

Cumberland Piedmont Network Water Quality Report

February 2005

Kings Mountain National Military Park

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Introduction

In early 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.

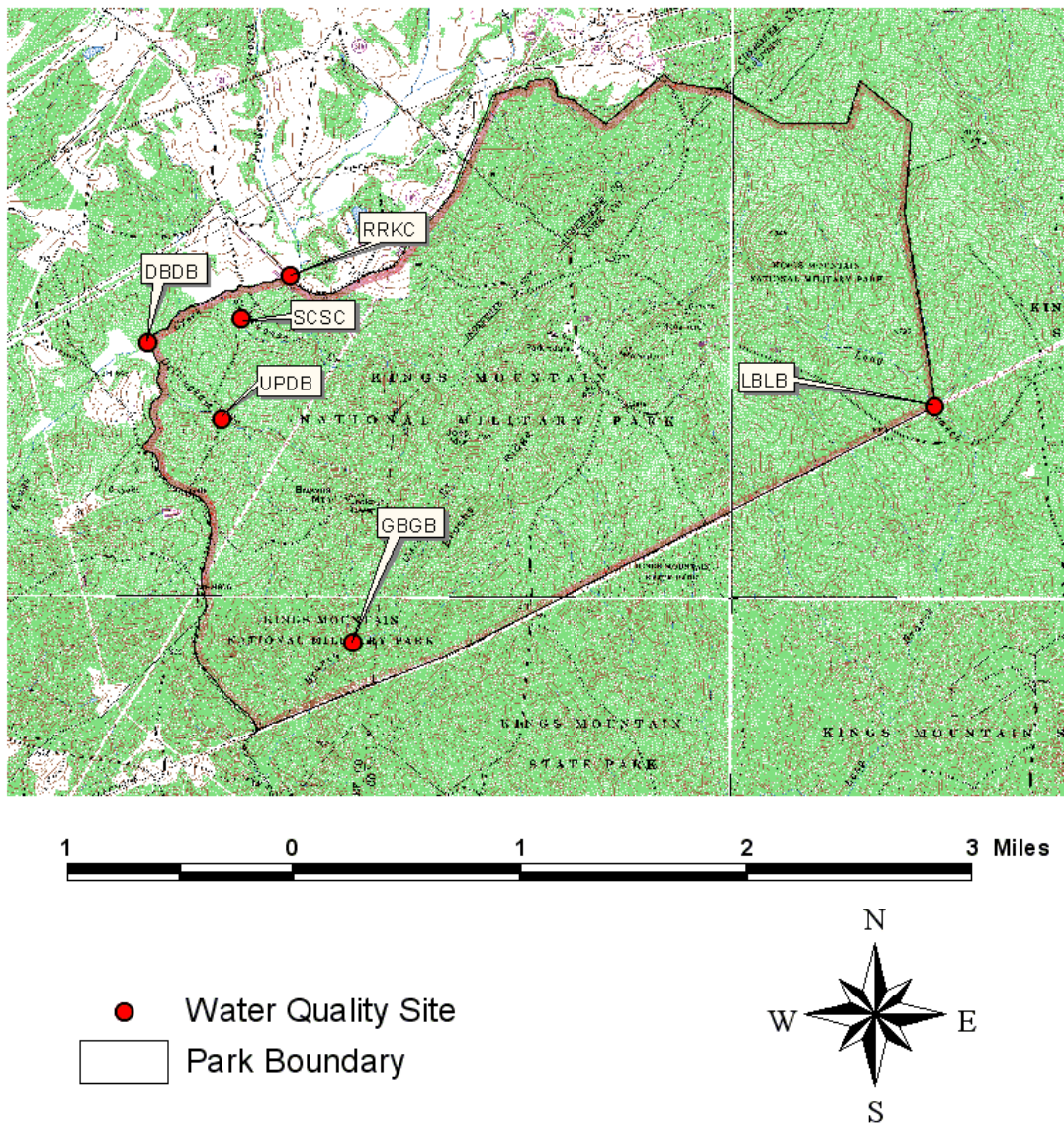
The CUPN Science and Technical Committee (STC) recently reviewed field and laboratory quality and has made their recommendations to the CUPN Board of Directors. Data quality was reviewed based upon the Relative Percent Difference (RPD) between a field sample and its duplicate. In general the STC found 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, 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 KIMO. During each bi-monthly sampling round each site was visited and an additional Quality Assurance-Quality Control sample was extracted. Bi-monthly sampling occurred during fiscal year 2003.

KIMO, Water Quality Monitoring Sites



Description of Sampling Sites

Long Branch (LBLB): This stream, which drains the primary front-country attraction (Visitor Center area and Battlefield Trail) can be sampled at the boundary of the state park. The boundary is reached after a two kilometer trail hike from the Visitor Center. Access is easy and safe in all conditions.



Garner Branch (GBGB): This stream is located in the southwestern portion of the park and can be accessed via a hiking trail (about 1.5 km) from the Piedmont Road within the state park. The sampling location is within the National Park at the trail crossing. Access is easy and safe in all conditions.



Dellingham Branch (DBDB): This stream is primarily recharged by park lands with the exception of its final 0.5 km, which borders private, agricultural lands (primarily pasture). The stream can be sampled at its confluence with Kings Creek. Access to this point was granted by the landowner prior to sampling. Past sampling occurred approximately 250 meters above the confluence of Kings Creek. Access is easy and safe in all conditions.



Upper Dellingham Branch (UPDB): This site was added during the first year (FY03) of sampling based upon high fecal coliform levels found at the Dellingham Branch site. This site receives flow exclusively from the park. Access is easy and safe in all conditions.



Stonehouse Creek (SCSC): This stream is recharged entirely by park lands and can be sampled at its confluence with Kings Creek. Access is gained via a park road to the Stonehouse, which leads to the Kings Creek floodplain. Access is easy and safe in all conditions



Kings Creek (RRKC): The largest stream in the park can be sampled at the bridge of Rockhouse Road. This site is representative of waters entering the park from the private lands to the north. 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.

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 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 South Carolina water quality standards, please see:

South Carolina: Water Classifications and Standards (R.61-68) Classified Waters (R.61-69).

The table below shows that only Kings Creek is officially listed. Other streams of KIMO were “listed” (those sites in red text) by the author using the same criteria used by the state.

<i>Park</i>	<i>Code</i>	<i>Site</i>	<i>State</i>	<i>Designated Use</i>
KIMO	LBLB	Long Branch	SC	Freshwater
KIMO	GBGB	Garner Branch	SC	Freshwater
KIMO	DBDB	Dellingham Branch	SC	Freshwater
KIMO	UPDB	Upper Dellingham Branch	SC	Freshwater
KIMO	SCSC	Stonehouse Creek	SC	Freshwater
KIMO	RRKC	Kings Creek	SC	Freshwater

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 six consecutive bi-monthly rounds of sampling at KIMO. There are not enough data to form a full box plot, a convenient way of displaying data. With more data, the box-plot would also indicate 95th and 5th percentiles. The top and bottom of each box in the graphs below represent the 75th and 25th percentiles, while the horizontal line within the box is the median.

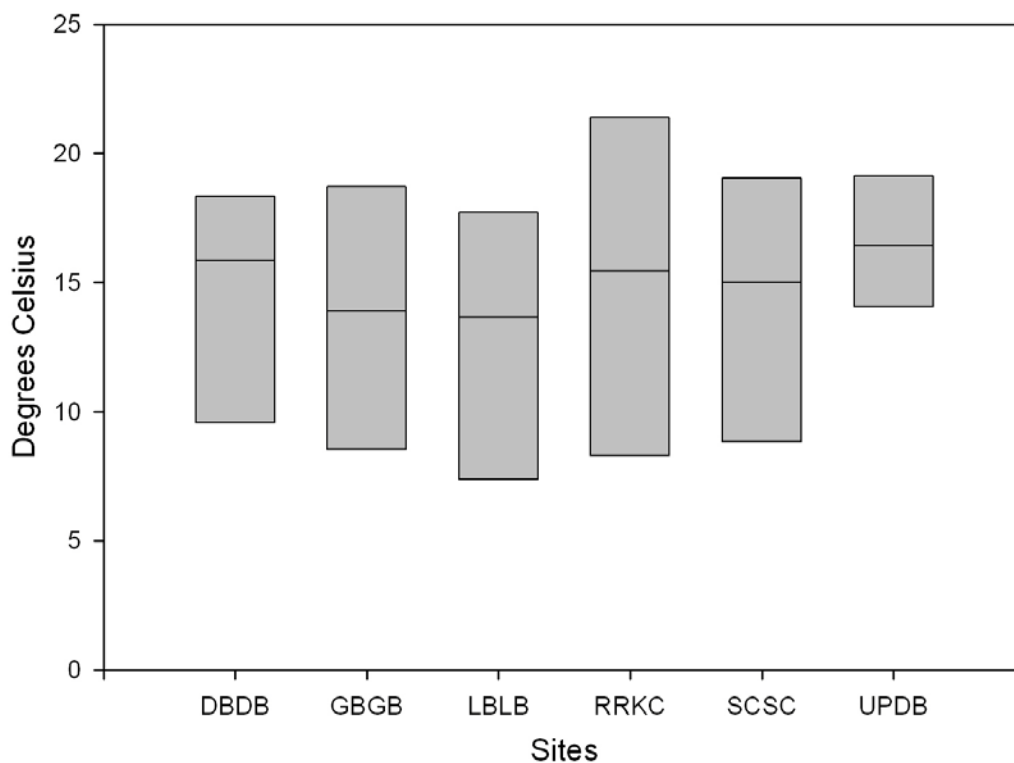
In addition to state water quality standards (where applicable), laboratory “Practical Quantitation Limits” (PQL) will be denoted. The PQL is five times the “Minimum Detection Limit” set by the laboratory. The PQL can be used as a means of determining if a particular parameter is worth monitoring in 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 Data

