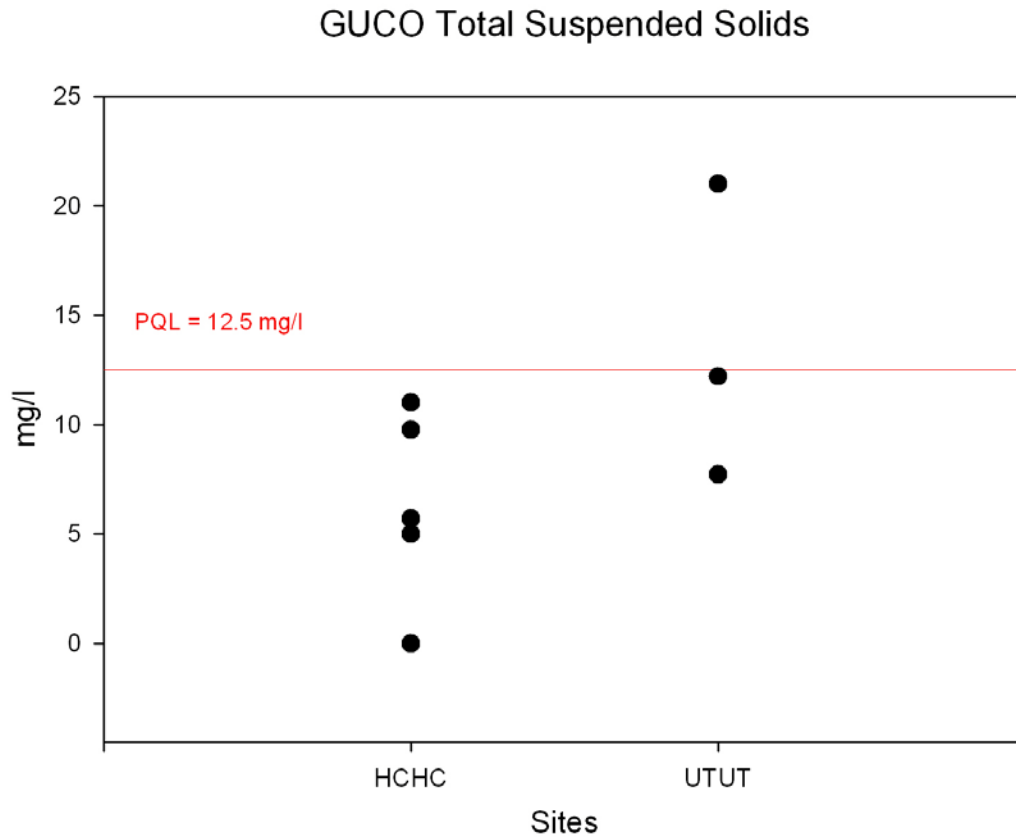
Chlorophyll-a

Chlorophyll-a analysis was only performed at Hunting Creek. Data reproducibility at the laboratory was not very good for this analyte, and even these few data points are suspect in terms of quality.



