

Cumberland Piedmont Network Water Quality Report

February 2005

Mammoth Cave National 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.

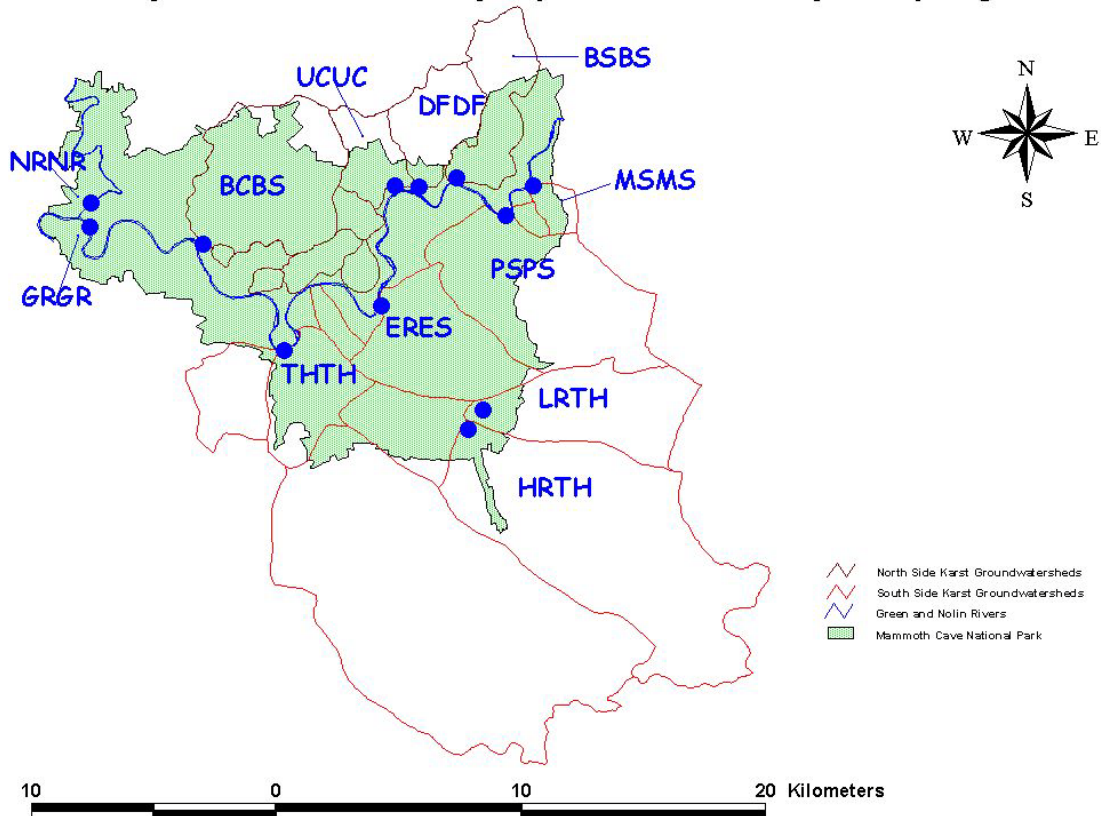
Unlike most other parks of the CUPN, there is a fairly complete picture of water quality at MACA. During two periods, March 1990 through September 1992, and again from October 1997 through September 1998, an intensive water quality monitoring program was initiated. Water quality analysis was done by either the USFS Research Laboratory (Berea, Kentucky), or the Kentucky Geological Survey Laboratory (Lexington, Kentucky). All samples were taken on a non-conditional synoptic monthly schedule at fixed integrator locations. Each site was sampled on the 10th day of the month.

MACA restarted its WQ monitoring program in July 2002, although it was slated to begin in October 2004 under the two-year-on five-year-off USGS National Water Quality Assessment Program of which the MACA program was based. During this time water quality analysis was done by the MACA laboratory, until July 2004 when the lab was merged with the Western Kentucky University lab, creating the WATERS laboratory. Data from these labs, as described above, are questionable in certain parameters. Data presented below are from the 1990-1992 and 1997-1998 dataset and will be used to determine the parameters to be monitored for the NPS Vital Signs Program.

Sampling Sites

Below is a map of water quality sampling sites at MACA. During each monthly sampling round each site was visited and an additional Quality Assurance-Quality Control sample was extracted. Monthly sampling commenced in March 1990 and continued until September 1992, and from October 1997 through September 1998, for a total of 55 sampling events.

Monthly Non-conditional Synoptic Water Quality Sampling Sites



Description of Sampling Sites

MSMS: The Mile 205.7 Spring groundwater basin (3.1 km²) is relatively small and much of it is contained within the park boundary (2.0 km²). The recharge area which lies outside the park boundary is sparsely populated with minimal human impact. Water quality data indicate relatively unaltered conditions.

PSPS: The recharge area of the Pike Spring groundwater basin (39.9 km²) contains both park (17.3 km²) and non-park lands (22.6 km²). Unlike the Turnhole Spring groundwater basin where there are significant numbers of feedlots, homes, and petroleum wells, the Pike Spring groundwater basin contains less agricultural, domestic, and urban development. This basin, whose main underground flow conduit has not been discovered by explorers, supports populations of endangered Kentucky Cave Shrimp.

BSBS: The Big Spring groundwater basin (15.2 km²), roughly bisected by the park boundary, is comprised of park, forest and light agricultural land-uses. It has been the focus of topical water quality studies including flood pulse and sulfate monitoring. Topical water quality data have reflected both park and private land-uses in time-resolved series.

DFDF: The Doyle's Ford groundwater basin (12.7 km²) has more active silviculture than Ugly Creek. The 11.2 km² of private lands of this watershed undergo a constant cycle of timber harvesting.

UCUC: The Ugly Creek groundwater basin (8.3 km²) contains both park lands (4.7 km²) and mostly forested private lands (3.6 km²). Water quality, in general, reflect the overall low disturbance and light land uses in this watershed. Like the neighboring Doyle's Ford basin, the major cave streams draining this watershed have not been discovered.

ERES: The Echo River groundwater basin, the type locality of the Kentucky Cave Shrimp, is almost entirely contained within park boundaries – 22.2 km² of its 23.2 km² are within the park. However, it does receive a large portion of its recharge from the adjacent Turnhole Spring basin (primarily agricultural lands) during periods of high flow. Research has allowed us to determine when, relative to stage condition, this overflow route is activated (Meiman and Ryan 1993). Water quality from this station is excellent during periods of low flow, but water quality is severely degraded during and immediately following high flow when the overflow route is active. There also exists a condition where if the stage of the Green is within 1.5-3 meters above base level, and the karst aquifer is in a stage of low discharge, a flow-reversal occurs. River water enters (at rates of over one cubic meter per second) River Styx Spring, flows into Mammoth Cave, and out Echo River Spring (total distance underground of about two kilometers). During these conditions, which occur for several weeks during the winter months, the recharge area of Echo River Spring is the entire Green River watershed upstream of River Styx Spring. Water quality signatures are obvious in low flow, overflow, and flow reversal states.

THTH: The drainage area of the Turnhole Spring groundwater basin is clearly much smaller than that of the Green River, but the potential for acute pollution of the cave aquatic ecosystem is much greater. The Turnhole basin will be sampled at its resurgence on the Green River. The vast majority of this 245.4 km² karst basin lies on private lands (215.1 km²), including some of the most intensely farmed land in the state. Sub-basins of the Turnhole are sampled at Hawkins and Logsdon Rivers (below).

HRTH: Hawkins River, drains the 72.4 km² Patoka Creek karst watershed, 68.9 km² beyond park boundaries. The basin's recharge is dominated by the sinkhole plain and one of the larger perennial surface streams (Patoka Creek, in the watershed's headwaters on the Glasgow Uplands). Land uses includes the town of Park City and agricultural production.

LRTH: Logsdon River, as is Hawkins, is sampled under any flow condition through a well and sample pump. Logsdon drains the Cave City Sub-basin (25.0 km²), including both park (2.8 km²) and non-park lands (22.2 km²). The land-use of this basin includes a moderate amount of agriculture and a corridor of expanding tourism-based businesses.

BCBS: The Buffalo Spring groundwater basin (32.9 km²) is the only large perennial watershed that is virtually contained within park boundaries (27.6 km²). This basin and Mile 205.7 Spring serve as natural controls against which to compare more impacted sites. Although the Buffalo Creek drainage basin has been devoid of gross human-derived impacts for nearly fifty years, and water quality trends at this site should reflect near pristine conditions, an increase in the amount of back-country use may impact water quality.

GRGR: The **Green River** is the regional base-level stream as is sampled just upstream from its confluence with the Nolin. Aquatic fauna of the Green, just within the park, ranks among the most diverse in North America. Six species of freshwater mussels are listed as Endangered, and four more are classed as Category 2, as are two species of fish. The Green River, with more than 80 species of fish (including five endemics), and 170 species of benthic macroinvertebrates, including 53 species of freshwater mussels, has been designated an Outstanding Resource Water by the Kentucky Environmental Protection Cabinet. The flow at this site originates primarily as surface water from the upper Green River, and its chemistry reflects those land-uses rather than local influences.

NRNR: The **Nolin River**, roughly forming the western park boundary, is sampled upstream from its confluence with the Green River. Discharge from the entire Nolin River basin will be sampled at this station. Land-use in the Nolin River basin primarily consists of forest, agriculture, and hydrocarbon extraction. This site is 12 kilometers downstream from the Nolin River dam. Data have demonstrated a correlation between water release patterns and water quality.

Parameters for Water Quality Inventory

Discharge is 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 karst aquifer.

Specific Conductance provides a quick analysis of where, temporally, the sample is taken relative to the last flood pulse. For a given site, a relatively low specific conductance indicates that the system is not at base flow and still affected by a recent recharge event. Specific conductance also indicates the overall dissolved solid load.

Water temperature is a low-cost method of rapidly assessing relative transport times of the water sampled. A water temperature close to that of antecedent recharge would indicate rapid transfer and flow rates. These data may be used to demonstrate the hydrogeologic provenance of a contaminant.

Dissolved oxygen is another field measurement that provides information on the general biological condition of the water. This measurement is a gross indicator of aquatic ecosystem health. Field measurements provide the investigators "real time" analysis of samples which may alert park managers to declining conditions.

The **pH** of each sample will be taken to determine the hydrogen activity of the water. Besides being a fundamental ecologic parameter, pH is needed to calculate carbonate saturation indices.

Turbidity is a low-cost approximation of the total suspended sediment load of the water. A high suspended sediment load indicates a high erosion rate within the recharge basin. In a highly vadose flow system, high turbidity is a harbinger of an approaching flood pulse. Our research has also show a high correlation between turbidity and pesticides.

Fecal coliform bacteria is a simple test to approximate the general bacterial load of the water. The presence of coliforms in sufficient numbers indicates fecal contamination of water by a warm-blooded animal. Past fecal coliform levels have ranged from 0-8000 colonies per 100 ml.

Triazine-class herbicides represent the most common and durable pesticides used in the Mammoth Cave area. The compounds, including atrazine, simazine, and cyanazine, are analyzed using an immuno-assay method. While this method, which has been in use at Mammoth Cave since 1990, cannot yield accurate quantitative results, samples which qualitatively indicate a concentration of greater than 1 ppb are sent to a contract laboratory for mass spectrographic/gas chromatographic analysis. This method can be thought of as a screening test which greatly reduces the need for expensive organic analysis. The current program uses a refined and approved assay technique for all samples.

Nitrate-nitrogen values can be a useful predictor of eutrophication. A high nitrogen-nitrate concentration indicates a high nutrient load, which, depending upon other parameters such as bacterial counts, may be from septic waste, animal waste, and fertilizer sources.

Chloride is an inexpensive test which may indicate the presence of oil field brines, road salts, or other sources. A natural concentration of chloride between 5 and 15 ppm exists in the Mammoth Cave area.

Bromide occurs in the groundwaters of the Mammoth Cave region that are impacted by oil field brines. There has been an explosion in oil and gas exploration adjacent to the park in the past two years.

Sulfate can be coupled with chloride analysis to suggest the type of pollution. Low chloride and high sulfate may indicate natural dissolution of sulfate minerals if the mass flux is relatively constant, high chloride with low sulfate may indicate contamination by road salt, and high chloride and high sulfate may indicate brines.

Calcium, magnesium, and alkalinity (bicarbonate ion) are the dominant natural cations and anion found in carbonate aquifers. These ions are useful in determining the temporal and hydrologic position of the sample relative to the last recharge event. More specific than conductance, these ions may indicate the provenance of a contaminant as related to transfer and storage.

Inorganic metals to be monitored in this program include *aluminum*, antimony, arsenic, barium, beryllium, boron, cadmium, *calcium*, chromium, cobalt, copper, gold, *iron*, *lead*, lithium, *magnesium*, manganese, nickel, *phosphorous*, *potassium*, selenium, *silicon*, silver, *sodium*, *strontium*, *sulfur*, thallium, tin, vanadium, and *zinc*. Elements in italics were found during the 1990-1992 Water Quality Inventory Project. Although not every element listed is needed to track water quality, they were included at no additional cost in the ICP analysis.

Methods

The following method list was from the KGS laboratory, who ran the vast majority of the samples. The MDLs, which are listed, will be used to derive the PQLs, Practical Quantitation Limits on the following graphs. The PQL is five times the MDL.

PARAMETER	METHOD
Discharge	Wading staff and Marsh-McBirney 201D velocity sonde
Specific Conductance	Omega CDH-70 SPC/Temp. meter (+/- 0.001 mS), or eq.
Water Temperature	Omega CDH-70 SPC /Temp. meter (+/- 0.1 °C), or eq.
Dissolved Oxygen	Hach DO175 meter (+/- 0.01 mg/L), or eq.
pH	Hach EC10 meter (+/- 0.01 units), or eq.
Alkalinity	Hach, phenolphthalein sulfuric acid titration (+/- 5 mg/L)
Turbidity	Turner 40-100 nephelometer (+/- 0.1 to +/- 1.0 ntu)
Fecal Coliform	Millipore membrane filter method, MFC broth (+/- 1)
Triazine Assay	Millipore immuno-assay (+/- 0.001 mg/L)
Nitrate-Nitrogen	Hach, cadmium-reduction/spectrometer (+/- 0.1 ppm)
Chloride	SW846-9056 (MDL 1 mg/L)
Bromide	SW846-9056 (MDL 1 mg/L)
Sulfate	SW846-9056 (MDL 5 mg/L)
Inorganic Metals	
Aluminum	EPA 200.7 and SW846-6010A,B (ICP) (MDL 19 ug/L)
Antimony	EPA 200.7 and SW846-6010A,B (ICP) (MDL 51 ug/L)
Arsenic	EPA 200.7 and SW846-6010A,B (ICP) (MDL 50 ug/L)
Barium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 0.7 µg/L)
Beryllium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 2.4 ug/L)
Boron	EPA 200.7 and SW846-6010A,B (ICP) (MDL 23 ug/L)
Cadmium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 6 ug/L)
Calcium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 23 ug/L)
Chromium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 8 ug/L)
Cobalt	EPA 200.7 and SW846-6010A,B (ICP) (MDL 12 ug/L)
Copper	EPA 200.7 and SW846-6010A,B (ICP) (MDL 7 ug/L)
Gold	EPA 200.7 and SW846-6010A,B (ICP) (MDL 12 ug/L)
Iron	EPA 200.7 and SW846-6010A,B (ICP) (MDL 6 ug/L)
Lead	EPA 200.7 and SW846-6010A,B (ICP) (MDL 71 ug/L)
Lithium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 3 ug/L)
Magnesium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 30 ug/L)
Manganese	EPA 200.7 and SW846-6010A,B (ICP) (MDL 2 ug/L)
Nickel	EPA 200.7 and SW846-6010A,B (ICP) (MDL 49 ug/L)
Phosphorus	EPA 200.7 and SW846-6010A,B (ICP) (MDL 121 ug/L)
Potassium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 1210 ug/L)
Selenium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 129 ug/L)
Silicon	EPA 200.7 and SW846-6010A,B (ICP) (MDL 34 ug/L)
Silver	EPA 200.7 and SW846-6010A,B (ICP) (MDL 6 ug/L)

Sodium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 18 ug/L)
Strontium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 1 ug/L)
Sulfur	EPA 200.7 and SW846-6010A,B (ICP) (MDL 30 ug/L)
Thallium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 68 ug/L)
Tin	EPA 200.7 and SW846-6010A,B (ICP) (MDL 426 ug/L)
Vanadium	EPA 200.7 and SW846-6010A,B (ICP) (MDL 4 ug/L)
Zinc	EPA 200.7 and SW846-6010A,B (ICP) (MDL 4 ug/L)

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 Kentucky water quality standards, please see:

Kentucky: 401 KAR 5:026. Designation of Uses of Surface Waters.