Water Temperature

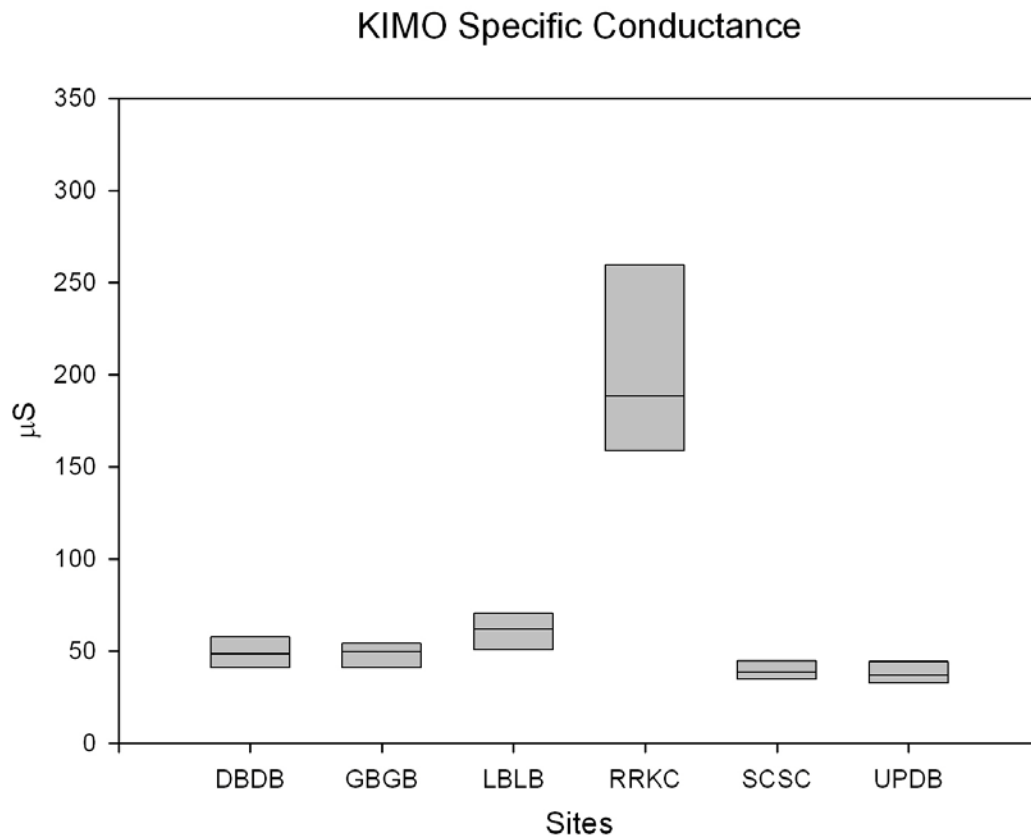
Water temperatures of KIMO are considered to be within range to support native aquatic life. The apparent higher, yet compressed temperature range at UPDB is due to this being a site that was added following the winter months. The site was added to help elucidate the relatively high fecal coliform levels at DBDB at the downstream end of the Dellingham Branch watershed.

KIMO Water Temperature



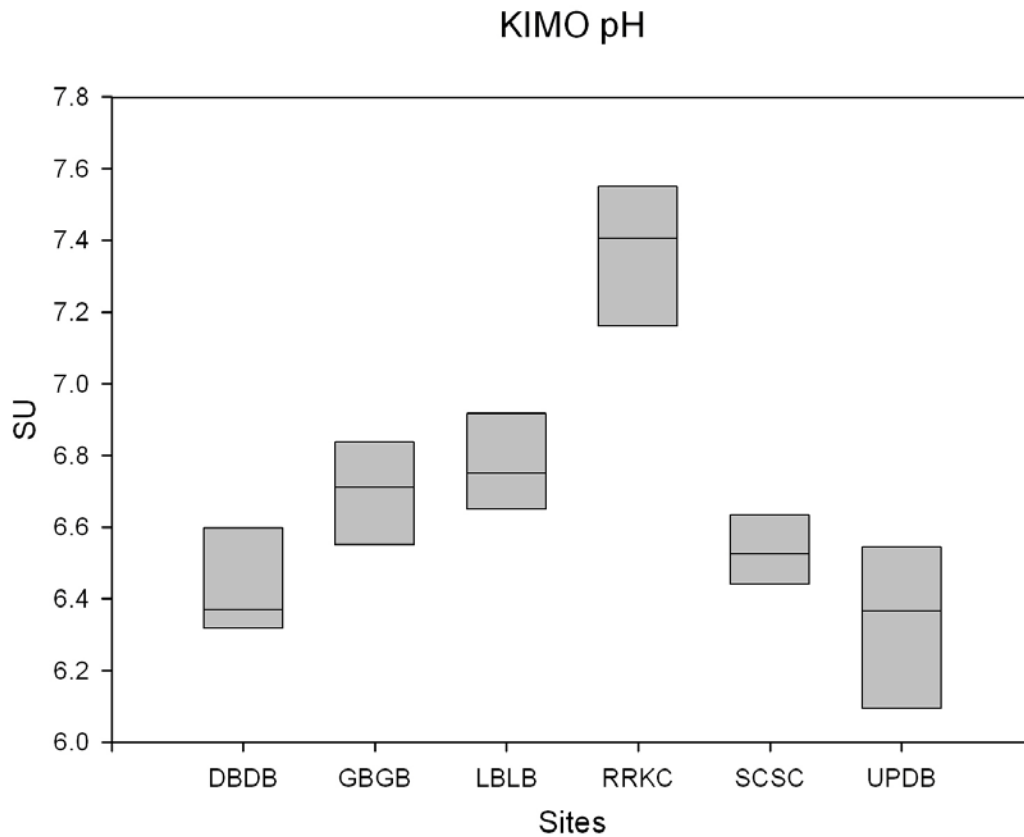
Specific Conductance

The distribution of specific conductance (SPC) of KIMO are, with exception of RRKC, reflective of low ionic-strength waters. The lithology of the park is largely crystalline and are relatively insoluble, thus the dissolved load is limited. Kings Creek, however, is a much larger watershed, bringing waters from far beyond park boundaries, and its higher SPC is indicative of a different, more soluble stratigraphy. It is also possible that non-point (runoff) sources are contributing to higher SPC values. This scenario is presented later.



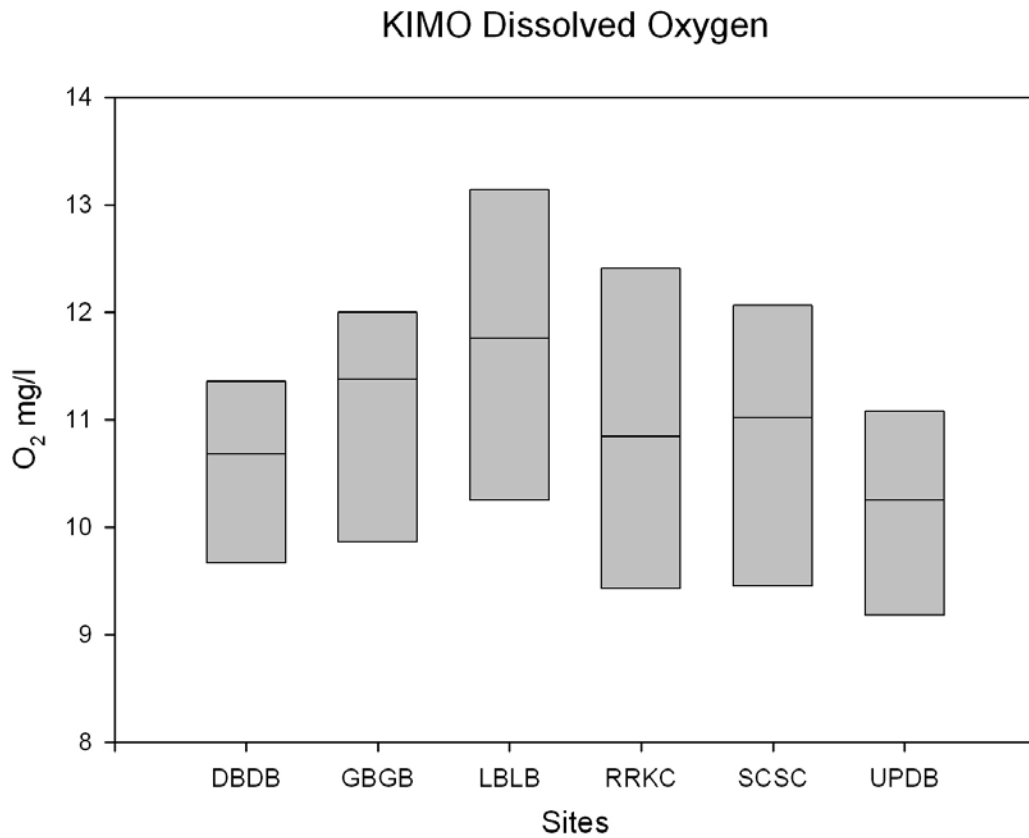
pH

Waters of KIMO, again with the exception of RRKC, are slightly acidic. The sites higher within a particular watershed tend to a bit more acidic that lower. This may be an effect of contributing basin size – that is, sites like LBLB and GBGB are near their headwaters and have less contact with buffering agents. The slightly alkaline waters of RRKC, as will be seen in the forthcoming ANC graph, is due to a higher load bicarbonates. State standards for freshwater pH are between 6.0 and 9.0 SU. We can see that both Dellingham Branch sites are approaching the lower pH limit.



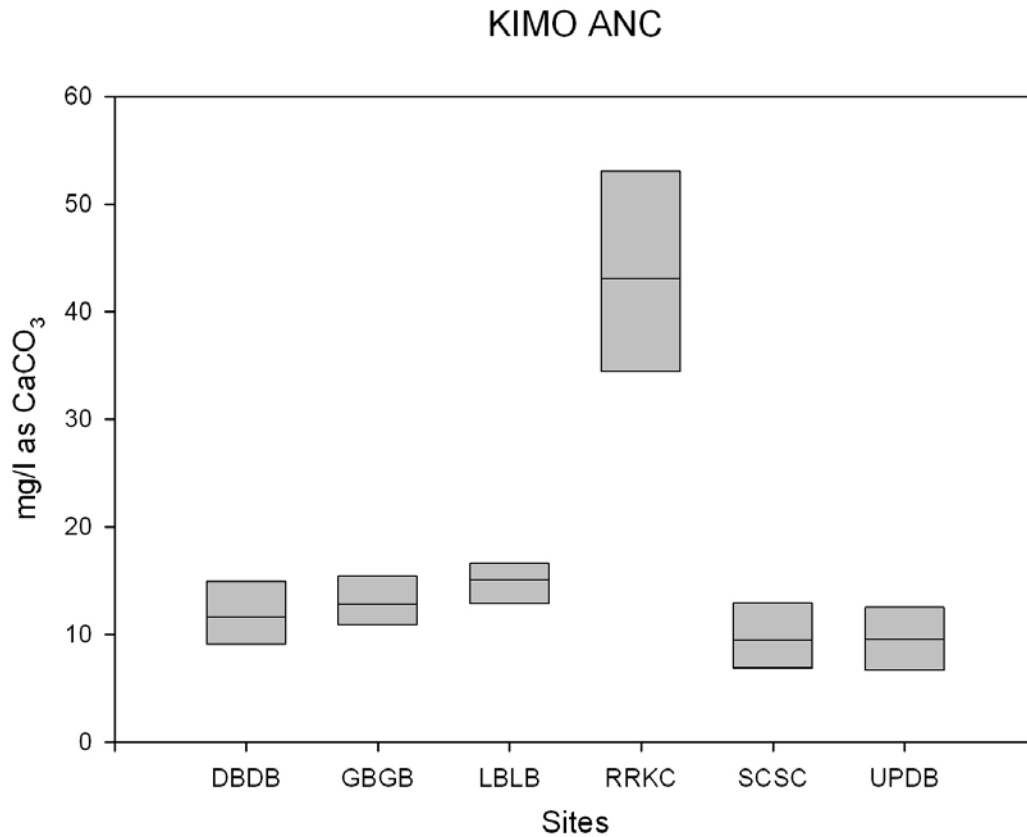
Dissolved Oxygen

All waters monitored at KIMO are saturated, or even supersaturated with oxygen. Even when dipping into the 9 mg/l range, these waters are capable of supporting aquatic life. This should not be surprising as there is limited nutrient loading and numerous occasions of the water to be fully aerated as it cascades down Kings Mountain. State standards require freshwaters to contain at least 4.0 mg/l oxygen.



Acid Neutralizing Capacity

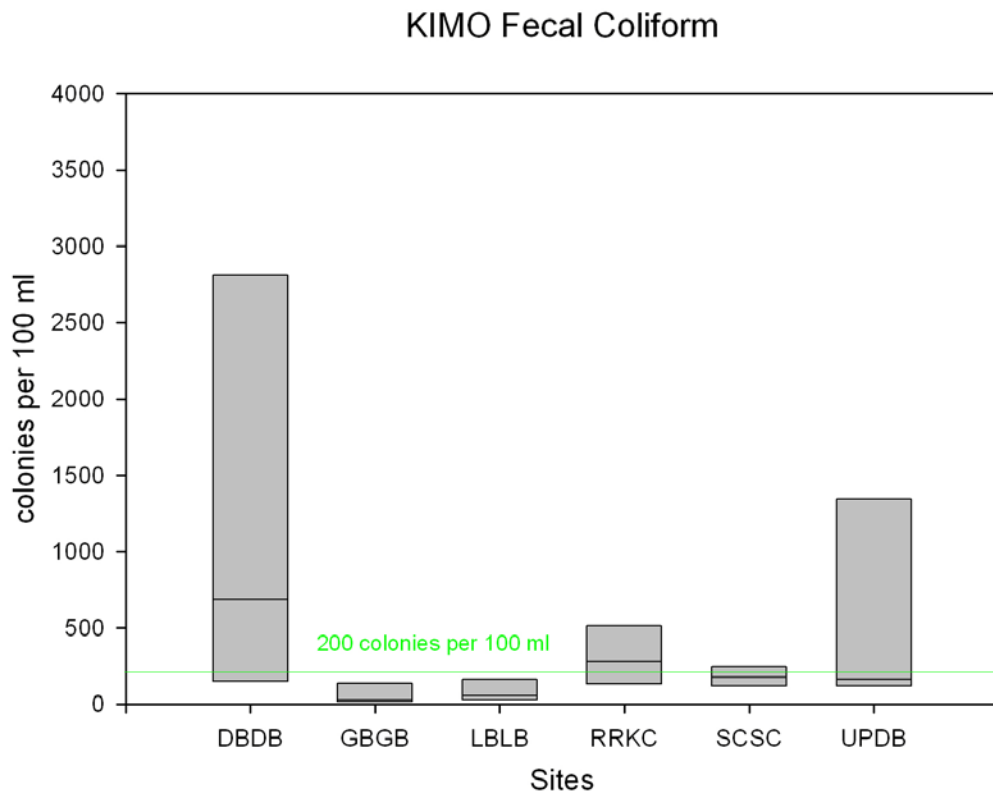
A nearly identical signature as was seen with SPC. Acid neutralizing capacity (ANC) of KIMO waters is fairly low, indicating a lack of contact with carbonate strata – with exception of Kings Creek. Low ANC levels make waters more susceptible to acid precipitation as there are limited amounts of bicarbonates available to counter additional acids. Kings Creek must have a source of bicarbonates – likely carbonate rock – within its watershed upstream of the park



Fecal Coliform

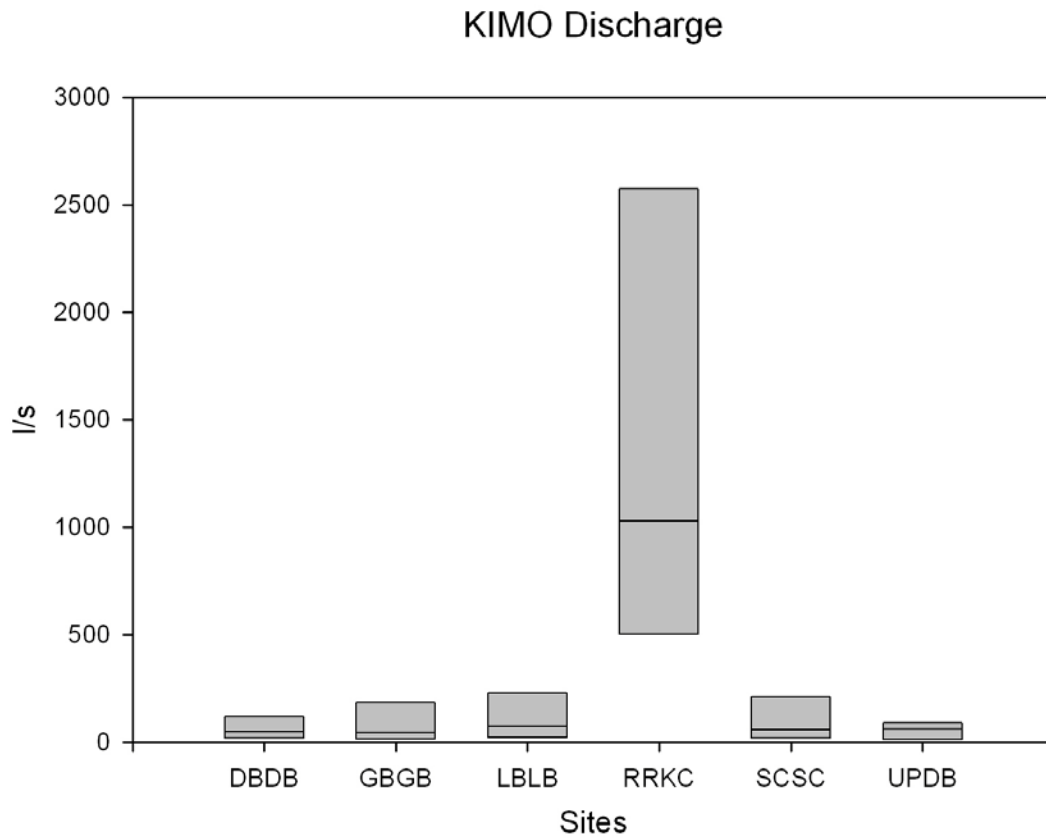
The range of fecal coliform are expected for natural waters with high wildlife populations, with the exception, this time, of Dellingham Branch. While all other sites have relatively low levels – and the higher end of their ranges are coincidental to runoff following rainfall events – both the mouth of Dellingham (DBDB) and its Upper Dellingham (UPDB) site are consistently higher than other sites. The UPDB site was added after high fecal coliform levels were detected at DBDB. The upper site receives water only from the park. First thoughts were that horse-back riding trails were contributing to these levels, but a map produced by CUPN data manager does not support this idea. At this time further investigation to pin-point the source(s) will be needed if the park is interested.

The state standard for freshwaters is a geometric mean of 200 colonies per 100 ml, based on a series of 5 consecutive samples taken within a 30 day period. We can expect that both sites on Dellingham Branch would exceed that standard if sampling frequency was increased. The bi-monthly sampling at KIMO would not automatically place these waters in violations of state standards as a series of samples as samples were taken bi-monthly. It is reasonable to assume that if such sampling frequency occurred, Dellingham Branch, and likely Kings Creek would exceed the standard. Stonehouse Creek at times exceeds the 200 colonies per 100 ml threshold, but its waters are generally low in fecal coliform.



Discharge

These data are presented to give the reader a sense of magnitude of flow at the six sampling sites are KIMO. Kings Creek obviously shows up as the largest stream. Discharge data (l/s) are of particular use in combination with concentration data (mg/l), thus producing mass flux or loading of a particular parameter (mg/s). Flow data are also of use in interpreting the discharge condition in which sampled.

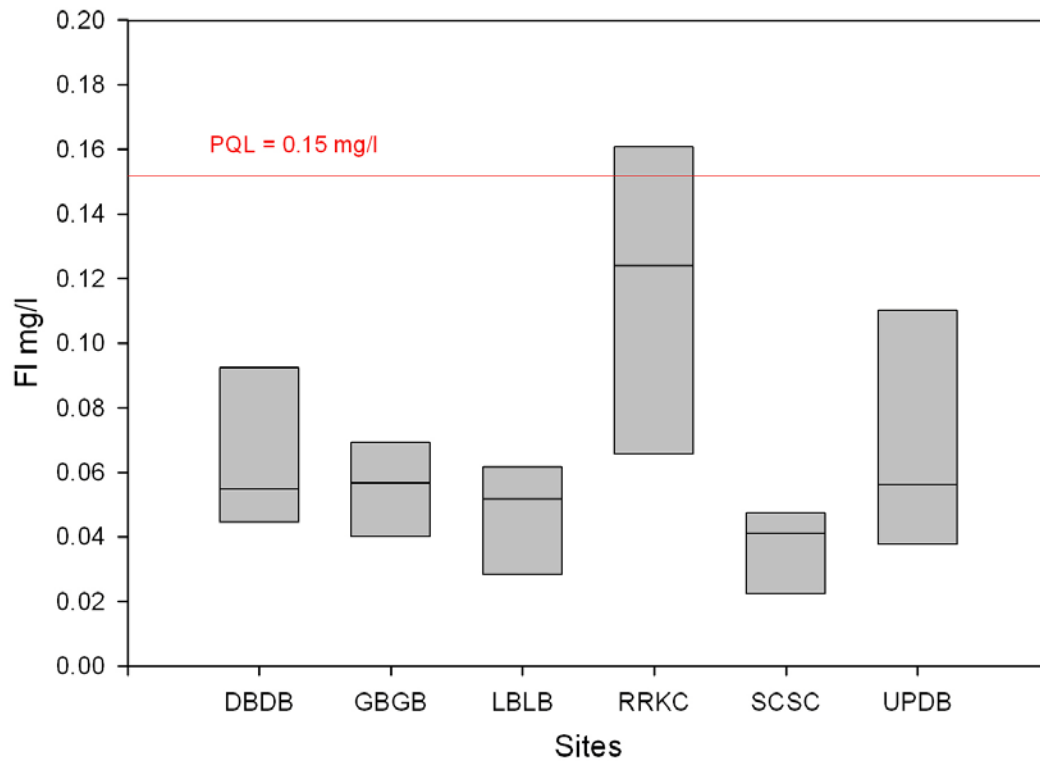


Laboratory Data

Fluoride

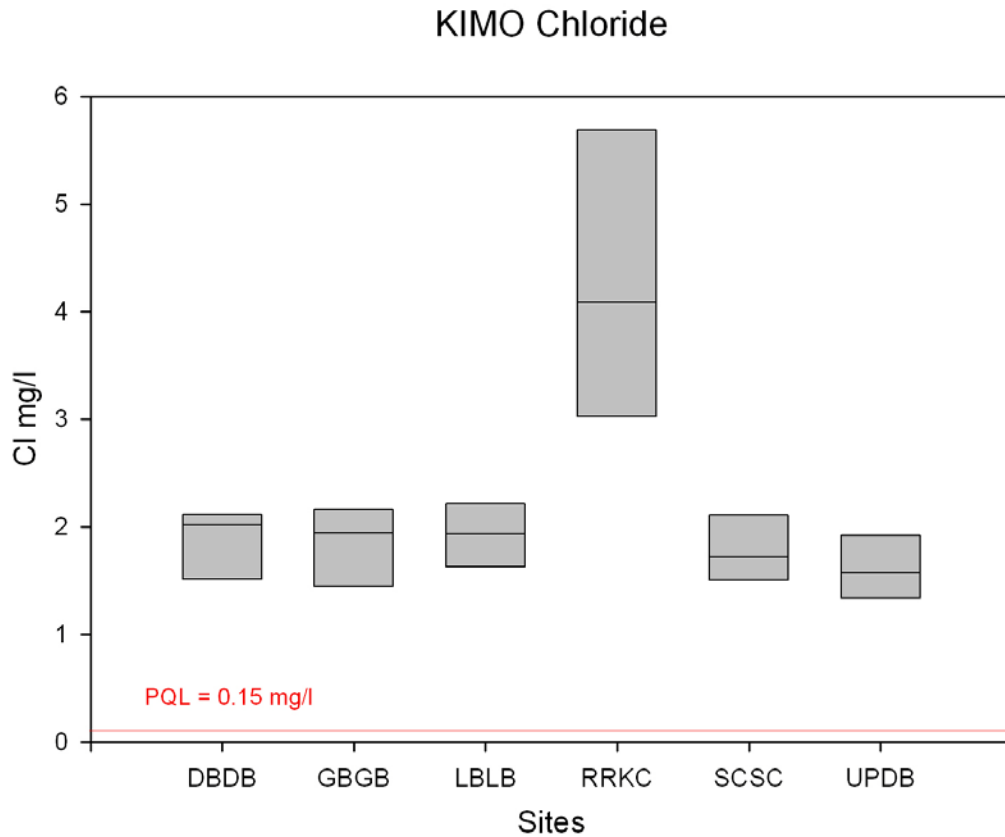
Fluoride concentrations of KIMO waters are very low. In all samples, except one at Kings Creek, concentrations were below the PQL of 0.15 mg/l. There is no state standard for fluoride in freshwaters.

KIMO Fluoride



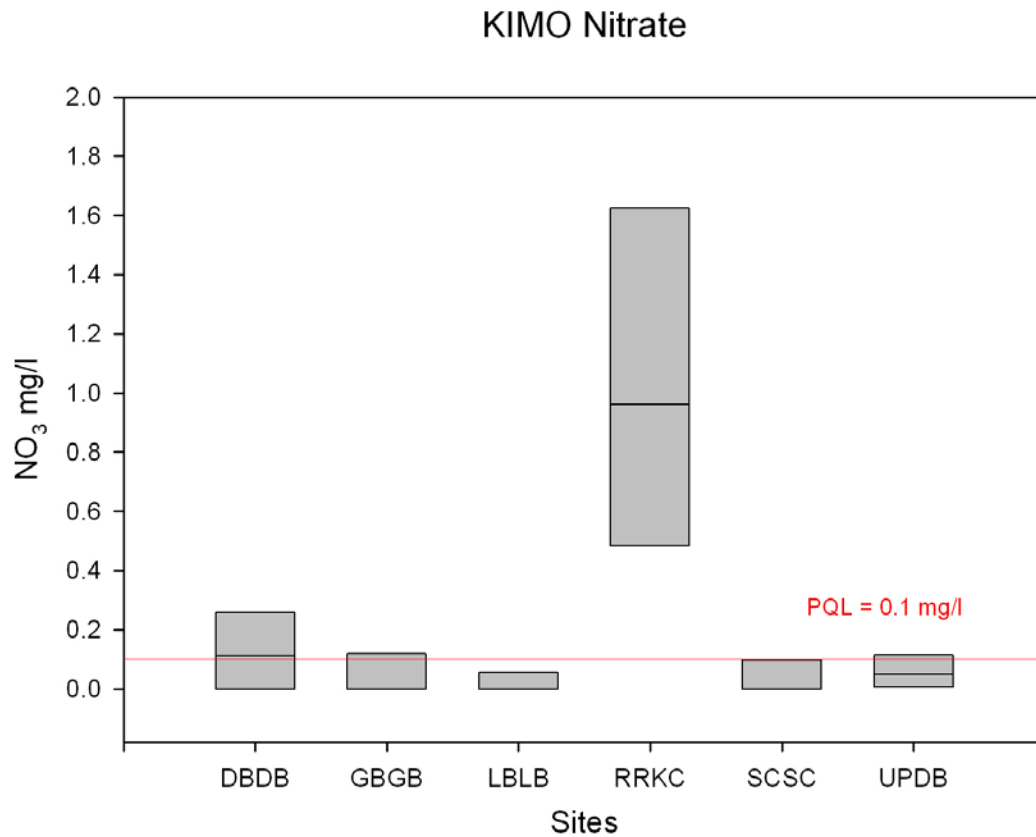
Chloride

While all samples were above the PQL of 0.15 mg/l, no samples exceeded the state standard for chloride, as there is no standard. Even with that in mind, the concentrations of chloride are not very great when compared with other freshwaters. The higher chloride concentrations found in Kings Creek may be simply a function of its larger and more complex watershed. Chloride is found as natural background and concentrations are typical to those found in other freshwaters.



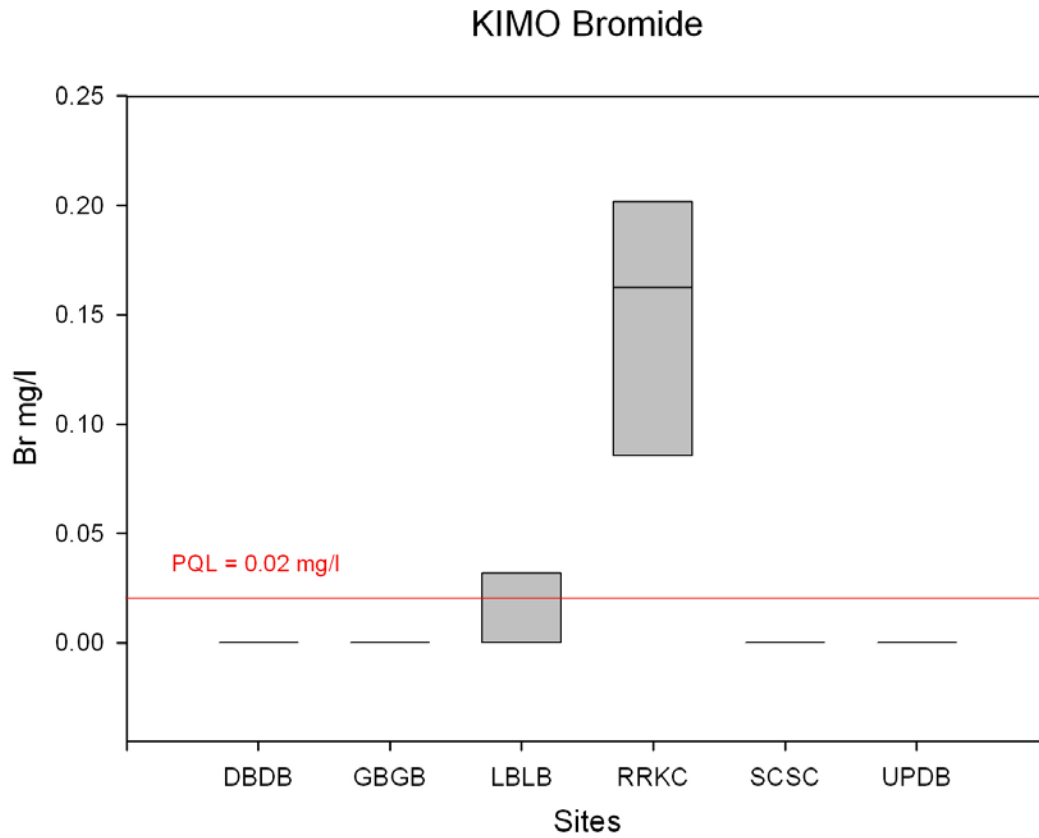
Nitrate

Surprisingly there is no state standard for nitrate in freshwaters. The general national standard for drinking water as N-NO₃ is 10 mg/l, or 45 mg/l as NO₃ as graphed below. At any rate, no KIMO samples are even close to the drinking water standard, and with the exception of 2 samples at DBDB and all samples are RRKC, KIMO waters are rather devoid of nitrate as can be detected with an ion chromatograph. Again the Kings Creek site is higher as a reflection of its larger watershed that is generally beyond park boundaries.



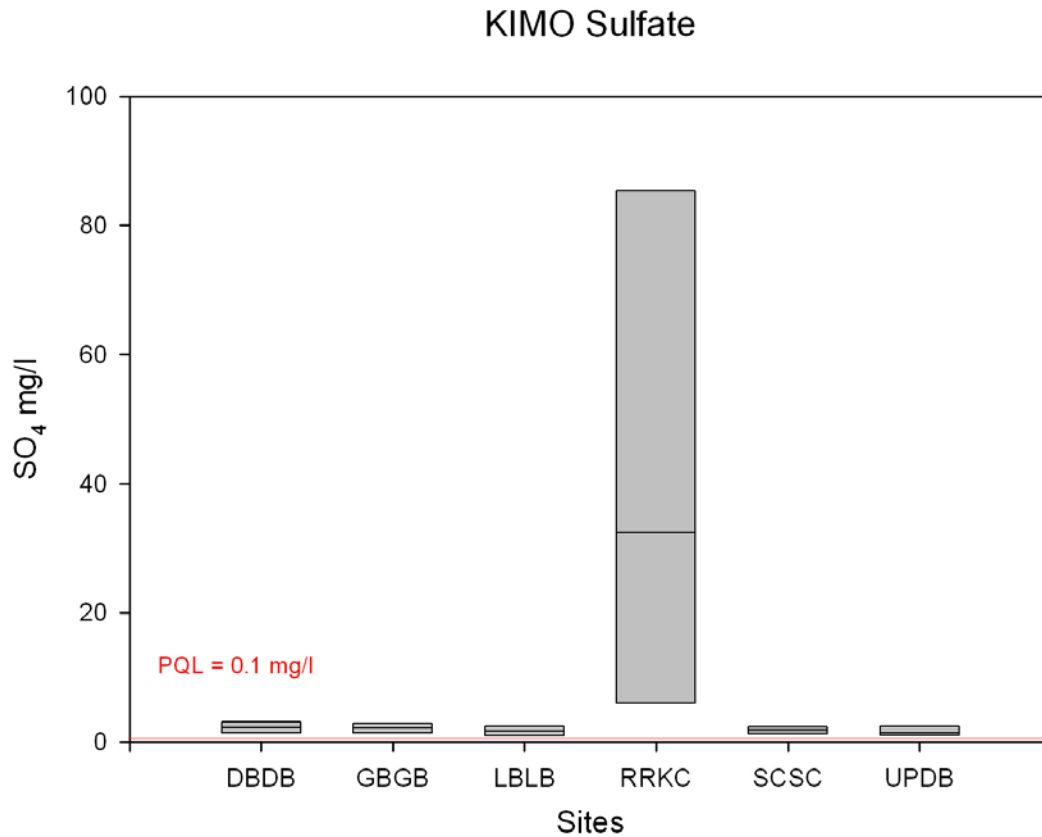
Bromide

No state standard exists for bromide. Kings Creek contains a small amount of this anion, and one sample from Long Branch had detectable levels. In any case, bromide is quite low, and non-detected at the other four sites.



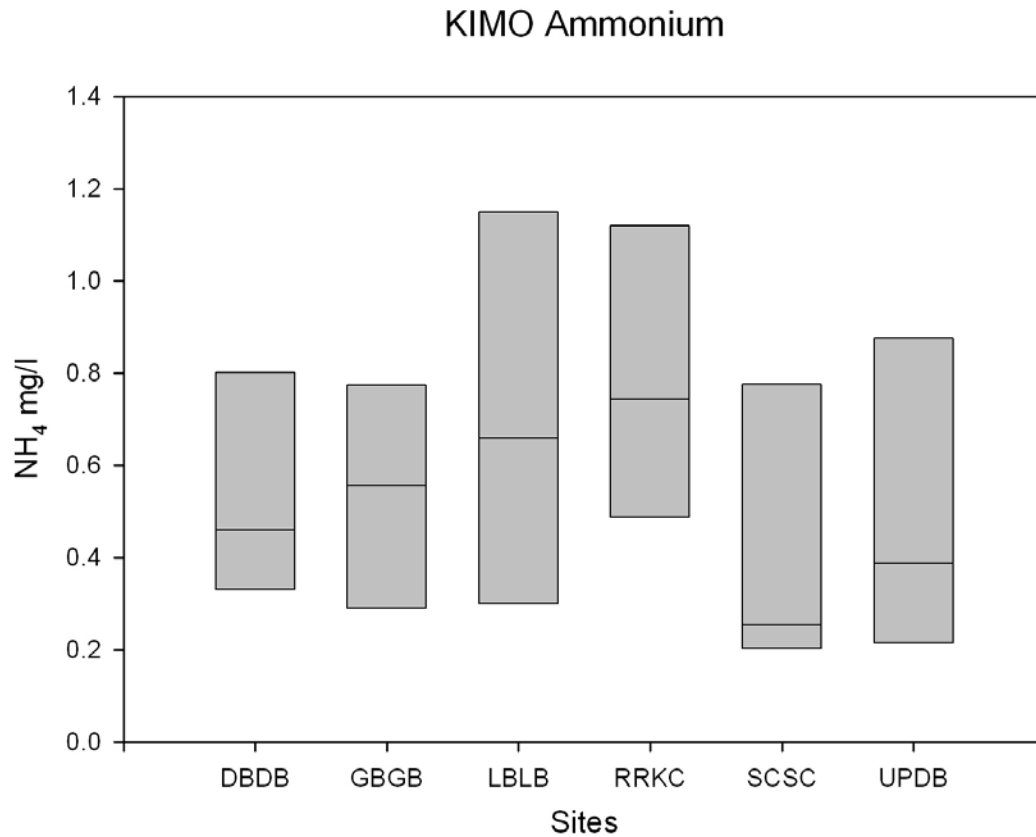
Sulfate

Waters of KIMO are low in sulfate, with exception of Kings Creek. No sulfate standard exists for South Carolina's freshwater designated use category. It is curious that the levels of sulfate are so high at RRKC. These concentrations, although not at levels harmful to aquatic life, are generally higher than most streams of the state. For comparison, the High Quality Water standard for North Carolina is 250 mg/l.



Ammonium

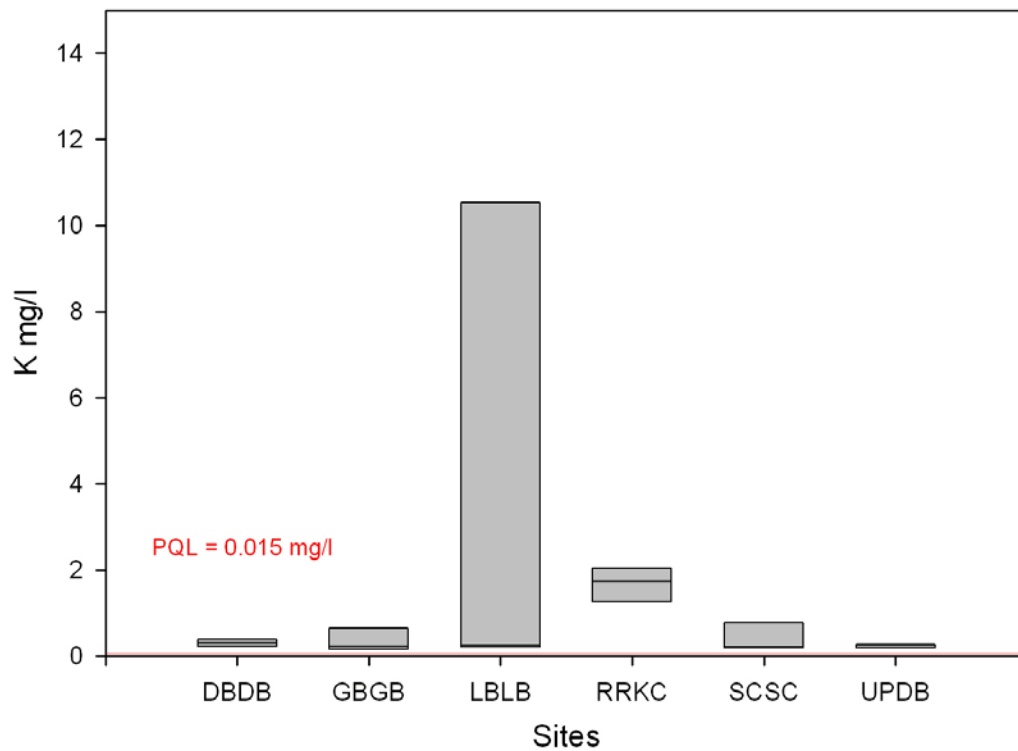
Ammonium levels at all sites are low. It should be noted that the laboratory did not perform ammonium analysis by an approved method. General ammonium reproducibility from the lab is considered unacceptable, and these data are presented in this light and not for management actions or decisions. As dissolved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



Potassium

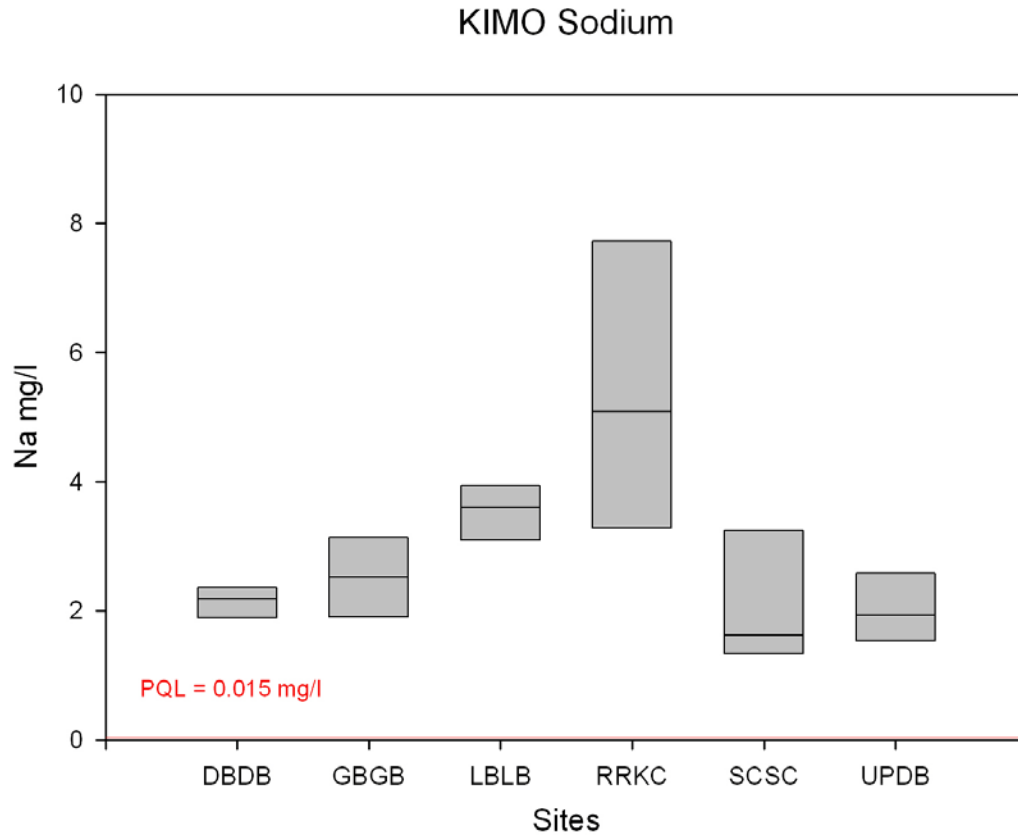
With the exception of one sample at Long Branch, potassium levels at KIMO are low. This point, an extreme outlier of 42.1 mg/l, is unexplainable. A review of laboratory records confirms this lofty value. Since it is greatly different than any other value – over an order of magnitude higher than any other sample – it will, for the time, be disregarded. There is no potassium standard for freshwaters.

KIMO Potassium



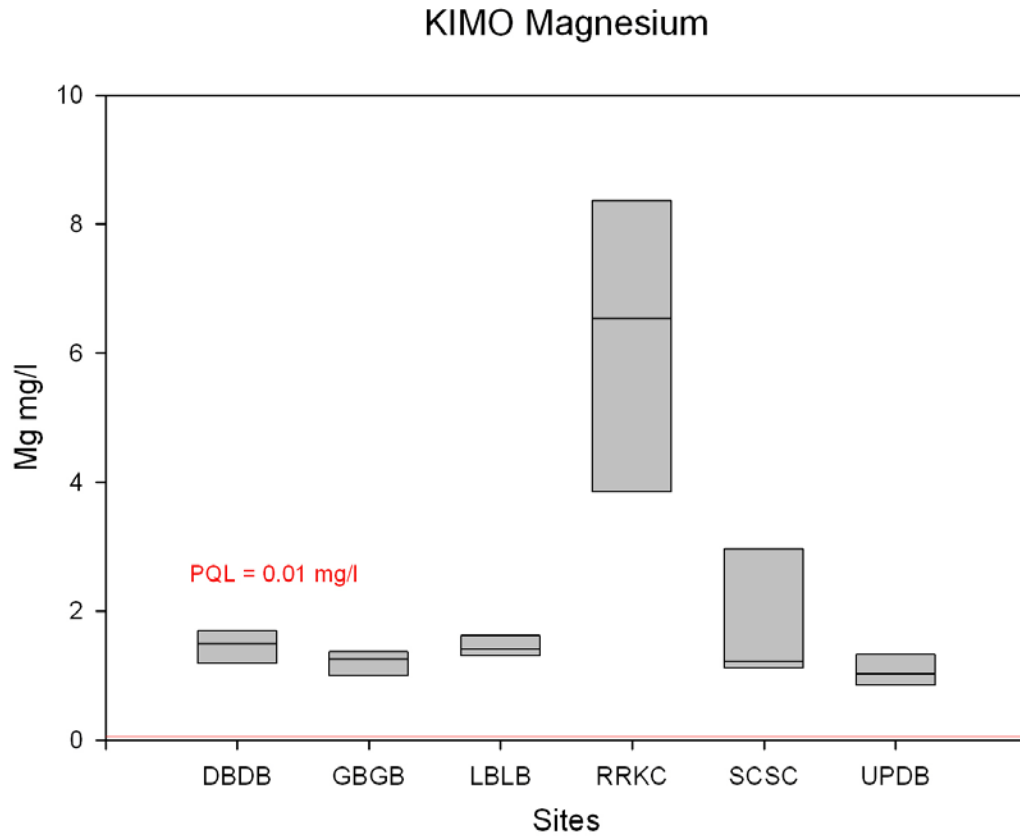
Sodium

The occurrence of sodium mirrors that of chloride. These two ions are commonly found in all freshwaters of the world and are primary products the 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 KIMO, and there is no freshwater standard for South Carolina.



Magnesium

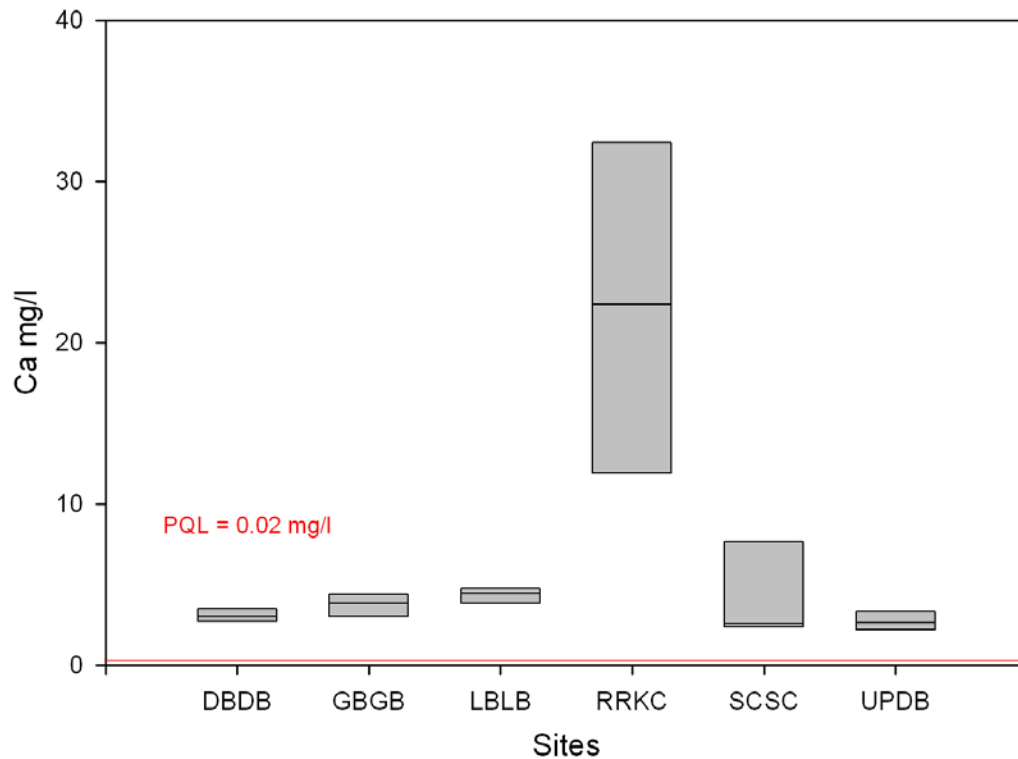
Similar to most other ionic data, the waters of Kings Creek contain far more dissolved constituents than other streams of KIMO. This general signature is very evident in the specific conductance graph shown earlier. There is no magnesium standard for this designated use.



Calcium

Relative concentrations of the calcium ion mirror that of magnesium. Both divalent cations, calcium and magnesium are often found replacing one another in mineral crystalline matrices. Recall the ANC graph above. The notable higher calcium levels of RRKC are matched in the higher ANC values of this stream. It is likely that there are outcroppings of calcium carbonate somewhere within the Kings Creek watershed. There is no state standard for calcium.

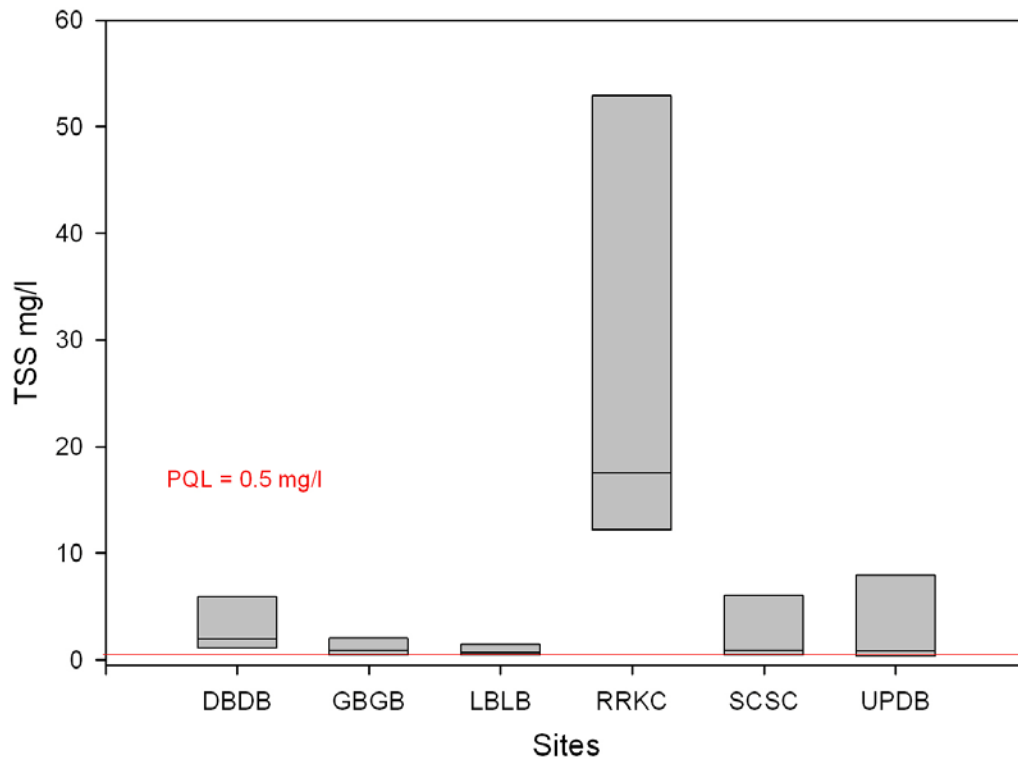
KIMO Calcium



Total Suspended Solids

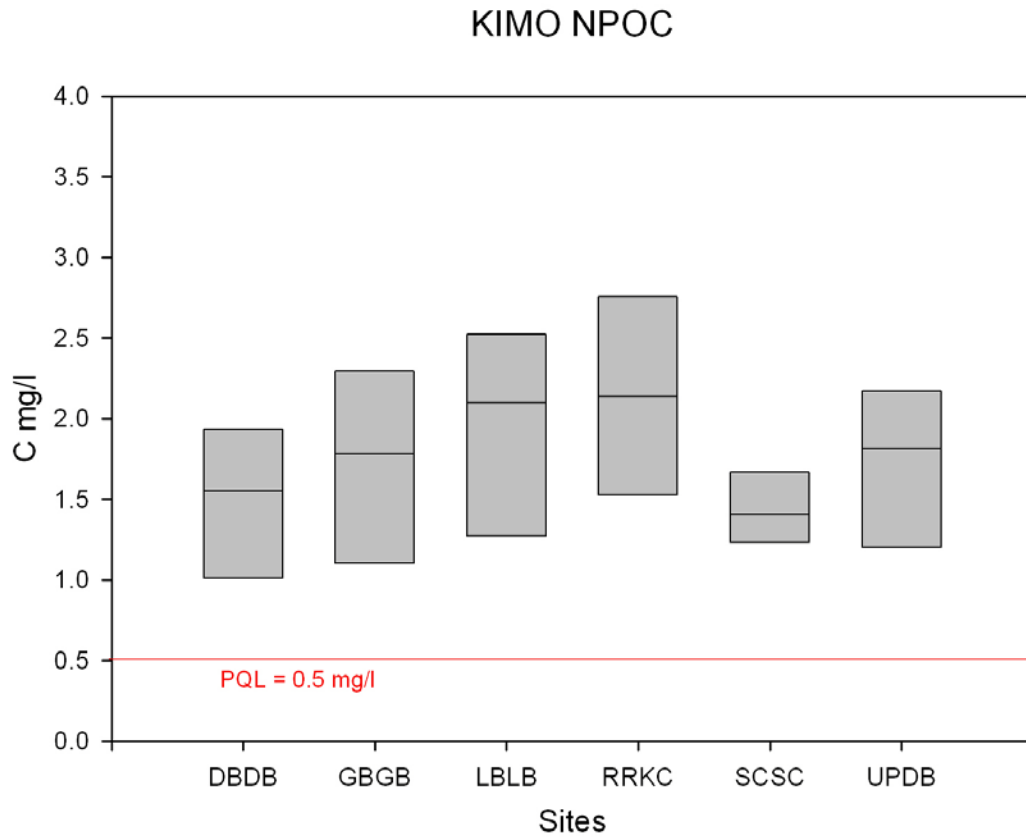
The laboratory reproducibility for suspended solids was not very good. However one can easily see a higher load of suspended sediments in Kings Creek – which given its larger discharge and the fact that almost all of the watershed lies upon “developed” lands outside the park – this can be expected. The lab also reduced solids data into two subsets, fixed and volatile solids. Results are not worth presenting here. There are no state standards for TSS in freshwaters.