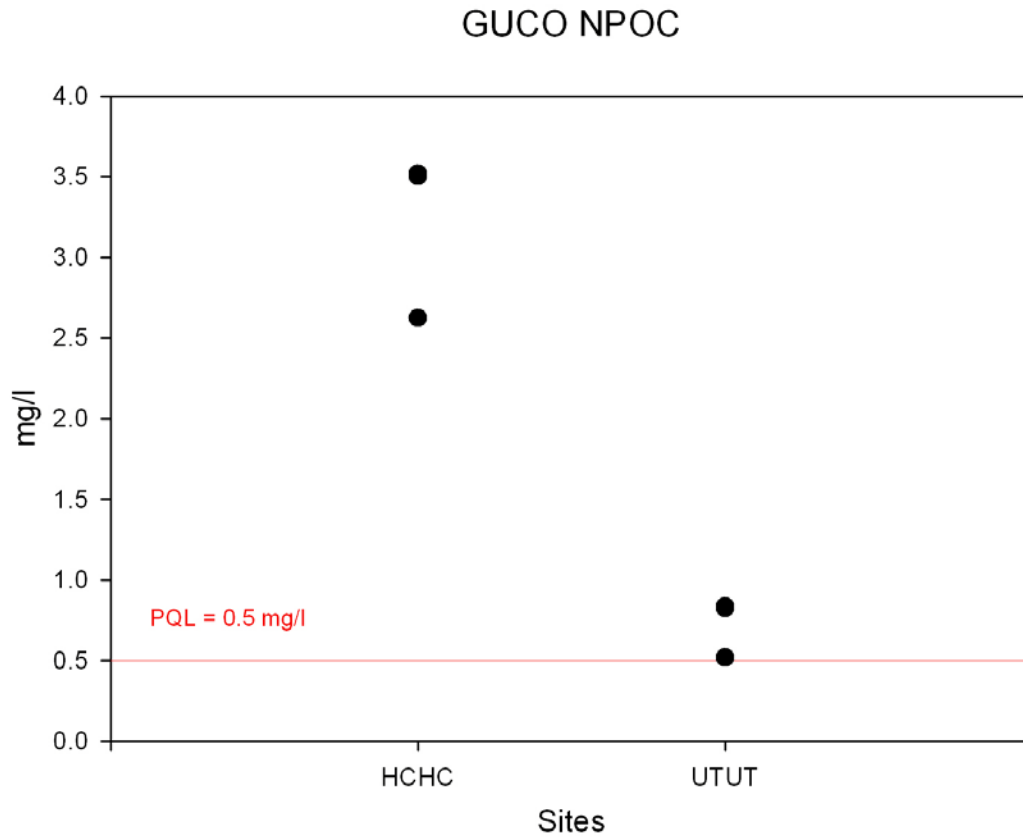
Total Suspended Solids

The laboratory reproducibility for suspended solids was not very good. The lab also reduced solids data into two subsets, fixed and volatile solids. Results are not worth presenting here. While the state standard for TSS is 20 mg/l, the data are of such questionable quality that it should not cause alarm. The highest value found at the Unnamed tributary is a possible result of sampling a very small water body and stream bed sediments may have been disturbed and inadvertently entered the sample bottle.



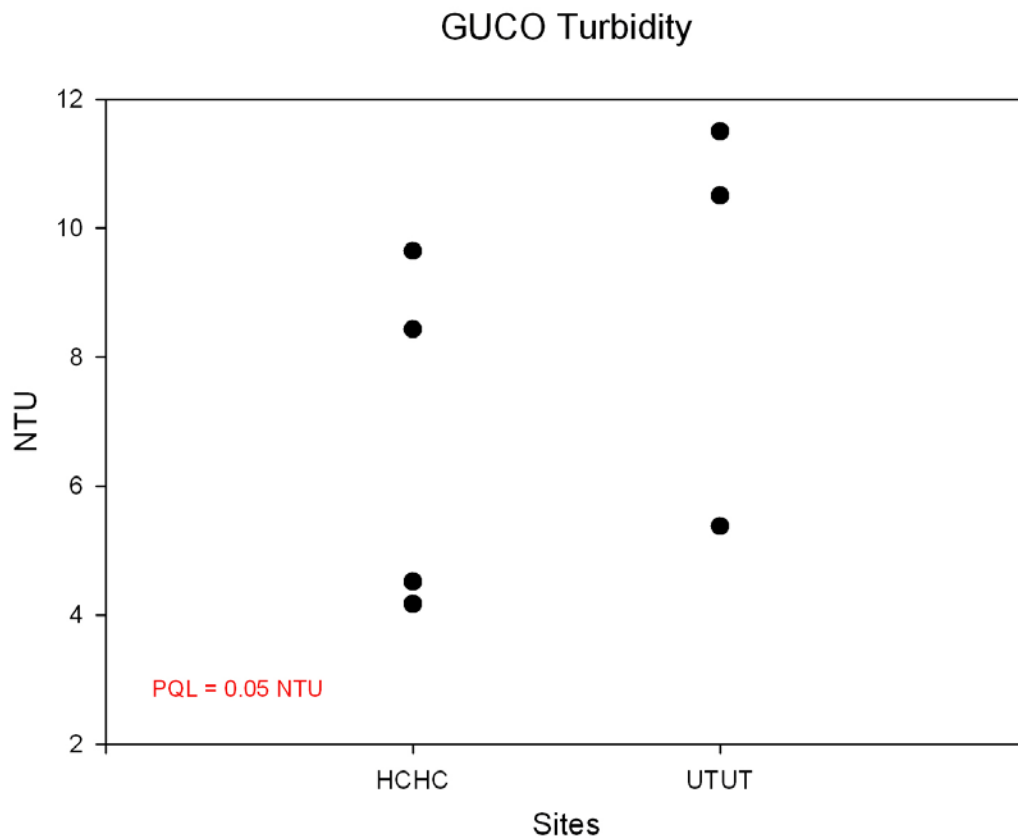
Total Organic Carbon

Total organic carbon, or in the case of most natural waters, non-purgeable organic carbon, is moderate to very low in the waters of GUCO. There is no standard for TOC in either designated use category.