The Commonwealth of Kentucky, as every state in the Union, must, under guidance of the USEPA, promulgate law to set both designated uses for streams, and set water quality standards. The sampling sites at Mammoth Cave National Park fall into these basic designated uses categories, from highest to lowest standards (401 KAR 5:031, Section 2):

Outstanding Resource Waters: Waters designated by the Natural Resources and Environmental Protection Cabinet as an outstanding resource water pursuant to 401 KAR 5:031. This list includes all underground streams and the main stem of the Green within Mammoth Cave National Park. This designated use category, as it is the most restrictive and the highest quality in the state, will be used as a minimum standard for these waters.

Cold Water Aquatic Habitat: Waters and associated substrate that will support indigenous cold water aquatic life or self-sustaining trout populations on a year-round basis. All cave streams within the park meet the Cold Water Aquatic Habitat criteria. Although the state stocks rainbow trout in the tailwaters of the Nolin dam just upstream of the park's boundary, the population is not self-sustaining.

Warm Water Aquatic Habitat: Waters and associated substrate that will support indigenous warm water aquatic life. The Green and Nolin Rivers can be considered under this category, although the Outstanding Resource Waters designation of the Green supersedes this category.

Primary Contact Recreation: Those waters suitable for full body contact recreation during the recreation season of May 1 through October 31. Both the Green and Nolin fall under this category.

Secondary Contact Recreation: Those waters that are suitable for partial body contact with minimal threat to public health to water quality. All park waters would fall into this minimum category.

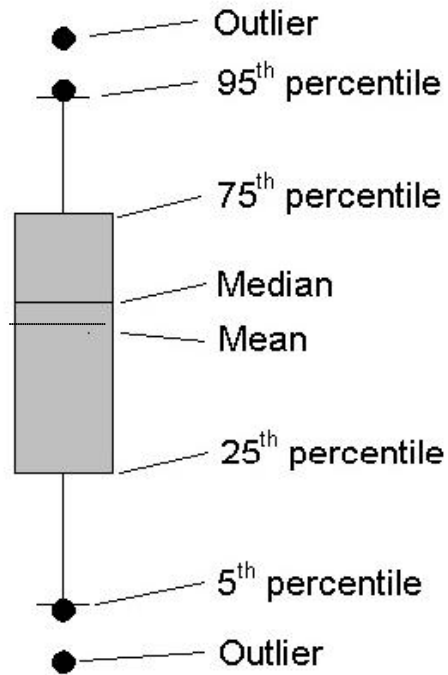
The following table summarizes designated uses for monitored park waters. Any designations in red are made by the author. They are based upon direct observations of visitor use and use the same criteria as used by the state.

<i>Park</i>	<i>Code</i>	<i>Site</i>	<i>State</i>	<i>Designated Use</i>
MACA	MSMS	Mile 205.7 Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	PSPS	Pike Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	BSBS	Big Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	DFDF	Doyle's Ford Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	UCUC	Ugly Creek	KY	Coldwater Habitat Secondary Contact Recreation
MACA	ERES	Echo River Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	THTH	Turnhole Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	HRTH	Hawkins River	KY	Coldwater Habitat
MACA	LRTH	Logsdon River	KY	Coldwater Habitat
MACA	BSBC	Buffalo Spring	KY	Coldwater Habitat Secondary Contact Recreation
MACA	GRGR	Green River	KY	Warmwater Habitat Primary Contact Recreation Secondary Contact Recreation
MACA	NRNR	Nolin River	KY	Warmwater Habitat Primary Contact Recreation Secondary Contact Recreation

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

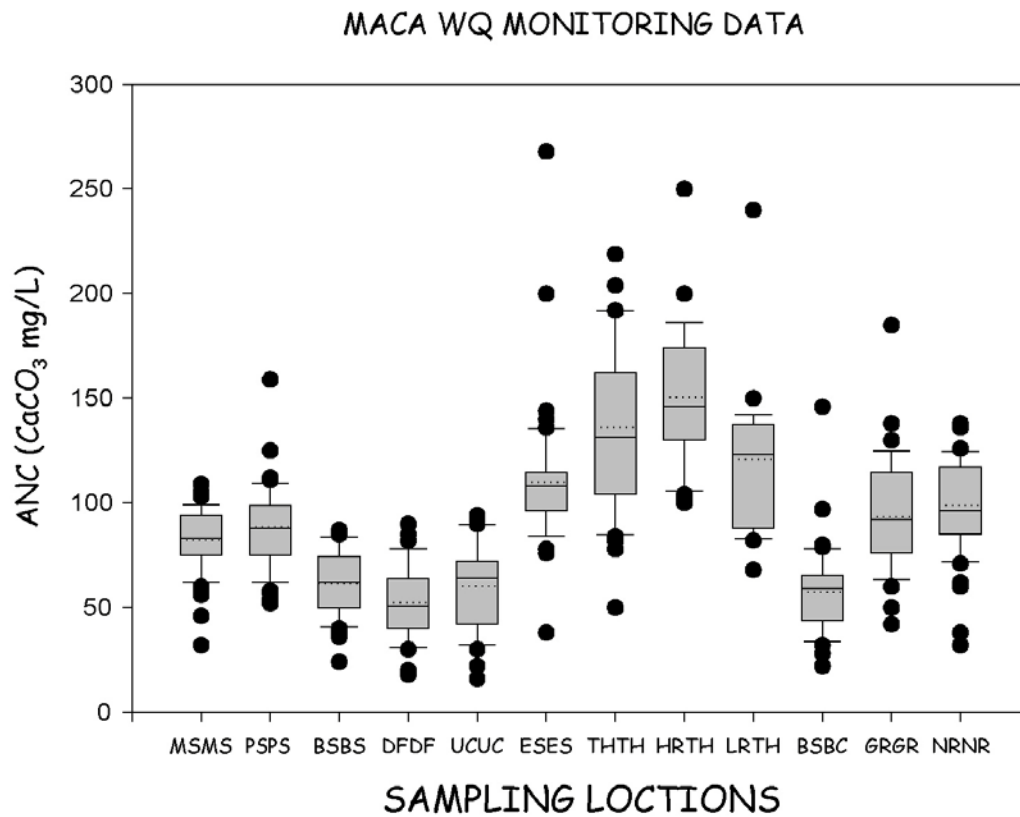
The following graphs are a composite of 55 monthly rounds of sampling at MACA. There are represented in the graphs below as box-plots. Here is a key to understanding the structure of a box-plot:



Field Parameters

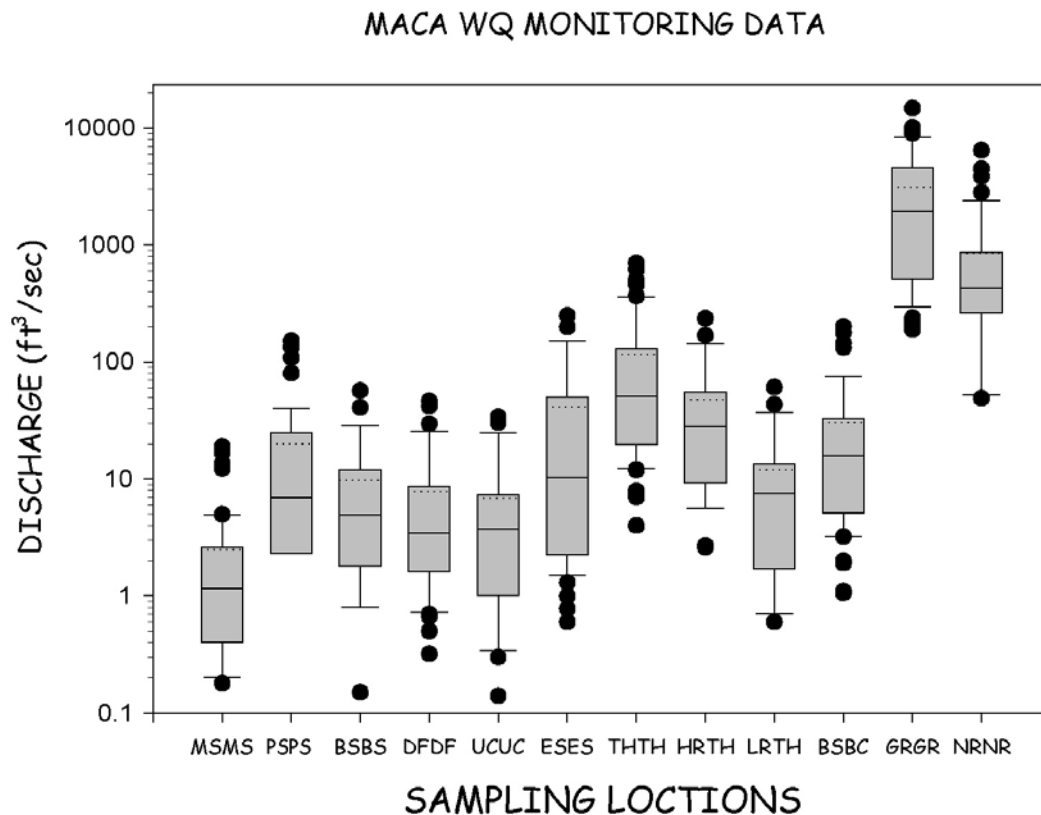
Acid Neutralizing Capacity

Acid neutralizing capacity (ANC, the same test as bicarbonate alkalinity, except that the sample is not filtered prior to analysis) is, as expected, quite high in these limestone-dominated watersheds. There seems to be a correlation between the amount of ANC and the amount of surfacially-exposed limestone within individual watersheds, and transport time (contact time) with the limestone. In any case, the high ANC values bode well in the system's ability to counter the effects of acid precipitation, prevalent throughout Southcentral Kentucky



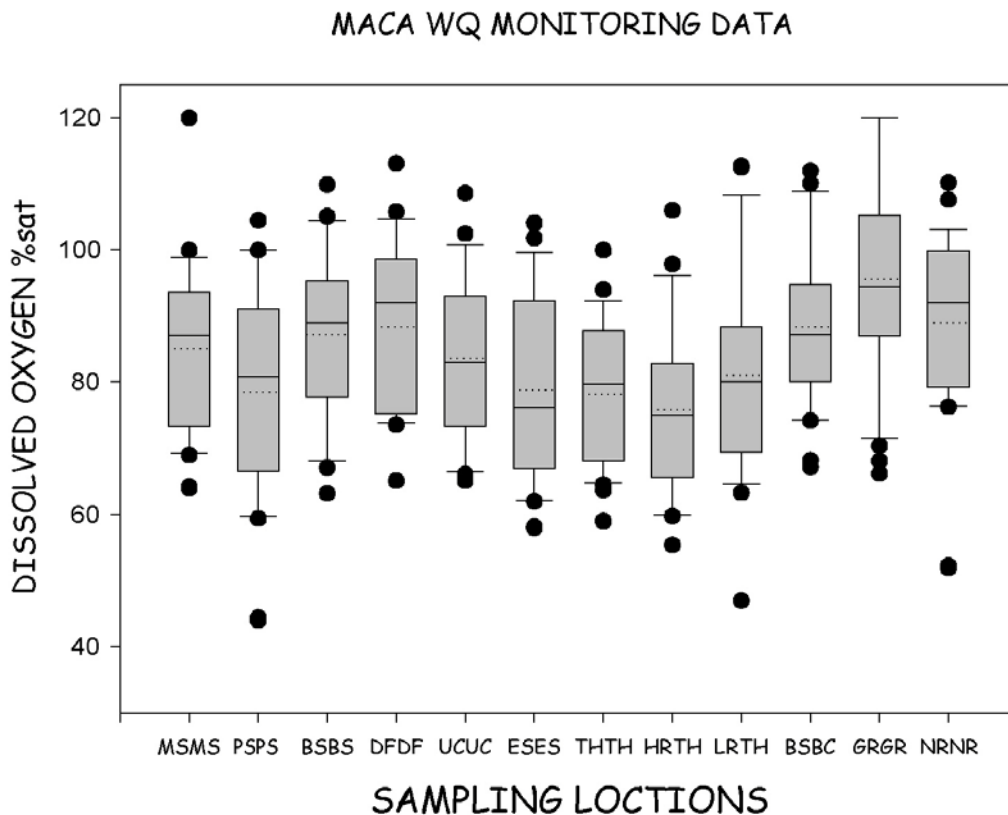
Discharge

As it is logistically impossible to measure discharge at every site on every visit (high water conditions typically interfere) these data – with exception of GRGR and NRNR which are continually monitored by the USGS – are a combination of actual measurements and extrapolations. Through years of measurements we have calculated “unit base flow” for each watershed. If a few sites are measured on a given high flow day, their actual measurements are compared to their base flow values and the percentage over base flow is determined. This “percent above base flow” is entered to the unmeasured sites, and combined with their unit base flow values, discharge is extrapolated. QA/QC checks indicate that these estimates are within 5-10% of actual. General assumptions are that the rainfall was equally distributed over all watersheds, and that each basin is generally synchronized in their response to the event.



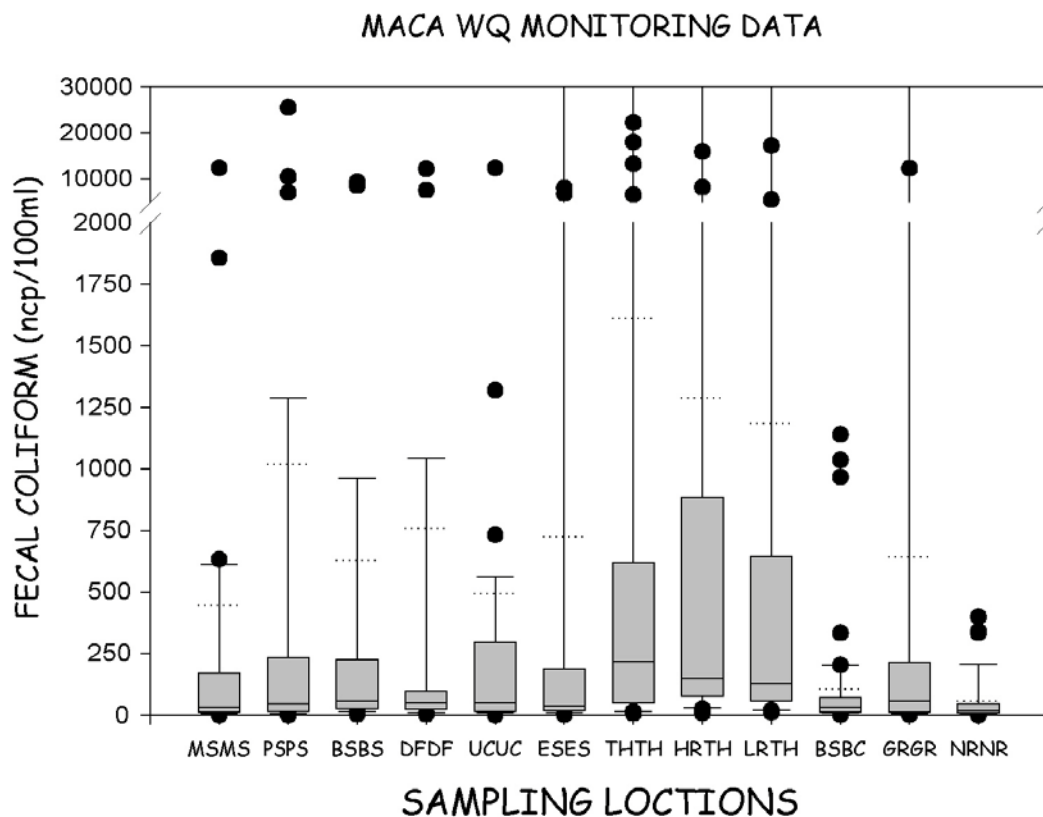
Dissolved Oxygen

Dissolved oxygen levels, for the most part are near or at saturation for all park waters. Values at all current sampling locations show very robust DO levels, reflecting relatively low biological oxygen demand and aerated flow, both in the surface rivers and cave streams. The state DO limits are reported in concentration values (mg/l), and thus do not reflect saturation levels which are governed by temperature – the higher the temperature, the less oxygen is required to maintain saturation. In any case, DO values of park waters are well over the lower limit of 5.0 mg/l.



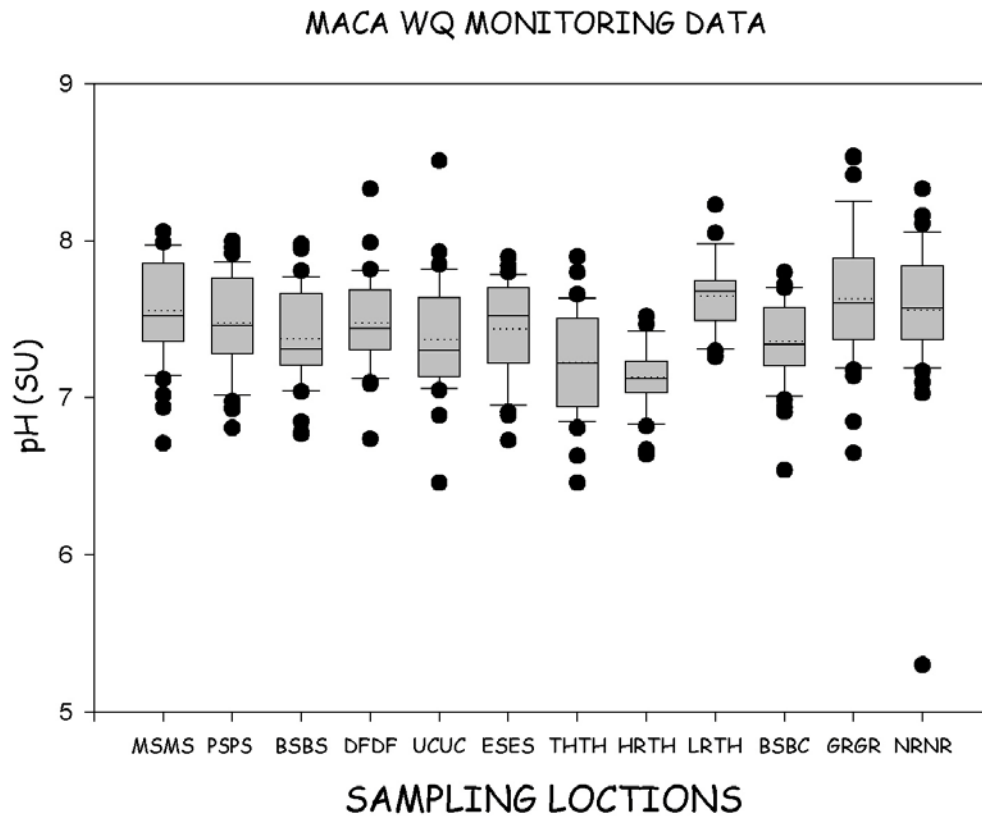
Fecal Coliform

Fecal coliform, although not pathogenic to humans, is derived from the digestive tract of warm-blooded animals, and can be considered an indicator of pathogens. The state's primary recreational contact limit is 200 colonies/100 ml, based on a geometric mean of not less than 5 samples per month, nor exceed 400 col/100 ml in more than 20% of all samples taken during the month. Park waters are sampled only once per month, but if sampled more often, results would be very similar to those of the monthly samples. Fecal coliform contamination is very high for nearly all park waters – the lowest values are found in watersheds primarily drained by park lands (MSMS, BSBC) and the Nolin River, where sampling is about 11 km downstream of the dam with little contribution from developed lands within that stretch. High fecal coliform levels are always associated with flood events as the recharge areas flush animal waste into the waterways, and fecal levels are in the 10,000 to 20,000 range. Background levels, when the systems are recharged by stored waters, are low.



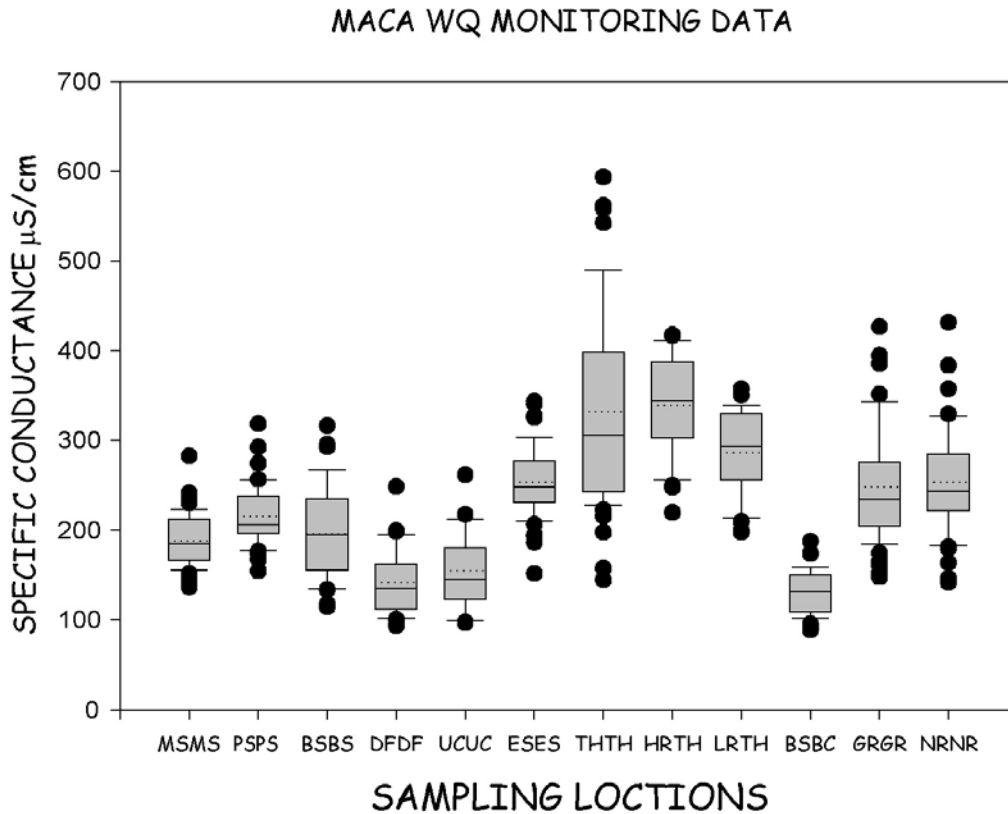
pH

As one would expect in waters with high bicarbonate alkalinity that drain large expanses of carbonates, pH remains well within the state standards of 6.0 to 9.0 SU. The lower values typically accompany storm events as the higher readings with base flow, paralleling calcium, magnesium, and bicarbonate ions, which is in large part dictated by residence time of the water in contact with limestone. The one outlier is from a January 10, 1991 sample at NRNR. All other parameters with this sample are within normal ranges, however the very low bacterial count with this sample may indicate it is associated with releases from the Nolin Reservoir.



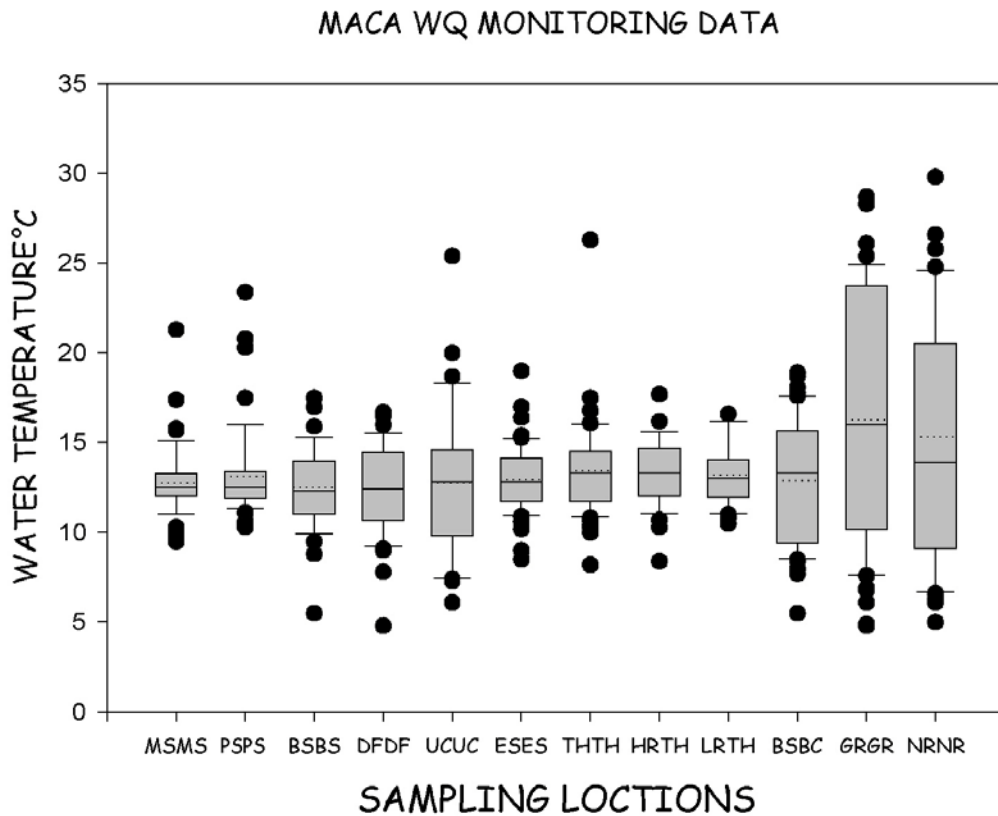
Specific Conductance

Specific conductance (SPC), a measure of the ability of water to conduct an electrical current, has no set standards at either the state or federal level. THTH, with its large expanse of carbonates and oil field brines has the highest values, while the limited carbonate exposure and rapid through-put times of BSBC has the lowest readings. During times of flood, when recharge has little residence time with the rock, SPC values are low, and conversely, base-flow times yield the highest values.



Water Temperature

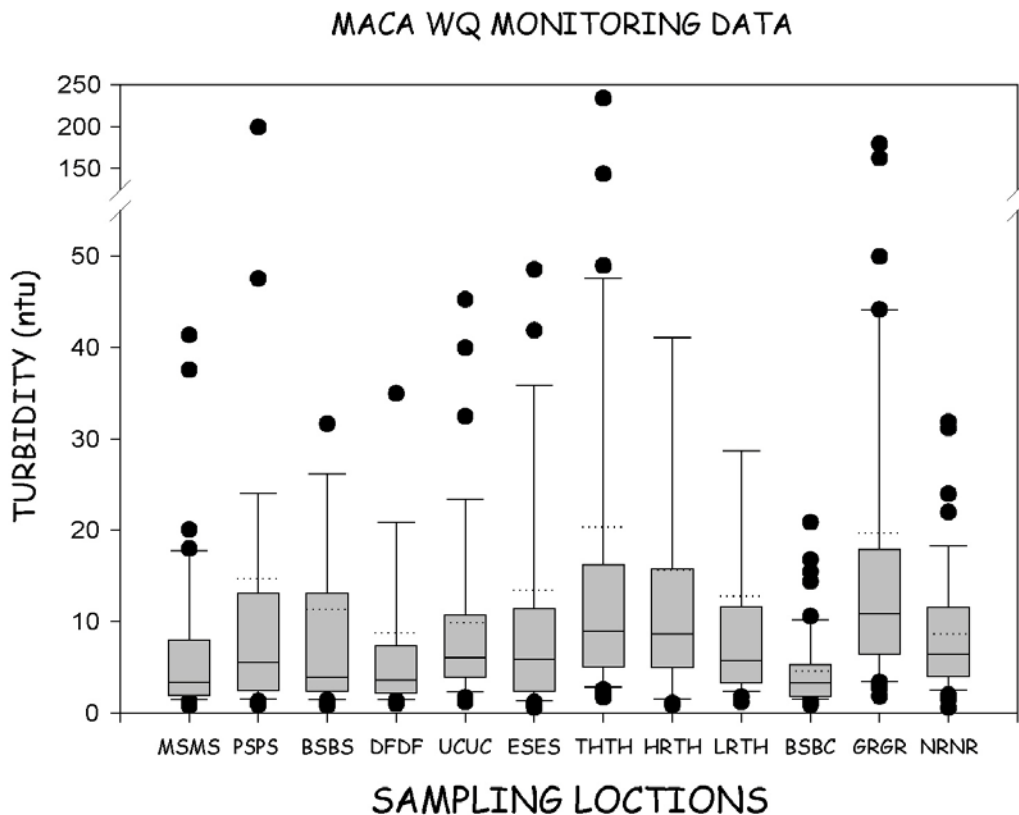
All park waters meet state requirements for water temperature as per their designated uses (all springs and cave streams are Cold Water Aquatic Habitat), while the rivers are classified as Warm Water Aquatic Habitat). The few outliers on the spring sites are due to a sampling event occurring while the Green River was backed up into the spring orifice. The somewhat wider ranges at DFDF and UCUC are caused by the sampling site being located more than 100 m from the spring (within the spring run), while the wider ranges for BSBS and BSBC are influenced by rapid through-flow.



Laboratory Parameters

Turbidity

Turbidity is roughly correlative to suspended solids. No state or federal standard exists for turbidity. All sites experience very high turbidity during times of flood flow, as soil particles are washed into streams with the runoff. A pattern is obvious, especially when the means and 75th percentiles are examined, between turbidity and land use (addressed in the next major section). Watersheds, such as THTH, GRGR, and HRTH, with the highest percentage of agricultural land use have the highest turbidity values. For background comparison, look at the range of BSBC (with nearly all of the watershed within the park) when compared to other watersheds. It is worth noting, similar to fecal coliform, that a substantial background of turbidity exists even within relatively pristine karst watersheds.

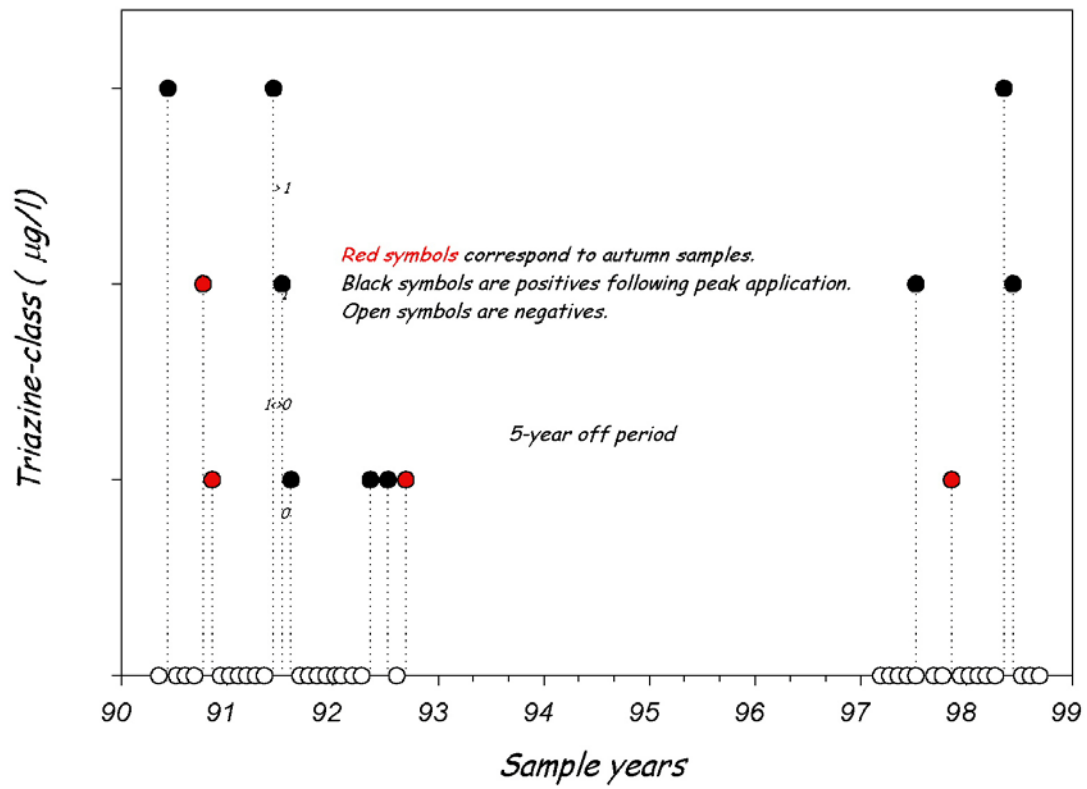


Atrazine

As a parameter of the park's monthly non-conditional synoptic sampling program, pesticide analysis has confirmed hypotheses on spatial and temporal occurrence of these compounds. For example, watersheds with a dominance of agricultural activities have the highest amounts of pesticides in their waters. The water quality data set (1990-1992, and 1997-1998) relied on immuno-assay screening for triazine-class herbicides (atrazine, by far the most commonly applied and commonly found, followed by simazine and cyanazine) and if positive, the master sample is sent to a laboratory for full analysis (MS/GC). Monthly samples found atrazine (2-chloro-4-ethylamine-6-isopropylamino-S-triazine) in the largest agricultural watersheds; Turnhole Spring, Pike Spring, Echo River (during periods of overflow from Turnhole), the Green and Nolin Rivers, immediately following peak application periods (April – June). Atrazine concentrations were commonly found in the 1.0 ppb range. Metolachlor was the second most common pesticide and typically below 0.5 ppb. Sporadic low concentrations of Linuron, and Alachlor were found as well.

More surprising was the re-occurrence of atrazine in autumn in the Green River, and to a lesser extent, the Nolin. This pattern has been observed each year. Discussions with local NRCS conservationists confirmed that atrazine was only applied prior to and immediately following spring planting. It is interesting that this re-appearance of atrazine is coincidental with draw-down of the Green and Nolin River Lakes. It seems that the lakes, which fill to summer recreation pool while the atrazine is applied in the spring, are acting as atrazine capacitors. These capacitors release their charge (atrazine) when the lakes are lowered to winter pool. This alone would not explain the sudden re-appearance of this chemical, as the lakes discharge water throughout the year. However, shortly after peak application, the lake undergoes a thermal stratification, and just prior to draw-down, the lakes “turn-over” or more accurately, de-stratify. Atrazine, both long-lived and with a high affinity for fine organic particles, may be “stored” within the organic-rich and anoxic “floc-zone” comprising the lower two meters of the lake. When the lake destratifies, the floc is mixed into the lake and released into the river.

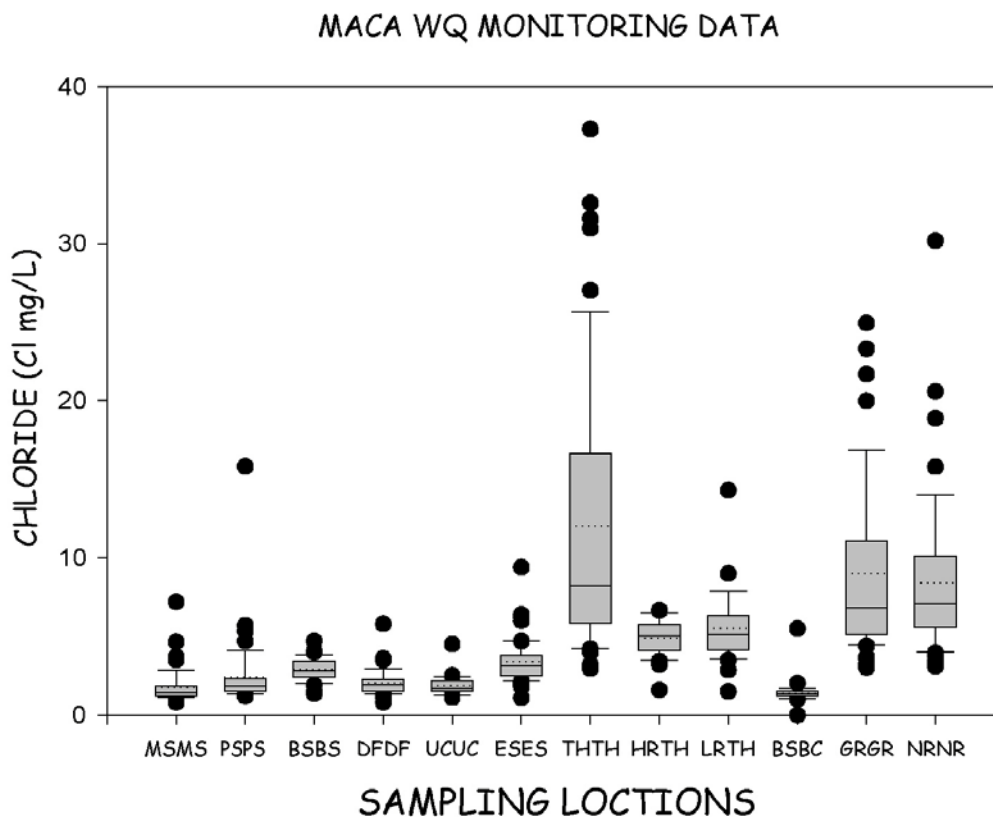
Green River immuno-assay screen



Anions

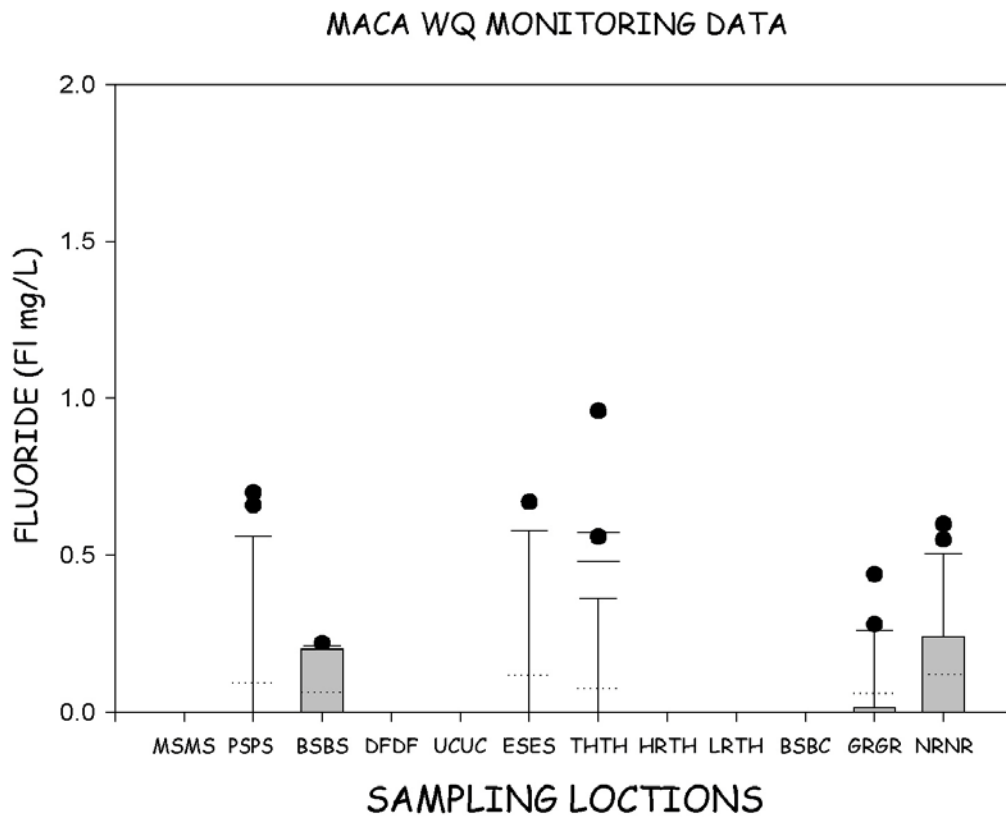
Chloride

The state's strictest standard, Cold Water Aquatic habitat, places the upper limit on chloride at 600 mg/l. The highest levels reported in this database range in the 30 mg/l range at THTH. Generally chloride levels are low and are derived from wet atmospheric precipitation. This chemically conservative ion readily passes through soils and bedrock and acts as a natural "tracer". The Green River, which had historic high levels of chloride of over 100 mg/l from oil field brine pollution in the late 1950's has returned to background levels. Brines are likely the source of elevated chloride levels in THTH, and are known to be high in the Mill Hole portion (western) of the watershed and joins the conduit system above THTH but below HRTH and LRTH. A documented brine source is found in Sulfur River of Parker Cave 4 km upstream of Mill Hole. Other brine-related ions, sodium, sulfate and barium, are also higher in THTH than elsewhere.



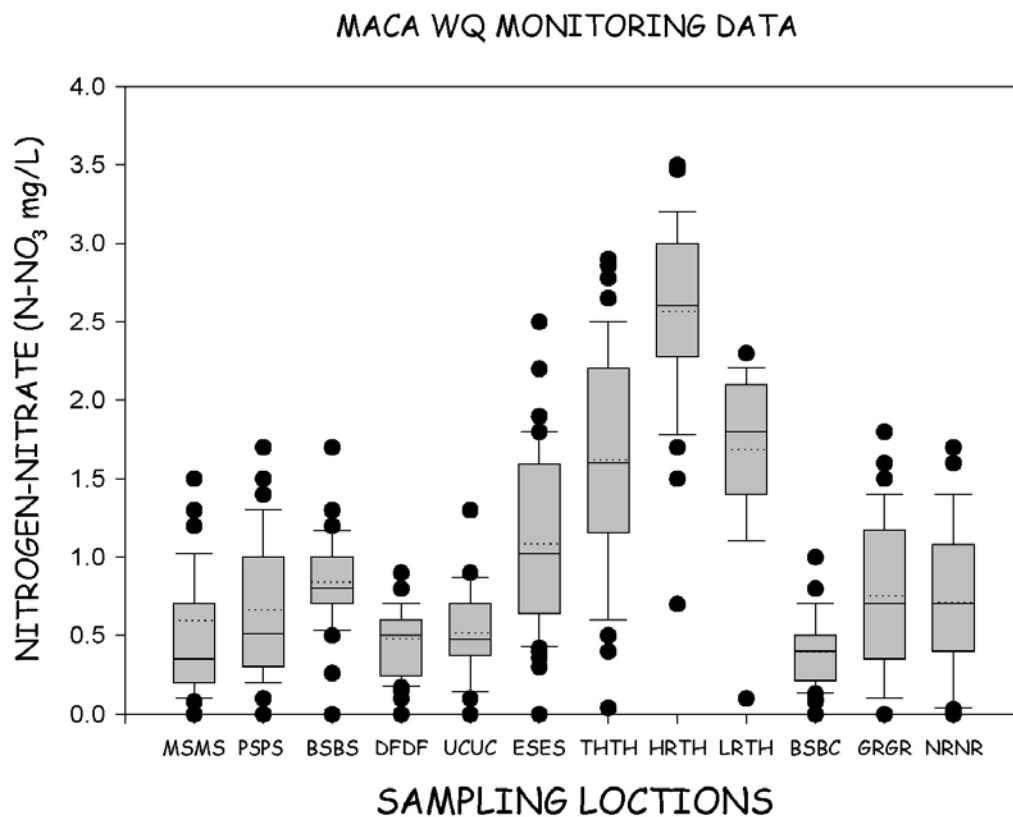
Fluoride

The only state standard for fluoride is for Domestic Water Supply Use, and is set at 2.0 mg/l. Fluoride levels in monitored park waters are usually zero. A few outliers, with seemingly random occurrence, have been reported, but all below 1.0 mg/l. These minute levels may be derived from weather rock or leaching from soils. In any case, levels are very low.



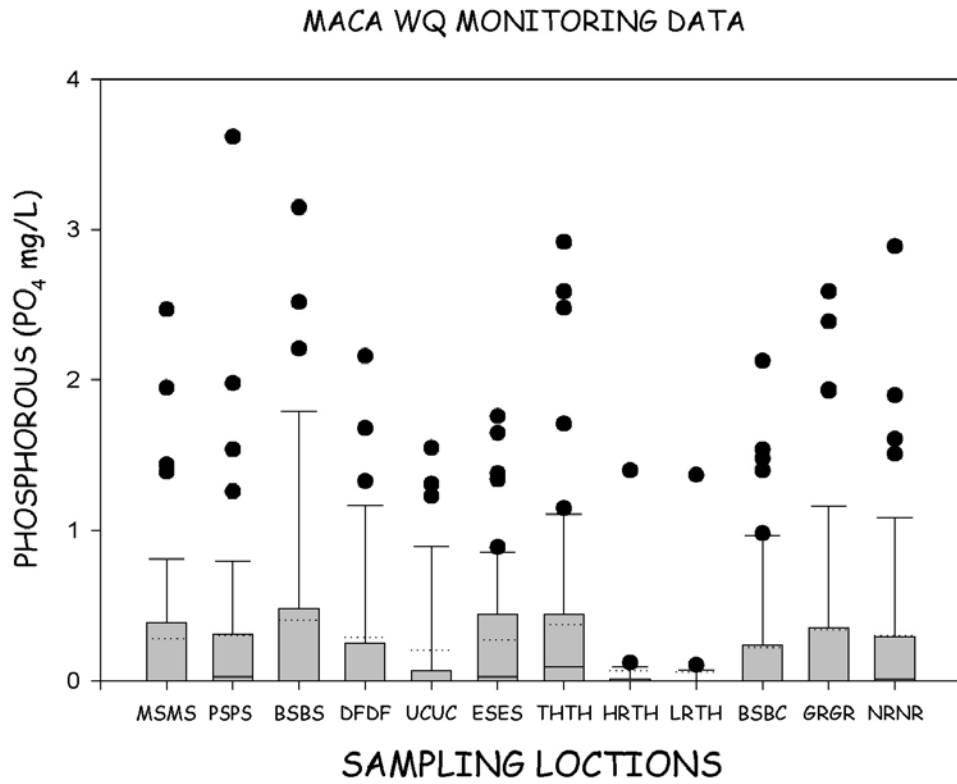
Nitrogen-Nitrate

State standards for nitrogen-nitrate are set at 10.0 mg/l and are based on human health issues associated with methemoglobinemia, “blue-baby syndrome”. Nitrate levels of monitored park waters have low concentrations of nitrogen-nitrate and rarely exceed 3.0 mg/l. Watersheds of HRTH, LRTH, and THTH have the highest levels and have the highest amounts of agricultural and urban development. It is worth noting that atmospheric precipitation of nitrogen-nitrate has a mean of 1.3 mg/l. The highest precipitation nitrate value between September 2002 and October 2003 (the first year the park became a National Precipitation Deposition Program site) was 5.4 mg/l. It is interesting that atmospheric precipitation concentrations of this ion are found near or above that is found in park waters.



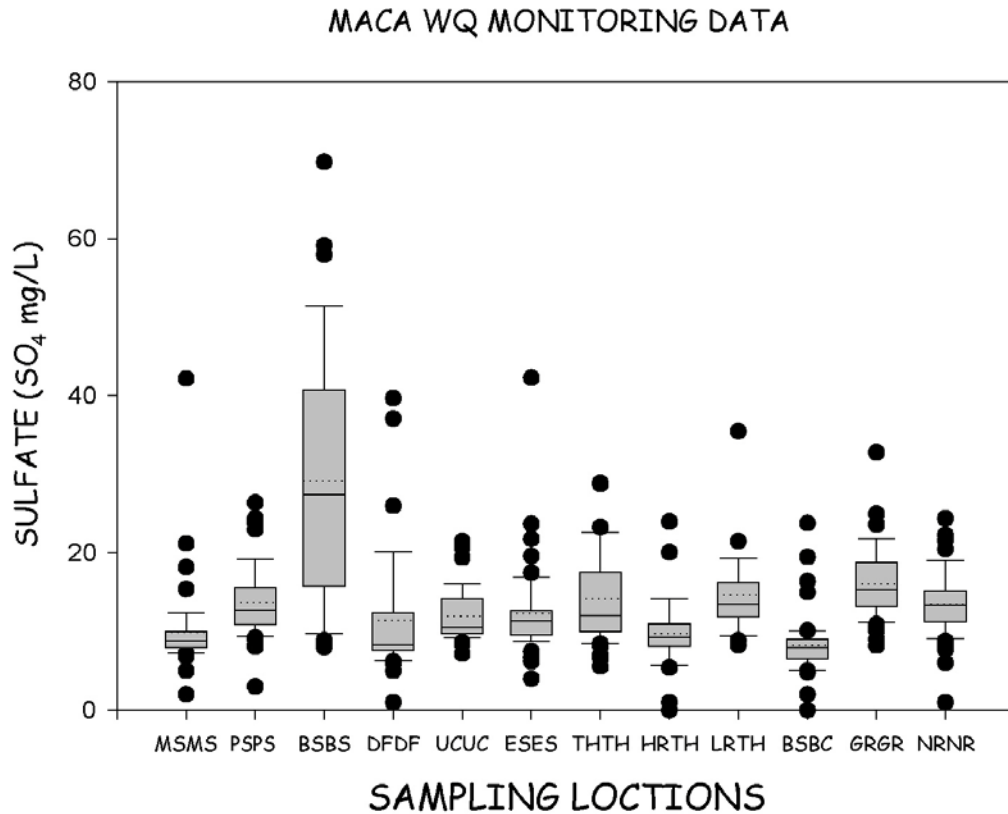
Phosphorous

Phosphorous is generally considered the limiting nutrient for eutrophication. There are no state or USPEA standards for phosphorous. Overall, phosphorous levels are fairly low, commonly under 1.0 mg/l in monitored waters.



Sulfate

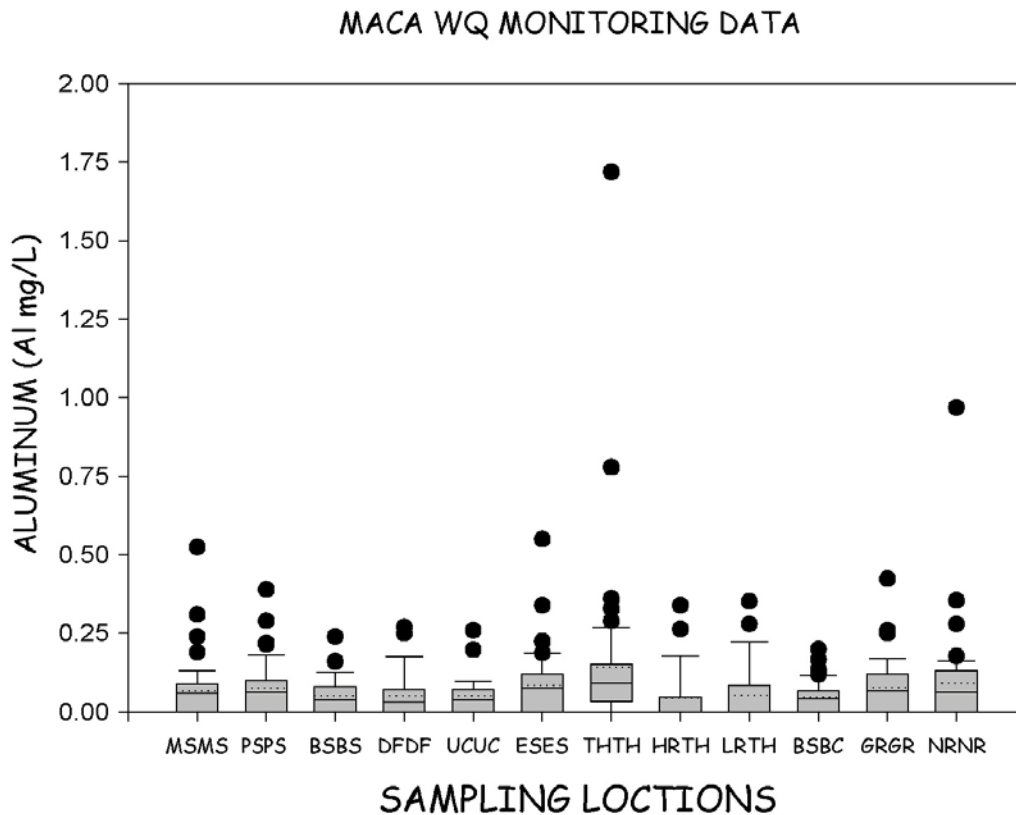
The state standard for sulfate is 250 mg/l (Domestic water supply use). Even the highest outlier (BSBS) is about 70 mg/l. It is interesting that sulfate levels among the different watersheds parallel strontium values, with the exceptions of HRTH-LRTH and NRNR-GRGR in comparison (the formers higher than latters in strontium but lower in sulfate). These ratios may be of interest to those wishing to further explore the hydrogeochemistry of the watersheds.



Cations

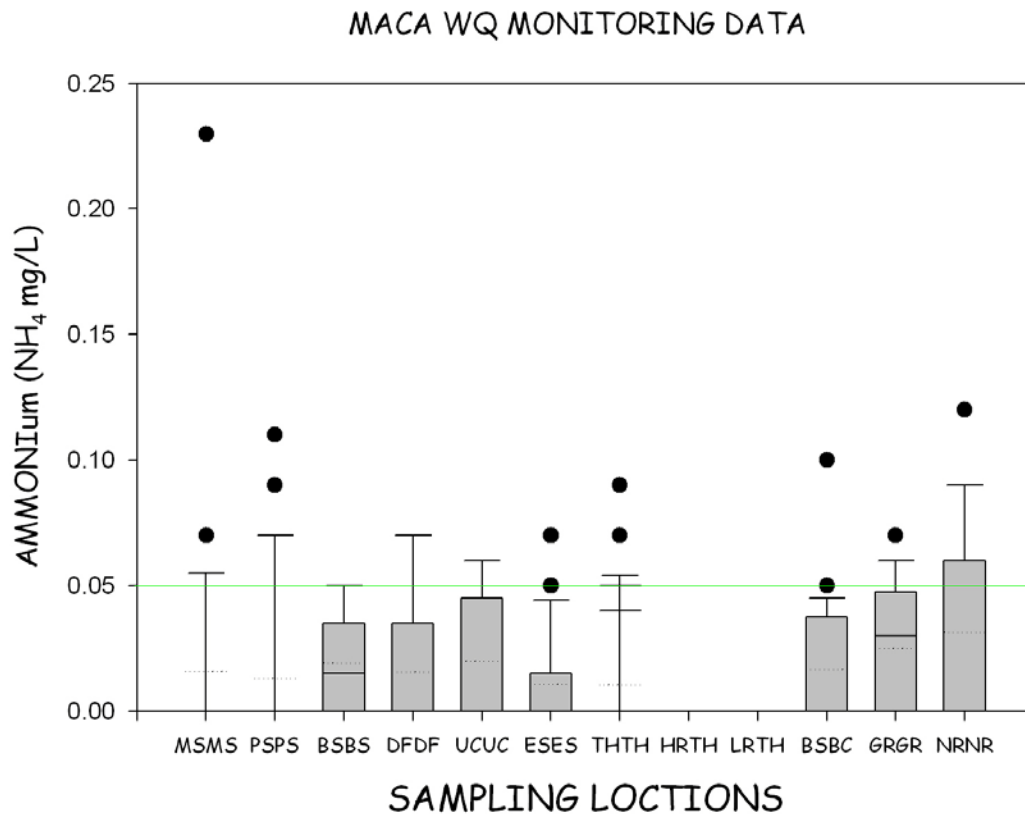
Aluminum

No state standard exists for aluminum. In general, aluminum concentrations are low, with the exception of a few outliers. The highest value was taken in Owl Cave (just upstream of Turnhole Spring, and is sampled when Turnhole's flow does not reach the surface of its rise-pool, typical for summer, low flow conditions) on August 10, 1992. Other data from this sample collection are within normal ranges, and do not match other outliers at the Nolin River and Echo River Spring. There is no evidence that these outliers represent a significant threat to park water quality as they are isolated occurrences and not associated with a particular flow condition. Potential sources of aluminum include weathered bedrock.



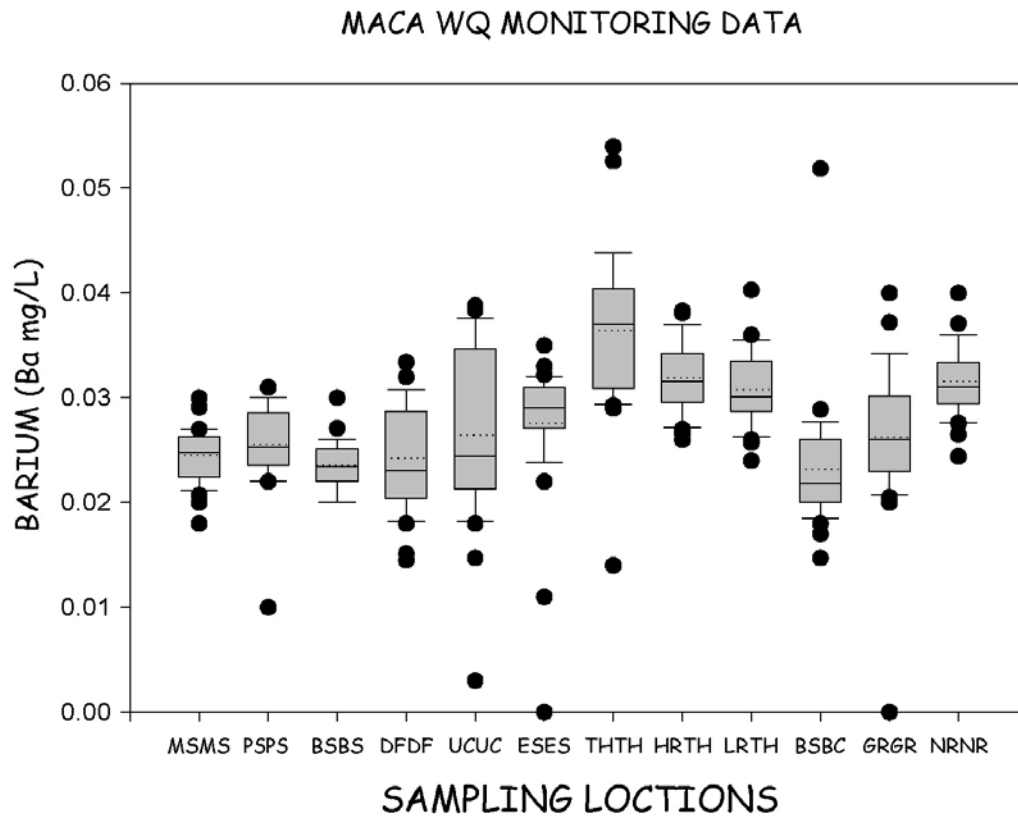
Ammonium

The state warm water aquatic standard for ammonium is 0.05 mg/l. The 95th percentile for most park waters approach this limit, and on occasion – mostly during drought flow conditions, exceed this standard. It is worth noting the number of samples in the accompanying data, which are lower than most parameters as ammonia was not always included in laboratory testing. Highest ammonia levels are found in the Green and Nolin rivers, and in springs on the north side of the park (BSBS, DFDF, UCUC, and BSBC). Ammonia sources include sewage, but it is unlikely the source for these north side sites as there is little development within their watersheds.



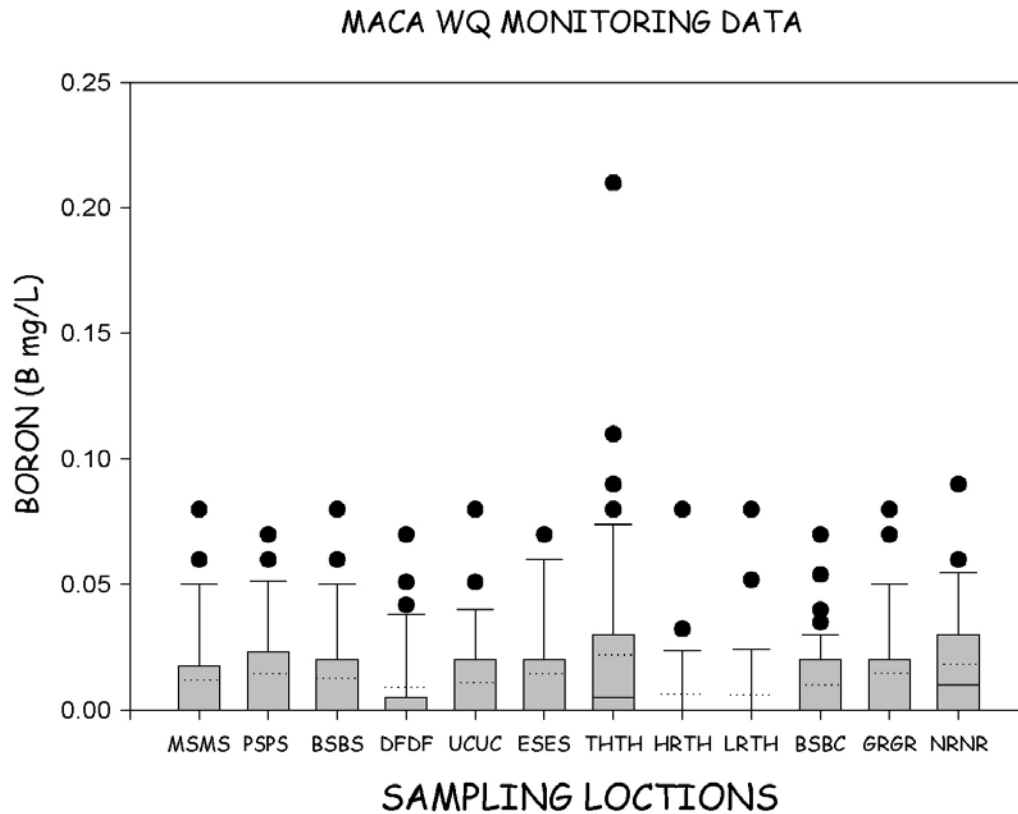
Barium

The Domestic Drinking Water Source standard for barium is 0.2 mg/l. All samples taken are well below this limit (mean values are nearly one order of magnitude below this threshold). Again, Turnhole had the highest values. Potential sources of barium include erosion of bedrock. As the Turnhole basin is the largest groundwater watershed monitored, with a wide variety of different rock types, this may explain the slightly higher levels, although it may be derived from oil field brines leaking into the aquifer. In any case, barium remains low, even when compared to Buffalo Spring (BSBC) which can be considered a background reference site. The PQL for barium is 0.0035 mg/l.



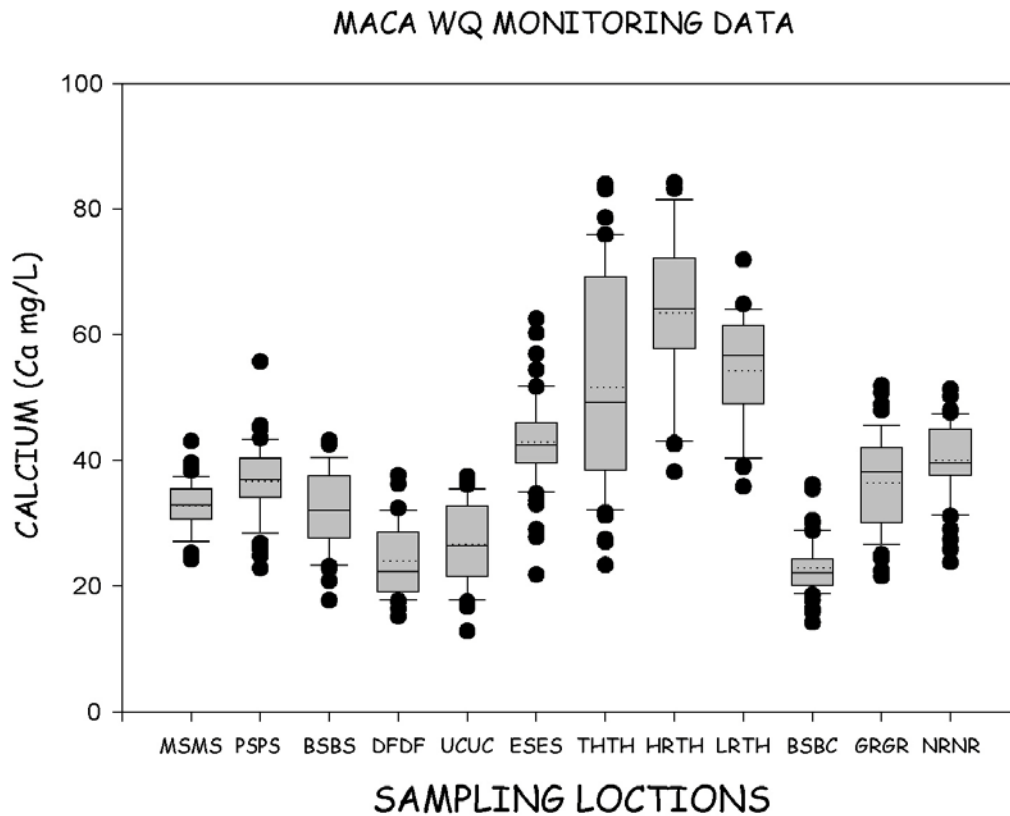
Boron

No water quality standard exists for boron, and levels are very low. It is curious that boron, along with most other “trace” elements are typically higher at Turnhole Spring than other sites. No obvious source of boron is known. The PQL for boron is 0.115 mg/l.



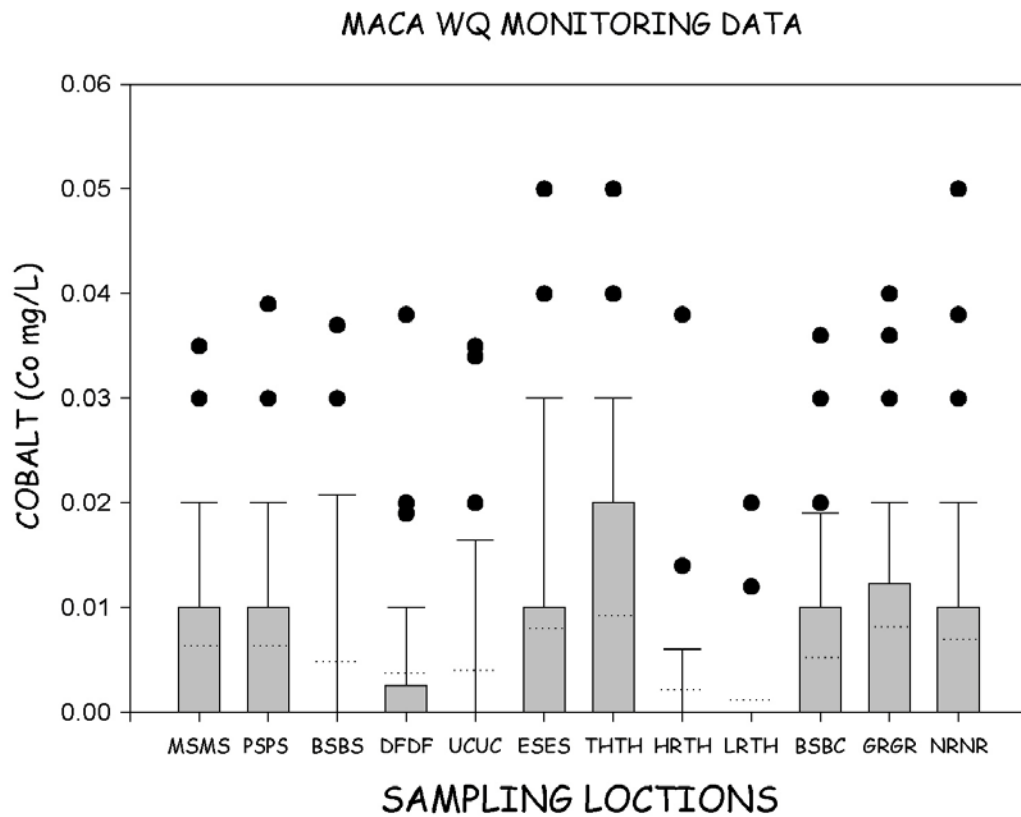
Calcium

No standard exists for calcium, and as obvious, calcium levels are very high in the karst waters of the park. Like ANC, there seems to be a correlation between the amount of exposed limestone and contact within the watersheds and calcium levels. Buffalo Creek, where there is little exposed limestone and transfer rates are very high, has a tight range of low values when compared to Turnhole (THTH). The wide range of values of THTH reflect flood and drought flow, which has strikingly different chemistries over these flow conditions (drought flow = high ionic strength waters, flood flow = low ionic strength waters). This pattern is also seen in SPC. The PQL for calcium is 0.115 mg/l.



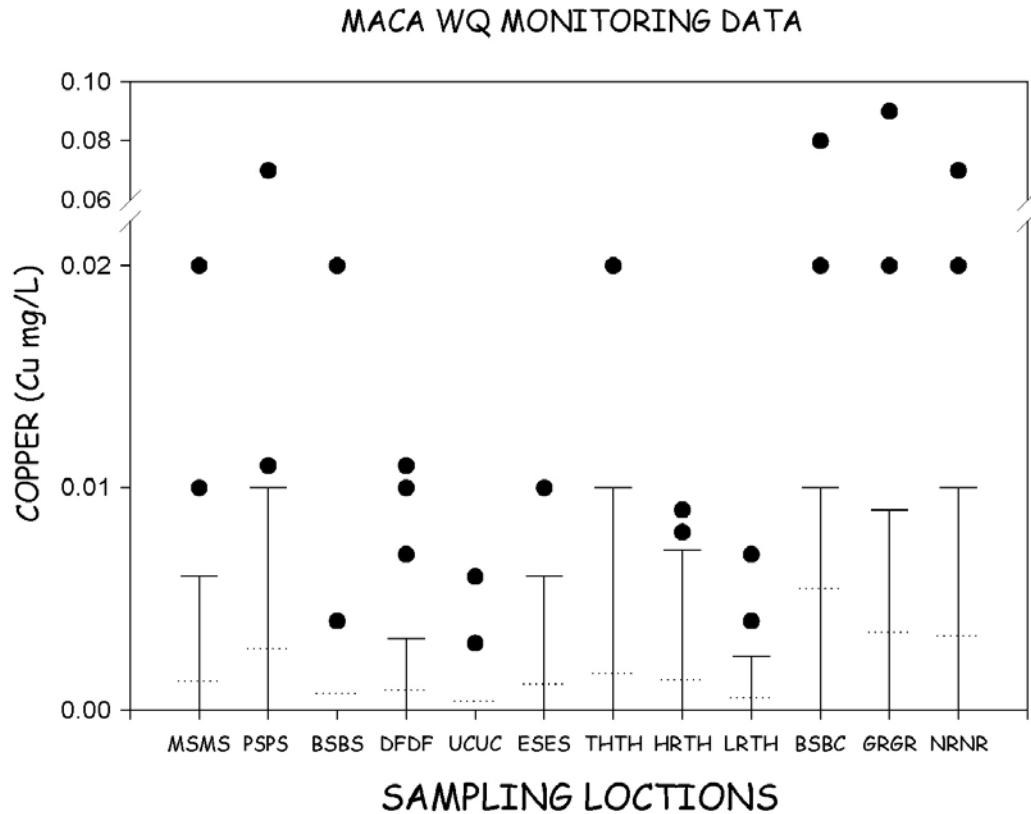
Cobalt

No water quality standard exists for cobalt, and the Florida Geological survey states that aquatic life tolerates cobalt concentrations over a wide range (3-10 mg/l), and that mineral weathering is a common source. Cobalt levels in the park's waters are very low and all sites range from 0.0 mg/l to about 0.04 mg/l, well below what is considered detrimental to aquatic life. All samples fell below the PQL for cobalt of 0.060 mg/l.



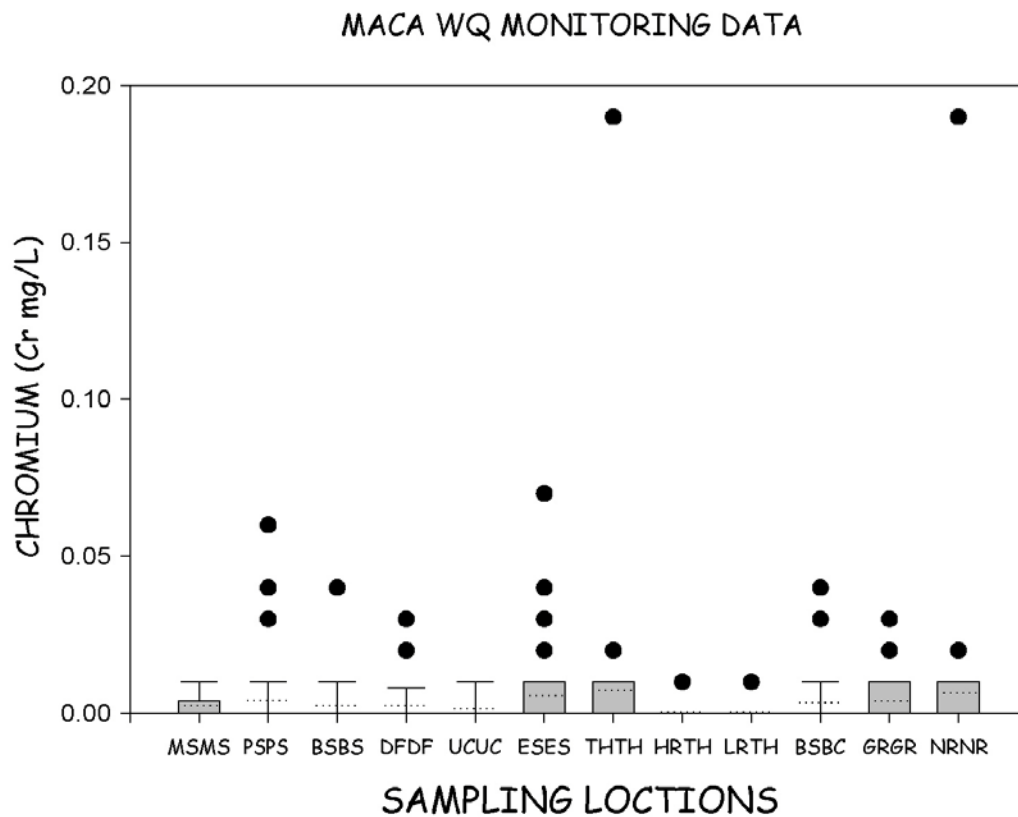
Copper

Copper limits, as with many metals, are governed by hardness values; the greater the hardness, the less likely copper exists in a dissolved phase and therefore less toxic to aquatic life. Copper values in park waters are very low, and are generally below detection limits. There is no correlation between copper values and watersheds, as all are low. The PQL for copper is 0.035 mg/l. More on copper, chromium, lead, and zinc is found at the end of this section.



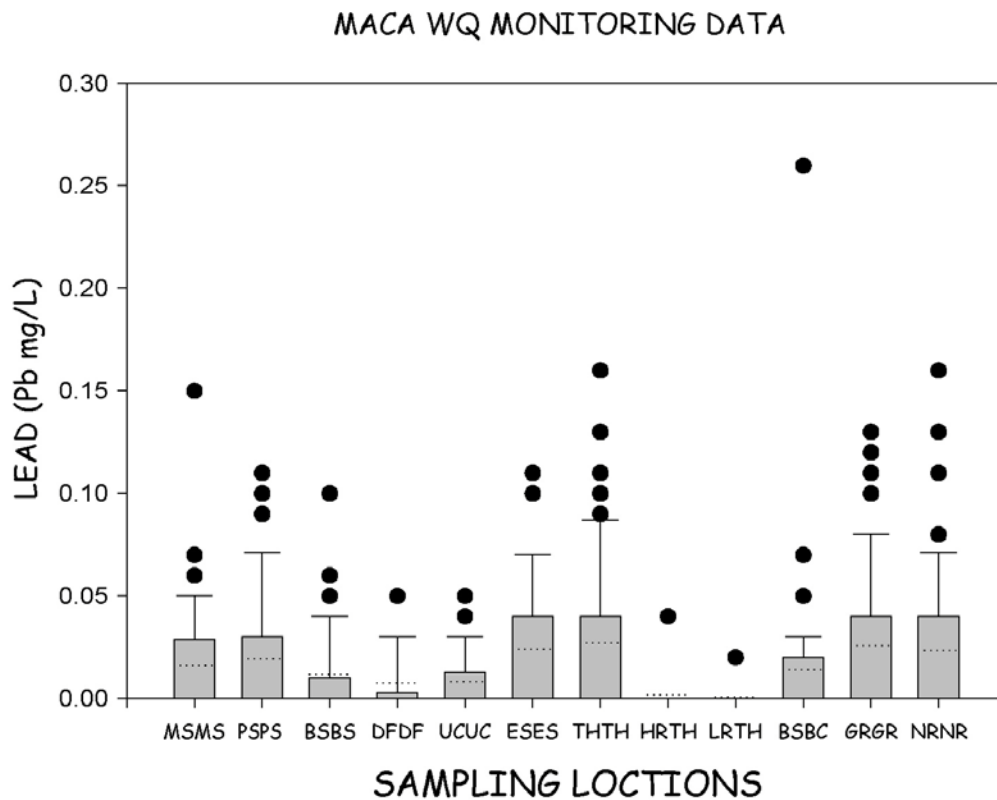
Chromium

With the exception of two outliers (THTH and NRNR) of 0.190 mg/l, chromium values were bordering on the range of detection (0.008 mg/l), and below the state standards for chronic exposure for warm water aquatic life. One would not expect chromium to be in a dissolved phase in waters with high bicarbonate alkalinities and relatively high pH values that are common throughout park waters. Metals, such as chromium, are only mobile under very low pH ranges and tend to form relatively insoluble carbonate-complexes in highly alkaline waters. The PQL for chromium is 0.040 mg/l. More on copper, chromium, lead, and zinc is found at the end of this section.



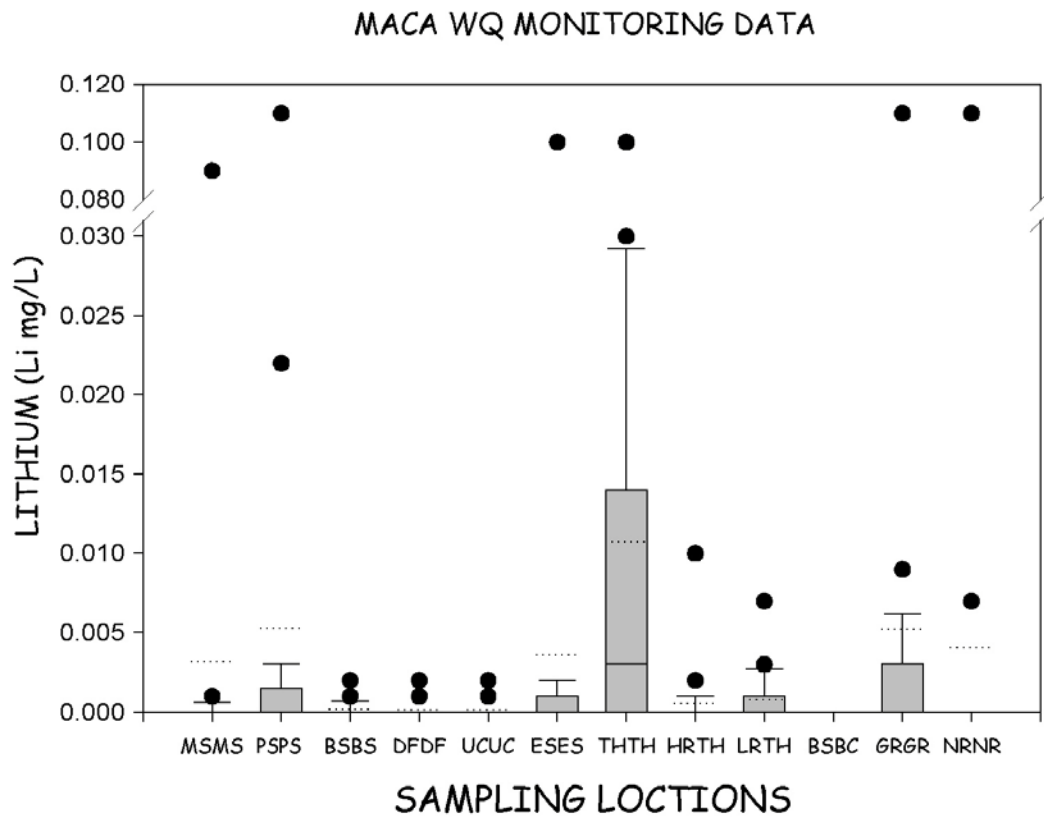
Lead

Lead occurs with a mean concentration of approximated 0.02 mg/l, with outliers generally between 0.10 and 0.15 mg/l. There is no obvious explanation of the distribution of lead levels and land use, however there seems to be a slight increase at sites being drained from outside the park. It is quite possible that lead, as in several other trace metals, that “detectable quantities” may be an artifact of the laboratory. For example, the only “detectable” levels of lead were found by the USFS laboratory, while the KGS lab did not find detectable concentrations. More on copper, chromium, lead, and zinc is found at the end of this section.



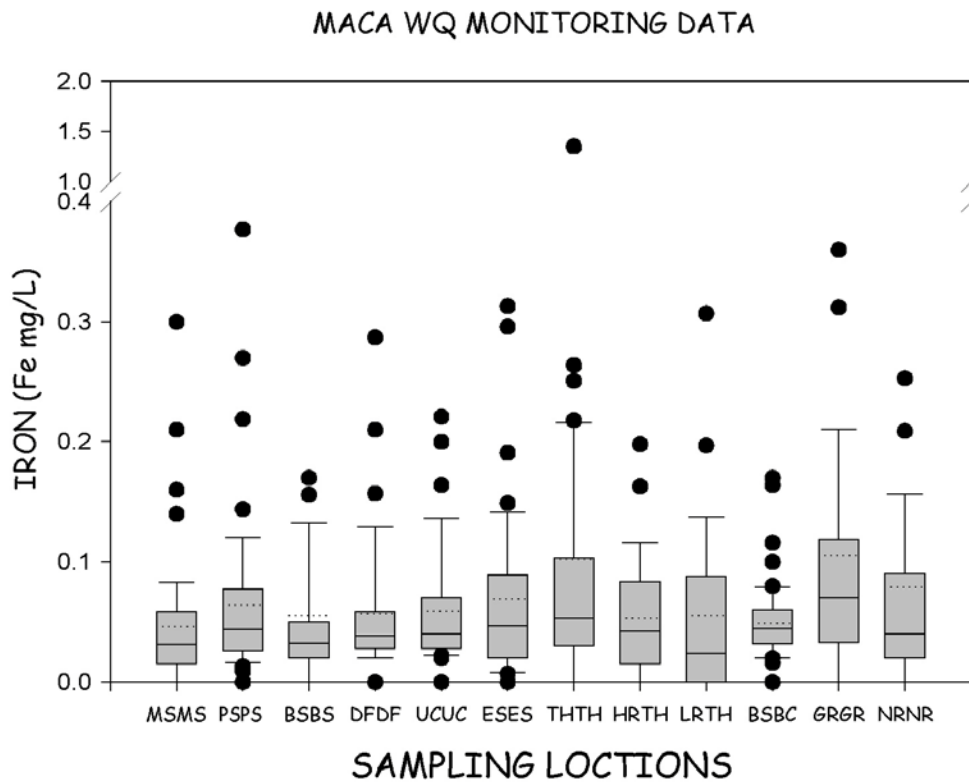
Lithium

The state sets no standards for lithium, and the USEPA Water Quality Criteria (1994) reports that, with respect to human health, it is beneficial in concentrations less than 1.25 mg/l. Lithium values remain very low in all monitored sites, generally not rising above 0.005 mg/l, however THTH consistently had values higher, with a mean of 0.011 mg/l. The PQL for lithium is 0.015 mg/l.



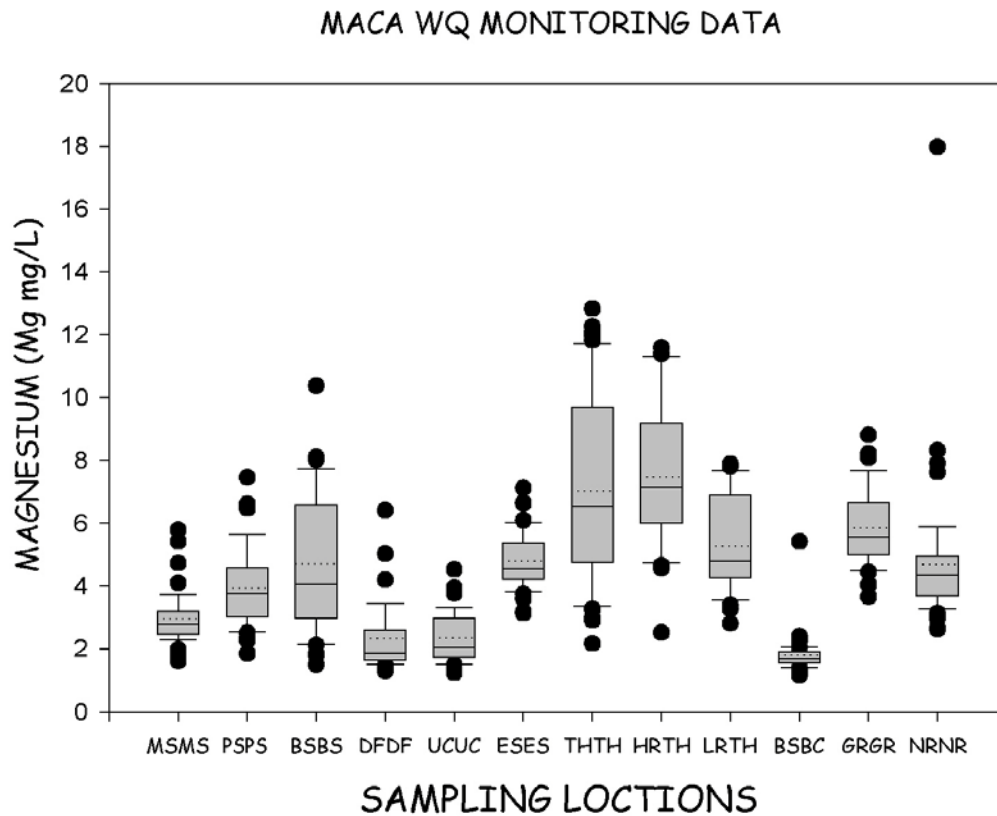
Iron

Iron levels, set by the state for chronic exposure of warm water aquatic life is 1.0 mg/l. Iron, like most metals, does not exist in large concentrations in high-alkaline waters common to limestone terranes – one reason why Kentucky produces the best whiskies in the world by using limestone spring waters, which are largely devoid of iron that imparts a bitter taste to the distillate. With the exception of one outlier at THTH (1.35 mg/l) iron concentrations are very low, generally less than 0.10 mg/l. Likely iron sources are from the weathered siliclastic bedrock which contains minor amounts of pyrite. The PQL of iron is 0.355 mg/l.



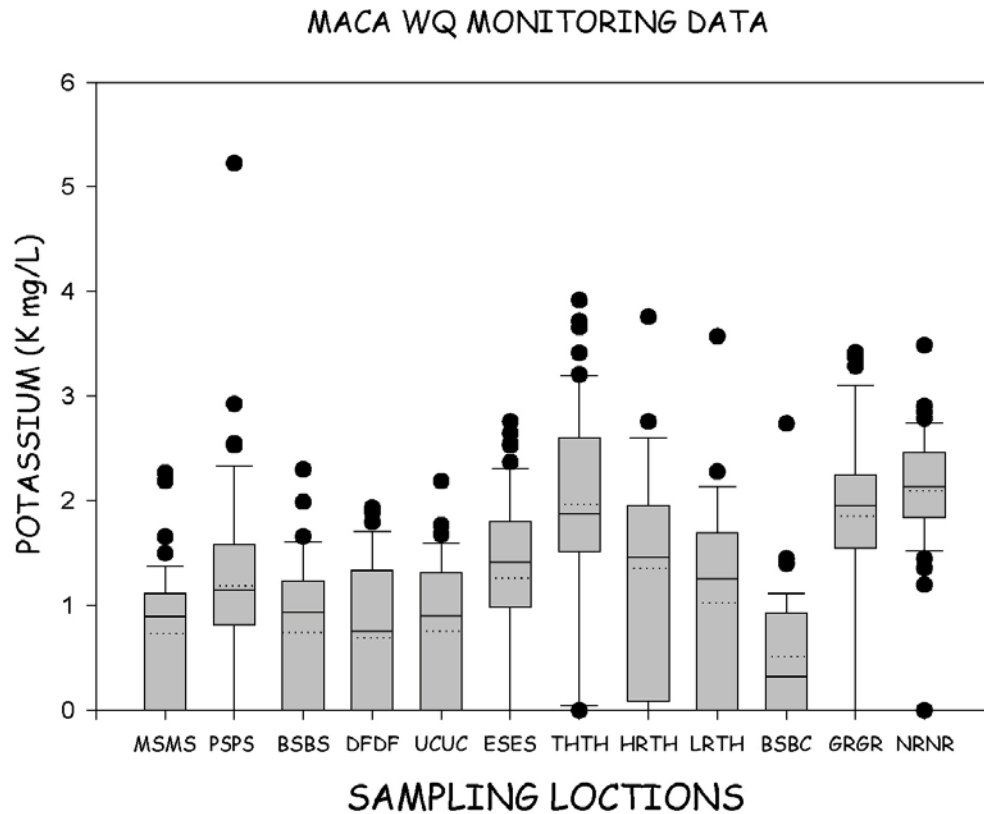
Magnesium

Limits are not set for magnesium at state or federal agencies. Magnesium sources are weathering of bedrock, like the ubiquitous dolostone found throughout the basal carbonate aquifer. Magnesium, like calcium, tell us something about the hydrogeology of the watershed. THTH has the widest range, bracketed by lower concentrations during flood flow, and higher levels during base flow, as reflected in longer residence times of the water in this carbonate-dominated watershed. Conversely, the limited exposure of carbonates in the BSBC watershed, coupled with rapid groundwater transfer, narrow the magnesium range. The PQL of magnesium is 0.150 mg/l.



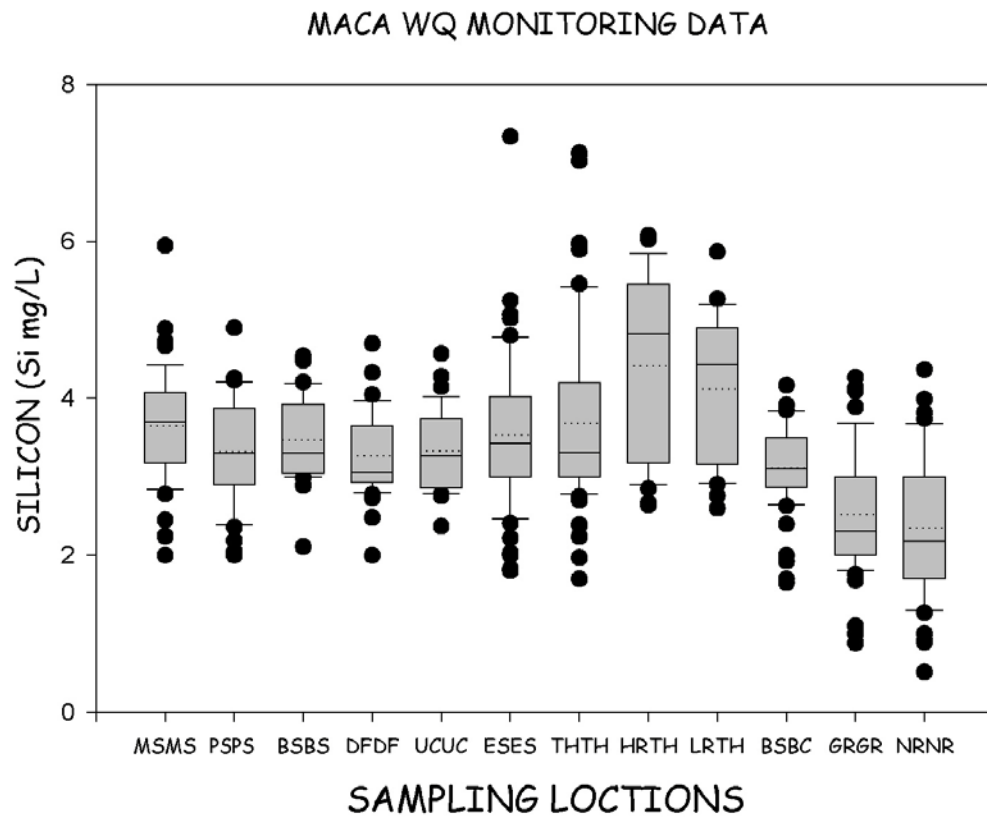
Potassium

No state standard exists for potassium, and sources include commercial fertilizers and natural weathering from bedrock. Potassium levels range from zero to an overall mean of about 1 mg/l. THTH consistently had the highest levels of this ion, perhaps reflective of the agricultural-dominated land use of its watershed. The PQL for potassium is 6.0 mg/l.



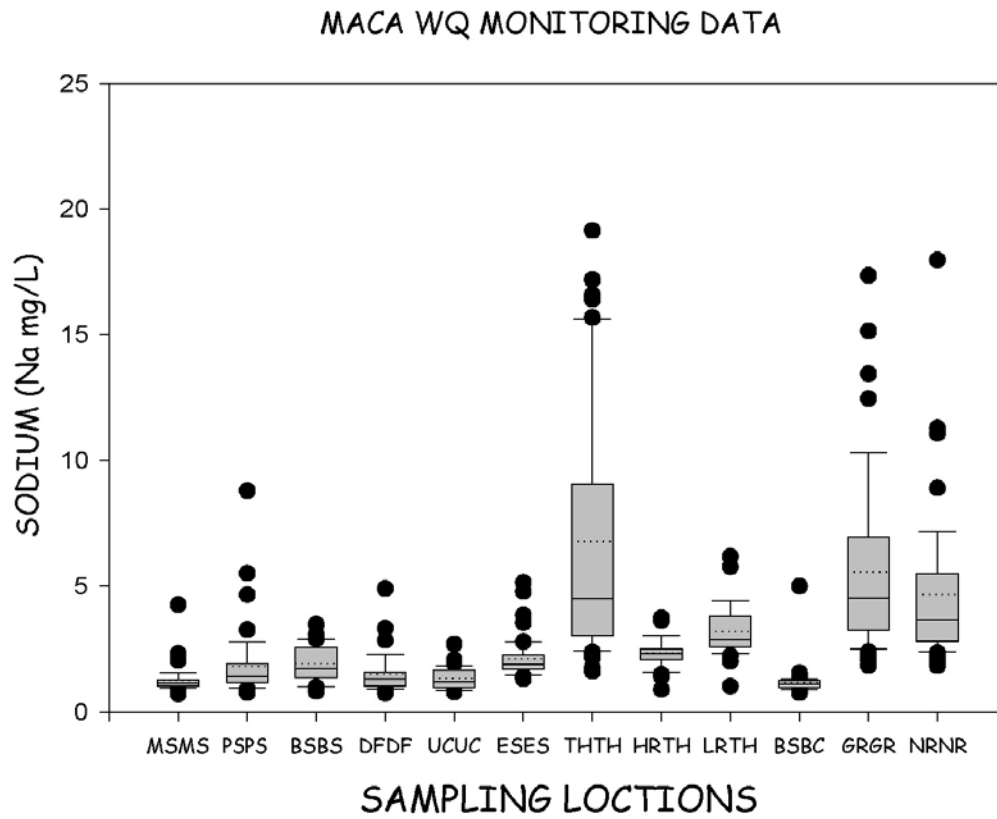
Silicon

There are no state or federal limits on silicon, and these data were collected as an element in the broad-spectrum of ion analysis. The most likely source of silicon is from weathered siliclastic grain cement, common throughout all watersheds. Range variations may be caused by the amount of available siliceous strata within a given watershed. The PQL for silicon is 0.170 mg/l.



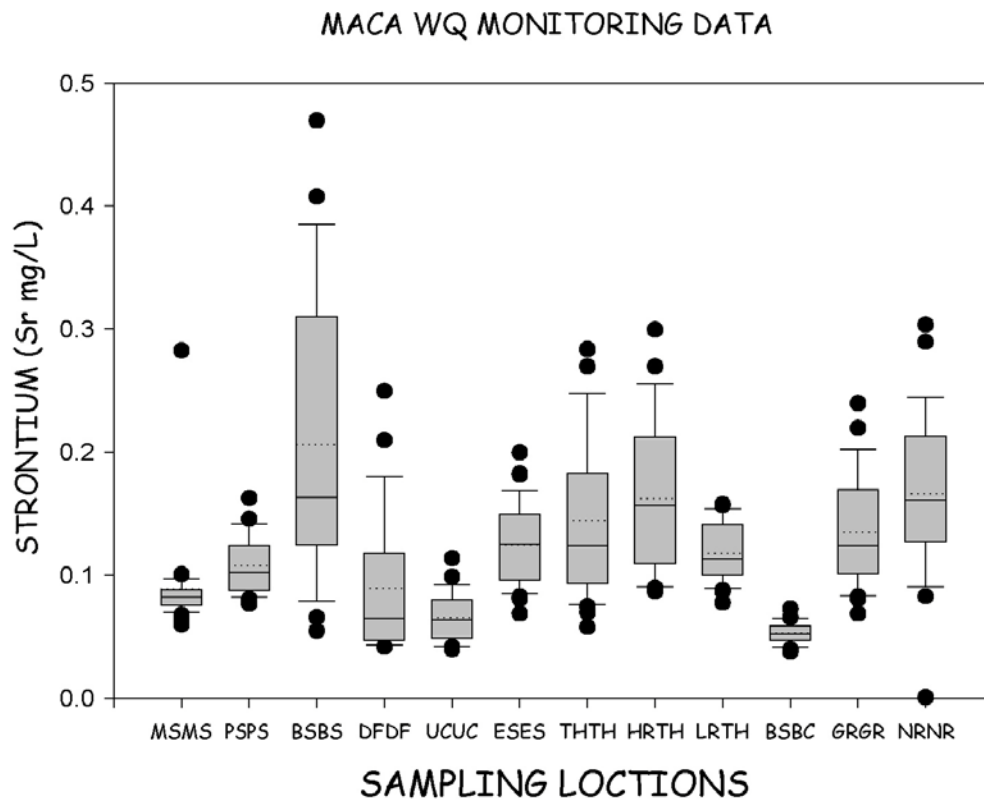
Sodium

No state or federal limits are set for sodium. Relative concentrations of sodium parallel those of chloride in every watershed. Sodium sources are natural background from precipitation and oil field brines. The PQL for sodium is 0.090 mg/l.



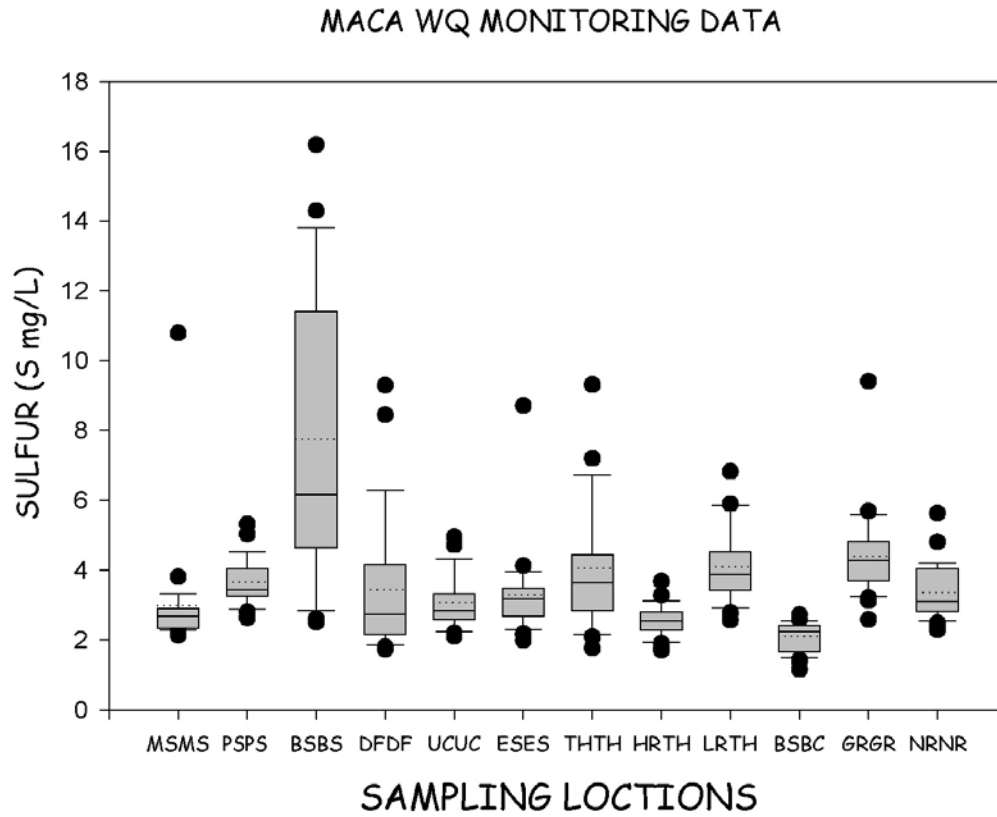
Strontium

No state standard exists for strontium, and the USEPA (also with no set limit) claims that strontium (is believed essential for human and animal health) is no more toxic than calcium. Strontium levels are predictable per watershed with the highest found in BSBS. Dye tracing of the Big Spring watershed suggests that strontium is migrating upwards along a the Cub Run fault from the evaporite beds of the lower St. Louis Limestone. These beds contain gypsum and anhydrite, and celestite (SrSO_4) is commonly found with these calcium-sulfate minerals. Strontium variations in other watersheds may simply be indicative of the amount of celestite being dissolved into their waters. The PQL for strontium is 0.005 mg/l.



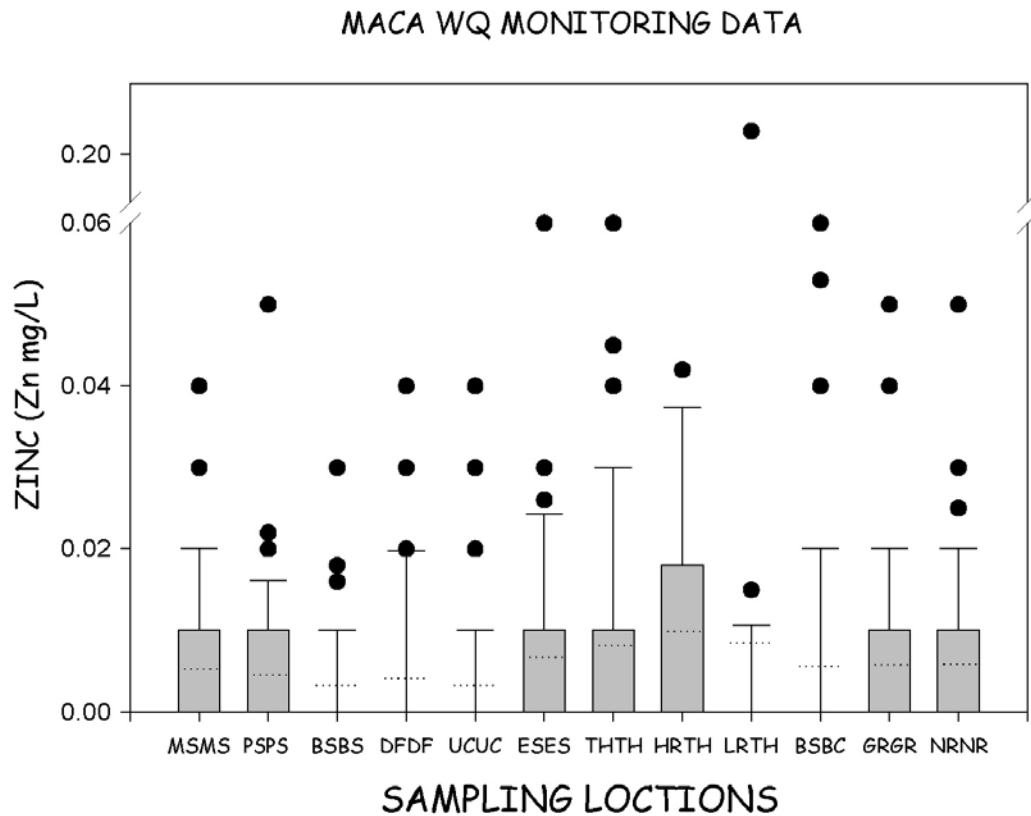
Sulfur

Sulfur, of course, is a component of the sulfate molecule, and produces the same pattern across the watersheds as does sulfate. There are no state or federal standards for sulfur. The PQL for sulfur is 0.150 mg/l.



Zinc

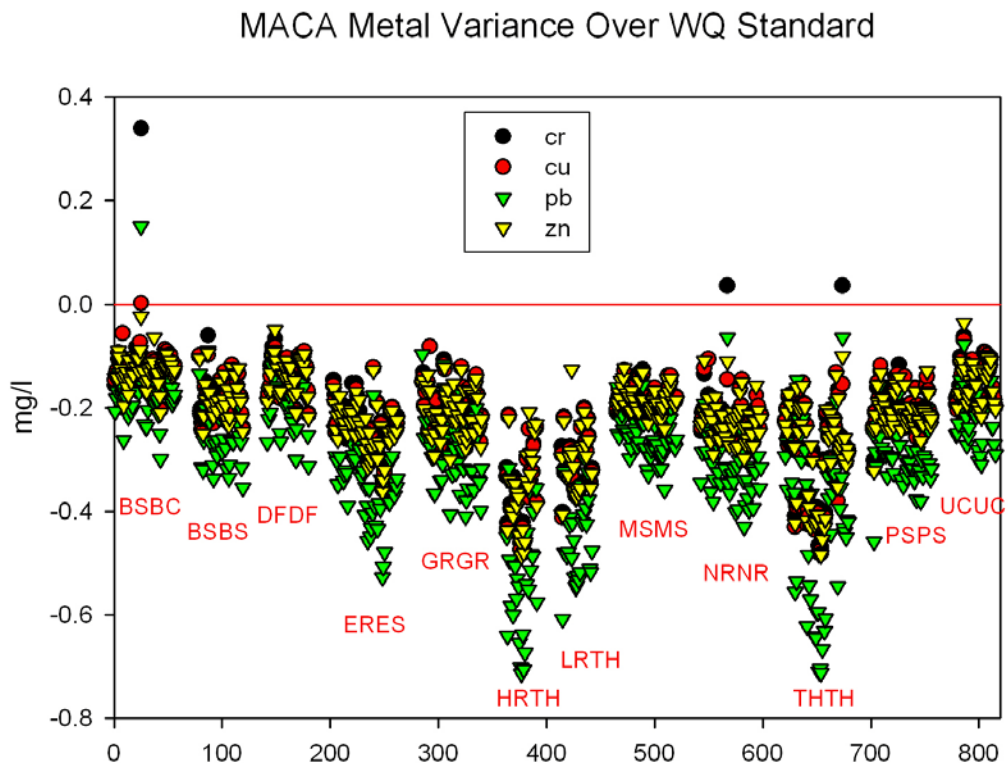
The state sets a low limit for zinc (the highest standard set by Chronic Warm Water Habitat). The USEPA Secondary Maximum Contaminant Level is set at 5.000 mg/l. The highest value found in the data was an outlier of 0.2 mg/l at LRTH. Zinc values are essentially zero across all monitoring locations, as would be expected as dissolved phase zinc, like most heavy metals, can only exist in waters of very low pH. The state standard for zinc is 0.106 mg/l in a hardness of 100 mg/l CaCO_3 . The PQL of zinc is 0.020 mg/l. More on copper, chromium, lead, and zinc is found at the end of this section.



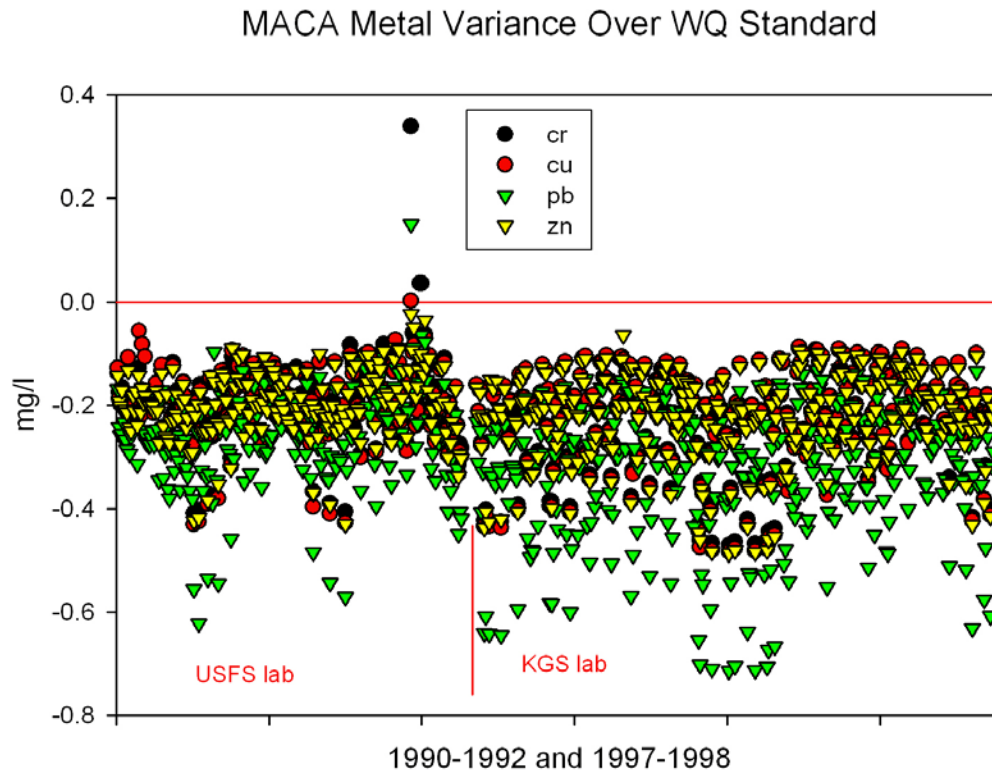
Metals

Dissolved chromium, copper lead and zinc were analyzed and presented above. State water quality standards are not as easy to apply as others. Rather than a simple standard, these metals require a calculation relative to water hardness, as metal toxicity is a function of hardness. The “harder” the water, the less toxic the metal, thus a higher concentration is set as a standard. The following graph is plotted as variances in mg/l above or below chronic exposure levels in warm water aquatic habitats (no specific standard is set for cold water). Each plot in the graph is calculated with calcium hardness as expressed as mg/l CaCO_3 to create a “standard” for a specific sample. Then this standard was subtracted from the metal concentration and plotted. Any variance above the zero line is above the chronic exposure standard for the time the sample was taken. Samples in this graph are grouped by site.

There are five apparent violations of a metal standard in the database. It is curious that each case shares a common sample date, March 10, 1992. Based on this coincidence, it is possible that these apparent violations are an artifact of the sampling or analysis. At no other time, with a data set of nearly 600 samples, was a standard violated.



Metals can also be viewed in a relative time-series. In the following graph, the same dataset as above is presented over time, to see if any obvious trends exist. There are no apparent trends, either positive or negative. The March 10, 1992 sampling event with the “apparent” violations is obvious. It is also interesting that the time-series shows no apparent shift in reported concentrations as laboratories were changed between June and August 1992. Review of both graphs do not suggest that these metals warrant long-term monitoring.



General Water Quality Status

Water quality of the 12 sites sampled at MACA is both good and bad. It is good in respect to most dissolved ions, however bacteria and turbidity levels are quite high after runoff-producing rainfall events. Atrazine is found in park waters, namely the rivers and within the Turnhole Spring karst watershed following the application season – spring and summer. Atrazine is also found in the rivers coincidental to fall draw-down of the lakes.

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. With exception of the aforementioned turbidity and bacteria issue, all other parameters were below state standards. The park should consider expanding its capabilities of suspended sediment quantification. While total suspended sediment analysis could shed more light on sediment levels – more accurately than turbidity – it is labor-intensive and reports a rather homogenized value. As the park is the recipient of many conservation efforts within its watershed, the ability to quantify suspended sediment into size classes may be very beneficial to the conservation efforts. The use of a particle size analyzer may be most cost-effective in the long run. It is recommended that the core four field parameters plus suspended sediment quantification, bacteria, and atrazine 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
E. coli and Total Coliform
Suspended Sediment Quantification
Atrazine*

* Atrazine sampling should include: Green and Nolin Rivers, Pike Spring, Echo River Spring, Logsdon and Hawkins Rivers, and Turnhole Spring from February through July; and the Green and Nolin Rivers from October through December.

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