KIMO Total Suspended Solids



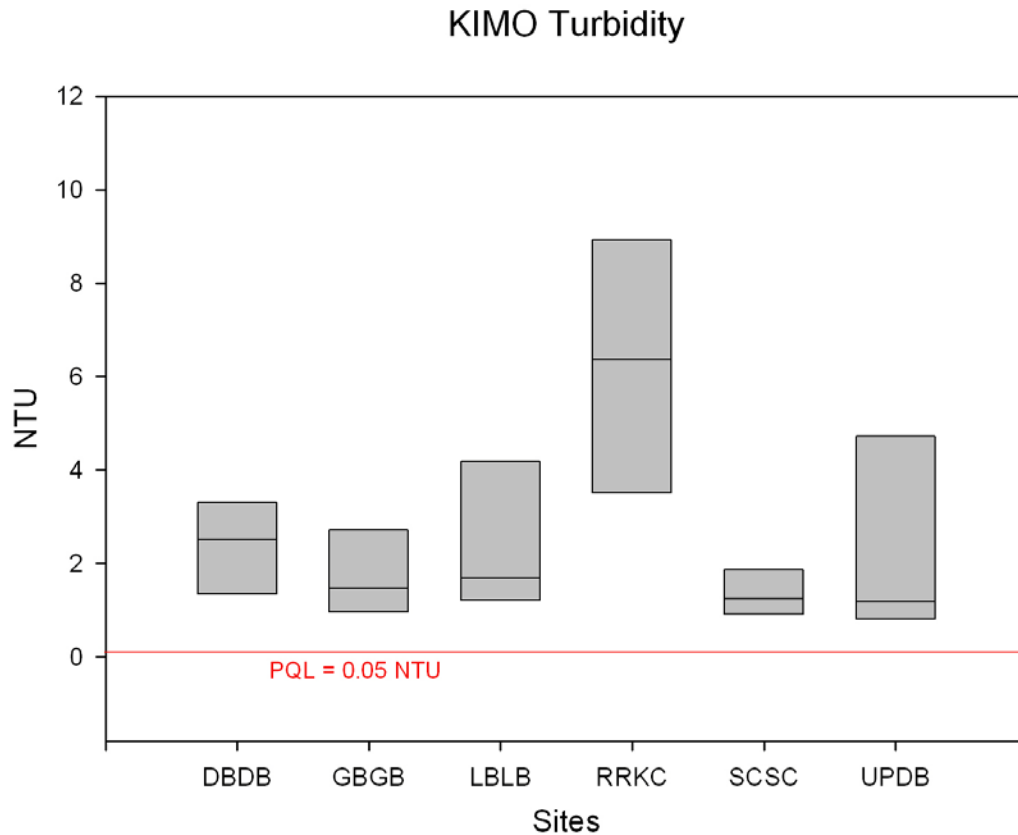
Total Organic Carbon

Total organic carbon, or in the case of most natural waters, non-purgeable organic carbon, is fairly low in the waters of KIMO. There is no South Carolina standard for TOC in freshwaters.



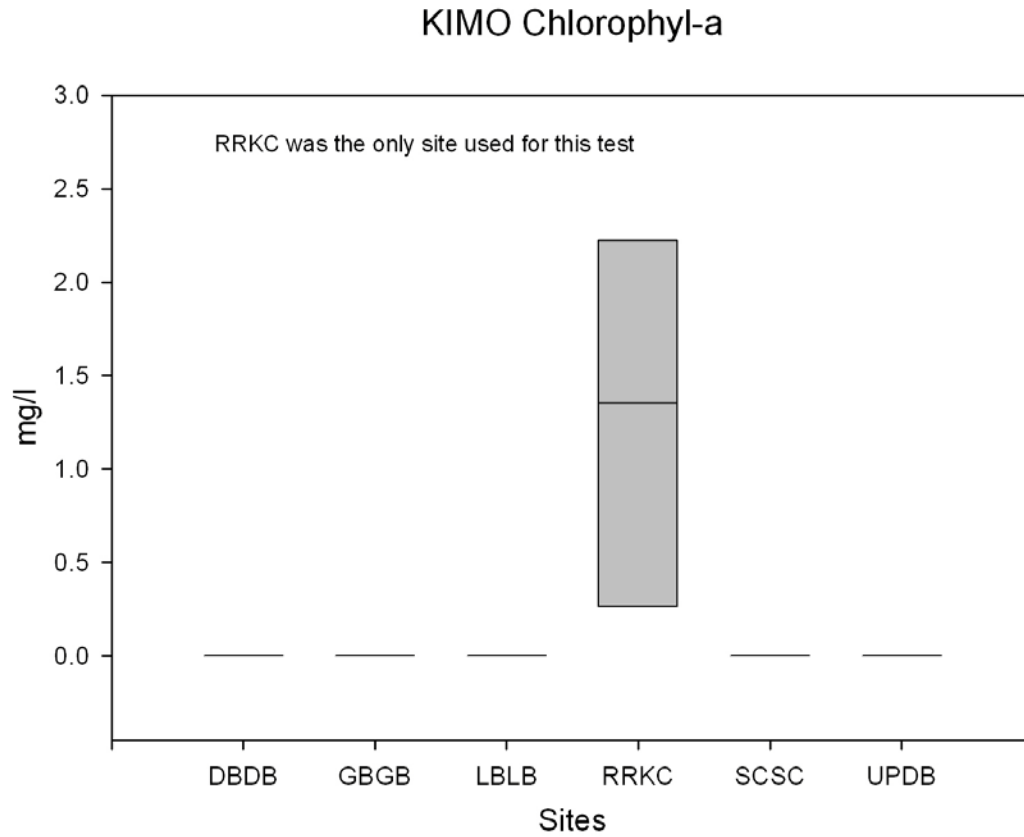
Turbidity

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. Kings Creek, as it drains a large area outside the park has higher turbidities than other sites. In general, all turbidity values taken at KIMO represent clear to very clear waters.



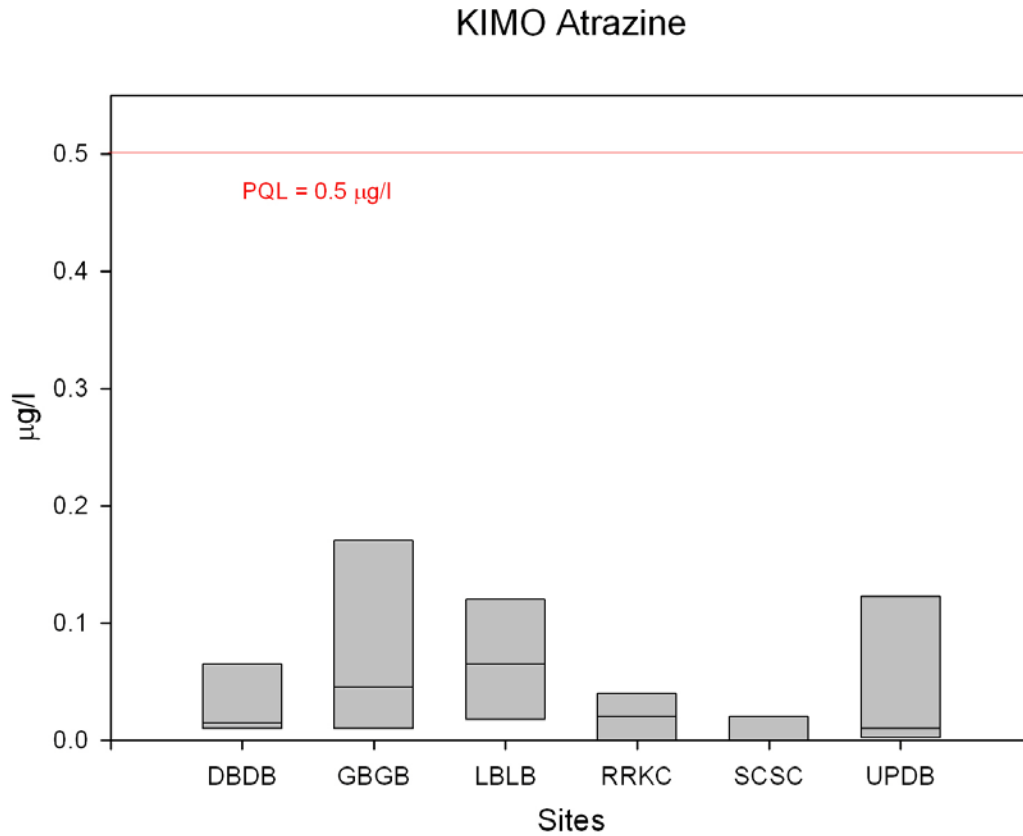
Chlorophyll-a

Chlorophyll-a analysis was only performed at Kings 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.



Atrazine

All atrazine samples were below the PQL of 0.5 µg/l. There are no state standards for atrazine in freshwaters. A national drinking water standard of 3.0 µg/l can be used as a general comparison to what was found at KIMO.



General Water Quality Status

For the most part, water quality of the six sites sampled at KIMO is very good. The only exception is the relatively high bacterial (fecal coliform) levels at Dellingham Branch. It is recommended that, if the park is interested in determining the source of the bacteria, a rather simple, low-cost sampling strategy could be easily devised.

Waters of KIMO, with the exception of Kings Creek, are naturally low in ANC, and pH. The historically and naturally low ANC and pH values are not much of an issue. However, with the increase in acid precipitation over the past decades, streams with low buffering capacity and low pH, such as those at KIMO are susceptible to becoming more acidic.

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. No evidence of nutrient loading (nitrate and phosphate) was found. All other parameters were well below the few state standards that exist, with exception of fecal coliform. Nitrite and phosphate ions were also analyzed but all samples were found to be below detection limits. 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