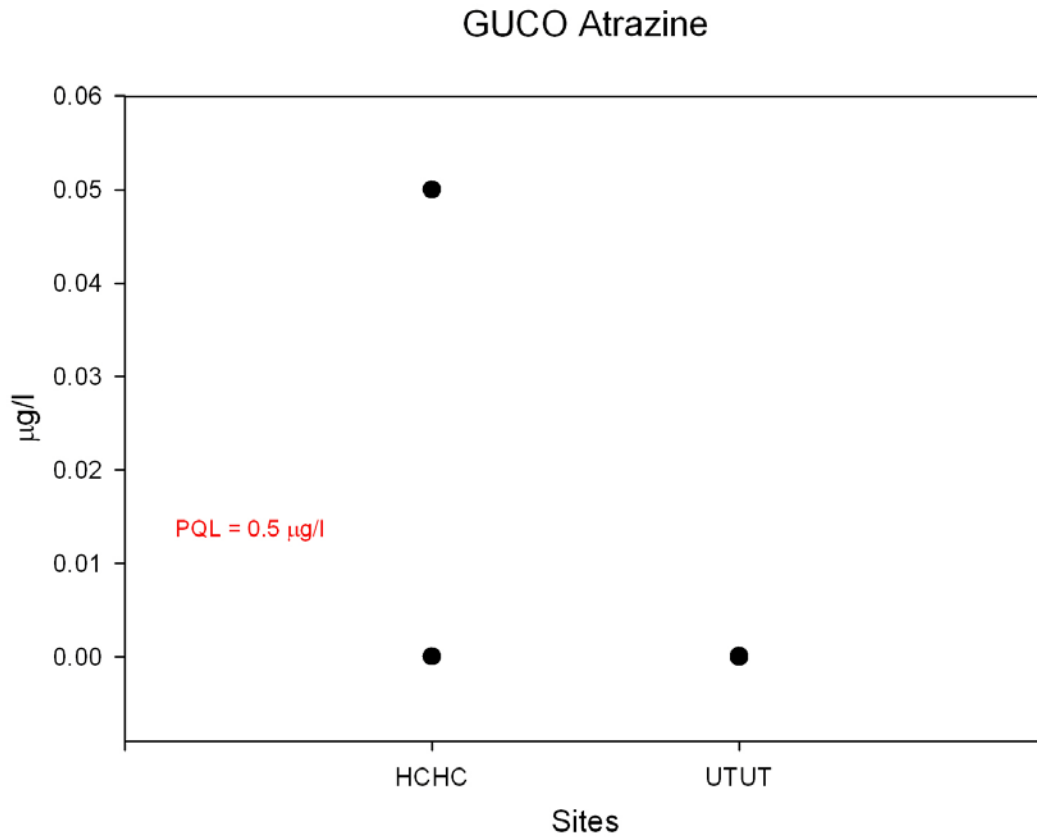
Turbidity

Turbidity is a general measure, or approximation of the amount of suspended material in the water. It is not directly correlative to suspended solids as particle size, shape and color all play a role in the transmission of light through the water column. In general, the higher turbidity values are associated with muddy or turbid waters. Waters of GUCO are clear to slightly murky. Turbidity limits in the designated use category is 50 NTU.



Atrazine

All atrazine samples were well below the PQL of 0.5 µg/l. There are no state standards for atrazine in the designated use category. Some studies have seen a hermaphroditization of amphibians at concentrations of one part per billion. A national drinking water standard of 3.0 µg/l can be used as a general comparison to what was found at GUCO.



General Water Quality Status

The water quality of the two sites sampled at GUCO is fair. This might be expected in a park that is immediately downstream from a well-developed watershed. Within the CUPN, perhaps only Stones River National Battlefield has a greater encroachment of development upstream of the park.

Future Water Quality Monitoring Recommendations

This inventory of water quality greatly reduces the number of parameters that need long-term monitoring for the Vital Signs program. Nitrite, bromide, and phosphate ions were also analyzed but all samples were found to be below detection limits.

Not totally surprisingly, fecal coliform levels are high in Hunting Creek, as it is fed by public lakes immediately upstream with large populations of water fowl. It was surprising that the small spring-fed stream of the Unnamed tributary was also fairly high in fecal coliform. If interested the park may wish to further investigate the source of the bacteria. A rather low-cost sampling strategy could be implemented to determine the source.

Dissolved oxygen levels approach the state limit, and since a potentially critical (summer) sampled was missed due to a malfunctioning sensor, this parameter must be monitored. Also the naturally low ANC values require this parameter to be included

It is recommended that the core four field parameters plus ANC and bacteria should be continued for the long-term. It is likely that the CUPN will adapt a new protocol for bacteria. Rather than use the “membrane filtration” method for fecal coliform, a “most probable number” technique will most likely be used. This technique quantifies both *E. coli* and total coliform bacteria.

Long-Term Monitoring will include:

Water Temperature
Specific Conductivity
pH
Dissolved Oxygen
Acid Neutralizing Capacity
E. coli and Total Coliform

List of Abbreviations

ANC	Acid Neutralizing Capacity
Br	Bromide
C	Carbon
Ca	Calcium
CaCO ₃	Calcium carbonate
Cl	Chloride
DO	Dissolved Oxygen
Fl	Fluoride
K	Potassium
km	kilometer
l/s	liters per second
MDL	Minimum Detection Limit
Mg	Magnesium
mg/l	milligrams per liter
µg/l	micrograms per liter
NaCl	Sodium Chloride
NH ₄	Ammonium
NO ₃	Nitrate
NTU	Nephelometric Turbidity Unit
PQL	Practical Quantitation Limit
NPOC	Non-purgable Organic Carbon
RPD	Relative Percent Difference
SPC	Specific Conductance
SO ₄	Sulfate
SU	Standard Unit (pH)
TOC	Total Organic Carbon
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey