

# Water Quality in the Upper Crystal River and Coal Creek Basin

Prepared for Roaring Fork Conservancy



by

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## Executive Summary

The 363 square mile Crystal River Sub-watershed is located in the southwestern part of the Roaring Fork Watershed, extending from peaks in the Elk Mountain Range to the Town of Carbondale, where the Crystal River joins the Roaring Fork River. The Crystal River Sub-watershed contributes more than one-half of the peak flows to the Roaring Fork Watershed. The sub-watershed has a long mining history, and extensive areas of sedimentary rock formations significantly influence its landscape, vegetation patterns, and water quality.

Roaring Fork Conservancy, among others, is concerned about human impacts on the Crystal River and in the sub-watershed's Coal Basin, such as development in and near the riparian corridors, the lingering effects of coal mining activities, and associated land uses, including roads, logging and grazing. Colorado Mesa University analyzed water quality data gathered over more than 50 years, by several third party sources, in order to assess water quality in the Crystal River and Coal Basin and prepare this report. Focusing on 9 sites (5 along the Crystal River and 4 in Coal Basin) it examined the water quality data with the following questions in mind:

- For those parameters that have water quality standards, are the streams in compliance with those standards?
- For each site and water quality parameter, is there a trend over time?
- For each parameter, are there useful or interesting comparisons between sites?
- Are there any other generalizations suggested by the data?
- Does the data adequately characterize existing conditions? Are there any data gaps?
- What recommendations are suggested for future water quality monitoring?

The analysis concluded that the primary water quality problem in the Crystal River and Coal Basin is the iron content in sediments being washed into the river and streams. Approximately 15% of the samples analyzed for total recoverable iron exceeded the Colorado water quality standard for this parameter, which is designed to protect aquatic life.

Dissolved oxygen results fell below the aquatic life-based water quality standard in approximately 8% of all samples. The majority of these problematic results occurred in the Crystal River at Penny Hot Springs in the mid- to late-1990's. It appears to be a localized problem.

Recoverable arsenic results exceeded the water quality standard in approximately 8% of the samples analyzed. This particular standard is based on the use of a stream for a domestic water supply, which is not taking place in the Upper Crystal River or Coal Creek at the present time. Arsenic does not present a problem for aquatic life.

Approximately 7% of the water temperature results were found to be higher than the temperature limits designated in the applicable Colorado water quality standards, which are also based on protection of aquatic life. However, because these temperature measurements were not conducted in the manner specified in the water quality regulations, they do not represent definite

exceedances of the standard. The majority of the high temperature results occurred at Site 3 - the Crystal River above Avalanche Creek. This may be due to the discharge from Penny Hot Springs. More generally, higher temperatures that sometimes occur throughout the area may be a result of shallow water found in channels that have become overly wide due to human activities.

Several other water quality parameters examined exceeded standards less frequently than those described above and are not considered to be a widespread or on-going problem. These parameters include pH, nitrate, cadmium, copper, lead, and selenium.

The purpose of monitoring water quality parameters is not only to compare conditions against state standards, but to detect any trends or patterns that are occurring, such as improvements due to restoration work or degradation due to the occurrence of new problems. The report recommends a quarterly water quality monitoring program to establish a baseline for the Crystal River Sub-watershed. Ideally, all parameters with state standards would be monitored. However, if funding is scarce, monitoring could be limited to parameters that reveal basic aspects of water quality and those that are of the most concern based on historical data and current issues. This list could include temperature, pH, dissolved oxygen, total phosphorous, dissolved iron, total recoverable iron, and selenium. In all cases it is recommended that specific conductance be measured, since it is an easy way to observe changes in total dissolved solids. The following locations are recommended:

- Coal Creek immediately upstream from its confluence with the Crystal River;
- The Crystal River immediately above the confluence with Coal Creek; and
- The Crystal River at a location downstream from the confluence with Coal Creek.

While there is concern about large inputs of sediment into Coal Basin from disturbed areas within its watershed, and input of sediment from Coal Creek into the Crystal River, existing data is inadequate to determine the true extent of this issue. Future water quality monitoring should also include a program to address this data gap.

Annual collections of macroinvertebrates and pebble counts are also recommended for the Crystal River Sub-watershed. Benthic macroinvertebrates are a preferred biological indicator for the assessment of biological integrity, and they are particularly valuable for capturing impacts from episodic events, such as intense rainfall, that routine water quality sampling may miss.

## 1.0 Introduction

The purpose of this report is to evaluate and interpret existing water quality data for the Crystal River and Coal Basin, and present recommendations for future water quality monitoring efforts. Roaring Fork Conservancy (RFC) and its partners are concerned about human impacts on the Crystal River and in Coal Basin, such as development in and near the riparian corridors, the lingering effects of historic coal mining activities, and associated land uses such as roads, logging and grazing. Preliminary results were presented by the author at the [Coal Basin & Crystal River Area Restoration Workshop](#) in May of 2012, which helped RFC and its partners set restoration priorities and identify ‘next steps’. In particular, three specific near-term projects were identified at the *Workshop*:

- Establish a priority list of water quality parameters and sites for baseline water quality monitoring and detection of future changes. Conduct water quality sampling at regular and frequent intervals to facilitate building correlations and detecting trends. Measure stream flow and storm events (precipitation) and correlate concentrations of water quality parameters with stream discharge and magnitude of storms.
- Conduct regular macroinvertebrate sampling at previous sampling sites to develop a more robust data set for Coal Basin and the Crystal River. Correlate the results with various stages in the stream hydrograph.
- Collect in-channel sediment data (*e.g.*, grain size, mineral content) at the same time as water quality sampling and macroinvertebrate sampling are being conducted.

## 1.1 Data used and site selection

Colorado Mesa University analyzed data gathered by several sources for this report, including data from: U.S. Geological Survey (USGS), U.S. Forest Service (USFS), Colorado Department of Public Health and Environment (CDPHE), Colorado Parks and Wildlife’s Colorado River Watch Program (CPW-RW), and RFC staff and volunteers. Surface water quality data was collected at 30 sites. Data on groundwater or spring water quality was collected at 9 sites. Overall, the data extended from 1960 through 2012, although nearly all sites had a much shorter period of record. Many of these sites were only sampled in the 1970’s and are located near earlier Mid-Continent Resources coal production activities. Nine sites with data for at least 3 years were selected to be the focus of this study (collectively, the “Sites”). The Sites are listed in [Table 1](#) and shown on the map in [Figure 1](#).

Water quality data was examined with the following questions in mind:

- For those parameters that have water quality standards, are the streams in compliance with those standards?
- For each site and water quality parameter, is there a trend over time?
- For each parameter, are there useful or interesting comparisons between sites?

- Are there any other generalizations suggested by the data?
- Does the data adequately characterize existing conditions? Are there any data gaps?
- What recommendations are suggested for future water quality monitoring?

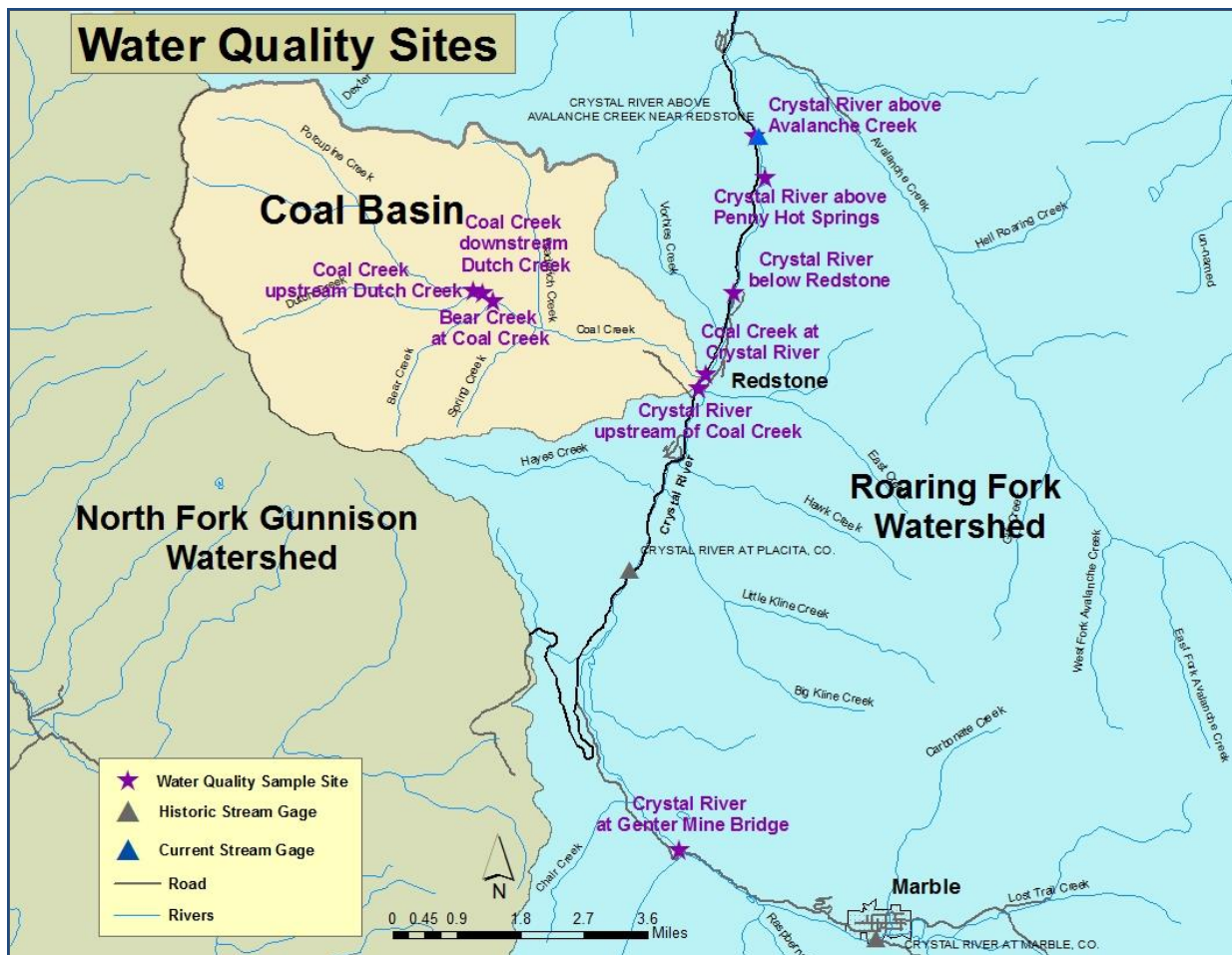
**Table 1. Sites selected as the focus of this study and associated data sources.**

**Crystal River**

- Site 1 - Crystal River at Genter Mine Bridge (CPW-RW)
- Site 2 - Crystal River upstream of Coal Creek (CDPHE)
- Site 3 - Crystal River below Redstone (CDPHE and RFC)
- Site 4 - Crystal River above Penny Hot Springs (CPW-RW)
- Site 5 - Crystal River above Avalanche Creek (USGS), co-located with stream gage

**Coal Creek Basin**

- Site 6 - Coal Creek upstream of Dutch Creek (USFS)
- Site 7 - Coal Creek downstream of Dutch Creek (USFS and RFC)
- Site 8 - Bear Creek at Coal Creek (USFS)
- Site 9 - Coal Creek at Crystal River (CDPHE and RFC)



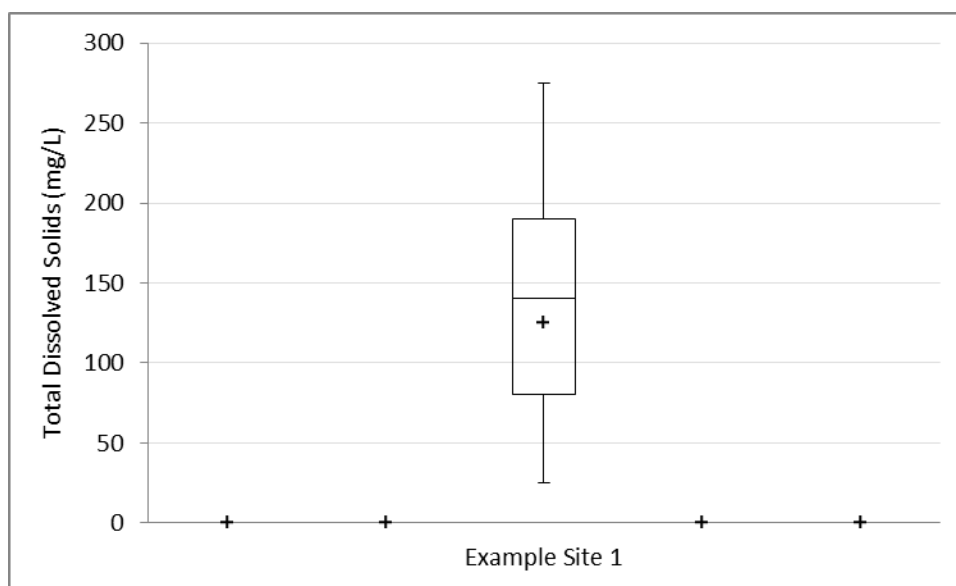
**Figure 1. Location of sites.**



## 1.2 Data analysis and presentation

A simple, direct inspection of the data was used to detect conditions such as exceedances of water quality standards. A statistical software package specifically designed for water quality data, WQSTAT Plus (version 9.4), was used to calculate summary statistics, compare sites, look for trends, and perform statistical tests.<sup>1</sup> Microsoft Excel was used for repetitive calculations, such as hardness-dependent standards for metals, and pH- and temperature-dependent standards for ammonia.

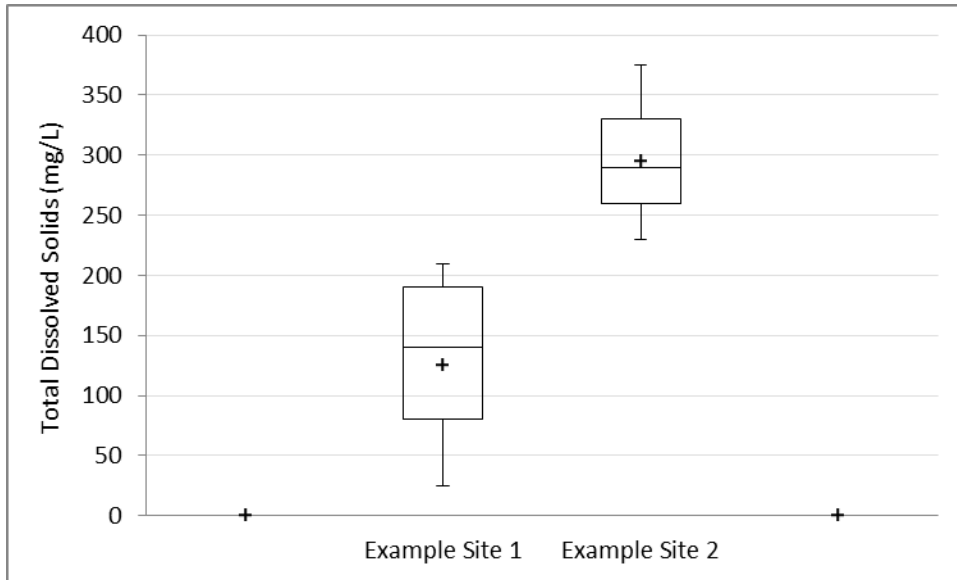
Box plots will be used extensively in this report to display data. A box plot is a convenient way of showing characteristics of a data distribution. In the example box plot shown below (Figure 2), the bottom of the box is the 25<sup>th</sup> percentile, the “+” is the average of all the data, the line within the box indicates the 50<sup>th</sup> percentile, and the top of the box is the 75<sup>th</sup> percentile. (Twenty-five percent of all the values in the data set being analyzed are below the 25<sup>th</sup> percentile, and seventy-five percent of the values are below the 75<sup>th</sup> percentile. Half of all values are below the 50<sup>th</sup> percentile, which is also known as the middle value or median.) The end of the lower “whisker” is the smallest value among the data, and the end of the upper whisker is the highest value.



**Figure 2. Example of a box plot.**

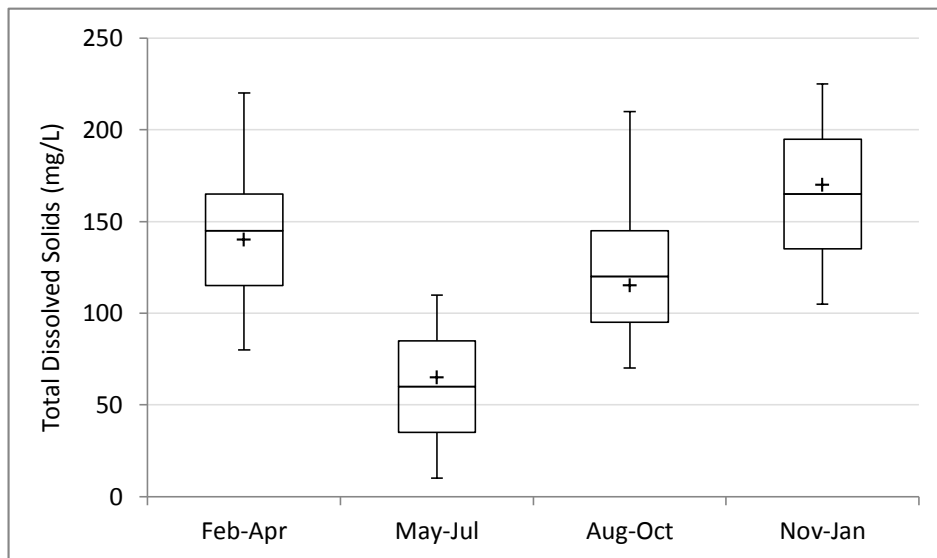
Multiple box plots can be shown in the same figure as a way of comparing data for two or more sites. In Figure 3 below, it is easy to see that there is a difference in the concentration of total dissolved solids between the two sites.

<sup>1</sup> Additional information on this software package is available at <http://www.sanitastech.com/wqstats/wqstats.html>.



**Figure 3. Example of a graph using multiple box plots.**

Multiple box plots can also be used to compare data from one year to another, or between seasons, as shown in [Figure 4](#) below.



**Figure 4. Example of a graph using multiple box plots to compare data over time.**

We are often interested in comparing two data sets to see if there is a significant difference between them (i.e., whether the values in one set tend to be smaller or larger than the values in the other set). The Wilcoxon rank sum test will be used in this study to make such comparisons. This statistical test is specifically designed to be valid for any data distribution—there is no requirement for the data to have a bell-shaped distribution, which is the case for more commonly used statistical tests, such as the student's  $t$  test.

We are also interested in viewing values of a water quality parameter versus the date of measurement to see if there is an upward or downward trend in the values of the parameter. The Sen slope test will be used in this study to determine whether statistically significant trends exist. Like the Wilcoxon rank sum test, this test is valid regardless of the distribution of the data.

## 2.0 Relevant watershed characteristics

The [\*2008 State of the Roaring Fork Watershed\*](#) report provides an overview of the Crystal River Subwatershed (Clarke *et al.* 2008), located in the southwestern part of the Roaring Fork Watershed. The 363 square mile sub-watershed extends from peaks in the Elk Mountain Range (13,513 feet) to the Town of Carbondale (6,052 feet), where the Crystal River joins the Roaring Fork River. Although only a quarter of the land area, the Crystal River Subwatershed contributes more than 50 percent of the peak flows to the Roaring Fork Watershed. The main tributaries to the Crystal River include the North and South Forks of the Crystal River, and Yule, Coal, Avalanche, and Thompson Creeks. The main valley is accessed by State Highway 133, a designated Scenic Byway, from Carbondale over McClure Pass (9,500 feet in elevation) to the North Fork of the Gunnison Basin and its communities of Paonia and Hotchkiss. The Crystal River is one of the few rivers on Colorado's West Slope not affected by dams or transbasin diversions.

The subwatershed is known for its mining history. The Mid-Continent Resources Coal Mine operated in Coal Creek Basin, and historic coke ovens can still be seen at the Town of Redstone, along with Redstone Castle, all originally developed by Charles Osgood. Marble mining continues at the Yule quarry near Marble, and a historic water-driven ore-processing mill remains at the old town site of Crystal.

Extensive areas of sedimentary rock formations significantly influence the sub-watershed's landscape, vegetation patterns, and the water quality of its streams and rivers. The Eagle Valley evaporite is an important source of the dissolved salts found in surface and groundwater. Mancos Shale is a source of selenium, as well as other salts. Limestone and other sedimentary formations in the sub-watershed are soluble enough to be additional sources of salts and minerals dissolved in its river and streams.

Several riparian and instream species of concern are found in the Crystal River Subwatershed, including: flannelmouth sucker; Colorado River cutthroat trout; mountain whitefish; boreal toad; Northern goshawk; bald eagle; American peregrine falcon; boreal owl; northern pygmy-owl; black swift; Lewis's woodpecker; Williamson's sapsucker; olive-sided, willow, and Cordilleran flycatchers; American dipper; purple martin; MacGillivray's and Wilson's warblers; brown-capped rosy finch; Townsend's big-eared bat; pine marten; Canada lynx; American yellow lady's slipper; helleborine; large-flower globe-mallow; canyon bog-orchid; Brandegees fumewort-tall fringed bluebells herbaceous vegetation; beaked spikerush herbaceous vegetation; montane and lower montane riparian forest; narrowleaf cottonwood riparian forest, montane and lower montane willow carrs; lower montane riparian forest, and cattail herbaceous vegetation.

Some key findings from the *State of the Roaring Fork Watershed Report* include:

- Reductions in late summer/fall stream flows in the lower Crystal River and Thompson Creek are due to agricultural and municipal diversions.
- A 2003 study by Grand River Consulting estimated that in the lower Crystal River 27 percent of the years between 1955 and 2000 would have had an irrigation shortage in the month of August. It was further estimated that 66 percent of the years would have had stream flows below the presently-established Colorado Water Conservation Board's (CWCB) instream flow right (ISF) in the month of August, 75 percent in September, and 44 percent in October.
- Nettle Creek, the municipal water supply for Carbondale, shows significant flow alteration for most of the year.
- The following constituents exceeded water-quality standards on more than one occasion at the sub-watershed's monitoring sites on the Crystal River and Coal Creek: total phosphorus, dissolved oxygen, total recoverable iron, selenium, and total recoverable aluminum.
- Coal Creek contributes to the higher suspended solid concentrations observed downstream of its confluence with the Crystal River.
- Throughout much of its length, the Crystal River has been channelized. Road cuts have resulted in the removal and degradation of streambank vegetation and habitat loss on 27 percent of the segment. Agricultural and residential development in the riparian zone has impacted 39 percent of native riparian habitat. Weeds impact more than 50 percent of the surveyed reaches.
- Riparian habitat on both banks is heavily modified or severely degraded on more than 70 percent of the surveyed reaches.
- Along much of the surveyed segment, native cottonwood woodlands that historically lined the river banks are dying and not being replaced. Nesting by Lewis's woodpecker, a species of concern, has been documented in a few of those sites where cottonwood stands remain.
- Colorado Natural Heritage Program (CNHP) identified nine Potential Conservation Areas and the Stream Health Initiative (SHI) identified seven Conservation Areas of Concern.
- No high quality instream habitat is present in the assessment area – with 7 percent 'slightly modified', 18 percent 'moderately modified', 56 percent 'heavily modified', and 19 percent 'severely degraded'.
- In general, brown trout are found in the lower reaches of the sub-watershed, mixed stocks of brook trout and brown trout in middle reaches, and brook trout in the upper reaches. Whirling disease is present in the Crystal River, causing limited natural reproduction of rainbow trout.

- Six tributary streams within the sub-watershed have populations of Colorado River cutthroat trout.

## **3.0 Water quality – a primer**

### **3.1 What determines “water quality”?**

A water quality evaluation determines what substances other than water are present in streams, rivers, ponds, lakes, wetlands, and groundwater. Some substances are beneficial or even crucial (such as dissolved oxygen), while the presence of other substances generates concern because of their potential toxicity. Whether aquatic organisms or any other organisms contacting the water are harmed depends on how much of the substance is present (*i.e.*, its concentration, typically expressed as milligrams of substance per liter of water, or mg/L). Smaller concentrations are less likely to create adverse effects; larger concentrations are more likely. A second key factor is the inherent toxicity of the substance itself—some substances are much more potent than others.

#### **3.1.1 Geochemical effects**

Geochemical influence is one of the most basic factors determining the chemistry of a specific body of water. Natural waters are in contact with soil and rock, and there is the opportunity for any minerals or other chemicals present in that soil and rock to dissolve into the water. Thus, the chemistry of the water can be a reflection of the chemistry of these geologic materials. As an example, consider the water quality parameter called “total dissolved solids” (TDS), which is primarily a measure of how salty the water is. TDS will be low in waters occurring in watersheds dominated by outcrops of igneous rock, such as granite, and soils derived from this rock; TDS will be high in waters where the rock and soils are associated with sedimentary rocks of marine origin, such as the Mancos Shale that is so common in western Colorado. This difference occurs because the marine sedimentary rocks contain an abundance of salts that are soluble in water, while granite is composed of minerals that have a very low solubility. It is important to realize that many toxic substances (such as arsenic and selenium) do occur in natural waters because of their presence in soil and rock. Thus, there is a natural baseline water quality that occurs independent of the presence or absence of people.

#### **3.1.2 Atmospheric effects**

Atmospheric influence is the second most basic factor determining the chemistry of natural waters. Molecules of gas present in the air (such as oxygen and carbon dioxide) are always in motion in random directions. By chance, this random motion brings some of these molecules to the water surface, where they may enter the water and dissolve. The amount of dissolved oxygen present is a water quality parameter that is especially critical to aquatic life, most of which needs oxygen to survive. Dissolved carbon dioxide influences how acidic or basic the water is, which also is important to aquatic life.

“Wet deposition” is another process that transfers gases from air into the water. The random motion of gas molecules sometimes brings them into contact with droplets of water in the air, providing an opportunity for these molecules to dissolve in the droplets. Eventually the droplets may fall to the land surface as rain or snow, bringing those gas molecules with them. An example of this process is acid rain, which occurs when sulfur dioxide or nitrogen dioxide gas are present in the air. When acid precipitation ends up in a stream or pond, it may acidify that water. (The degree to which this occurs depends on the alkalinity of the water, which is discussed in [Section 4.7.](#))

Airborne particulate matter (dust) may find its way into surface water as well. One process is “dry deposition”, in which the particles settle to the land or water surface because of gravity. The other process is wet deposition, described above. Chemical components of the dust may dissolve into the water.

### **3.1.3 Biological effects**

Biological influence is yet another water quality factor. Aquatic animals excrete waste materials into the water, and some of these materials may dissolve in the water or react with other chemicals already in the water. When any aquatic organism dies, the decomposition process releases a variety of substances into the water.

Water from a typical stream may include calcium, sodium, potassium, chloride, sulfate, and carbonate from soils and rock; dissolved oxygen, dissolved carbon dioxide, and carbonic acid from air; and ammonia, other nitrogen compounds, and phosphorous compounds from aquatic life. All of these are naturally-occurring chemicals. Even in the absence of any pollution from human activities, these geochemical, atmospheric, and biological influences lead to a variety of chemicals in natural waters beyond just H<sub>2</sub>O.

### **3.1.4 The effect of point and non-point source pollution**

Human actions can be viewed as a perturbation of the baseline water quality. Say “water pollution,” and many people picture a pipe from a factory discharging wastewater of an unnatural color into a stream or pond, or a pipe discharging raw sewage. Water can also become contaminated from leaks, spills, and illegal dumping of toxic substances. These are the classic examples of “point sources”—where the discharge takes place at a clearly discernible, well-defined location such as a pipe. Inputs allowed under wastewater discharge permits, and other legal activities, affect water quality as well.

“Non-point sources” are also important. Non-point source pollution is most commonly associated with storm water runoff. Any substance on the land surface has the potential to end up in the nearest stream or pond when storm water dissolves or otherwise washes the material downhill across the land surface. Just what substances are involved depends on the land use within the watershed. In agricultural areas, we deliberately apply materials such as fertilizers, herbicides, and pesticides to the land surface, and we may find measurable amounts of these in storm water runoff that ultimately finds its way into surface water. Roads and parking lots may

contribute sediment, de-icing salts, fuel, oil, and grease. Because these pollutants originate from a broad and somewhat ill-defined area of land, we classify them as “non-point source” pollutants.

Groundwater is often another input to surface water that comes from a broad, ill-defined area. Some of the contaminated storm water on the land surface will infiltrate into the soil and may eventually percolate downward to groundwater, thus leading to groundwater contamination. Where underground onsite wastewater treatment systems (a/k/a septic systems) are used, their malfunction can lead to groundwater contamination. If groundwater is contaminated, it becomes another non-point source of pollution. Yet another form of non-point source pollution is the introduction of atmospheric pollutants into surface water by wet deposition.

In order to tie together the different influences on water chemistry, it's useful to think about the distinction between “pure water”, “natural water”, and “polluted water”. Pure water would be nothing but H<sub>2</sub>O. Natural water would be H<sub>2</sub>O plus a number of naturally-occurring substances, as described above. Polluted water would be natural water plus pollutants from point and/or non-point sources.

### **3.1.5 The influence of streamflow**

There is one more influence on water quality that is important to recognize—the effect of flow on chemical concentrations in surface water. First, consider periods of high flow originating either from the spring snowmelt or from large storms during any part of the year. Heavy surface runoff has a relatively short time in which it is in contact with soil and rock, and thus it has less opportunity to dissolve salts and minerals from soils and rock. This means that the surface runoff will have only low concentrations of dissolved materials. During the spring snowmelt, we find that many substances present in our streams and rivers have lower concentrations than at other times of the year because they are being diluted by the purer runoff. Similarly, a point-source discharge that occurs at essentially the same discharge rate throughout the year will be more diluted, and have less effect on water quality, during periods when the stream is receiving lots of runoff. It is important to keep in mind two complications within this simple picture. One is that we often find that the “first flush” of storm water runoff is much more polluted than runoff later on in a storm event. This is especially true if a long time has elapsed since the last storm, allowing more materials to accumulate on the land surface for the runoff to transport into the stream. The other complication is that if the soils or rock in a watershed are highly erodible, there can be considerable input of suspended sediment to the stream. Suspended sediment inputs can also be increased by any human activities (*e.g.*, mining, roads, agriculture, and development) that decrease infiltration and increase runoff. That chocolate milk appearance that some rivers take on after a storm is a result of eroded sediment.

Now consider periods of low flow. In western Colorado, most of the winter months are rather dry, and the precipitation that does fall in the high country is stored in the form of snow. The water that you see in stream channels at this time of year is primarily baseflow, which is groundwater that is seeping into the stream channel. That groundwater has been in close, extended contact with soils and rock and, if the geochemistry of the saturated zone is conducive, will have high concentrations of substances dissolved from the soils and rock. On the other hand, since there is less input from surface runoff, and the in-stream water velocity is low due to the

low flow, we will see less suspended sediment in the stream. Any point-source discharges that occur at essentially the same discharge rate throughout the year will be less diluted, and will have more effect on water quality.

### 3.2 Water quality standards

The modern era of strong regulation of water quality originated with the Federal Water Pollution Control Act of 1972. Federal regulation was updated and extended by the Clean Water Act of 1977, and subsequent amendments in 1987 and 1990. These federal laws focus on surface waters (ponds, lakes, streams, rivers, and wetlands).

Water quality standards are established by a process that involves both the U.S. Environmental Protection Agency (EPA) and state environmental regulatory agencies, such as the CDPHE and the Colorado Water Quality Control Commission (CWQCC). Using the results of extensive toxicity testing, EPA develops "water quality criteria" for important water quality parameters. Criteria are developed for protection of aquatic life, protection of drinking water supply, and protection of human consumption of fish. Each state is required to designate specific uses for each body of water within its borders. Use designations employed by Colorado include aquatic life, recreation, water supply, and agriculture. States then set standards for each relevant water quality parameter that protect each of the designated uses. The standards can be based on EPA water quality criteria or can be developed using other scientifically-defensible approaches. Standards *do* vary from one body of water to another when the designated uses are different.

Each state is responsible for collecting water quality data for its surface waters and monitoring compliance with the state standards. Every two years, the state submits a report to EPA listing all surface waters and pollutants that do not meet their standards. States must then develop plans for bringing each of those bodies of water back into compliance for the relevant pollutants. The key to this effort is development of a "total maximum daily load" (TMDL). The TMDL is the maximum amount of the pollutant that the water body can receive over the course of a day without violating its water quality standard. Portions of the maximum load are allocated among the sources of the pollutant, with the expectation that each source will reduce its generation of that pollutant to fit within its allocation. Individual TMDL's can be difficult to develop; they must be created for each body of water and each pollutant not meeting the standard.

In Colorado, water quality standards applicable to the Crystal River and Coal Basin are specified in "Basic Standards and Methodologies for Surface Water" (5 CCR 1002-31) and "Classifications and Numeric Standards" (5 CCR 1002-33). Within the latter document, the Crystal River is segment 8 and Coal Creek is segment 9 under Region 12, Basin: Roaring Fork. Both the Crystal River and Coal Creek have the same designated uses, which are listed and defined below:

- Aquatic Life Cold 1: Waters with this designation "presently support aquatic life uses as described below, or such uses may reasonably be expected in the future due to the suitability of present conditions, or the waters are intended to become suitable for such uses as a goal... Class I - Cold Water Aquatic Life: These are waters that (1) currently are capable of sustaining a wide variety of cold water biota, including sensitive species,



or (2) could sustain such biota but for correctable water quality conditions. Waters shall be considered capable of sustaining such biota where physical habitat, water flows or levels, and water quality conditions result in no substantial impairment of the abundance and diversity of species.”

- Recreation E – Existing Primary Contact Use: “These surface waters are used for primary contact recreation or have been used for such activities since November 28, 1975... ‘PRIMARY CONTACT RECREATION’ means recreational activities where the ingestion of small quantities of water is likely to occur. Such activities include but are not limited to swimming, rafting, kayaking, tubing, windsurfing, water-skiing, and frequent water play by children.”
- Domestic Water Supply: “These surface waters are suitable or intended to become suitable for potable water supplies. After receiving standard treatment (defined as coagulation, flocculation, sedimentation, filtration, and disinfection with chlorine or its equivalent) these waters will meet Colorado drinking water regulations and any revisions, amendments, or supplements thereto.”
- Agriculture: “These surface waters are suitable or intended to become suitable for irrigation of crops usually grown in Colorado and which are not hazardous as drinking water for livestock.”

### **3.3 Water quality sampling and analysis**

Water quality monitoring programs typically include field measurements, sample collection, and subsequent analysis of those samples in laboratories. Field-portable meters are commonly used for measuring temperature, pH, specific conductance, and sometimes dissolved oxygen. These measurements are typically carried out by inserting a probe from the meter directly into the stream being tested.

Most parameters are not measured in the field due to a lack of suitable field-portable instrumentation. Instead, samples are collected and sent to fixed-base commercial or government laboratories where analysis is performed by specialists using standard methods approved by the EPA. The organizations carrying out the monitoring (such as CDPHE, CPW-RW, USFS, or USGS) collect the samples using standard procedures that ensure sample integrity. If the organization wants to quantify only the dissolved form of a chemical, the sample will be filtered in the field to remove suspended sediments that might also contain that chemical. If the organization wants to quantify the chemical in both the dissolved form and in sediments, the sample will not be filtered.

Monitoring objectives and budget constraints drive the selection of water quality parameters analyzed. For example, if the objective is to monitor compliance with water quality standards, only those parameters that actually have standards may be analyzed. If the standard specifies that filtered samples are to be used, then that may be the only type of sample that is collected. On other occasions, the goal may be to learn more about how a particular chemical occurs. Does it occur only in a dissolved form, or does it also occur in the sediment that is suspended in the

water? In this case, both filtered and unfiltered samples would likely be analyzed. Each monitoring organization may have different objectives and these objectives may change over time. Thus, there is considerable variability across the data base of results examined in this report—not every sample was analyzed for every parameter.

The standard methods and instrumentation used in the laboratory all have “detection limits”, which are thresholds below which the concentration of the substance is too small to be sensed by the analytical instrumentation. Laboratories report these results as less than the value of the detection limit. For example, a result reported as “<30 mg/L” indicates that the detection limit was 30 milligrams of substance per liter of water. This result means that the true value for the concentration of that substance could be any number less than 30 mg/L, including but not exclusively zero. Thus, we never know if there is truly none of that substance present in the water.

## **4.0 Water quality parameters**

### **4.1 Temperature**

Our interest in water temperature stems from its effects on aquatic life. Because temperature directly influences the metabolism, reproduction, and survival of aquatic organisms, each organism thrives only within a range of temperatures characteristic of that species. Thermal shock from sudden temperature changes is also a concern. Temperature has relevant indirect effects as well. The solubility of dissolved chemicals depends on temperature, so temperature changes that increase the concentration of toxics or reduce the concentration of desirable constituents (such as oxygen) may stress aquatic organisms.

Aquatic life is commonly grouped into either warm water or cold water species. In Colorado, warm water fish species in streams include shiners, darters, dace, chub, and most suckers. Trout are the classic example of species requiring cooler water.

Several factors affect water temperature. Streamside vegetation cools the water by shading it, thus removal of this vegetation may lead to warming of the water in narrow channels. Shallow water, which can be caused by low flows or unnaturally wide channels, is more readily warmed by sunlight than deeper water. Streams may also be warmed by discharges of process water from industrial facilities and cooling water from power plants.

Both Coal Creek and the Crystal River are classified as Aquatic Life Cold 1, meaning that they are currently capable of sustaining a wide variety of cold water species, including sensitive species, or could sustain such species except for the presence of correctable water quality conditions. Physical habitat, flows, water depth, and water quality are the key factors that determine this capability. Colorado regulations include a general requirement that “temperature shall maintain a normal pattern of diurnal [daily] and seasonal fluctuations with no abrupt changes and shall have no increase in temperature of a magnitude, rate, and duration deemed deleterious to the resident aquatic life.”

The specific standards associated with the Aquatic Life Cold 1 classification vary with time of year and the duration of the warmer water. For June through September, the daily maximum temperature must not exceed 21.2°C (70°F) more than once in 3 years and the maximum weekly average temperature must not exceed 17.0°C (63°F) more than once in 3 years. For October through May, the daily maximum temperature must not exceed 13.0°C (55°F) more than once in 3 years and the maximum weekly average temperature must not exceed 9.0°C (48°F) more than once in 3 years. Exceptions are allowed for periods of unusually hot weather and periods of unusually low flows. “Daily maximum temperature” is defined in the regulations to be the highest 2-hour average water temperature observed over a twenty-four hour period. “Weekly average temperature” is defined as an average of at least 3, equally-spaced temperature measurements each day over 7 consecutive days. [Table 2](#) below (excerpted from Appendix 3.5.1 of the 2008 *State of the Roaring Fork Watershed* report) shows the average maximum tolerable water temperatures for four species and three life stages of trout. The upper limit for thriving brown trout is 18.9°C (66°F). CPW may close a stretch of river to fishing if daily maximum temperature exceeds 23.3°C (74°F) or daily average temperature exceeds 22.2°C (72°F).

**Table 2. Optimal and lethal average maximum water temperatures for trout.**

| Species   | Average Maximum Water Temperature |               |
|---|-----------------------------------|---------------|
|   | Optimal Range                     | Lethal        |
| <b>Rainbow Trout</b><br>Adult, Juvenile & Fry   | 12.2-17.8°C (54-64°F)             | 26.1°C (79°F) |
| <b>Brown Trout</b><br>Adult & Juvenile          | 12.2-17.8°C (54-66°F)             | 27.2°C (81°F) |
| Fry   | 7.2-15.0°C (45-59°F)              | 26.1°C (79°F) |
| <b>Brook Trout</b><br>Adult, Juvenile & Fry     | 10.0-16.1°C (50-61°F)             | 22.2°C (72°F) |
| <b>Cutthroat Trout</b><br>Adult, Juvenile & Fry | 11.1-16.1°C (52-61°F)             | 22.2°C (72°F) |

Out of 898 temperature measurements collected in our data, there were a number of measurements that were greater than the standard: 62 measurements greater than the 9.0°C standard for maximum weekly average during October through May; 3 measurements greater than the 13.0°C standard for daily maximum for the months of October through May; and 11 measurements greater than the 17.0°C standard for maximum weekly average for the months of June through September. No measurements exceeded the 21.2°C standard for daily maximum for June through September. Only one temperature measurement was included in each sampling event, thus we cannot evaluate compliance with the daily maximum and maximum weekly average temperatures, which require more than one measurement. Still, the occurrence of single temperatures exceeding these limits would suggest the *possibility* of non-compliance, and noting the exceedances will contribute to our understanding of these streams.

The majority of the high temperature results occurred at Site 3 - the Crystal River above Avalanche Creek. Perhaps this is due to the Penny Hot Springs, which discharge into the river

not far upstream of this site. More generally, higher temperatures that sometimes occur throughout the study area may be a result of shallow water found in channels that have become overly wide due to human activities.

## 4.2 Suspended solids

“Suspended solids” can include a variety of materials, with sediment being the most common. Sediment can be material mobilized from the stream bed by current and turbulence, with smaller particles being more readily suspended than larger particles. Suspended sediment is also composed of soil particles eroded into the water body from the surrounding land. Another type of material is organic debris, such as fragments of dead aquatic organisms, as well as twigs and leaves from the surrounding land.

Even an undisturbed body of water will have naturally-occurring suspended solids in noticeable amounts on at least some occasions. Problems arise when excessive amounts occur. A high concentration of suspended solids reduces the penetration of sunlight into the water, which limits photosynthesis and growth of aquatic plants (including algae) and, in turn, the populations of herbivores and carnivores. As excessive amounts of suspended solids settle to the stream or lake bottom, “siltation” occurs – smaller particles fill in the spaces between gravel and cobble, which damages aquatic insect habitat, smothers the insects themselves, and ruins gravel beds used for spawning by trout. The depth of pools can be reduced by excessive siltation, reducing their effectiveness as refuges from high flow and temperature and as rearing habitat for fish. Excessive suspended silt can kill fish through abrasion of gills. Suspended solids in water used for irrigation can leave crusts on soil that limit infiltration, plant emergence, and soil aeration. As this water evaporates from leaf surfaces, it may leave a film that impedes photosynthesis. Settling of sediment in reservoirs, canals, and ditches reduces water-holding capacity. In water used for drinking water supply, suspended solids create a surface for bacterial growth and complicate disinfection of the water. People find cloudy water in streams and lakes to be less aesthetically pleasing than clear water. The poor visibility associated with suspended solids can be a safety problem in waters used for swimming.

Suspended solids typically increase during the spring runoff and following rain events. Suspended solids occur in higher amounts in streams whose watersheds have highly erodible soils, large areas of sparse vegetative cover, steep slopes, and high annual precipitation or intense storms that produce locally large amounts of storm water runoff. Vegetative cover is a key watershed characteristic, whether it reflects only natural influences, or both natural and human influences. Natural disturbances such as fire and avalanche can reduce vegetative cover. Human disturbances such as roads adjacent to streams, road crossings, clearing for any purpose (*e.g.*, mining, agriculture, and development), overgrazing, and recreational overuse also reduce cover.

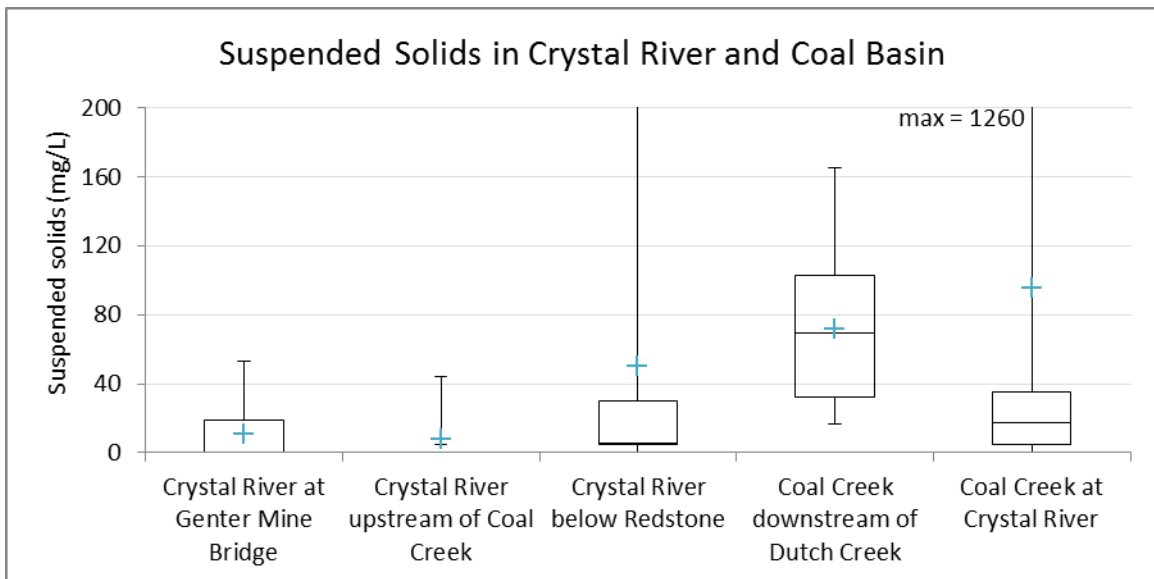
No Colorado water quality standards exist for suspended solids. The organizations that monitored the Crystal River and Coal Creek included total suspended solids in their list of parameters to be analyzed for 5 out of the 9 sites included in this report: the Crystal River at Genter Mine Bridge (Site 1), upstream of Coal Creek (Site 2), and below Redstone (Site 3); and Coal Creek below Dutch Creek (Site 7) and at Crystal River (Site 9). Measureable suspended solids were found in 103 of 191 samples. There were minimal total suspended solids in the 2

Crystal River sites upstream from Coal Creek (the median value at each site was a non-detectable value) and somewhat greater in the Crystal River below Redstone (median value of 5.5 mg/L). See Figure 5. The two Coal Creek sites had the highest median values (69 and 17 mg/L). These results indicate that Coal Creek typically carries a higher concentration of suspended solids than the Crystal River. The results also suggest that suspended solids in the Crystal River below Redstone, which is also downstream of Coal Creek, are a result of the input of suspended solids from Coal Creek. Most of the higher values of suspended solids occurred on dates that likely coincided with spring runoff, when a greater input of sediment from erosion can be expected. The other high values may coincide with storms or possibly with human activities in the riparian zone causing transient inputs of eroded soil.

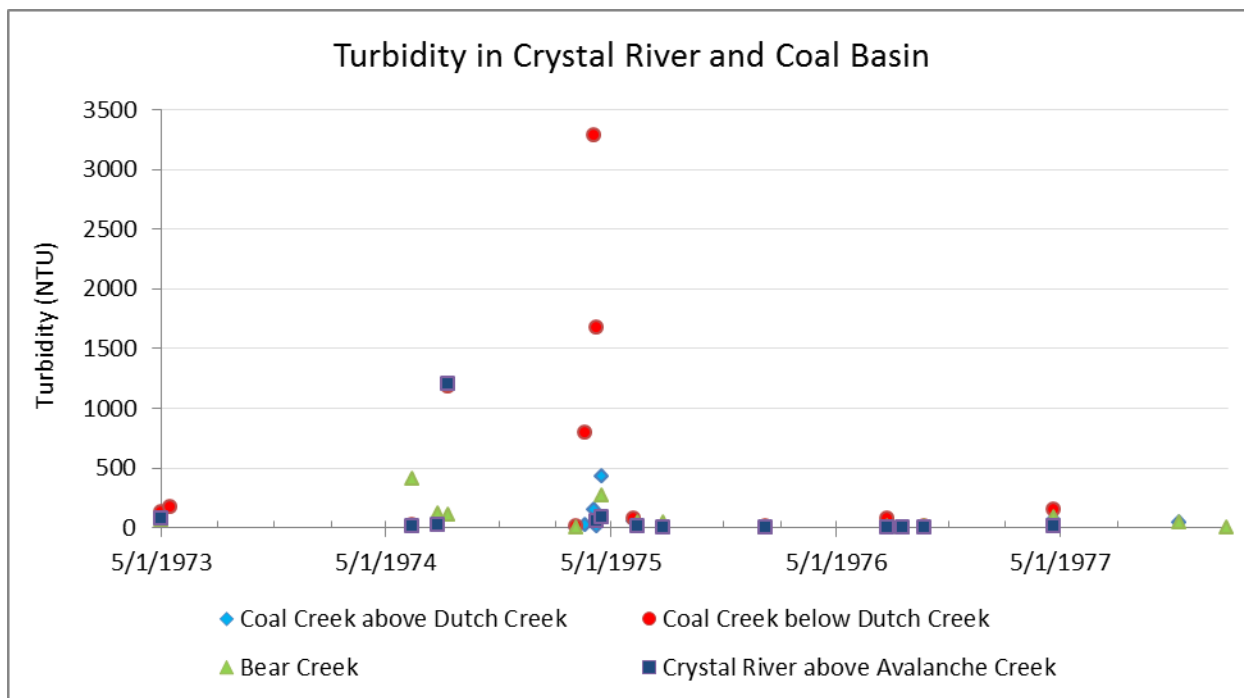
Turbidity, another water quality parameter, varies with the amount of suspended solids. Turbidity quantifies the extent to which light shining through the water is scattered by suspended materials. The greater the amount of suspended materials, the greater the fraction of incoming light that is scattered off in other directions, and the greater the turbidity, which is measured in “nephelometric turbidity units (NTU)”.

Turbidity was measured at only 4 sites covering a period of less than 5 years. See Figure 6. A spike in turbidity occurred in late March and early April in 1975 for Coal Creek above and below the Mid-Continent Resources mining operations. During that period, turbidity below the plant was much greater than turbidity above the plant, suggesting that either the coal processing area was a significant source of additional suspended solids input to Coal Creek or there was a large input of suspended solids from Dutch Creek. Most other values are much lower and are consistent with turbidity in streams carrying significant sediment loads from their watershed. Occasional higher values are attributable to spring runoff, intense rain, or human activities.

Turbidity measurements were also collected in the Crystal River above Avalanche Creek from 1973 to 1977 (Figure 6), with results that largely mirror those in Coal Creek.



**Figure 5. Suspended solids in Crystal River and Coal Basin.**

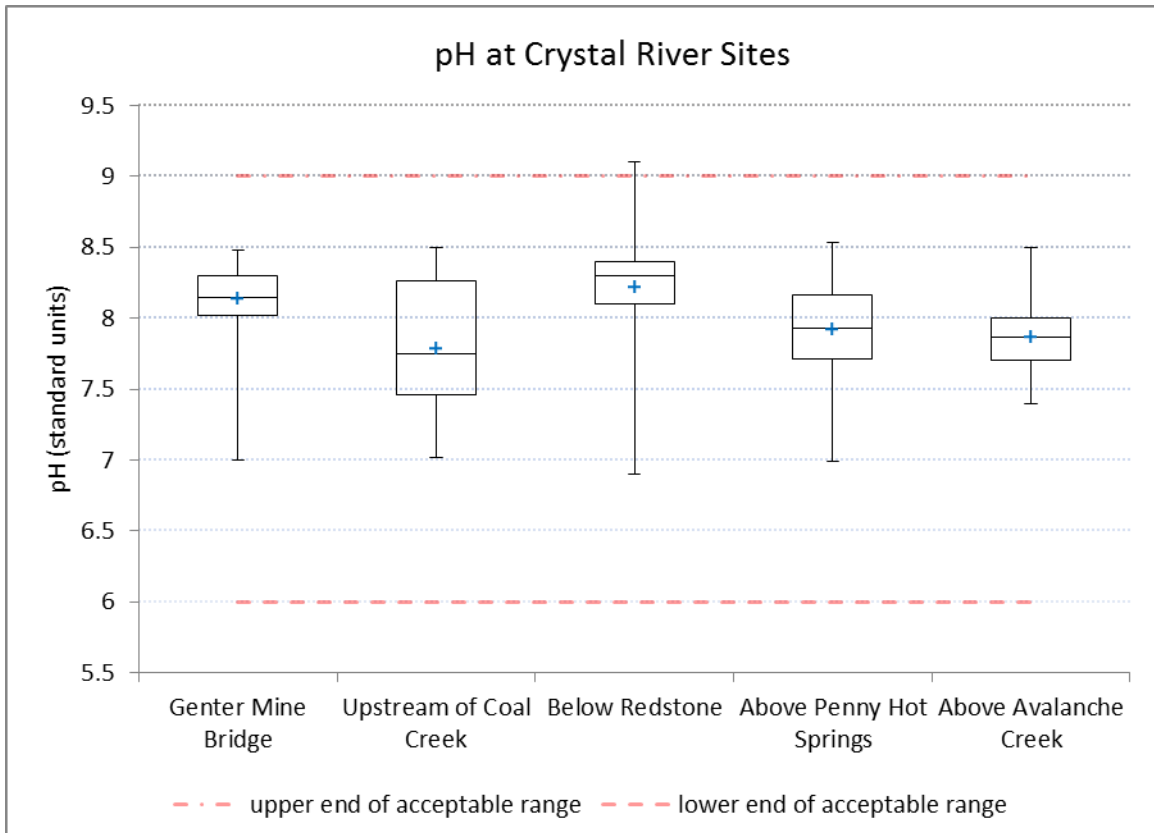


**Figure 6. Turbidity in Crystal River and Coal Basin.**

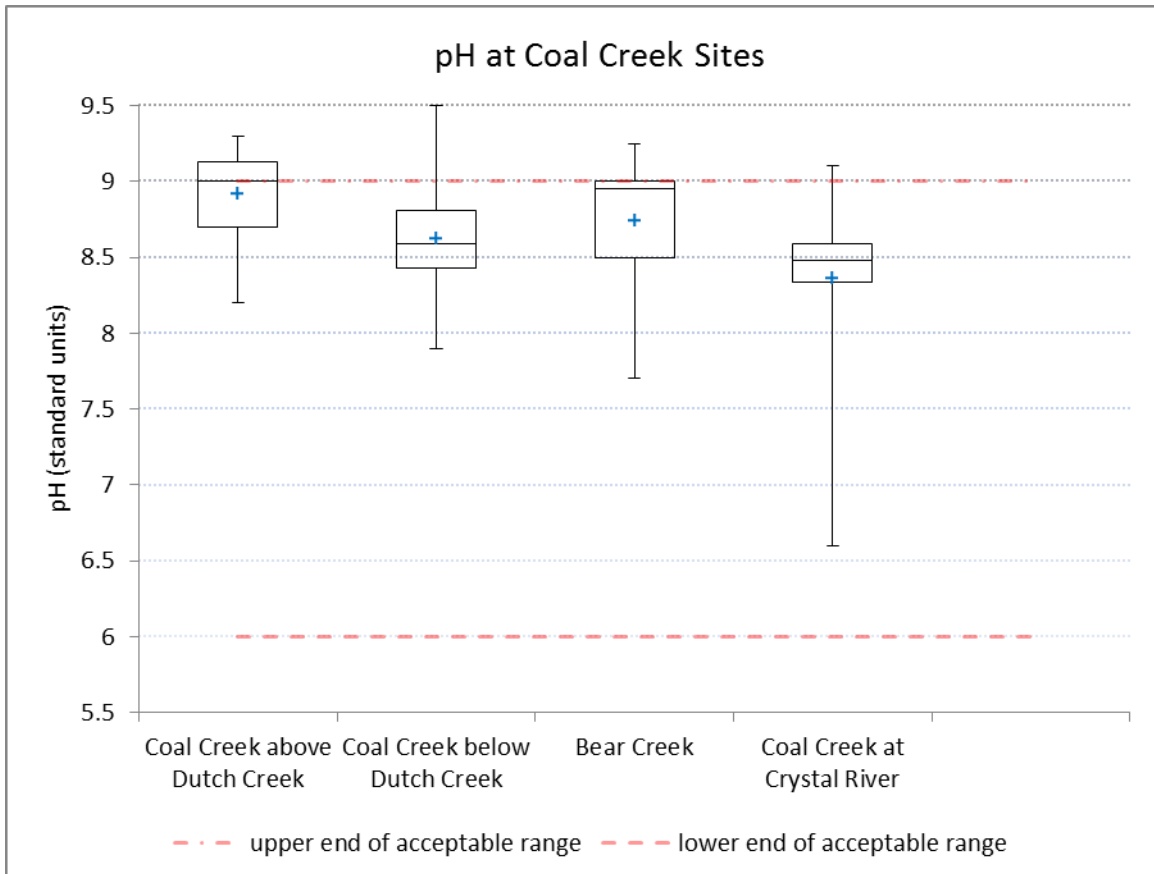
### 4.3 pH

pH is a measure of how acidic or basic the water is. The pH scale for water ranges from 0 to 14.0, with the middle value of 7.0 representing a neutral solution—one that is neither acidic nor basic. In general, aquatic life can tolerate a range of pH from 6.0 to 9.0 and the Colorado water quality standard requires pH to fall within this range. Changes in pH away from the mid-range can increase the degree to which some minerals may dissolve into the water. pH may be altered to unacceptable values by acid rain, acid mine drainage, and discharges of industrial wastewater.

The organizations monitoring the Crystal River and Coal Basin conducted pH measurements at all 9 sites, but pH was not measured in every sampling event. pH was measured on 449 occasions in the Crystal River; results ranged from 6.9 to 9.1 with a median of 8.1 (Figure 7). Only one result, 9.1 in the Crystal River below Redstone, fell outside the range of 6.0 to 9.0. Results in Coal Basin ranged from 6.6 to 9.5 with a mean of 8.6 (Figure 8). Only 6 out of 109 values in Coal Basin exceeded 9.0; all of these occurred between 1974 and 1976. There was no seasonal variation in pH in Crystal River or Coal Basin. The mean values are similar to those found in other Western Slope streams in a similar geochemical setting.



**Figure 7. pH at Crystal River sites.**



**Figure 8. pH at Coal Basin sites.**

#### 4.4 Total dissolved solids and salinity

In fresh water, total dissolved solids (TDS) is usually dominated by just a few ions—sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ )—and a non-ionic dissolved solid, silica ( $\text{SiO}_2$ ). These ions are present because of the dissolution of salts such as sodium chloride ( $\text{NaCl}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), calcium chloride ( $\text{CaCl}_2$ ), and calcium carbonate ( $\text{CaCO}_3$ ). TDS is expressed as milligrams of dissolved solids per liter of water (mg/L). “Salinity” is essentially the same property as TDS, but is often expressed in units of parts per thousand, which is equivalent to grams per liter (g/L).

The primary source of these dissolved solids is the soil and rock in the watershed. A typically lesser amount of dissolved solids arrive by way of wet and dry deposition from the atmosphere. Certain industrial wastewater discharges are a human source of TDS. Irrigation return water is a significant source in some locations. (Irrigation water that isn’t lost by evaporation or absorbed by plants either runs off the land surface or infiltrates and percolates to groundwater. Either way, this water makes a lot of contact with soil and rock, and thus has the potential to carry high concentrations of dissolved solids into lakes and rivers.)



High TDS creates an excessively salty taste in drinking water and a laxative effect when this water is consumed. To the extent that TDS is high because of high sodium concentrations, the water may contribute to hypertension. Corrosion and encrustation may occur on metallic surfaces in contact with high TDS water. Osmotic regulation of internal salt concentrations within aquatic organisms is disrupted by high TDS. When this water is used for irrigation, it can disrupt osmotic equilibrium in plants, adversely affect soil structure, and reduce water infiltration into the soil. There is no Colorado water quality standard for TDS. The following categories are sometimes used to classify TDS:

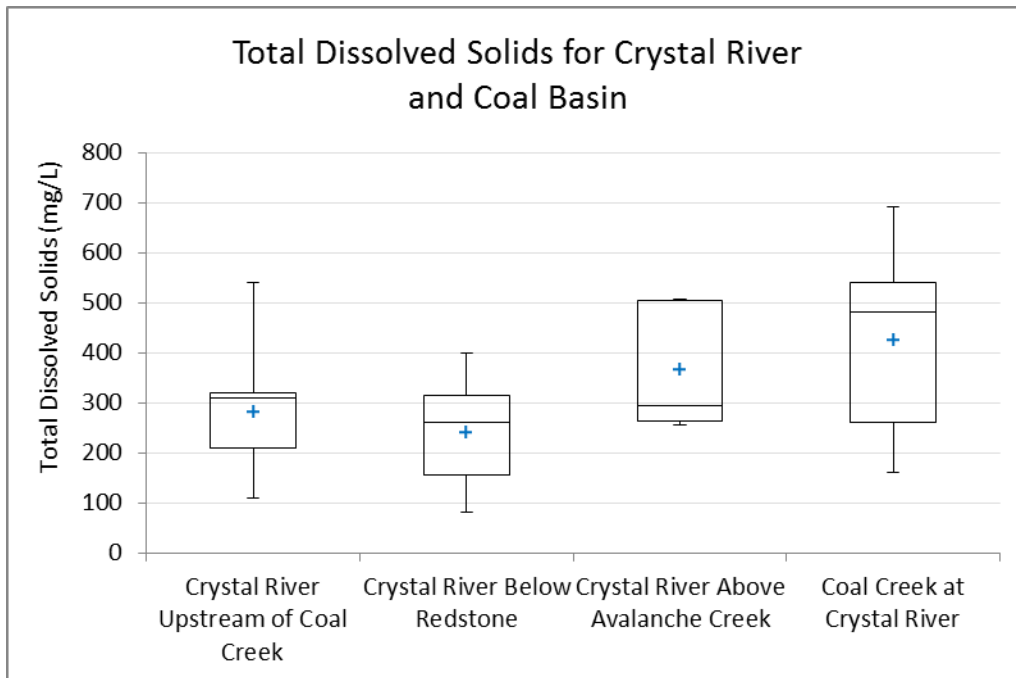
- Fresh                                    TDS less than 1,500 mg/L
- Brackish                                TDS between 1,500 mg/L and 5,000 mg/L
- Saline                                    TDS greater than 5,000 mg/L

How much TDS is “too much” depends on how we hope to use the water. Some guidelines for TDS are:

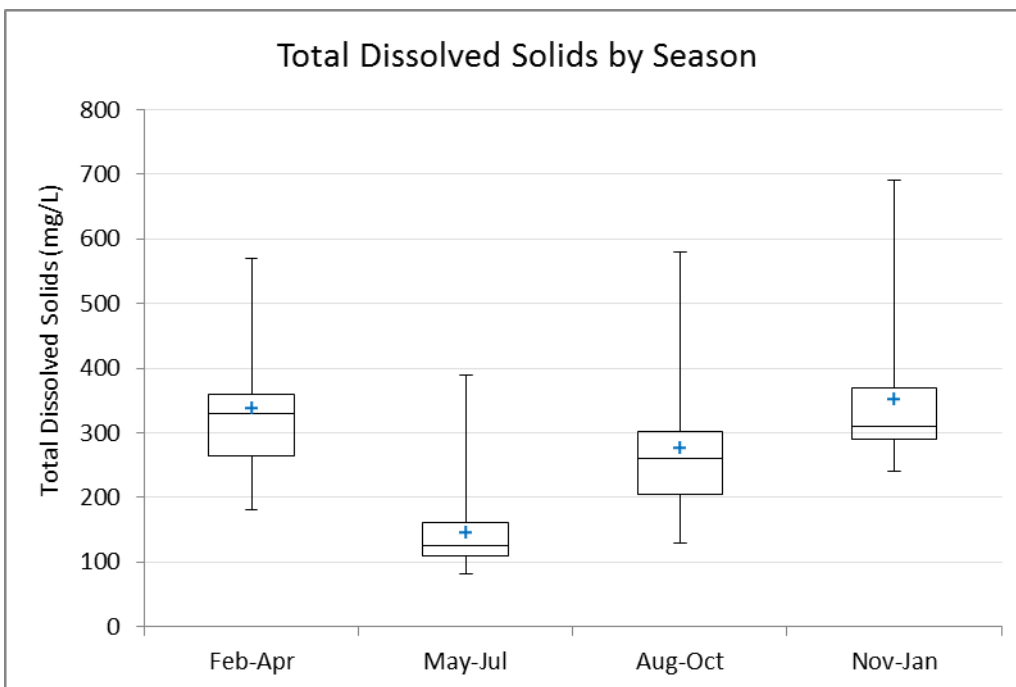
- Less than 200 mg/L                    for human consumption
- Less than 10,000 mg/L                for livestock consumption
- Less than 10,000 mg/L                for freshwater fish (varies with species)
- Less than 500 mg/L                    for irrigation of salt-sensitive crops
- Less than 1,000 mg/L                  for irrigation of most other crops
- Less than 3,000 mg/L                  for irrigation of salt-tolerant crops

The organizations that sampled the Crystal River and Coal Basin included total dissolved solids in their list of parameters to be analyzed for 4 of the 9 sites: the Crystal River upstream of Coal Creek (Site 2), below Redstone (Site 3), and above Avalanche Creek (Site 5); and Coal Creek at Crystal River (Site 9). Measureable TDS was reported in all 174 samples. The Crystal River sites showed median TDS values between 260 and 290 mg/L while the Coal Creek site had a median of 480 mg/L ([Figure 9](#)). Sixty-five out of 152 TDS values in the Crystal River exceeded the 200 mg/L threshold that is considered undesirable for human consumption, while 19 out of 22 TDS values in Coal Creek exceeded that threshold. Both streams may have too much TDS to be usable for drinking water without treatment to remove salts.

Given the geochemistry of the Crystal River watershed, with the presence of the salt-rich Eagle River evaporates and Mancos Shale, we expect TDS values to tend toward greater numbers. We also expect to see TDS values lowest during the spring runoff, when salt-free snow-melt dilutes the input of salt-rich groundwater to the stream channels ([Figure 10](#)).



**Figure 9. TDS at Crystal River and Coal Basin sites.**



**Figure 10. TDS at Crystal River and Coal Basin sites by season.**

#### 4.5 Dissolved oxygen

Given that most aquatic organisms can't survive without sufficient oxygen dissolved in the water, dissolved oxygen concentration is a crucial water quality parameter. The solubility of

oxygen decreases with increasing temperature and with increasing elevation above sea level. Both effects are demonstrated in [Table 3](#) below. Note the magnitude of the difference in oxygen solubility between cold water at sea level and warm water at higher elevations.

**Table 3. Water temperature and elevation - effect on oxygen solubility.**

| Water Temperature<br>°C (°F) | DO Solubility at<br>Sea Level (mg/L) | DO Solubility at<br>4,600 ft (mg/L) | DO Solubility at<br>9,842 ft (mg/L) |
|------------------------------|--------------------------------------|-------------------------------------|-------------------------------------|
| 0 (32)                       | 14.6                                 | 12.3                                | 10.1                                |
| 10 (50)                      | 11.3                                 | 9.5                                 | 7.8                                 |
| 20 (68)                      | 9.1                                  | 7.7                                 | 6.3                                 |
| 30 (86)                      | 7.6                                  | 6.4                                 | 5.3                                 |

DO comes from two sources. One is the diffusion of O<sub>2</sub> from the atmosphere into the water. The other is photosynthetic organisms, such as algae and aquatic plants. There are also DO “sinks”—processes that remove DO from the water. The primary sink for DO is respiration by aquatic organisms. In situations where the DO is supersaturated, diffusion from the water to the air (reestablishing the air-water equilibrium) is also a sink. Another sink is a process called biochemical oxygen demand (BOD) that occurs when dissolved organic substances (*i.e.*, those with a chemical structure based on a carbon-carbon bond framework) are abundant in the water. Microorganisms tend to proliferate because many of these organics can serve as a food source for microorganisms. Large microorganism populations consume more DO through respiration and can deplete the water of DO faster than it can be replenished by its sources.

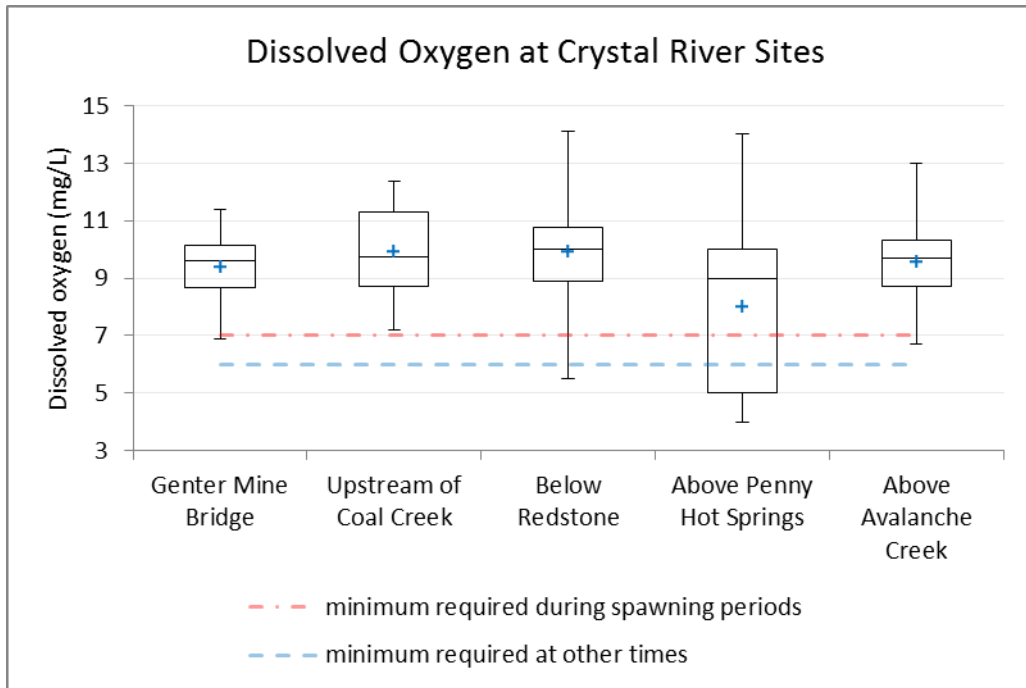
The vast majority of aquatic organisms (everything except for anaerobic bacteria) require DO for respiration. The typical water quality standard for the maintenance of a healthy aquatic ecosystem is for DO to be at least 5.0 mg/L, based on observed impairment of fish growth and the effect of simultaneous stresses involving temperature, disease, and pollutants. Trout and many of the aquatic insect species common in trout habitat require at least 6.0 mg/L. However, some aquatic organisms do tolerate DO well below 5 mg/L. Organisms that dwell in the sediments on the bottom of streams and ponds are a good example. These bottom sediments tend to have low DO because they are usually far away from the sources of DO—the atmosphere, and the well-lit shallow water where aquatic plants thrive and produce DO by photosynthesis.

The temperature dependence of DO solubility underlies the occurrence of low DO during periods of low stream flow. When water levels are extremely low, the water is readily warmed by sunlight, reducing the amount of DO present. Low-flow, high-temperature conditions are most likely to occur in late summer in normal years and throughout the summer in drought years. This is one aspect of the heat stress that can be deadly to fish during low-flow periods.

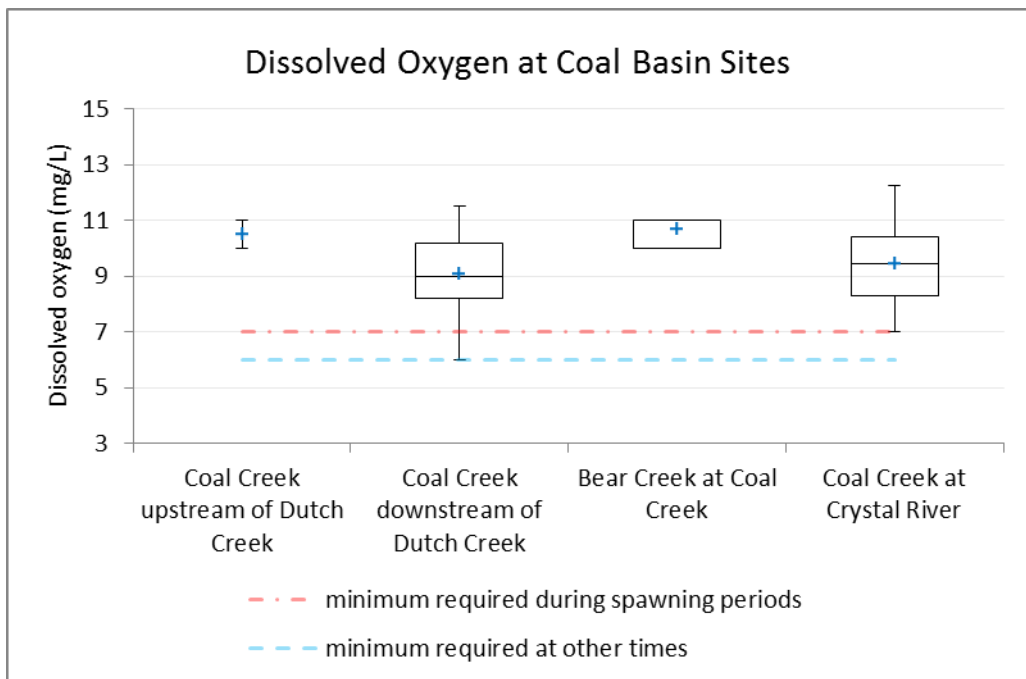
The standard for the Crystal River and Coal Creek is a minimum DO concentration of 6.0 mg/L, with a more stringent minimum of 7.0 mg/L during spawning periods. Box plots for all sites are shown in [Figures 11 and 12](#).

The organizations monitoring the Crystal River and Coal Creek had samples from all 9 sites analyzed for DO, but DO was not measured in every sample. Dissolved oxygen was detected in

all 527 samples. Results ranged from 4 mg/L to 14.1 mg/L with a median of 9.6 mg/L. There were 44 occasions when the 7.0 mg/L standard was not met and 25 occasions when the 6.0 mg/L standard was not met.



**Figure 11. Dissolved oxygen for Crystal River sites.**



**Figure 12. Dissolved oxygen for Coal Creek Basin sites.**

Two occasions when DO did not meet a standard occurred in Coal Creek at the Crystal River. All other occasions were in the Crystal River. One occasion occurred in the Crystal River at Genter Mine Bridge, another occurred in the Crystal River above Avalanche Creek, and the 39 other occasions all occurred in the Crystal River at Penny Hot Springs from 1994 until regular sampling stopped in 1997. One might expect that water at this site was warmer than at other Sites because of nearby geothermal features, which would decrease DO solubility. However, a comparison of water temperature between the Crystal River below Redstone and the Crystal River at Penny Hot Springs using the Wilcoxon rank sum test shows that there was no significant difference in temperature at the 95% confidence level. Another cause of low DO would be the presence of organics in high enough concentrations to create a significant biochemical oxygen demand. Still another possible explanation could be a systematic error on the part of the analysts. Available information does not provide a clear indication of the cause for the low DO. Analysis of water from this site could be resumed to determine if low DO is currently a problem.

## 4.6 Hardness

The property that we call hardness is defined as the concentration of all ions in the water having an electrical charge of +2. Calcium and magnesium ions are by far the most abundant of these ions, so hardness is usually referred to in terms of just these two ions (the concentration of  $\text{Ca}^{2+}$  plus the concentration of  $\text{Mg}^{2+}$ ). Hardness is expressed in units of “mg/L as calcium carbonate ( $\text{CaCO}_3$ )”, which means that a sample has the same hardness that the water would have if this number of mg of  $\text{CaCO}_3$  was dissolved in 1 liter of water.

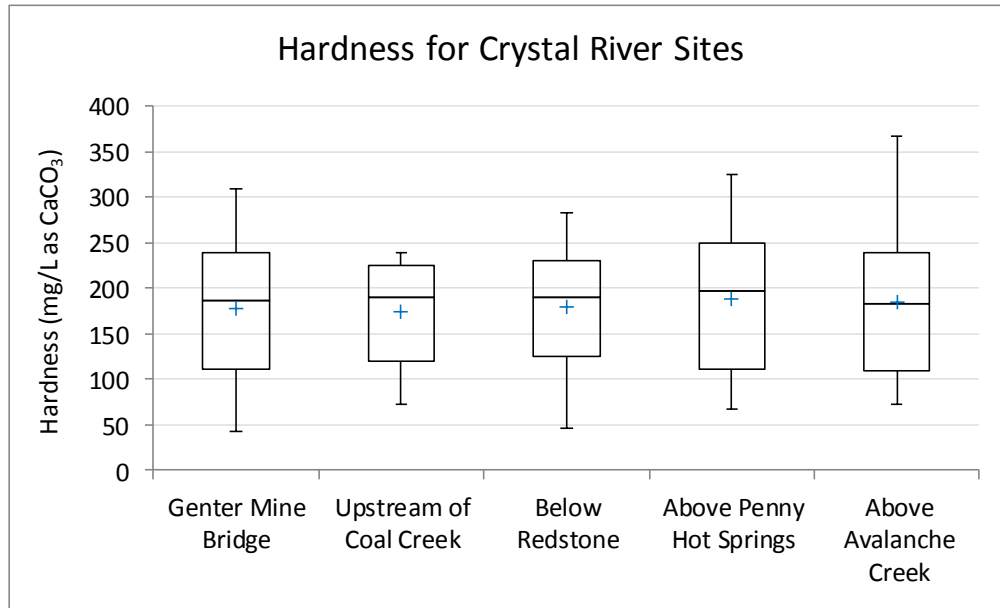
The most basic source of hardness is minerals and salts containing calcium or magnesium that dissolve in the water. Limestone, dolomite, and gypsum are all high in calcium, while dolomite is high in magnesium as well. Hardness may also be associated with discharges from industries and mines. A possible sink for hardness is the precipitation of minerals containing calcium and magnesium.

There are two factors that make large values of hardness undesirable. One arises when we want to use the water for domestic purposes, such as washing. The calcium and magnesium ions react with soap to form an undesirable soap scum. Hardness leads to the precipitation of  $\text{CaCO}_3$  from hot water to form “scale”, which can clog hot water pipes and boilers. Also, where there is high hardness, you may also have high TDS, with all its implications. When very hard water is used for irrigation, the hazard is associated with the effects of TDS. There is one factor that makes hardness desirable—its effect on the toxicity of certain metals that may be dissolved in the water. We find that the toxicity of certain metals to aquatic organisms decreases as the hardness of the water increases.

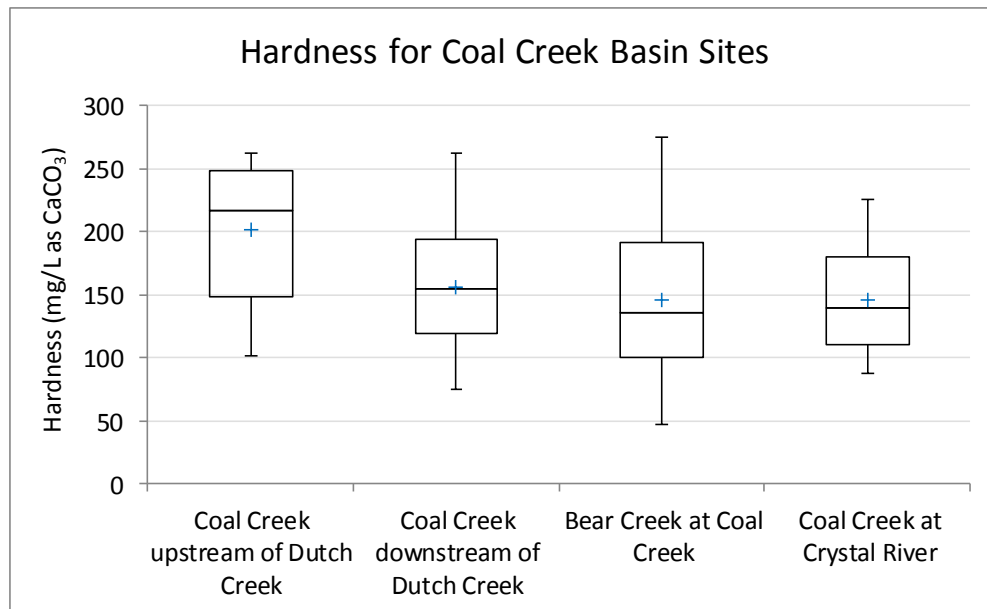
Hardness is sometimes categorized according to this scheme (U.S. Geological Survey):

- |                   |  |
|-------------------|--|
| ▪ Soft            | hardness less than 60 mg/L as $\text{CaCO}_3$        |
| ▪ Moderately hard | hardness between 61 and 120 mg/L as $\text{CaCO}_3$  |
| ▪ Hard            | hardness between 121 and 180 mg/L as $\text{CaCO}_3$ |
| ▪ Very hard       | hardness greater than 180 mg/L as $\text{CaCO}_3$    |

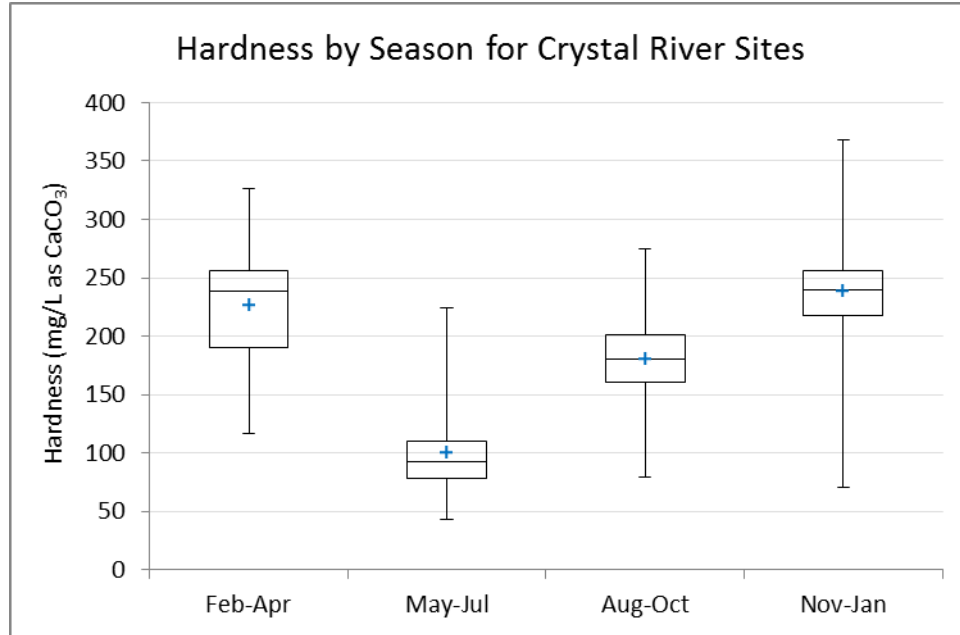
The organizations monitoring the Crystal River and Coal Creek had samples from all 9 sites analyzed for hardness, but hardness was not measured in every sample. Hardness was detected in all 555 samples analyzed for this parameter, with results ranging from 43 to 368 mg/L as CaCO<sub>3</sub> with a mean of 184 mg/L as CaCO<sub>3</sub>. Most of these hardness results are between 100 and 250 mg/L (Figures 13 and 14), making this water moderately hard to very hard. A seasonal box plot for Crystal River sites shows that hardness decreases during spring runoff, as expected (Figure 15). The source of the calcium and magnesium measured in these samples is the dissolving of salts and minerals containing these elements in the Eagle River evaporates and sedimentary rocks of this watershed.



**Figure 13. Hardness for Crystal River sites.**



**Figure 14. Hardness for Coal Creek Basin sites.**



**Figure 15. Hardness by season for Crystal River sites.**

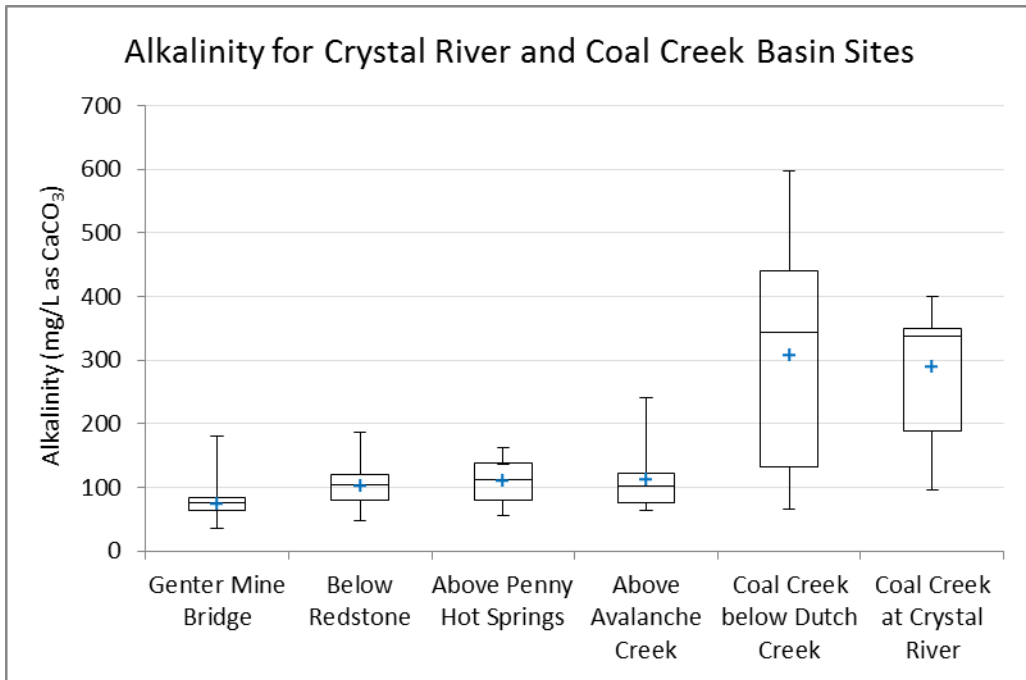
## 4.7 Alkalinity

Alkalinity is a property of water’s acid-base chemistry. Alkalinity is defined as the water’s capacity for neutralizing a strong acid and is sometimes called “acid neutralizing capacity” instead of alkalinity. Alkalinity will be high if there is a high concentration of bases in the water; the bases will react with and neutralize any acid that might be added. The most common bases found in water are hydroxide, bicarbonate, and carbonate. Alkalinity comes primarily from the dissolution of carbon dioxide gas and carbonate minerals into the water. Alkalinity is expressed as “milligrams per liter as calcium carbonate (mg/L as CaCO<sub>3</sub>)”. For example, an alkalinity of 100 mg/L as CaCO<sub>3</sub> means that the water has the same alkalinity that would be produced by dissolving 100 mg of CaCO<sub>3</sub> into 1 L of pure water.

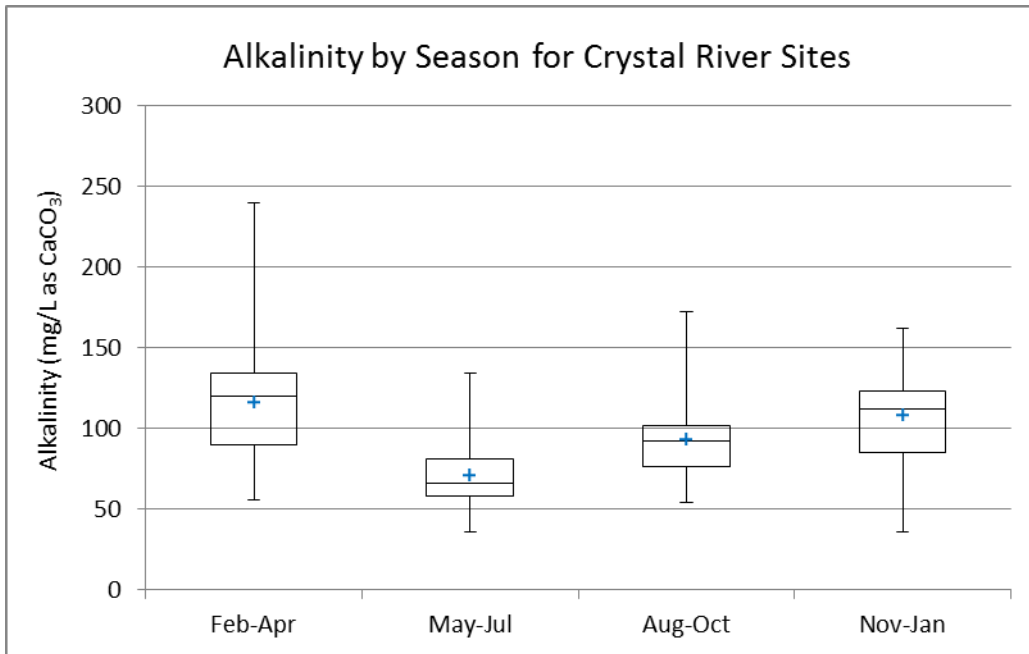
It is common to find alkalinity values ranging from 0 mg/L to a few hundred mg/L, depending on the geochemistry of the soil and rock in the watershed. There is no rule about how much is good and how much is bad. It is important to have some alkalinity present to buffer the water against acid rain, acid mine drainage, and decreases in pH due to production of carbonic acid by photosynthesis. Water that has a high alkalinity is likely to also have high TDS, which affects the usability of the water, as discussed in [Section 4.4](#). When used for irrigation, high alkalinity water that is also high in hydroxide can precipitate iron from soil water, which can cause chlorosis in plants.

The organizations monitoring the Crystal River and Coal Creek analyzed for alkalinity at all sites except for the Crystal River upstream of Coal Creek, Coal Creek above Dutch Creek, and Bear Creek. Alkalinity was detected in all 429 samples that were analyzed for this parameter, with results ranging from 36 mg/L as CaCO<sub>3</sub> to 598 mg/L as CaCO<sub>3</sub> with a median of 100 mg/L as

CaCO<sub>3</sub> (Figure 16). Alkalinities show a decrease during high flow, as expected (Figure 17). The available data suggest that streams in the Crystal River watershed have an alkalinity that is expected for the local geochemistry.



**Figure 16. Alkalinity for Crystal River and Coal Creek Basin sites.**



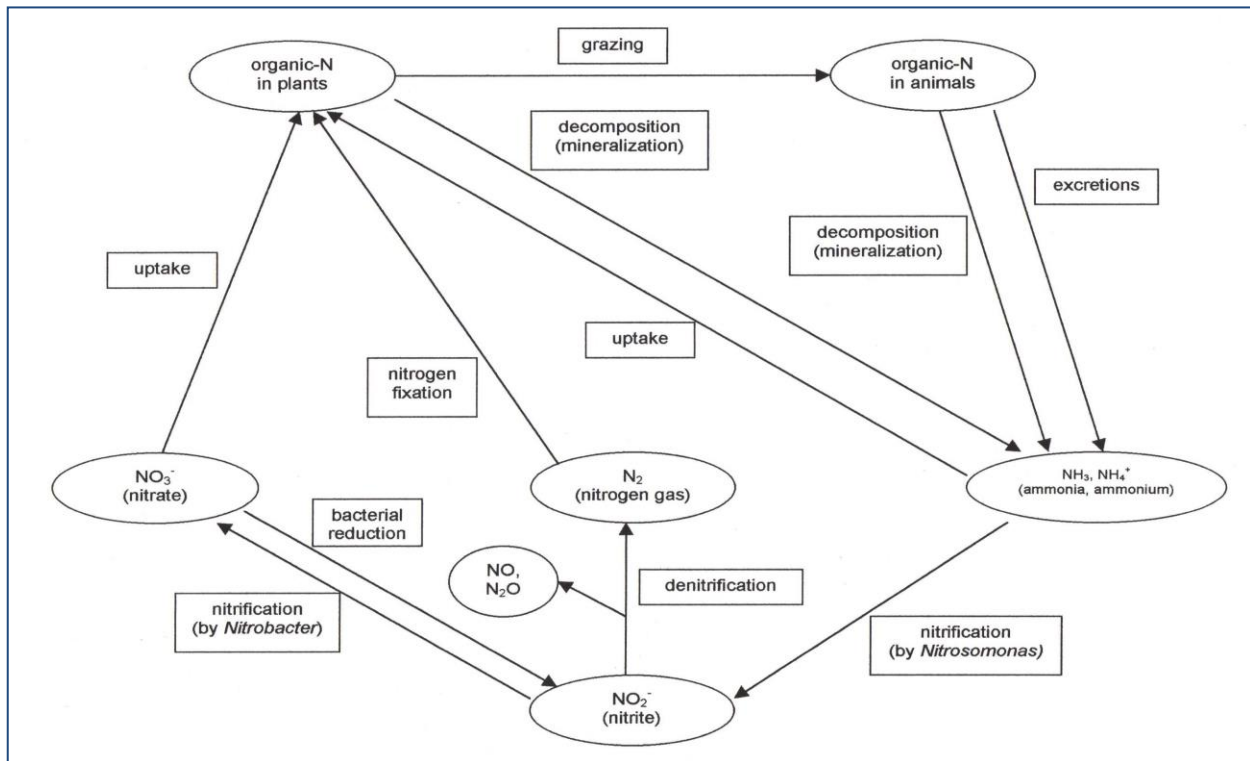
**Figure 17. Alkalinity for Crystal River sites by season.**



## 4.8 Nitrogen

Nitrogen (N) commonly occurs in several different forms in natural waters: nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), ammonia ( $\text{NH}_3$ ), ammonium ( $\text{NH}_4^+$ ), and organic nitrogen (organic-N), which is nitrogen incorporated into organic molecules.

The chemistry of nitrogen in an aquatic system can be understood in terms of the nitrogen cycle (Figure 18). Nitrogen is an essential nutrient for plants. Nitrate in the water is taken up by aquatic plants, which incorporate the nitrogen into organic-N compounds. Eventually, some plants will be consumed by herbivores (with nitrogen remaining as some type of organic nitrogen compound in the herbivore), while other plants will die and be decomposed by microorganisms (with nitrogen being released back into the water as ammonia - either through urine-like excretions, or through microbial decomposition of the dead animals). The pH of the water determines whether this nitrogen occurs as ammonia or ammonium. Both forms may be taken up by plants, or oxidized to nitrite by *Nitrosomonas* bacteria in a process called nitrification. The nitrite can be converted to molecular nitrogen ( $\text{N}_2$ ), nitric oxide (NO), or nitrous oxide ( $\text{N}_2\text{O}$ ) gases, or further oxidized to nitrate, again by a bacterial process. The reverse process, reduction of nitrate to nitrite, also occurs. Finally, certain plants can convert molecular nitrogen into organic nitrogen by the process of fixation.



**Figure 18.** The nitrogen cycle in an aquatic system.

In addition to the sources displayed in the nitrogen cycle, nitrite may also enter an aquatic system through discharges of industrial wastewater. Nitrite is very toxic to aquatic animals, often because of its ability to damage gill tissue, thus reducing the ability of the gills to absorb oxygen from the water. Nitrite is also toxic to people, and infants in particular. When absorbed into the

body, nitrite binds with hemoglobin in the blood, which prevents oxygen from binding with hemoglobin and circulating throughout the body. Nitrite is generally not found in concentrations higher than a few mg/L, and normally much less. The water quality standard for nitrite in Crystal River and Coal Creek is 0.05 mg/L as nitrogen (in other words, the concentration of nitrite that includes 0.05 mg/L due to the nitrogen in the nitrite). The organizations monitoring the Crystal River and Coal Creek had samples analyzed for nitrite at only 3 of the 9 sites: Crystal River upstream of Coal Creek, below Redstone, and above Avalanche Creek. Of the 63 samples analyzed, 2 had nitrite concentrations exceeding the standard. The exceedances were slight—a maximum value of 0.12 mg/L as nitrogen versus 0.05 mg/L as nitrogen for the standard.

In addition to the sources shown in the nitrogen cycle, nitrate can enter an aquatic system in wastewater discharges from industrial facilities, discharges of treated water from sewage treatment plants, in surface runoff from agricultural land in particular, and by deposition from the atmosphere. Nitrate has little *direct* toxicity to aquatic animals and people, but it can be converted to nitrite within the organism. Nitrate is not usually found in natural waters in concentrations higher than about 20 mg/L unless there are anthropogenic sources present. The water quality standard for nitrate in Crystal River and Coal Creek is 10 mg/L as nitrogen (in other words, the concentration of nitrate that includes 10 mg/L due to the nitrogen in the nitrate.) All but 4 of the 9 sites had samples analyzed for nitrate: Crystal River at Genter Mine Bridge, below Redstone, and at Penny Hot Springs; and Coal Creek at Crystal River. None of the 77 samples analyzed for nitrate exceeded the standard.

Ammonia and ammonium have essentially the same additional sources as nitrate. The pH of the water determines whether we have ammonia or ammonium. When we have a more acidic (*i.e.*, lower) pH, we have less ammonia and more ammonium and *vice versa*. Temperature is also a factor, with higher temperatures favoring ammonia over ammonium. At a pH of 6 and a temperature of 0°C (32°F), we have 0.01% ammonia and 99.99% ammonium. At a pH of 9 and a temperature of 25°C (77°F), we have 36% ammonia and 64% ammonium. The difference is important to aquatic life—ammonia is much more toxic to aquatic animals than ammonium.

Because of this dependence on pH and temperature, the water quality standard for ammonia varies with these parameters according to an equation specified in Classifications and Standards for the Upper Colorado River Basin (5 CCR 1002-33). There is one equation based on short-term (acute) exposures of aquatic life to ammonia, and a second equation for long-term (chronic) exposures. The standards generated from these equations were calculated for a plausible range of temperature and pH. The standards are expressed in units of mg/L as N, (meaning the concentration of ammonia that includes that number of mg/L of nitrogen in the ammonia.) Ammonia is generally not found in concentrations higher than about 1 mg/L unless anthropogenic sources are present.

Ammonia was quantified and reported in six different ways, depending on the organization conducting the sampling and the dates of the sampling:

|  |  |
|--|--|
| Ammonia, filtered, mg/L as N               | Ammonia, filtered, mg/L as NH <sub>3</sub>   |
| Ammonia, unfiltered, mg/L as N             | Ammonia, unfiltered, mg/L as NH <sub>3</sub> |
| Ammonia, un-ionized, calculated, mg/L as N | Total ammonia, mg/L                          |

The organizations monitoring the Crystal River and Coal Creek had samples from all but 3 of the 9 sites analyzed for ammonia: Crystal River at Penny Hot Springs, Coal Creek above Dutch Creek, and Bear Creek. Ammonia was detected in 104 of the 129 unfiltered samples that were analyzed for this parameter. There were no exceedances of either the acute or chronic ammonia standards.

The available data suggest that neither nitrate, nitrite, nor ammonia have been a significant water quality problem in the Crystal River and Coal Basin.

## 4.9 Phosphorous

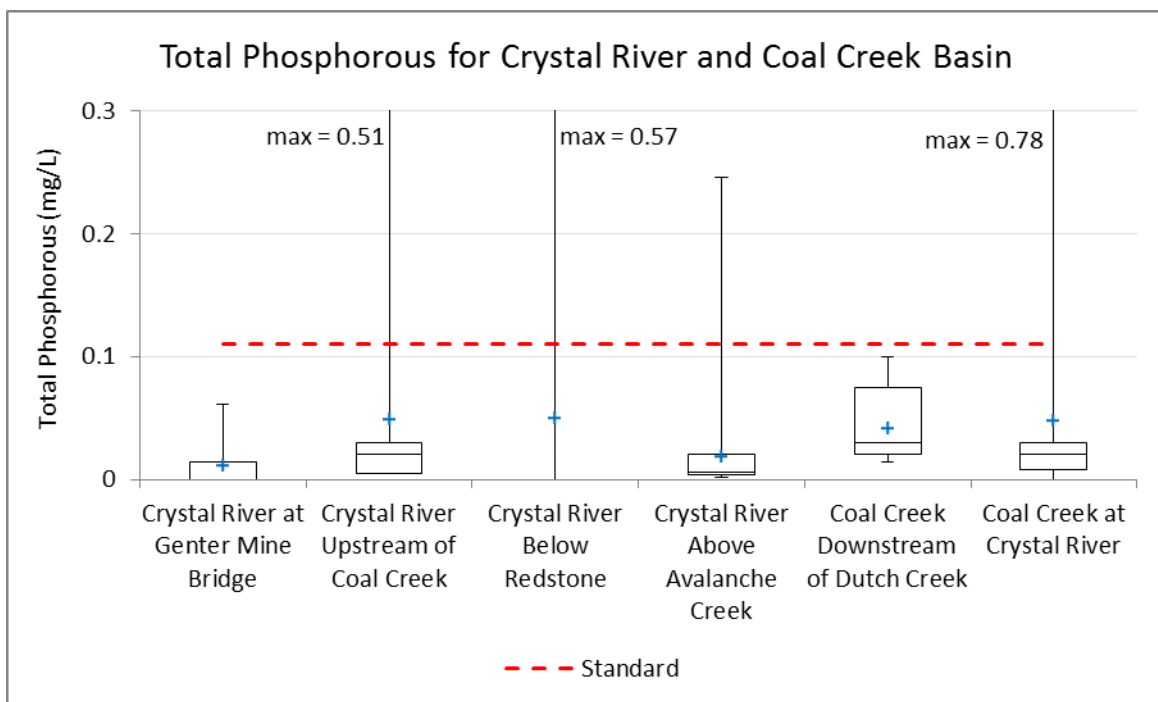
Phosphorous (P) occurs primarily in three forms: phosphate or orthophosphate ( $\text{PO}_4^{3-}$ ), condensed phosphates (such as  $\text{P}_2\text{O}_7^{4-}$ ), and organic phosphate (organic-P), which is phosphorous that has been incorporated into plant and animal tissue. About 90% of all the phosphorous present in a typical aquatic system occurs as organic phosphorous. The concentration of a phosphorous-containing compound is often expressed as “mg/L of P”, which specifically refers to the amount of phosphorous present in that compound. (For example, a “phosphate concentration of 0.1 mg/L as P” means that the amount of phosphorous due to this concentration of phosphate is 0.1 mg/L.)

Natural sources of phosphorous in aquatic systems include the dissolution of phosphorous-containing minerals (such as apatite) from soil and bedrock, decomposition of plant and animal matter, and excretions from aquatic animals. Human sources include seepage from onsite wastewater treatment systems, discharge of treated water from sewage treatment plants, discharges of industrial wastewater, discharges containing phosphate detergents, and surface runoff from animal wastes and fertilizers associated with agricultural lands. Phosphorous in aquatic systems can be absorbed by aquatic plants and incorporated into organic-P, converted between orthophosphate and condensed phosphates through microorganism-mediated reactions, and accumulated in the bottom sediments of the stream or pond. This accumulation takes place by the precipitation of phosphate minerals out of the water and the sorption or “sticking” of phosphate to sediment surfaces because of attractive forces. The majority of all the phosphorous in an aquatic system is commonly found in the bottom sediments rather than as dissolved phosphorous.

The amount of phosphorous present in an aquatic system is usually the limiting factor in the growth of aquatic plants. The greater the amount of phosphorous, the greater the growth of algae and macrophytes (“pondweeds”) will be. When human actions lead to unusually large amounts of phosphorous, cultural eutrophication may occur. Mats of algae cover the surface of the water; clumps wash onto shore and rot. Cyanobacteria (formerly known as blue-green algae), in particular, are associated with eutrophication and are especially undesirable because they secrete a toxin that can be lethal to fish and wildlife. Dead algae sink to the bottom and decompose, creating a biochemical oxygen demand. The resulting oxygen depletion kills or drives away many of the aquatic species present. Eutrophication is mostly associated with ponds and lakes rather than streams.

At this time, there is no Colorado water quality standard for phosphorous, but as of 2012 there are “interim values” set forth in Section 31.17 of Regulation 31 of the CWQCC. The interim values currently function as water quality goals, but are intended to serve as a basis for water quality standards that regulation requires to be established by 2022. As cold-water streams, the Crystal River and Coal Creek are subject to an interim value of 0.11 mg/L as phosphorous for total phosphorous. Compliance is assessed by comparing the annual median of total phosphorous to 0.11 mg/L, with no more than 1 exceedance in a 5-year period.

Total phosphorous was detected in 128 of the 245 unfiltered samples that were analyzed for this parameter. Phosphorous values exceeded 0.11 mg/L as phosphorous on 13 occasions: once in the Crystal River upstream of Coal Creek, 8 times in the Crystal River below Redstone, once in the Crystal River above Avalanche Creek, and 3 times in Coal Creek above Crystal River (Figure 19). The 8 results greater than 0.11 mg/L below Redstone took place at irregular intervals during the period 1976 to 2003. None of the other values above 0.11 mg/L occurred more recently than 2003. These data suggest that neither the Crystal River nor Coal Creek have a current problem with phosphorous. The new Redstone wastewater treatment plant, constructed in 2012, should help prevent future problems in the Crystal River below Redstone.



**Figure 19. Total phosphorous for Crystal River and Coal Creek Basin sites.**

#### 4.10 Chloride

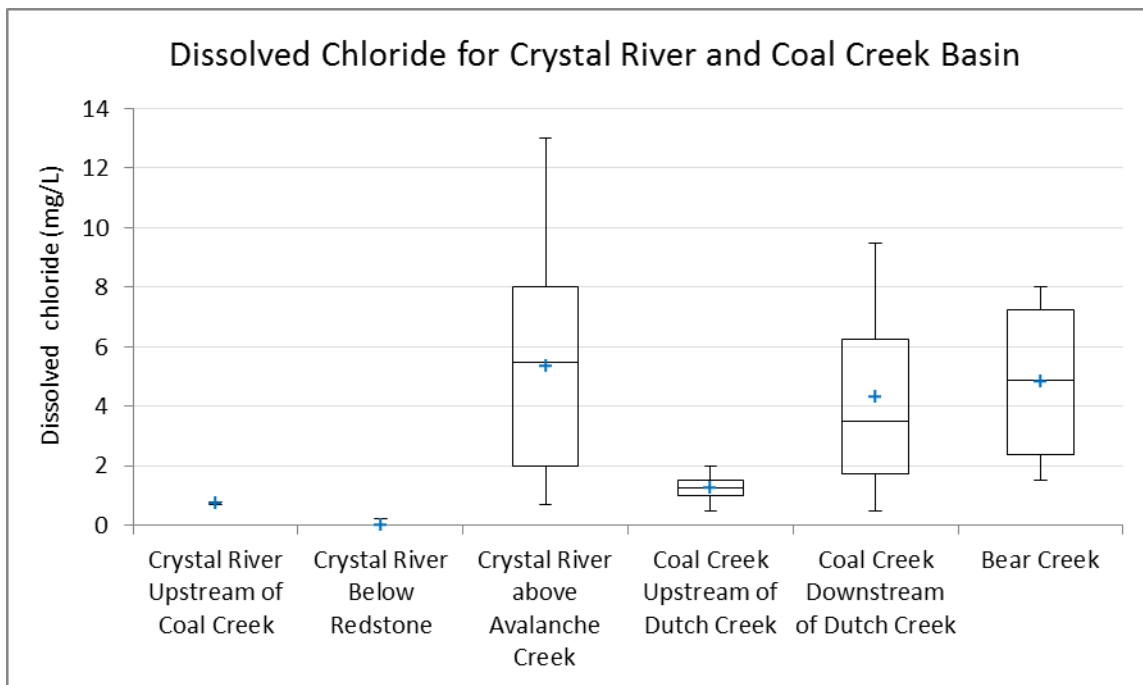
Chloride (Cl<sup>-</sup>) is commonly found in surface water in concentrations of up to a few hundred mg/L, depending on the geochemistry of the watershed. Chloride comes from dissolution of minerals containing chloride, discharges from sewage treatment plants and certain industries, and salts from road de-icing. In general, there are no significant sinks.

Chloride shows little toxicity to aquatic life. However, if the chloride concentrations are very high (*i.e.*, hundreds of mg/L), the water is also likely to be high in TDS. The Colorado water quality standard applicable to the Crystal River and Coal Basin is based on the potential use of these waters for drinking. The standard for chloride is set at 250 mg/L in unfiltered samples based on taste—people in general find the taste of water objectionable as the concentration increases beyond 250 mg/L.

Chloride was detected in 51 of the 72 unfiltered samples that were analyzed for this parameter. For the unfiltered samples, results ranged from non-detectable to 33 mg/L with a median of 1.5 mg/L (Figure 20). There were no exceedances of the 250 mg/L standard.

Dissolved chloride was detected in 70 out of 90 filtered samples. Results ranged from non-detectable to a maximum of 20 mg/L with a median of 2 mg/L (Figure 21). There is no water quality standard for dissolved chloride.

The available data suggest that chloride does not present a water quality problem in the Crystal River and Coal Basin.



**Figure 20. Chloride in filtered samples for Crystal River and Coal Creek Basin sites.**

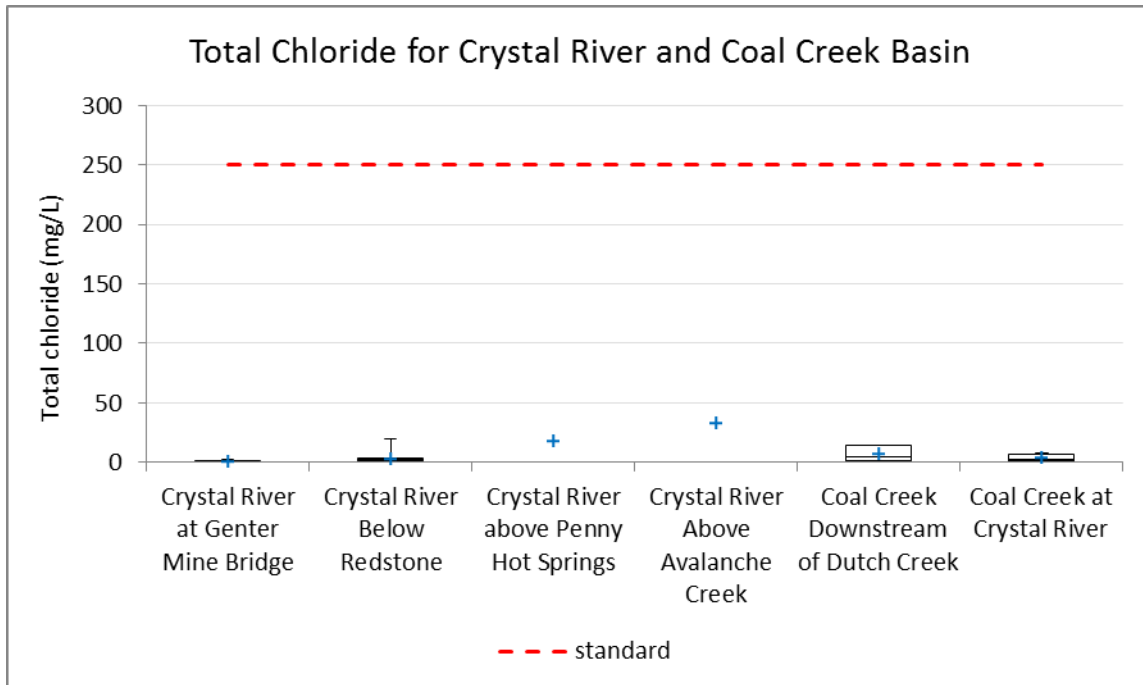


Figure 21. Chloride in unfiltered samples for Crystal River and Coal Creek Basin sites.

#### 4.11 Sulfur

Sulfur occurs in several different forms in aquatic systems: sulfate ( $\text{SO}_4^{2-}$ ), elemental sulfur (S), inorganic sulfide ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ), and organic sulfide (organic-S), which is sulfur incorporated into plant and animal tissues.

Sulfate commonly occurs in natural waters because of the dissolution of sulfate-containing minerals, such as gypsum ( $\text{CaSO}_4$ ). Deposition of sulfate in acid rain may sometimes be a significant factor. Additional mechanisms involve microorganisms. When conditions are favorable, microorganisms can cause the oxidation of dissolved sulfides to sulfate. Similarly, there is the microbial oxidation of sulfide minerals (such as iron sulfide,  $\text{FeS}$ ) to sulfate, with dissolution of the sulfate into water. This latter process is the origin of acid mine drainage. Sulfates and sulfides may be a component of industrial wastewater discharges into surface waters as well. Sinks for sulfate include microbial reduction to sulfide. (Different bacteria are involved in the reduction reaction than are involved in the oxidation reactions.) Under certain conditions, sulfate can precipitate out of the water as a sulfate mineral or salt.

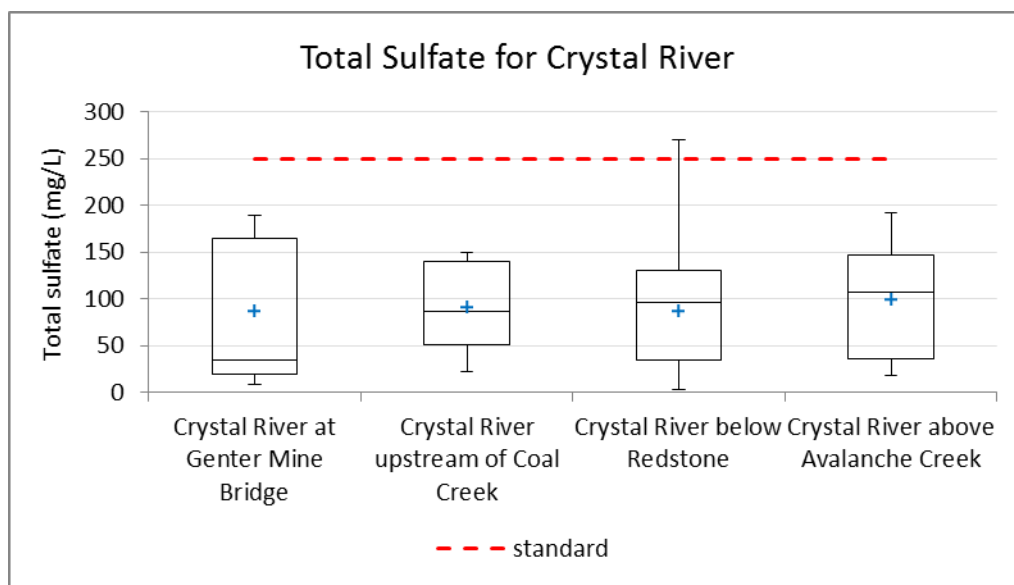
There is little toxicity to aquatic organisms associated with sulfate. However, if the sulfate concentration is very high (*i.e.*, hundreds of mg/L), the water is also likely to be high in TDS. The Colorado water quality standard applicable to the Crystal River and Coal Basin is based on the potential use of these waters for drinking. The standard for sulfate is set at 250 mg/L in unfiltered samples and is based on taste—people in general find the taste of water objectionable as the concentration increases beyond 250 mg/L.

Sulfate was detected in 276 of the 279 unfiltered samples analyzed for this parameter with results ranging from non-detectable to a maximum of 270 mg/L with a median of 72 mg/L (Figures 22 and 23). The only exceedance of the standard was 270 mg/L in the Crystal River below Redstone on 20 February 2003.

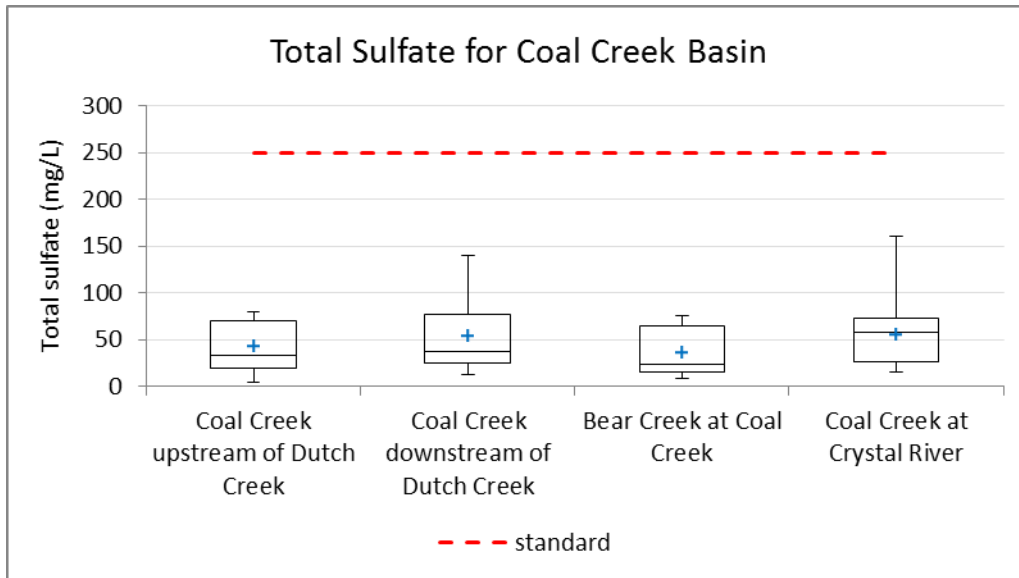
Dissolved sulfate was detected in 14 of the 15 filtered samples that were analyzed for this parameter. Results ranged from non-detectable to a maximum of 240 mg/L with a median of 75 mg/L. There is no water quality standard based only on dissolved sulfate.

Sulfides in natural waters are also of interest. When plant and animal matter decomposes, organic sulfur compounds in the plant and animal tissue are decomposed by microorganisms to soluble sulfide. Sinks for sulfide include the microbial oxidation to sulfate and the precipitation of solid iron sulfides from solution. Hydrogen sulfide (H<sub>2</sub>S) in particular is very toxic to aquatic life.

The Colorado water quality standard for hydrogen sulfide is 0.002 mg/L. The occurrence of this compound in the Crystal River and Coal Basin cannot be evaluated because none of the samples recorded in the data base were analyzed for this compound. Hydrogen sulfide is unlikely to occur very long in persistent, significant concentrations in well-oxygenated surface waters. Dissolved oxygen data for the Crystal River and Coal Basin show no evidence of poor oxygenation, so hydrogen sulfide is unlikely to be a problem in these waters.



**Figure 22. Sulfate in unfiltered samples for Crystal River sites.**



**Figure 23. Sulfate in unfiltered samples for Coal Creek Basin sites.**

The available data suggest that sulfate does not present a water quality problem in the Crystal River and Coal Basin. The available data are insufficient to demonstrate that hydrogen sulfide is not a problem, but the apparent absence of hydrogen sulfide sources suggests that there should not be a problem.

#### 4.12 Cyanide

Cyanide includes hydrogen cyanide (HCN) and the cyanide ion (CN<sup>-</sup>). Cyanide is released into the environment from biogenic processes in bacteria, fungi, and plants. Human sources of cyanide include certain industries, precious metal extraction in particular.

The Colorado water quality standard for cyanide is 0.005 mg/L based on protection of aquatic life. Of the 26 samples in the data base that were analyzed for cyanide, all were from the Crystal River below Redstone and only 2 had detectable concentrations. Both of these samples exceeded the standard: 0.01 mg/L on 18 December 1980 and 0.014 mg/L on 18 November 1981. Of the 24 samples in which cyanide was not detected, 16 had a detection limit of 0.01 mg/L, which is above the standard. This presents the possibility that actual cyanide concentrations exceeded the standard even though no cyanide was detected.

The available data are insufficient to demonstrate that cyanide is not a problem in the Crystal River and Coal Basin. However, the apparent absence of cyanide sources suggests that a problem is unlikely.

#### 4.13 Boron

Boron may occur in aquatic systems in the form of borate (BO<sub>3</sub><sup>3-</sup>) if borate minerals are present in the watershed. Human sources of boron include certain industrial discharges. Boron has very



little toxicity to aquatic life. The Colorado water quality standard of 0.75 mg/L for dissolved boron is based on the sensitivity of crops to boron in irrigation water. Only one sample in the data base was analyzed for dissolved boron and no boron was detected.

The available data are insufficient to demonstrate that boron is not a problem in the Crystal River and Coal Basin. However, the apparent absence of boron sources suggests that a problem is unlikely.

#### **4.14 Metals**

The term “metals” is broadly used by environmental professionals to mean the elements in the first two columns of the periodic table (such as sodium, calcium, and magnesium), the “transition metals” in the middle of the periodic table (such as cadmium, lead, and mercury) and certain other “metalloids” (such as arsenic and selenium). Metals in aquatic systems are distributed between the dissolved and solid forms. In the solid form, metals occur within the minerals that make up the suspended sediments and bottom sediments, within insoluble compounds that have precipitated out of the water, and sorbed to sediment surfaces due to attractive forces. The relative amount present in each of the various possible forms depends on other properties of the water, such as pH, oxidation potential, other substances dissolved in the water, and the chemistry of the sediments. Metals may also be found sequestered in the tissue of aquatic organisms.

There are two approaches to studying metals in aquatic systems. To quantify only the dissolved form of a metal, water is passed through a filter that will trap particles greater than 0.45 micrometers in size before sample analysis. To quantify the total amount of a metal, a digestion process is used to release the metal from any sediments present in the sample, allowing the metal to be measured along with its dissolved form. This and similar procedures are referred to as analysis for “total metals”, “recoverable metals”, or “total recoverable metals”.

All the metals occur naturally in the earth’s crust, and thus occur in soil and natural waters due to weathering of the crust. Each metal also has human sources, with each metal linked to certain industries. Most metals have a significant toxicity to aquatic organisms, with effects ranging from death, to impairment of reproduction, to a variety of other adverse physiological conditions. Water quality criteria for metals are derived from studies that identify concentrations that are lethal to the selected aquatic species that are particularly convenient for toxicity testing. Acute water quality standards are established to protect aquatic life from transient high concentrations of the metal. Chronic standards provide protection from concentrations present over periods of 30 days or longer. In some cases, additional standards are set for protection of particular fish species, such as trout and sculpin.

The toxicity of several metals (including cadmium, copper, lead, manganese, and zinc) depends on the water hardness. The greater the hardness, the lower the toxicity of the metal and the less stringent the water quality standard is. Aquatic toxicologists have developed equations specific to each metal that give an appropriate standard for a specific value of hardness. In order to compare the metal concentration in a water sample with the standard, the hardness of the sample must be measured and a sample-specific standard calculated using equations specified in 5 CCR 1002-33.6(3) Table Value Standards.

#### **4.14.1 Arsenic**

The Colorado water quality standards for arsenic that apply to the Crystal River and Coal Basin are an acute standard for protection of aquatic life and a standard for protection of water supplies. The acute standard of 340 µg/L is based on analysis of dissolved arsenic in filtered samples. The water supply standard is 0.02 µg/L, based on analysis of total recoverable arsenic in unfiltered samples.

Dissolved arsenic was detected in 14 of the 167 samples analyzed for this parameter. Results ranged from non-detectable to 290 µg/L. None of the results exceeded the acute standard of 340 µg/L.

Total recoverable arsenic was detected in 10 of the 121 samples analyzed for this parameter. Results ranged from non-detectable to 250 µg/L, with all 10 of the detectable concentrations exceeding the water supply standard of 0.02 µg/L. The sites represented by these 10 samples were the Crystal River at Genter Mine Bridge, Crystal River upstream of Coal Creek, Crystal River below Redstone, and the Crystal River above Avalanche Creek, along with Coal Creek at Crystal River.

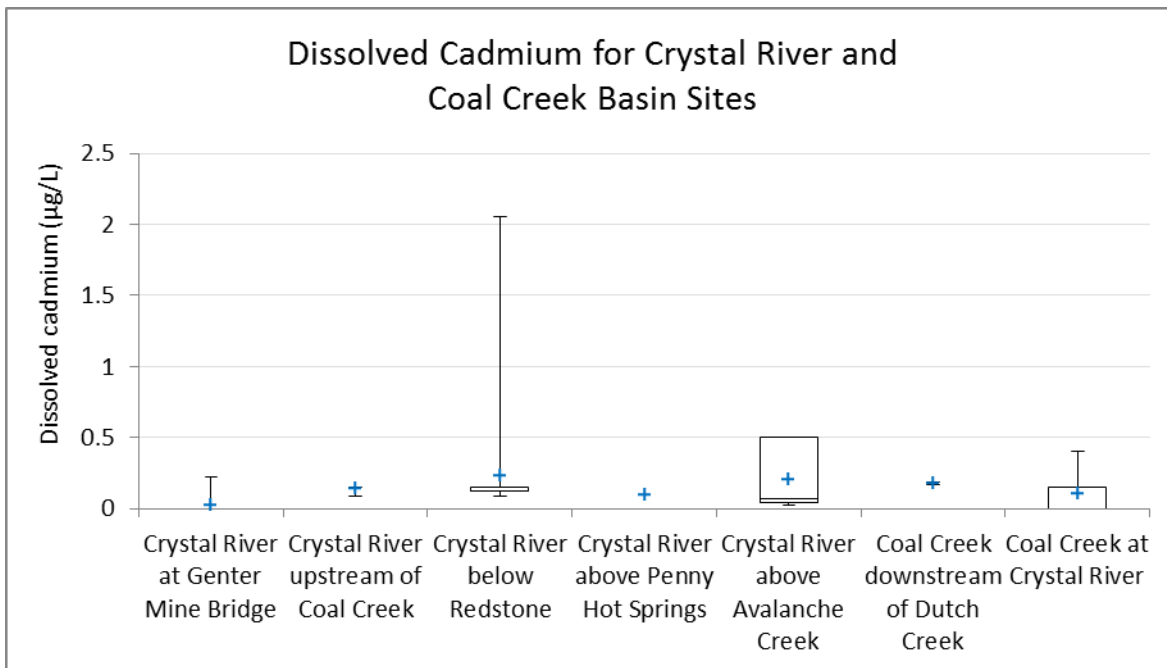
Total recoverable arsenic includes both dissolved arsenic and arsenic associated with sediments suspended in the water. If dissolved arsenic exceeds the 0.02 µg/L standard, one can reasonably assume that total recoverable arsenic would also exceed this standard. Six of the samples having detectable dissolved arsenic concentrations were not also analyzed for total recoverable arsenic. All six of these samples had results that exceeded the 0.02 µg/L standard and can be considered evidence of additional occasions when arsenic exceeded the water supply standard of 0.02 µg/L.

The available data indicate that arsenic may be a problem if the Crystal River and Coal Creek were to be used as a drinking water supply. Arsenic does not present a problem for aquatic life.

#### **4.14.2 Cadmium**

The Colorado water quality standards for cadmium are based on the protection of aquatic life. The standards applicable to the Crystal River and Coal Basin are an acute standard, an acute standard specific to trout waters, and a chronic standard. Each standard varies with water hardness and is based on dissolved cadmium measured in filtered samples. Cadmium was detected in 32 of the 215 samples that were analyzed for dissolved cadmium. Results ranged from non-detectable to 2.1 µg/L (Figure 24). Hardness-based standards were calculated for each sample that was analyzed for both hardness and dissolved cadmium. The acute standard for trout waters ranged from 1.3 µg/L to 4.2 µg/L. The chronic standard ranged from 0.4 µg/L to 0.9 µg/L. There were no exceedances of the acute standard or the acute standard for trout. The chronic standard was slightly exceeded in the Crystal River below Redstone on 4 occasions, all between June 2000 and March 2001.

The available data suggest that cadmium has not been a significant water quality problem in the Crystal River or in Coal Basin.



**Figure 24. Box plots of all results for cadmium in filtered samples.**

#### 4.14.3 Chromium

Chromium commonly occurs in two forms, chromium(III) and chromium(VI), each of which has its own Colorado water quality standard. The water quality standards for chromium(VI) that apply to the Crystal River and Coal Basin are for protection of aquatic life. The acute standard of 16 µg/L and the chronic standard of 11 µg/L are both based on analysis of dissolved chromium(VI) in filtered samples. There is an additional standard of 50 µg/L for protection of drinking water based on analysis of total recoverable chromium(III) in unfiltered samples. The regulations require that unless it is clearly demonstrated that the chromium present is in the form of chromium(III), the measured chromium concentrations must be compared with the standard for chromium(VI). Also, the sum of chromium(III) and chromium(VI) (or total chromium, when the analysis does not distinguish between these two forms) must not exceed 50 µg/L.

The analyses reported in the data base did not distinguish between the two forms of chromium. Only 20 samples in the data base had been analyzed for dissolved chromium, and none showed any detectable chromium. Thus, the standards for protection of aquatic life have not been exceeded. Of the 54 samples that were analyzed for total recoverable chromium, only two had detectable chromium, with values of 21 µg/L and 0.74 µg/L, showing that the standard for protection of drinking water has not been exceeded.

The available data suggest that chromium has not been a water quality problem in the Crystal River and Coal Basin.

#### 4.14.4 Copper

The Colorado water quality standards for copper are based on the protection of aquatic life. Both the acute and chronic standards vary with water hardness and are based on dissolved copper measured in filtered samples. Copper was detected in 69 of the 267 samples that were analyzed for dissolved copper. Results ranged from non-detectable to 200 µg/L (Figure 25; two values exceeding 100 µg/L are omitted from this figure in order to preserve a vertical scale that permits better viewing of the majority of samples). Hardness-based standards were calculated for each sample that was analyzed for both hardness and dissolved copper. The acute standard ranged from 8.6 µg/L to 35.9 µg/L. The chronic standard ranged from 6.0 µg/L to 21.3 µg/L. Both the acute and chronic standards were exceeded on only 2 occasions: on 21 August 2002 in the Crystal River below Redstone, and on 20 February 2001 in Coal Creek at Crystal River.

The available data suggest that copper has not been a significant water quality problem in the Crystal River and Coal Basin.

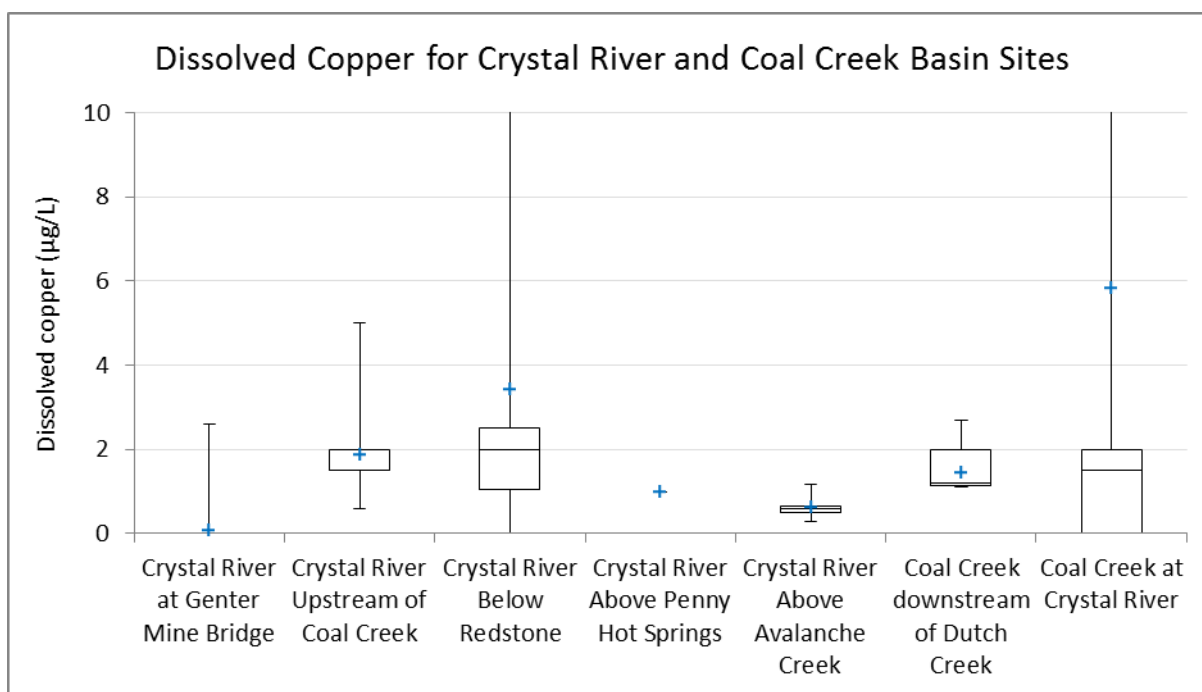


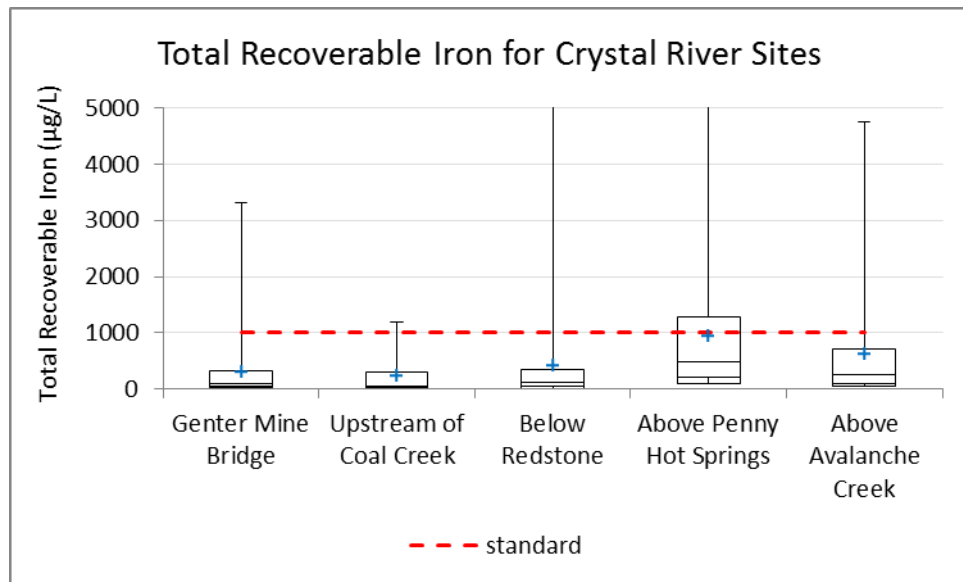
Figure 25. Box plots for selected results for copper in filtered samples.

#### 4.14.5 Iron

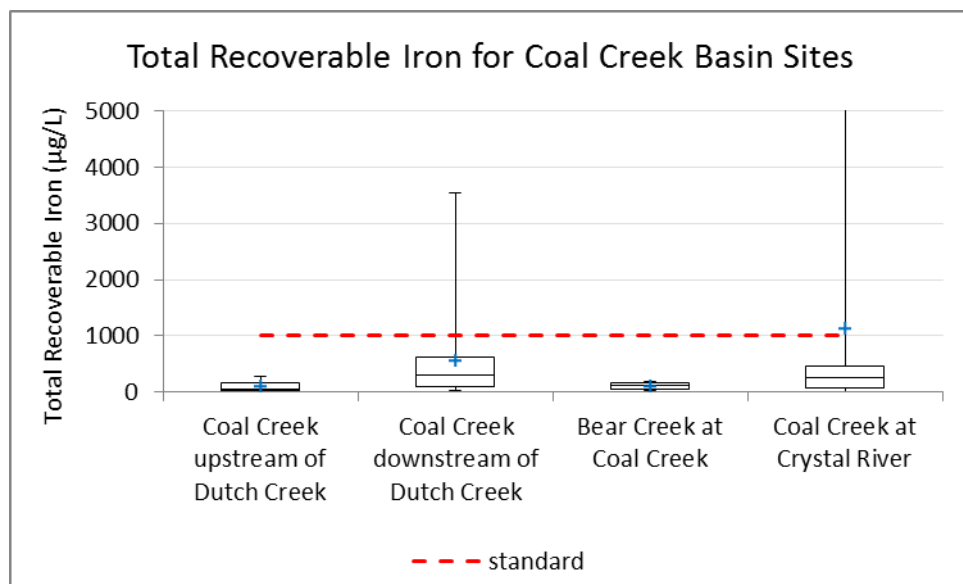
Colorado has one iron standard for protection of aquatic life and a second iron standard for protection of drinking water. Both apply to the Crystal River and Coal Basin. The standard for protection of aquatic life is 1,000 µg/L, based on analysis of total recoverable iron in unfiltered

samples. The standard based on water supply is 300 µg/L, based on analysis of dissolved iron in filtered samples.

Total recoverable iron was detected in all but 21 of the 469 samples that were analyzed for this parameter. Results ranged from non-detectable to 22,000 µg/L, with a median of 175 µg/L (Figures 26 and 27; values exceeding 5,000 µg/L are omitted from these figures in order to preserve a vertical scale that permits better viewing of the majority of samples). Total recoverable iron exceeded 1,000 µg/L in 69 of the samples, with exceedances occurring throughout the period of record and at every location except for Coal Creek above Dutch Creek and Bear Creek at Coal Creek, which were each studied for only a short period of time in the mid-1970's.

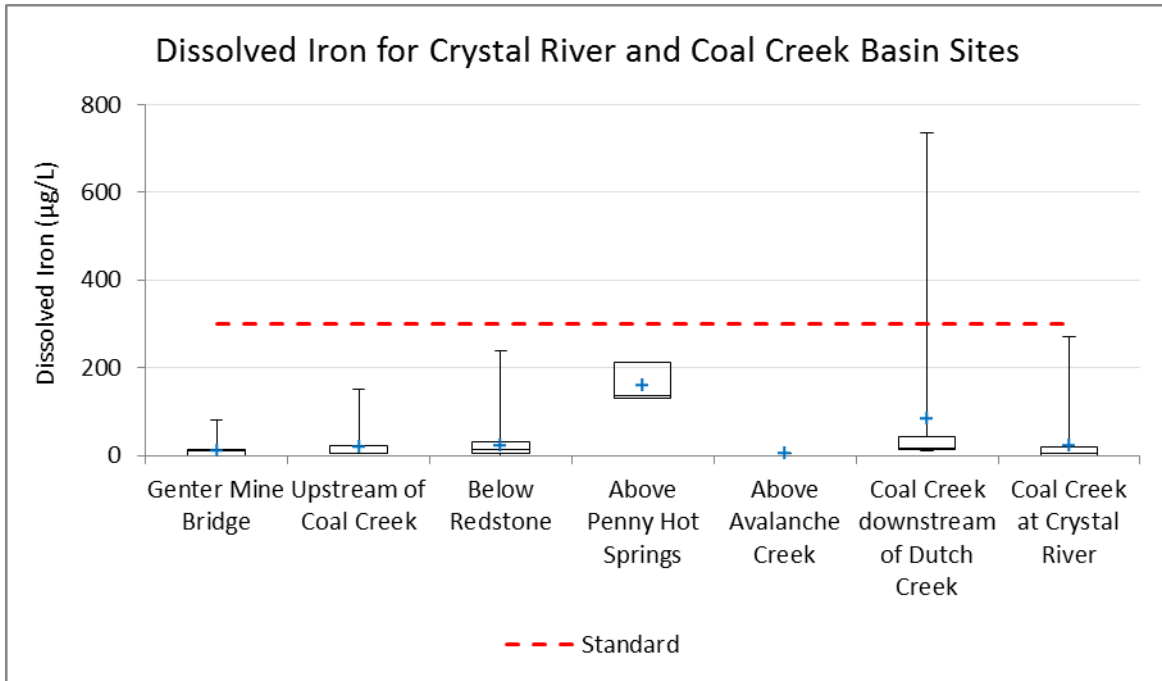


**Figure 26. Total recoverable iron for Crystal River sites.**



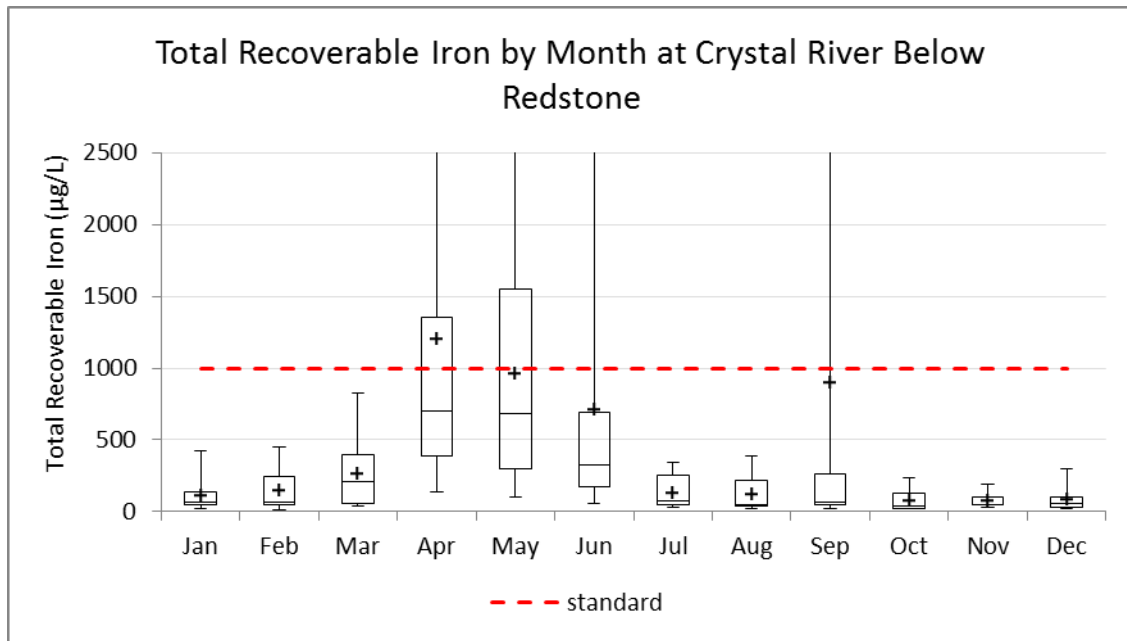
**Figure 27. Total recoverable iron for Coal Creek Basin sites.**

Dissolved iron was detected in 120 of the 225 samples that had been analyzed for this parameter. Results ranged from non-detectable to 736  $\mu\text{g/L}$  (Figure 28). The value 736  $\mu\text{g/L}$  in Coal Creek below Dutch Creek on 22 May 2003 was the only result that exceeded the water supply standard of 300  $\mu\text{g/L}$ .



**Figure 28. Iron in filtered samples for Crystal River and Coal Creek Basin sites.**

The total recoverable iron concentrations show a seasonal variation, with higher values occurring from March through June, as seen for the Crystal River below Redstone in Figure 29. Total recoverable concentrations are also much greater than dissolved iron concentrations. These patterns show that most of the total recoverable iron is associated with suspended sediments eroded from the land surface and stream bank during the spring runoff. Occasional high values of total recoverable iron at other times of year are likely to be a result of transient high concentrations of suspended sediments from stormwater runoff.



**Figure 29. Total recoverable iron for the Crystal River below Redstone.**

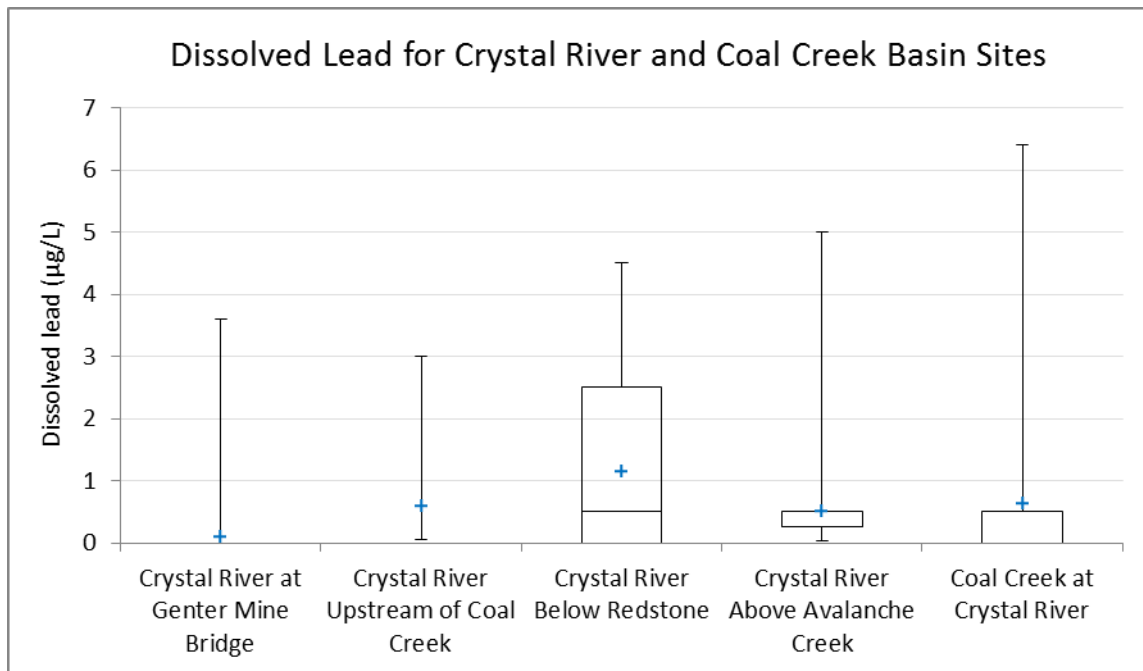
The data suggest that dissolved iron has not been a significant water quality problem. In contrast, the data show that total recoverable iron frequently occurs in concentrations exceeding the water quality standard for protection of aquatic life in the Crystal River and Coal Basin. Given that total recoverable iron concentrations are typically much greater than dissolved iron concentrations, the majority of the total recoverable iron is associated with sediment suspended in the water. The source of this sediment is soil and rock in the Crystal River watershed having significant iron content.

#### 4.14.6 Lead

Colorado has acute and chronic water quality standards for lead. Both standards vary with water hardness and are based on dissolved lead measured in filtered samples. Lead was detected in 11 of the 231 samples that were analyzed for dissolved lead. Results ranged from non-detectable to 6.4 µg/L (Figure 30). Standards were calculated for each sample that was analyzed for both hardness and dissolved lead. The acute standard ranged from 28 µg/L to 258 µg/L. The chronic standard ranged from 1.1 µg/L to 10 µg/L.

There were no exceedances of the acute standards for lead. The chronic standard was exceeded on 5 occasions: 17 May 1976 in the Crystal River above Coal Creek, 15 June 2000 in the Crystal River below Redstone, and 29 September 2003, 7 February 2008, and 17 February 2008 in Coal Creek at Crystal River. The Crystal River below Redstone also had 7 occasions between 1988 and 1991 when the detection limit was greater than the chronic standard, which presents the possibility that actual lead concentrations may have exceeded the standard.

The available data suggest that lead has not been a significant water quality problem in the Crystal River and Coal Basin.

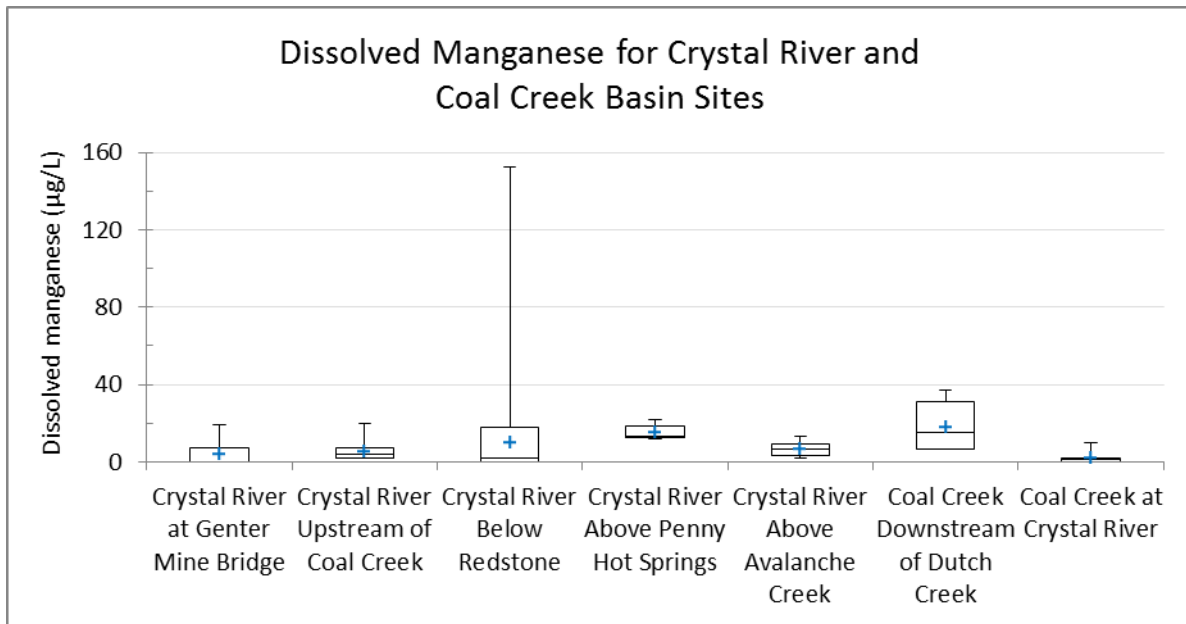


**Figure 30. Lead in filtered samples for Crystal River and Coal Creek Basin sites.**

#### 4.14.7 Manganese

Colorado has acute and chronic water quality standards for manganese. Both standards vary with water hardness and are based on analysis of filtered samples. Manganese was detected in 96 of the 245 samples that were analyzed for dissolved manganese. Results ranged from non-detectable to 152 µg/L (Figure 31). Standards were calculated for each sample that had been analyzed for both hardness and dissolved manganese. The acute standard ranged from 2,322 µg/L to 4,608 µg/L. The chronic standard ranged from 1,283 µg/L to 2,546 µg/L. All manganese concentrations were well below the standards.





**Figure 31. Manganese in filtered samples for Crystal River and Coal Creek Basin sites.**

The available data suggest that manganese has not been a significant water quality problem in the Crystal River and Coal Basin.

#### 4.14.8 Mercury

The applicable water quality standard for mercury is 0.01 µg/L, based on protection of aquatic life. This standard requires analysis of total mercury in unfiltered samples. Mercury was not detected in any of the 42 samples that were analyzed for total mercury. However, the detection limits for these analyses ranged from 0.1 µg/L to 0.5 µg/L, which presents the possibility that actual mercury concentrations may have exceeded the standard. An additional 41 samples in the data base had been analyzed for dissolved mercury in filtered samples. There were 2 detections of dissolved mercury. The measurement (recorded as an estimated value) from 7 June 2000 in the Crystal River above Avalanche Creek was the only result that exceeded the standard.

Mercury occurs in many water bodies in Colorado due to deposition from the atmosphere, which suggests the possibility that the Crystal River and Coal Basin may be affected. Given the limited number of samples analyzed for mercury, and the detection limits for the analyses, the available data are insufficient to demonstrate that mercury is not a problem for water quality in the Crystal River and Coal Basin.

#### 4.14.9 Nickel

Colorado has acute and chronic water quality standards for nickel. Both standards vary with water hardness and require analysis of dissolved nickel in filtered samples. Only 2 of the samples in the data base have been analyzed for nickel. Only 1 sample yielded a detectable value of nickel, with a result that was well below standards.

The available data are insufficient to demonstrate that nickel is not a problem for water quality in the Crystal River and Coal Basin, but there is no apparent reason to believe that nickel should be a problem.

#### 4.14.10 Selenium

Dissolved selenium has an acute standard of 18.4 µg/L and a chronic standard of 4.6 µg/L. Selenium was detected in 50 of the 226 samples that were analyzed for dissolved selenium. Results ranged from non-detectable to 17.3 µg/L (Figure 32).

All dissolved selenium concentrations were below the acute standard. The chronic standard was exceeded 8 times: on 23 November 2005 in the Crystal River at Genter Mine Bridge; on 15 June 2000, 9 August 2000, 13 September 2000, and 6 December 2000 in the Crystal River below Redstone; on 23 November 2005 and 16 February 2006 in Coal Creek downstream from Dutch Creek; and 17 September 2008 in Coal Creek at Crystal River.

The available data suggest that selenium has been a water quality problem in the Crystal River in 2000 and in Coal Creek from 2005 to 2008. Selenium is known to occur in the Mancos Shale formation that is present in the Crystal River watershed and thus its presence in these streams is not surprising. Occasional concentrations exceeding the water quality standard may be due to natural processes or to human actions that expose material from this formation to weathering and create an opportunity for surface runoff to transport selenium into the rivers.

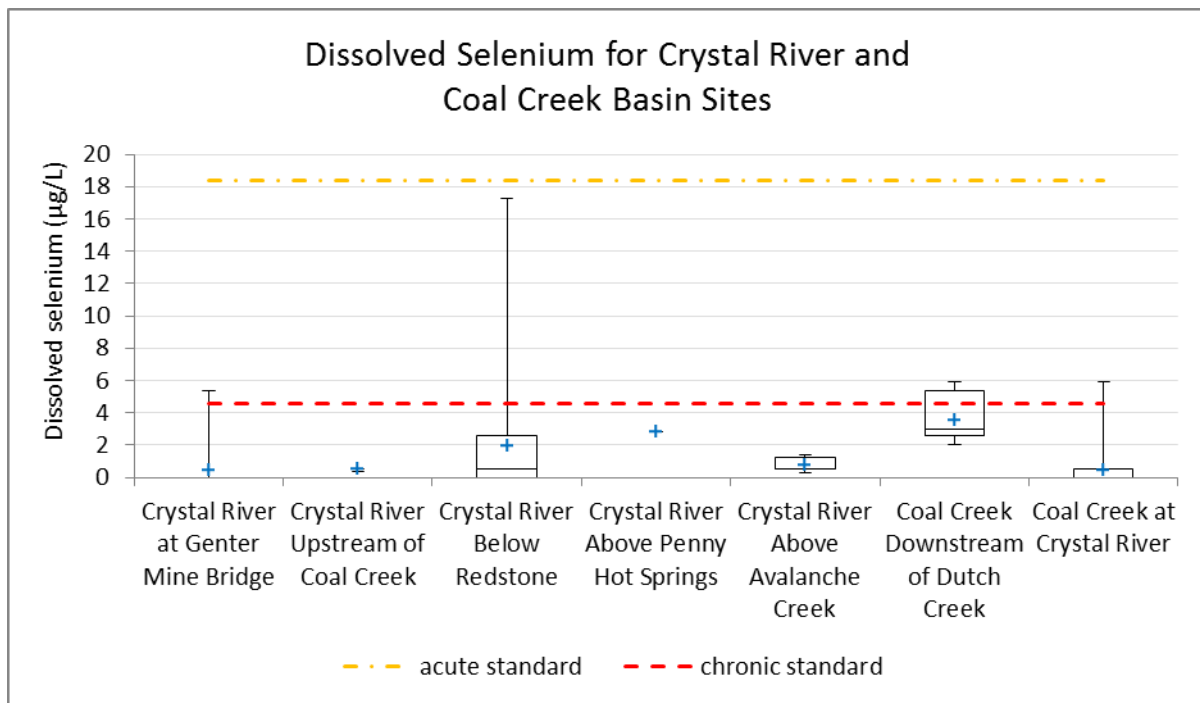


Figure 32. Selenium in filtered samples for Crystal River and Coal Creek Basin sites.

#### 4.14.11 Silver

Colorado has acute and chronic water quality standards for silver. Both standards vary with water hardness and are based on analysis of filtered samples. Silver was not detected in any of the 94 samples that were analyzed for dissolved silver. However, the silver detection limit for 42 of the samples was greater than the hardness-based standard, which presents the possibility that the actual silver concentration may be greater than the standard.

The available data are insufficient to rule out exceedances of the water quality standards for silver. However, if any exceedances have occurred, they have been slight.

#### 4.14.12 Zinc

Colorado has acute and chronic water quality standards for zinc. Both standards vary with water hardness and are based on analysis of filtered samples. Zinc was detected in 99 out of the 258 samples that were analyzed for dissolved zinc. Results ranged from non-detectable to 53  $\mu\text{g/L}$  (Figure 33). Standards were calculated for each sample that was analyzed for both hardness and dissolved manganese. The acute standard ranged from 75  $\mu\text{g/L}$  to 435  $\mu\text{g/L}$ . The chronic standard ranged from 65  $\mu\text{g/L}$  to 374  $\mu\text{g/L}$ . All zinc concentrations were below the standards.

The available data suggest that zinc has not been a significant water quality problem in the Crystal River and Coal Basin.

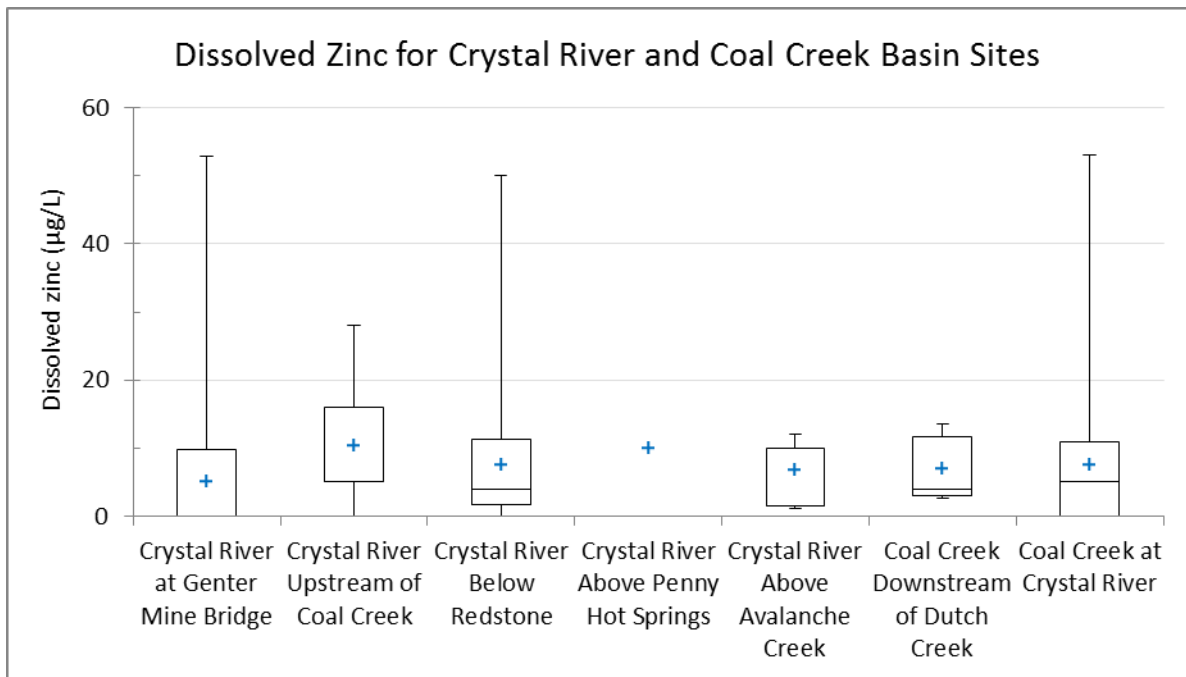


Figure 33. Zinc in filtered samples for Crystal River and Coal Creek Basin sites.

## 5.0 Water quality by Site

### 5.1 Crystal River at Genter Mine Bridge (Site 1)

The Crystal River was sampled at Genter Mine Bridge on County Road 3, approximately 3 road miles east of Colorado Highway 133. All other Crystal River sites are downstream from this location. Samples were collected by students at Marble Charter School (1998 to 2002, and 2005 to 2009) and RFC staff (2003 to 2004, and 2010 to present). There were 3 to 18 sampling events per year, beginning in December 1998. This report considers the 101 sampling events that occurred over a period of 13.5 years, through June 2012.

The classification and standards for the Crystal River at this location are found under Region 12, Roaring Fork Basin, Segment 8 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The river is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 4 shows each parameter that was studied, along with the number of samples in which that parameter was analyzed, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All of the results were below standards except for the following:

- One out of 95 temperature measurements, 11.0°C on 5 October 2000, was greater than the maximum weekly average temperature standard of 9.0°C for October through May. However, being a single result rather than an average of several measurements taken over a week, this result presents the possibility of an exceedance but is not evidence of an actual exceedance of the standard.
- One out of 94 dissolved oxygen measurements, 6.9 mg/L on 14 September 1999, was less than the minimum value of 7.0 mg/L required during spawning periods. If no fish were spawning at this time, the measurement would comply with the standard of 6.0 mg/L.
- The sum of nitrate and nitrite was quantified instead of the individual substances. If the entire sum was due to nitrate, there would be no exceedances of the nitrate standard. If the entire sum was nitrite, the nitrite standard would be exceeded on several occasions, but it is very unlikely for this to be the case. The dissolved oxygen results indicate that the Crystal River at this site has well-oxygenated water. Under these conditions nitrogen tends to occur as nitrate rather than nitrite.
- Four out of 92 results for total recoverable arsenic were greater than the chronic standard of 0.02 µg/L: 24 µg/L on 19 September 2006; 87 µg/L on 25 September 2007; 111 µg/L on 15 February 2008; and 36 µg/L on 15 September 2008. This standard is not to be exceeded more than once every 3 years on average. Four

exceedances over a period of 13.5 years complies with this limitation. However, it is noteworthy that all 4 exceedances occurred within a period of 1.5 years.

- Six out of 92 results for total recoverable iron were greater than the chronic standard of 1,000 µg/L: 3,306 µg/L on 25 September 2007; 1,449 µg/L on 4 June 2008; 1,403 µg/L on 2 February 2009; 1,743 µg/L on 29 September 2009; 2,858 µg/L on 9 June 2010; and 1,316 µg/L on 8 June 2011. This standard is not to be exceeded more than once every 3 years on average. Given that there were 6 exceedances over 13.5 years, the Crystal River at this site is not in compliance with the standard. Perhaps more importantly, the 6 exceedances all occurred within the last 5 years of data considered in this report.
- One out of 70 selenium results, 5.4 µg/L on 23 November 2005, was greater than the chronic standard for dissolved selenium of 4.6 µg/L. The Colorado water quality regulations specify that this standard is not to be exceeded more than once every 3 years on average. The single exceedance over 13.5 years of sampling complies with this limitation.

As expected, dissolved oxygen concentrations are slightly lower during the summer months when water temperature is higher (*see Section 4.5*). This behavior is consistent with oxygen having a lower solubility at higher water temperatures. Analysis using the Sen slope method shows dissolved oxygen decreasing by 0.06 mg/L per year, with the trend significant at the 95% confidence level. One might wonder whether this is a consequence of warming temperatures. However, Sen slope analysis shows a decreasing trend in water temperature rather than an increasing trend, although that decreasing trend is *not* significant at the 95% confidence level. Existing data do not provide an apparent explanation for the decreasing trend in dissolved oxygen.

Dissolved salts and dissolved metals associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, sodium, calcium, magnesium, hardness, dissolved manganese, and sulfate concentrations at this site do show this pattern. Values were generally lower during May and June than at other times of year.

The analysis for total recoverable iron and total recoverable arsenic includes not only the amount of iron and arsenic dissolved in the water, but iron and arsenic occurring in particulate form as well (*see Section 4.14*). Occasional elevated concentrations of particulates are likely to be a result of natural events and/or human actions that cause a large input of eroded soil or sediment to the river over a short time. Intense or extended storms and spring runoff are examples of such natural events; clearing of vegetation from the land surface and earthmoving are examples of such human actions. Particulate concentrations can be quantified by analyzing the water samples for TSS. Five of the 9 samples having excessive total recoverable iron or arsenic did occur on dates when results for TSS were relatively high. The other 4 samples were not analyzed for TSS. Because only 21 samples were analyzed for TSS out of 108 sampling events, a more definite correlation between TSS and total recoverable iron and arsenic cannot be established for this site. Given the month in which each of the highest values occurred, some may be attributed to

sediment input during the spring runoff (such as those occurring in June), while others may be associated with storms (such as those that occurred in September).

Several additional parameters for this site tend to show higher concentrations during spring runoff and on other isolated occasions that may possibly correspond with precipitation events. These parameters include total suspended solids, dissolved aluminum, total aluminum, dissolved iron, nitrite plus nitrate, total phosphorous, and total zinc. As described above for arsenic and iron, concentrations of total aluminum, total phosphorous, and total zinc are highly influenced by the presence of suspended sediments, so the occurrence of higher values during spring runoff is expected. Concentrations of dissolved aluminum and dissolved iron may also be enhanced by increased sediment input if these metals are occurring in the sediment in forms that have a significant water solubility.

Sen slope analysis of potassium concentrations showed a decreasing trend of 0.1 mg/L per year that was significant at the 95% confidence level. Available information does not suggest an explanation for this apparent trend. Future data collection may show that the trend is not real.

Other parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results above the detection limit for any patterns or trends to be evident.

The available data suggest that the Crystal River near Marble has good water quality except for occasional high values of total recoverable iron and total recoverable arsenic that may be a threat to aquatic life.

**Table 4. Summary of results for Crystal River at Genter Mine Bridge.**

| Parameter                               | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value    | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|-----------------|--------------------|-------------------------|
| Alkalinity (mg/L as CaCO <sub>3</sub> ) | 94                | 94                   | 36            | 180           | 75              | No                 | NA <sup>2</sup>         |
| Aluminum, dissolved (µg/L)              | 67                | 19                   | ND            | 84            | ND <sup>3</sup> | No                 | NA                      |
| Aluminum, total (µg/L)                  | 90                | 83                   | ND            | 3,141         | 75              | No                 | NA                      |
| Ammonia, total (mg/L as N)              | 20                | 3                    | ND            | 0.0147        | ND              | No                 | 0                       |
| Arsenic, dissolved (µg/L)               | 70                | 2                    | ND            | 51            | ND              | No                 | 0                       |

| Parameter                               | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Arsenic, total recoverable (µg/L)       | 92                | 4                    | ND            | 111           | ND           | No                 | 4                       |
| Cadmium, dissolved (µg/L)               | 70                | 8                    | ND            | 0.22          | ND           | No                 | 0                       |
| Calcium (mg/L)                          | 92                | 92                   | 10.8          | 99.4          | 63.0         | No                 | NA                      |
| Chloride, total (mg/L)                  | 21                | 7                    | ND            | 2             | ND           | No                 | 0                       |
| Copper, dissolved (µg/L)                | 70                | 3                    | ND            | 2.6           | ND           | No                 | 0                       |
| Discharge (cfs)                         | 9                 | 9                    | 80            | 350           | 204          | No                 | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> )   | 92                | 92                   | 43            | 309           | 187          | No                 | NA                      |
| Iron, dissolved (µg/L)                  | 70                | 39                   | ND            | 81            | 11           | No                 | 0                       |
| Iron, total recoverable (µg/L)          | 92                | 92                   | 24            | 3,306         | 105          | No                 | 6                       |
| Lead, dissolved (µg/L)                  | 70                | 2                    | ND            | 3.6           | ND           | No                 | 0                       |
| Magnesium (mg/L)                        | 92                | 92                   | 1.81          | 16.1          | 6.83         | No                 | NA                      |
| Manganese, dissolved (µg/L)             | 70                | 24                   | ND            | 19            | ND           | No                 | 0                       |
| Manganese, recoverable (µg/L)           | 92                | 36                   | ND            | 115           | 10.2         | No                 | NA                      |
| Nitrate plus nitrite, total (mg/L as N) | 21                | 19                   | ND            | 0.50          | 0.13         | No                 | NA                      |

| Parameter                            | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--------------------------------------|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Oxygen, dissolved (mg/L)             | 94                | 94                   | 6.9           | 11.4          | 9.6          | ↓ <sup>4</sup>     | 1                       |
| pH                                   | 91                | 91                   | 7             | 8.48          | 8.15         | No                 | 0                       |
| Phosphorus, total, unfiltered (mg/L) | 21                | 10                   | ND            | 0.0608        | ND           | No                 | 0                       |
| Potassium (mg/L)                     | 20                | 20                   | 0.350         | 1.237         | 0.722        | ↓                  | NA                      |
| Solids, total suspended (mg/L)       | 21                | 10                   | ND            | 53            | ND           | No                 | NA                      |
| Selenium, dissolved (µg/L)           | 70                | 9                    | ND            | 5.4           | ND           | No                 | 1                       |
| Selenium, unfiltered (µg/L)          | 92                | 21                   | ND            | 40.8          | ND           | No                 | NA                      |
| Sodium (mg/L)                        | 20                | 20                   | 0.745         | 3.266         | 2.144        | No                 | NA                      |
| Specific conductance (µS/cm)         | 7                 | 7                    | 133           | 576           | 501          | No                 | NA                      |
| Sulfate, total (mg/L)                | 21                | 21                   | 8.11          | 189           | 34.2         | No                 | 0                       |
| Temperature (°C)                     | 95                | 95                   | -2            | 16            | 5.06         | No                 | 1                       |
| Zinc, dissolved (µg/L)               | 69                | 25                   | ND            | 52.9          | ND           | No                 | 0                       |
| Zinc, total (µg/L)                   | 91                | 29                   | ND            | 113.4         | ND           | No                 | NA                      |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ND: Not detected

<sup>4</sup> ↓: Decreasing trend



## 5.2 Crystal River upstream of Coal Creek (Site 2)

The Crystal River was sampled approximately 0.3 river miles upstream from the mouth of Coal Creek, at the south end of Redstone. This site is approximately 8.6 river miles downstream from Site 1, the Crystal River at Genter Mine Bridge. Samples were collected by CDPHE on 20 occasions. Four events took place in 1976. The rest occurred from 1998 to 2002, with the majority occurring during 2001.

The classification and standards for the Crystal River at this location are found under Region 12, Roaring Fork Basin, Segment 8 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The river is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 5 shows each parameter that was studied, along with the number of samples for which that parameter was analyzed, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All of the results were below standards except for the following:

- One out of 15 temperature measurements, 12.8°C on 26 April 2001, was greater than the maximum weekly average temperature (MWAT) standard of 9.0°C for October through May. However, being a single result rather than an average of several samples taken over a week, this result presents the possibility of an exceedance but is not evidence of an actual exceedance of the standard.
- Nitrite was analyzed on 2 occasions but was not detected in either sample. The sum of nitrate and nitrite was quantified on 17 occasions and detected in 8 of those samples. If the entire result for those 8 samples was due to nitrate, there would be no exceedances of the nitrate standard. If the entire result was nitrite, the nitrite standard would be exceeded on all 8 occasions, but it is very unlikely for this to be the case. The dissolved oxygen results indicate that the Crystal River at this site has well-oxygenated water. Under these conditions nitrogen tends to occur as nitrate rather than nitrite.
- One out of 16 results for total phosphorous, 0.51 mg/L on 17 May 1976, was greater than the water quality goal for cold rivers of 0.11 mg/L. Compliance is defined as no more than one annual median exceeding 0.11 mg/L within a 5-year period. Out of the 6 years in which samples were collected and analyzed for total phosphorous, only 1976 had an annual median (0.27 mg/L) greater than 0.11 mg/L; thus the goal has been met.
- One out of 3 results for total recoverable arsenic, 0.5 µg/L on 19 May 1998, was greater than the chronic standard of 0.02 µg/L. This single exceedance complies with the requirement that the standard not be exceeded more than once every 3 years on the average.
- Two out of 17 results for total recoverable iron were greater than the chronic standard of 1,000 µg/L. These results were 1,200 µg/L on 17 May 1976 and 1,200 on 19 May 1998.

The Colorado water quality regulations specify that 1,000 µg/L is not to be exceeded more than once every 3 years on the average. The single exceedance during the more recent 4-year period of sampling complies with this limitation.

- One out of 16 results for dissolved lead, 3 µg/L on 17 May 1976, was greater than the chronic lead standard of 2.1 µg/L. This standard was calculated using the hardness value of 84 mg/L that was measured for this sample. This single exceedance complies with the requirement that the standard not be exceeded more than once every 3 years on the average.

The analysis for total recoverable iron and total recoverable arsenic includes not only the amount of iron and arsenic dissolved in the water, but iron and arsenic occurring in particulate form as well (*see Section 4.14*). Occasional elevated concentrations of particulates are likely to be a result of natural events and/or human actions that cause a large input of eroded soil or sediment to the river over a short time. Intense or extended storms and spring runoff are examples of such natural events; clearing of vegetation from the land surface and earthmoving are examples of such human actions. All 3 results for total recoverable iron and arsenic occurred in May, when spring runoff is underway.

As expected, dissolved oxygen concentrations are slightly lower during the summer months when water temperature is higher (*see Section 4.5*). This behavior is consistent with oxygen having a lower solubility at higher water temperatures.

Dissolved salts associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, total dissolved solids, hardness, and sulfate results at this site all show this pattern. Values were generally lower during May and June than at other times of year.

Analysis using the Sen slope method shows total dissolved solids increasing by 10 mg/L per year and specific conductance increasing by 13 µS/cm per year, with both trends significant at the 95% confidence level. These trends may be an artifact of data collection. For each parameter, the data set included 2 results in 1976 and no further measurements until the period 1998 to 2002, with both of the 1976 results occurring toward the lower range of the results from the later period. A greater number of measurements in the 1970's may have resulted in a range of results similar to that of 1998 to 2002, which would remove the trend.

The Sen slope method also showed total phosphorous decreasing by 0.01 mg/L per year at the 95% confidence level. This may also be an artifact of the data collection. Again, there were 2 results in 1976 and no further measurements until 1998 to 2002. One of the 1976 results is an outlier, being dramatically higher than all other results and creating a decreasing trend. A larger data set in the 1970's may have resulted in more results having values within the range of the non-outlier results, which could lead to a determination of no trend.

Other parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results above the detection limit for any patterns or trends to be evident.

The available data suggest that the Crystal River above Coal Creek at Redstone has good water quality except for occasional high values of total recoverable iron, total recoverable arsenic, and dissolved lead that may be a threat to aquatic life.

**Table 5. Summary of results for Crystal River upstream of Coal Creek.**

| Parameter  | Number of Samples | Number of Detections | Minimum Value   | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|-----------------|---------------|--------------|--------------------|-------------------------|
| Aluminum, dissolved (µg/L)                       | 15                | 3                    | ND <sup>2</sup> | 200           | 25           | No                 | NA <sup>3</sup>         |
| Aluminum, unfiltered (µg/L)                      | 3                 | 2                    | ND              | 800           | 120          | No                 | NA                      |
| Ammonia plus ammonium (mg/L)                     | 15                | 0                    | ND              | ND            | ND           | No                 | NA                      |
| Ammonia plus organic nitrogen, total (mg/L as N) | 16                | 2                    | ND              | 0.5           | 0.1          | No                 | NA                      |
| Ammonia, total (mg/L as N)                       | 2                 | 1                    | ND              | 0.103         | ND           | No                 | 0                       |
| Arsenic, dissolved (µg/L)                        | 15                | 1                    | ND              | 0.5           | ND           | No                 | 0                       |
| Arsenic, total recoverable (µg/L)                | 3                 | 1                    | ND              | 0.5           | ND           | No                 | 1                       |
| Bicarbonate (mg/L)                               | 2                 | 2                    | 70              | 87            | 78.5         | No                 | NA                      |
| Cadmium, dissolved (µg/L)                        | 15                | 0                    | ND              | ND            | ND           | No                 | 0                       |
| Calcium (mg/L)                                   | 2                 | 2                    | 28              | 53            | 40.5         | No                 | NA                      |
| Carbonate (mg/L)                                 | 2                 | 0                    | ND              | ND            | ND           | No                 | NA                      |

| Parameter  | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Chloride, dissolved (mg/L)                             | 2                 | 2                    | 0.7           | 0.8           | 0.75         | No                 | 0                       |
| Copper, dissolved (µg/L)                               | 15                | 2                    | ND            | 5             | 1.5          | No                 | 0                       |
| Discharge (cfs)  | 3                 | 3                    | 37            | 1,160         | 120          | No                 | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> )                  | 17                | 17                   | 72            | 240           | 175          | No                 | NA                      |
| Iron, dissolved (µg/L)                                 | 17                | 7                    | ND            | 150           | 5            | No                 | 0                       |
| Iron, total recoverable (µg/L)                         | 17                | 16                   | ND            | 1,200         | 33           | No                 | 2                       |
| Lead, dissolved (µg/L)                                 | 16                | 1                    | ND            | 3             | ND           | No                 | 1                       |
| Magnesium (mg/L)                                       | 2                 | 2                    | 3.5           | 5.7           | 4.6          | No                 | NA                      |
| Manganese, dissolved (µg/L)                            | 16                | 8                    | ND            | 10            | 4            | No                 | 0                       |
| Manganese, unfiltered (µg/L)                           | 4                 | 3                    | ND            | 31            | 13.5         | No                 | NA                      |
| Nitrate plus nitrite, total (mg/L as N)                | 17                | 8                    | ND            | 0.25          | 0.13         | No                 | NA                      |
| Nitrate, total (mg/L as NO <sub>3</sub> <sup>-</sup> ) | 2                 | 2                    | 0.08          | 0.11          | 0.095        | No                 | 0                       |
| Nitrite, total (mg/L as NO <sub>2</sub> <sup>-</sup> ) | 2                 | 0                    | ND            | ND            | ND           | No                 | 0                       |

| Parameter                                  | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Nitrogen, total (mg/L as N)                | 2                 | 2                    | 0.435         | 1.345         | 0.89         | No                 | 1                       |
| Oxygen, dissolved (mg/L)                   | 13                | 13                   | 7.2           | 12.37         | 9.73         | No                 | 0                       |
| pH   | 14                | 14                   | 7.02          | 8.5           | 7.75         | No                 | 0                       |
| Phosphate, dissolved (mg/L)                | 2                 | 1                    | ND            | 0.01          | ND           | No                 | NA                      |
| Phosphorous, total, unfiltered (mg/L as P) | 16                | 9                    | ND            | 0.51          | 0.02         | ↓ <sup>5</sup>     | 1                       |
| Potassium (mg/L)                           | 2                 | 2                    | 0.4           | 1.4           | 0.9          | No                 | NA                      |
| Selenium, dissolved (µg/L)                 | 16                | 1                    | ND            | 0.4           | ND           | No                 | 0                       |
| Selenium, unfiltered (µg/L)                | 3                 | 1                    | ND            | 0.6           | ND           | No                 | NA                      |
| Sodium (mg/L)                              | 2                 | 2                    | 1.4           | 2.3           | 1.85         | No                 | NA                      |
| Solids, total dissolved (mg/L)             | 17                | 17                   | 100           | 540           | 290          | ↑ <sup>4</sup>     | NA                      |
| Solids, total suspended (mg/L)             | 15                | 1                    | ND            | 44            | ND           | No                 | NA                      |
| Specific conductance (µS/cm)               | 15                | 15                   | 155           | 510           | 400          | ↑                  | NA                      |
| Sulfate, dissolved (mg/L)                  | 2                 | 2                    | 25            | 78            | 51.5         | No                 | NA                      |

| Parameter                  | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|----------------------------|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Sulfate, unfiltered (mg/L) | 14                | 14                   | 22            | 150           | 86           | No                 | 0                       |
| Temperature (°C)           | 15                | 15                   | 0.1           | 14            | 6.2          | No                 | 1                       |
| Turbidity (NTU)            | 2                 | 2                    | 1             | 20            | 10.5         | No                 | NA                      |
| Zinc, dissolved (µg/L)     | 15                | 8                    | ND            | 28            | 10.3         | No                 | 0                       |
| Zinc, unfiltered (µg/L)    | 4                 | 4                    | 8.5           | 20            | 16           | No                 | NA                      |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> ND: Not detected

<sup>3</sup> NA: Not applicable (there is no standard for this parameter)

<sup>4</sup> ↑: Increasing trend

<sup>5</sup> ↓: Decreasing trend

### 5.3 Crystal River below Redstone (Site 3)

The Crystal River was sampled at the Redstone Boulevard Bridge near the USFS campground north of Redstone, approximately 1.4 river miles downstream from the mouth of Coal Creek. This site is approximately 1.7 river miles downstream from Site 2, the Crystal River upstream of Coal Creek. CDPHE conducted 85 sampling events here from 1979 to 1992 and 1996 to 1997. Between 1 and 6 events occurred each year; in most years the sampling was bimonthly. RFC volunteers and staff have sampled 1 to 18 times per year since 1997, with monthly sampling events in 6 of those years. Overall, samples were collected in 31 out of the 34 years from 1979 to 2012. This report includes the 85 CDPHE events as well as the 108 RFC events that occurred through 13 June 2012.

The classification and standards for the Crystal River at this location are found under Region 12, Roaring Fork Basin, Segment 8 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The river is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 6 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All of the results were below standards except for the following:

- Twelve out of 181 temperature measurements were greater than the MWAT standard of 9.0°C for October through May. Most of these results occurred during the “shoulder” months—3 in October and 5 in May—when higher temperatures would be most likely. These 12 results all occurred between 1979 and 2004. One measurement, 17.2°C on 25 August 1980, exceeded the MWAT standard of 17.0°C for June through September. However, being single results rather than an average of several samples taken over a week, these results present the possibility of an exceedance but are not evidence of an actual exceedance.
- Nitrite was analyzed in 4 samples. Two of the results exceeded the nitrite standard of 0.05 mg/L as nitrogen. The sum of nitrate and nitrite was analyzed in 101 samples and detected in 19. If the entire result in these 19 samples was due to nitrate, there would be no exceedances of the nitrate standard. If the entire sum was nitrite, the nitrite standard would be exceeded in 17 of these 19 occasions, but it is very unlikely for this to be the case. The dissolved oxygen results indicate that the Crystal River at this site has well-oxygenated water. Under these conditions nitrogen tends to occur as nitrate rather than nitrite.
- Eight out of 109 results for total phosphorous exceeded the water quality goal for cold rivers of 0.11 mg/L. Compliance is defined as no more than one annual median exceeding 0.11 mg/L within a 5-year period. Out of the 26 years in which samples were collected and analyzed for phosphorous, only 2003 had an annual median (0.125 mg/L) greater than 0.11 mg/L, thus the goal has been met.
- Thirteen out of 158 results for total recoverable iron were greater than the chronic standard of 1,000 µg/L. These results ranged from 1,121 µg/L to 10,336 µg/L and were distributed from 1979 to 2011. The Colorado water quality regulations specify that 1,000 µg/L is not to be exceeded more than once every 3 years on the average. Thirteen exceedances over a period of 33 years averages to 1 exceedance every 2.5 years, thus this limitation has not been met.
- Two out of 3 results for recoverable arsenic, 0.5 µg/L on 19 May 1998 and 0.2 µg/L on 19 August 1998, exceeded the standard of 0.02 µg/L. The Colorado water quality regulations specify that 0.02 µg/L is not to be exceeded more than once every 3 years on the average. The only samples analyzed for recoverable arsenic were collected between May 1998 and February 1999. With 2 exceedances over a 10-month period, this limitation was not met.
- Four out of 49 results for dissolved selenium were greater than the chronic standard of 4.6 µg/L. These results ranged from 5.2 µg/L to 17.3 µg/L and all occurred between June 2000 and December 2000. The Colorado water quality regulations specify that 4.6 µg/L is not to be exceeded more than once every 3 years on the average. Samples were analyzed for dissolved selenium from 1996 through 2012. With only 4 exceedances over this period of 17 years, the limitation specified in the regulations was met. However, it is noteworthy that exceedances were concentrated within a 6-month period.

- One out of 61 results for dissolved lead, 4.5 µg/L on 15 June 2000, was greater than the chronic lead standard of 2.4 µg/L, which was calculated using the hardness value of 95 mg/L that was measured for this sample. This single exceedance complies with the requirement that the standard not be exceeded more than once every 3 years on the average.

As expected, dissolved oxygen concentrations are slightly lower during the summer months when water temperature is higher (*see Section 4.5*). This behavior is consistent with oxygen having a lower solubility at higher water temperatures.

The analysis for total recoverable iron and recoverable arsenic includes not only the amount of iron and arsenic dissolved in the water, but iron and arsenic occurring in particulate form as well (*see Section 4.14*). Occasional elevated concentrations of particulates are likely to be a result of natural events and/or human actions that cause a large input of eroded soil or sediment to the river over a short time. Intense or extended storms and spring runoff are examples of such natural events; clearing of vegetation from the land surface and earthmoving are examples of such human actions. For total recoverable iron, all but one result occurred during the spring runoff period, from April through June. The highest result occurred in September, likely as a result of a rain event. The same explanation applies to recoverable arsenic, for which one result occurred in May and the other in August.

Dissolved salts associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, calcium, magnesium, hardness, sulfate results at this site all show this pattern. Values were generally lower during May and June than at other times of year.

Four parameters showed decreasing trends at the 95% confidence level: chloride in unfiltered samples is decreasing by 0.042 mg/L per year; recoverable manganese is decreasing by 0.49 µg/L per year; selenium in unfiltered samples is decreasing by 0.027 µg/L per year, and dissolved zinc is decreasing by 0.15 µg/L per year. The source of these trends is not apparent. For the latter 3 of these parameters, there appears to be a cluster of unusually high values centered around the year 2001. All 3 of these parameters are associated with the sedimentary rocks found in this watershed. Perhaps there was some short-term disturbance in the vicinity of Redstone at that time, such as clearing of land, that provided a new, fresh area of contact between soil and water (such as surface runoff) that ultimately drained into the Crystal River.

Two parameters showed increasing trends at the 95% confidence level: ammonia in unfiltered samples is increasing by 0.00015 mg/L per year, and pH is increasing by 0.0055 per year. There is no obvious reason for these trends.

The available data suggest that the Crystal River below Redstone has good water quality except for total recoverable iron and possibly temperature. Recoverable arsenic exceeded its water quality standard, but only 3 samples were analyzed for this parameter. Future monitoring should include recoverable arsenic so as to determine whether the exceedance reported here is a recurring problem.



**Table 6. Summary of results for the Crystal River below Redstone.**

| Parameter  | Number of Samples | Number of Detections | Minimum Value   | Maximum Value | Median Value | Trend          | Exceedances of Standard |
|--|-------------------|----------------------|-----------------|---------------|--------------|----------------|-------------------------|
| Alkalinity (mg/L as CaCO <sub>3</sub> )          | 177               | 177                  | 48              | 186           | 104          | No             | NA <sup>1</sup>         |
| Aluminum, dissolved (µg/L)                       | 51                | 39                   | ND <sup>2</sup> | 147           | 18           | No             | NA                      |
| Aluminum, unfiltered (µg/L)                      | 86                | 80                   | ND              | 4,026         | 101          | No             | NA                      |
| Ammonia, total (mg/L as N)                       | 94                | 94                   | ND              | 0.06          | 0.0027       | ↑ <sup>3</sup> | 0                       |
| Ammonia, unfiltered, calculated (mg/L as N)      | 81                | 81                   | 0.00009         | 0.022         | 0.0033       | ↑              | 0                       |
| Ammonia plus ammonium (mg/L)                     | 91                | 12                   | ND              | 0.32          | ND           | No             | NA                      |
| Ammonia plus organic nitrogen, unfiltered (mg/L) | 76                | 7                    | ND              | 6.6           | ND           | No             | NA                      |
| Arsenic, dissolved (µg/L)                        | 38                | 7                    | ND              | 62            | ND           | No             | 0                       |
| Arsenic, recoverable(µg/L)                       | 3                 | 2                    | ND              | 0.5           | 0.2          | No             | 2                       |
| Bicarbonate (mg/L)                               | 2                 | 2                    | 114             | 138           | 126          | No             | NA                      |
| Cadmium, dissolved (µg/L)                        | 43                | 8                    | ND              | 2.05          | ND           | No             | 4                       |

| Parameter                             | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend          | Exceedances of Standard |
|---------------------------------------|-------------------|----------------------|---------------|---------------|--------------|----------------|-------------------------|
| Calcium (mg/L)                        | 104               | 104                  | 23            | 230           | 65           | No             | NA                      |
| Chloride, dissolved (mg/L)            | 21                | 1                    | ND            | 0.21          | ND           | No             | NA                      |
| Chloride, unfiltered (mg/L)           | 28                | 22                   | ND            | 20            | 1.9          | ↓ <sup>4</sup> | 0                       |
| Chromium, dissolved (µg/L)            | 20                | 0                    | ND            | ND            | ND           | No             | 0                       |
| Chromium, recoverable (µg/L)          | 53                | 1                    | ND            | 21            | ND           | No             | NA                      |
| Copper, dissolved (µg/L)              | 88                | 36                   | ND            | 131           | 2.0          | No             | 0                       |
| Discharge (cfs)                       | 39                | 39                   | 35            | 2,110         | 95           | No             | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> ) | 176               | 176                  | 47            | 284           | 190          | No             | NA                      |
| Iron, dissolved (µg/L)                | 72                | 36                   | ND            | 239           | 14           | No             | 0                       |
| Iron, total recoverable (µg/L)        | 158               | 138                  | ND            | 10,336        | 120          | No             | 13                      |
| Lead, dissolved (µg/L)                | 61                | 4                    | ND            | 4.5           | ND           | No             | 1                       |
| Magnesium (mg/L)                      | 104               | 104                  | 3             | 16            | 7.9          | No             | NA                      |
| Manganese, dissolved (µg/L)           | 64                | 12                   | ND            | 152           | ND           | No             | 0                       |
| Manganese, recoverable (µg/L)         | 111               | 47                   | ND            | 440           | ND           | ↓              | NA                      |

| Parameter                                    | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend | Exceedances of Standard |
|--|-------------------|----------------------|---------------|---------------|--------------|-------|-------------------------|
| Nitrate plus nitrite, unfiltered (mg/L as N) | 101               | 19                   | ND            | 1.3           | ND           | No    | NA                      |
| Nitrite, unfiltered (mg/L as N)              | 4                 | 3                    | ND            | 0.12          | 0.10         | No    | 2                       |
| Oxygen, dissolved (mg/L)                     | 189               | 189                  | 5.5           | 14.1          | 10           | No    | 0                       |
| pH   | 187               | 187                  | 6.9           | 9.1           | 8.3          | ↑     | 1                       |
| Phosphorous, total, unfiltered (mg/L as P)   | 109               | 33                   | ND            | 0.57          | ND           | No    | 8                       |
| Potassium (mg/L)                             | 24                | 1                    | ND            | 0.25          | ND           | No    | NA                      |
| Specific conductance (µS/cm)                 | 71                | 71                   | 47            | 610           | 380          | No    | NA                      |
| Selenium, dissolved (µg/L)                   | 49                | 20                   | ND            | 17            | ND           | No    | 4                       |
| Selenium, unfiltered (µg/L)                  | 52                | 26                   | ND            | 18            | 1.6          | ↓     | NA                      |
| Sodium (mg/L)                                | 7                 | 5                    | 2.5           | 10            | 5            | No    | NA                      |
| Solids, total dissolved (mg/L)               | 92                | 92                   | 82            | 400           | 260          | No    | NA                      |
| Solids, total suspended (mg/L)               | 112               | 58                   | ND            | 1550          | 5.5          | No    | NA                      |
| Sulfate, unfiltered (mg/L)                   | 115               | 113                  | ND            | 270           | 96           | No    | 1                       |

| Parameter               | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend | Exceedances of Standard |
|-------------------------|-------------------|----------------------|---------------|---------------|--------------|-------|-------------------------|
| Temperature (°C)        | 181               | 181                  | -0.1          | 17.2          | 7            | No    | 13                      |
| Zinc, dissolved (µg/L)  | 81                | 31                   | ND            | 50            | ND           | ↓     | 0                       |
| Zinc, unfiltered (µg/L) | 106               | 46                   | ND            | 260           | ND           | No    | NA                      |

<sup>1</sup> ND: Not detected

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ↑: Increasing trend

<sup>4</sup> ↓: Decreasing trend

#### 5.4 Crystal River above Penny Hot Springs (Site 4)

The Crystal River was sampled upstream from Penny Hot Springs, approximately 3.4 river miles downstream from the mouth of Coal Creek and approximately 1.7 river miles downstream from Site 3, the Crystal River below Redstone. This site was sampled by students from Roaring Fork High School as part of the River Watch program. Samples were collected between 3 and 23 times per year for a total of 97 sampling events between 1991 and 1997. One additional sampling event occurred in each of the years 2001 and 2002.

The classification and standards for the Crystal River at this location are found under Region 12, Roaring Fork Basin, Segment 8 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The river is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 7 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All of the results were below standards except for the following:

- Five out of 76 temperature measurements were greater than the MWAT standard of 9.0°C (4 April 1995, 29 March 1996, 29 April 1996, 21 March 1997, and 16 April 1997). However, being single results rather than an average of several samples taken over a week, these results present the possibility of an exceedance, but are not proof of an exceedance.
- The results for dissolved oxygen were less than the minimum required concentration of 6.0 mg/L for 25 out of 94 measurements. On 15 additional occasions the results were less than the minimum 7.0 mg/L required for periods when fish are spawning. All of the

exceedances occurred in the period 1994 through 1997; the exceedances occurred across all seasons.

- The results for total recoverable iron were greater than the chronic standard of 1,000 µg/L on 24 out of 74 occasions. The Colorado water quality regulations specify that 1,000 µg/L is not to be exceeded more than once every 3 years on the average. With 24 exceedances over a period of 9 years, this requirement is not met.

In contrast to what is seen at other sites, the median dissolved oxygen concentrations are *not* consistently lower during the summer months when water temperature is higher. This finding, along with the relatively high number of exceedances of the standard and the occurrence of exceedances throughout the year, suggests there are additional influences present other than seasonal variation of solubility with temperature. Analysis using the Sen slope method shows dissolved oxygen decreasing by 1.1 mg/L per year, with the trend significant at the 95% confidence level. One might wonder whether this is a consequence of warming temperatures. Sen slope analysis does show water temperature increasing 0.2°C per year, but this trend is not significant at the 95% confidence level. Dissolved oxygen concentrations show a distinct decrease beginning in May 1994, suggesting an abrupt change in conditions. The temperature record does not show a corresponding distinct change. A possible explanation is the onset of a new source of organic material into the river, which would increase biochemical oxygen demand and decrease dissolved oxygen concentrations.

The analysis for total recoverable iron includes not only the amount of iron dissolved in the water, but iron occurring in particulate form as well (*see Section 4.14*). Occasional elevated concentrations of particulates are likely to be a result of natural events and/or human actions that cause a large input of eroded soil or sediment to the river over a short time. Intense or extended storms and spring runoff are examples of such natural events; clearing of vegetation from the land surface and earthmoving are examples of such human actions. The timing of the exceedances suggests that particulate matter associated with runoff is the source of the high concentrations of total recoverable iron; 23 of the exceedances occur between late March and June, while the remaining exceedance occurs in September, perhaps as the result of a storm.

Sen slope analysis showed a statistically significant increasing trend (95% confidence level) of 0.04 units per year in pH. Available information does not suggest an explanation for this apparent trend. The highest value of pH (8.53) is still significantly less than the upper limit specified by the standard (9.00).

Sen slope analysis showed a statistically significant increasing trend (95% confidence level) of 7.6 µg/L per year for total zinc. Available information does not suggest an explanation for this apparent trend. Even the highest total zinc concentration (115 µg/L) is well below the standard for zinc (226 µg/L for the hardness measured in the sample with the highest zinc concentration).

Parameters associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, alkalinity, and hardness results at this site all show this pattern, with values generally lower

during May and June than at other times of year. Other parameters associated with specific conductance were not sampled often enough to show this pattern.

Recoverable manganese showed higher concentrations during spring runoff and on other isolated occasions that may possibly correspond with precipitation events. As described above for iron, concentrations of recoverable manganese are highly influenced by the presence of suspended sediments, so the occurrence of higher values during spring runoff is expected.

The remaining parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results for any valid patterns or trends to be evident.

The available data suggest that the Crystal River above Penny Hot Springs has acceptable water quality except for frequent low values of dissolved oxygen and high values of total recoverable iron, which may be a threat to aquatic life.

**Table 7. Summary of results for the Crystal River above Penny Hot Springs.**

| Parameter                               | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Alkalinity (mg/L as CaCO <sub>3</sub> ) | 95                | 95                   | 56            | 162           | 112          | No                 | NA <sup>2</sup>         |
| Aluminum, unfiltered (µg/L)             | 2                 | 2                    | 16            | 19            | 17.5         | No                 | NA                      |
| Cadmium, dissolved (µg/L)               | 1                 | 1                    | 0.1           | 0.1           | 0.1          | No                 | 0                       |
| Calcium (mg/L)                          | 2                 | 2                    | 90.3          | 95.5          | 92.9         | No                 | NA                      |
| Carbonate (mg/L)                        | 1                 | 1                    | 213           | 213           | 213          | No                 | NA                      |
| Chloride, unfiltered (mg/L)             | 1                 | 1                    | 17            | 17            | 17           | No                 | 0                       |
| Copper, dissolved (µg/L)                | 4                 | 4                    | 1             | 1             | 1            | No                 | 0                       |
| Discharge (cfs)                         | 41                | 41                   | 26            | 1,660         | 128          | ↑ <sup>3</sup>     | NA                      |

| Parameter                             | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---------------------------------------|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Hardness (mg/L as CaCO <sub>3</sub> ) | 94                | 94                   | 68            | 326           | 198          | No                 | NA                      |
| Iron, dissolved (µg/L)                | 3                 | 3                    | 129           | 211           | 136          | No                 | 0                       |
| Iron, total recoverable (µg/L)        | 74                | 74                   | 105           | 6,315         | 477          | No                 | 24                      |
| Magnesium (mg/L)                      | 2                 | 2                    | 12.0          | 12.8          | 12.4         | No                 | NA                      |
| Manganese, dissolved (µg/L)           | 5                 | 5                    | 12            | 21.8          | 13           | No                 | 0                       |
| Oxygen, dissolved (mg/L)              | 94                | 94                   | 4             | 14            | 9            | ↓ <sup>4</sup>     | 25                      |
| pH                                    | 89                | 89                   | 6.99          | 8.53          | 7.93         | ↑                  | 0                       |
| Selenium, dissolved (µg/L)            | 1                 | 1                    | 2.8           | 2.8           | 2.8          | No                 | 0                       |
| Selenium, unfiltered (µg/L)           | 2                 | 2                    | 1.7           | 2.6           | 2.15         | No                 | NA                      |
| Temperature (°C)                      | 76                | 76                   | 1             | 14            | 6            | No                 | 5                       |
| Zinc, dissolved (µg/L)                | 1                 | 1                    | 10            | 10            | 10           | No                 | 0                       |
| Zinc, unfiltered (µg/L)               | 52                | 52                   | 10            | 115           | 46.5         | ↑                  | NA                      |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ↑: Increasing trend

<sup>4</sup> ↓: Decreasing trend

## 5.5 Crystal River above Avalanche Creek (Site 5)

The Crystal River was sampled at the USGS gaging station approximately 1.2 miles upstream from the mouth of Avalanche Creek. This site is approximately 0.7 river miles downstream from Site 4, the Crystal River above Penny Hot Springs. There is an extensive record of water quality at this location. USGS has sampled every year from 1960 to the present, with the exception of 1970 to 1972 and 2006 to 2008. This report considers results from 432 different dates between June 1960 and October 2010.

The classification and standards for the Crystal River at this location are found under Region 12, Roaring Fork Basin, Segment 8 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The river is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 8 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All of the results were below standards except the following:

- Thirty-six out of 427 temperature measurements were greater than the MWAT standard of 9.0°C for the months October through May. Most of these exceedances occurred in October and May, the months bordering the warm summer months. Another 6 measurements exceeded the MWAT standard of 17.0°C for June through September. However, being single measurements rather than an average of several measurements taken over a week, these results present the possibility of exceedances but are not evidence of actual exceedances. Two temperature measurements exceeded the daily maximum standard of 13.0°C for the months October through May. The 36 measurements that were greater than a standard occurred in 31 different years distributed across the 50-year period of record.
- One out of 59 dissolved oxygen measurements was less than the minimum value of 7.0 mg/L required during spawning periods: 6.7 mg/L on 23 August 1976. If no fish were spawning at this time, the measurement would comply with the standard of 6.0 mg/L.
- Six out of 36 results for total recoverable iron were greater than the chronic standard of 1,000 µg/L: 1,855 µg/L on 24 May 1996; 2,655 µg/L on 14 May 1997; 2,025 µg/L on 22 May 1997; 2,110 µg/L on 28 July 1999; 1,195 µg/L on 18 July 2001; and 4,739 µg/L on 30 July 2002. This standard is not to be exceeded more than once every 3 years on average. Samples were analyzed for total recoverable iron over a period of 9 years. With 6 exceedances in 9 years, this condition is not met and the Crystal River was not in compliance with this standard for the period 1995 to 2004.
- One out of 57 results for total phosphorous exceeded the water quality goal for cold rivers of 0.11 mg/L: 0.25 mg/L on 27 May 2003. Compliance is assessed by comparing



the annual median for total phosphorous to the goal, with no more than 1 exceedance in a 5-year period. The results meet this condition.

Considerably more high temperature measurements occurred at this site than other sites in this study. The likely cause is the proximity of the site to Penny Hot Springs, which are immediately upstream.

As expected, dissolved oxygen concentrations are slightly lower during the summer months when water temperature is higher (*see Section 4.5*). This behavior is consistent with oxygen having a lower solubility at higher water temperatures.

The analysis for total recoverable iron includes not only the amount of iron dissolved in the water, but iron occurring in particulate form as well (*see Section 4.14*). Occasional elevated concentrations of particulates are likely to be a result of natural events and/or human actions that cause a large input of eroded soil or sediment to the river over a short time. Intense or extended storms and spring runoff are examples of such natural events; clearing of vegetation from the land surface and earthmoving are examples of such human actions. The data were examined to see if there was a correlation between stream flow and total recoverable iron. In spite of the 50-year data record, there were only 33 dates when both flow and total recoverable iron were measured. No significant correlation was found. (For example, the  $R^2$  value for a linear correlation was only 0.02.) Suspended solids were never measured at this site, so there was no opportunity to look for a correlation with this parameter. High values of total recoverable iron in May are likely to be associated with spring runoff. High values in July may be a result of human activities or rainfall events.

For dissolved ammonia, Sen slope analysis showed a decreasing trend significant at the 95% confidence level of 0.0013 mg/L as N per year. This trend is based on 36 detections over a 9-year period. It is noteworthy that a related parameter, the sum of ammonia plus organic-nitrogen in unfiltered samples, showed a decreasing trend with the same slope, although this trend was not significant at the 95% confidence level. Perhaps the dissolved ammonia trend is a result of a change in human actions in the Redstone area, such as improved management of livestock manure or improved sewage treatment.

Sen slope analysis showed a decreasing trend significant at the 95% confidence level of 0.00027 mg/L as P per year for phosphate. Perhaps this trend is a result of the same factors proposed for the dissolved ammonia trend. Given that the trend is based on only 11 detections of phosphate, a more extensive data record augmented by future sampling may not necessarily sustain this trend. The trend is a result of 6 values recorded in the mid-1970's that were all higher than the 5 values recorded in the years 1998 to 2000.

For total dissolved phosphorous, Sen slope analysis showed a decreasing trend significant at the 95% confidence level of 0.00047 mg/L as P per year. Perhaps this trend is a result of the same factors proposed for the dissolved ammonia and phosphate trends. However, given that the trend is based on only 6 detections of total phosphorous, a more extensive data record augmented by future sampling may not necessarily show this trend. It is interesting to note that for total

phosphorous in unfiltered samples there was a decreasing trend of 0.00021 mg/L as P per year, although this trend was not significant at the 95% confidence level.

Parameters associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see* Sections 4.4, 4.6, and 4.7). Specific conductance, alkalinity, bicarbonate, calcium, magnesium, hardness, sodium, potassium, bicarbonate, dissolved chloride, dissolved sulfate, total sulfate, dissolved manganese, and TDS (by sum of constituents) results at this site all show this pattern, with values generally lower during May and June than at other times of year.

Total recoverable iron, recoverable manganese, ammonia plus organic nitrogen unfiltered, total nitrogen unfiltered, total phosphorous unfiltered, showed higher concentrations during spring runoff and on other isolated occasions that may possibly correspond with precipitation events. As described above for iron, concentrations of these substances are highly influenced by the presence of suspended sediments, so the occurrence of higher values during spring runoff is expected.

The remaining parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results for any valid patterns or trends to be evident.

The available data suggest that the Crystal River above Avalanche Creek has acceptable water quality except for total recoverable iron and possibly high temperatures, both of which are threats to aquatic life. Nutrient concentrations may have decreased over time.

**Table 8. Summary of results for the Crystal River above Avalanche Creek.**

| Parameter  | Number of Samples | Number of Detections | Minimum Value   | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|-----------------|---------------|--------------|--------------------|-------------------------|
| Alkalinity (mg/L as CaCO <sub>3</sub> )              | 14                | 14                   | 63              | 240           | 101          | No                 | NA <sup>2</sup>         |
| Ammonia, dissolved (mg/L as N)                       | 55                | 36                   | ND              | 0.058         | 0.013        | ↓ <sup>4</sup>     | NA                      |
| Ammonia, unfiltered (mg/L as N)                      | 2                 | 2                    | 0.057           | 0.69          | 0.063        | No                 | 0                       |
| Ammonia plus organic nitrogen, dissolved (mg/L as N) | 42                | 13                   | ND <sup>3</sup> | 0.1           | 0.065        | No                 | NA                      |

| Parameter   | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Ammonia plus organic nitrogen, unfiltered (mg/L as N) | 57                | 35                   | ND            | 0.372         | 0.077        | No                 | NA                      |
| Bicarbonate (mg/L)                                    | 19                | 19                   | 64            | 180           | 132          | No                 | NA                      |
| Cadmium, dissolved (µg/L)                             | 37                | 10                   | ND            | 0.18          | ND           | No                 | 0                       |
| Calcium (mg/L)  | 40                | 40                   | 23            | 98            | 60           | No                 | NA                      |
| Carbonate (mg/L)                                      | 46                | 0                    | ND            | ND            | ND           | No                 | NA                      |
| Chloride, dissolved (mg/L)                            | 46                | 46                   | 0.69          | 13            | 5.5          | No                 | NA                      |
| Copper, dissolved (µg/L)                              | 37                | 11                   | ND            | 1.2           | 0.6          | No                 | 0                       |
| Discharge (cfs)                                       | 239               | 239                  | 26            | 2,530         | 135          | No                 | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> )                 | 54                | 54                   | 72            | 368           | 183          | No                 | NA                      |
| Iron, dissolved (µg/L)                                | 2                 | 1                    | ND            | 70            | 38           | No                 | 0                       |
| Iron, total recoverable (µg/L)                        | 36                | 36                   | 48            | 4,739         | 297          | No                 | 6                       |
| Lead, dissolved (µg/L)                                | 37                | 0                    | ND            | ND            | ND           | No                 | 0                       |
| Magnesium (mg/L)                                      | 40                | 40                   | 3.2           | 11            | 8.0          | No                 | NA                      |
| Manganese, dissolved (µg/L)                           | 39                | 34                   | 2.0           | 13            | 6.3          | No                 | 0                       |

| Parameter   | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Manganese, recoverable (µg/L)                               | 37                | 36                   | 5             | 143           | 12           | No                 | NA                      |
| Nitrate, dissolved (mg/L as NO <sub>3</sub> <sup>-</sup> )  | 61                | 22                   | ND            | 1.4           | 0.052        | No                 | NA                      |
| Nitrate, unfiltered (mg/L as NO <sub>3</sub> <sup>-</sup> ) | 2                 | 2                    | 0.06          | 0.13          | 0.095        | No                 | 0                       |
| Nitrate plus nitrite, dissolved (mg/L as N)                 | 57                | 56                   | ND            | 0.19          | 0.085        | No                 | NA                      |
| Nitrate plus nitrite, unfiltered (mg/L as N)                | 2                 | 2                    | 0.06          | 0.13          | 0.095        | No                 | NA                      |
| Nitrite, dissolved (mg/L as NO <sub>2</sub> <sup>-</sup> )  | 55                | 16                   | ND            | 0.02          | ND           | No                 | NA                      |
| Nitrite, unfiltered (mg/L as NO <sub>2</sub> <sup>-</sup> ) | 2                 | 0                    | ND            | ND            | ND           | No                 | 0                       |
| Nitrogen, total, dissolved (mg/L as N)                      | 42                | 12                   | ND            | 0.26          | ND           | No                 | NA                      |
| Nitrogen, total, unfiltered (mg/L as N)                     | 57                | 34                   | ND            | 0.80          | 0.15         | No                 | 0                       |
| Oxygen, dissolved (mg/L)                                    | 59                | 59                   | 6.7           | 13            | 9.7          | No                 | 1                       |
| pH  | 68                | 68                   | 7.4           | 8.5           | 7.9          | No                 | 0                       |
| Phosphate (mg/L)  | 63                | 11                   | ND            | 0.104         | ND           | ↓                  | NA                      |

| Parameter   | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Phosphorous, total dissolved (mg/L as P)              | 42                | 6                    | ND            | 0.016         | ND           | ↓                  | NA                      |
| Phosphorous, total, unfiltered (mg/L as P)            | 57                | 43                   | ND            | 0.25          | 0.0057       | No                 | 1                       |
| Potassium (mg/L)                                      | 40                | 40                   | 0.31          | 2.1           | 1.3          | No                 | NA                      |
| Selenium, dissolved (µg/L)                            | 37                | 10                   | ND            | 1.4           | ND           | No                 | 0                       |
| Solids, total dissolved (mg/L)                        | 4                 | 4                    | 256           | 505           | 398          | No                 | NA                      |
| Solids, total dissolved by sum of constituents (mg/L) | 39                | 39                   | 87            | 425           | 269          | No                 | NA                      |
| Sodium (mg/L)   | 40                | 40                   | 3.1           | 25            | 14           | No                 | NA                      |
| Specific conductance (µS/cm)                          | 319               | 319                  | 120           | 1,200         | 440          | No                 | NA                      |
| Sulfate, dissolved (mg/L)                             | 13                | 12                   | ND            | 240           | 54           | No                 | NA                      |
| Sulfate, total (mg/L)                                 | 40                | 40                   | 18            | 192           | 108          | No                 | 0                       |
| Temperature (°C)                                      | 427               | 427                  | 0.5           | 19            | 8            | No                 | 42                      |
| Turbidity (NTU)                                       | 15                | 15                   | 0.8           | 1200          | 8.6          | No                 | NA                      |
| Zinc, dissolved (µg/L)                                | 37                | 11                   | ND            | 12            | ND           | No                 | 0                       |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ND: Not detected

<sup>4</sup> ↓: Decreasing trend

## 5.6 Coal Creek upstream from Dutch Creek (Site 6)

This site is labeled as “Coal Creek above plant” in the data base prepared by RFC. However, the latitude and longitude reported for this site place it about 2 miles west of Coal Creek on an unnamed tributary of Dutch Creek, which flows into Coal Creek. The site appears to be upgradient from the wash plant at the confluence of Coal and Dutch Creeks. Water was sampled on 14 occasions at irregular intervals by the USFS from March 1975 through November 1977.

The classification and standards for this creek are found under Region 12, Roaring Fork Basin, Segment 9 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The creek is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 9 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All results met standards except for pH.

Two values for pH exceeded the upper limit of 9.0 specified in the standards: 9.25 on 9 April 1975 and 9.20 on 23 July 1976. All other results met standards. Given that this site is believed to be upgradient of coal operations, the high pH values may be a reflection of the geochemistry of the site. For 23 July 1976, pH also exceeded the upper limit of 9.0 at Coal Creek below the plant and at Bear Creek, which were sampled by the same organization sampling this site. On 9 April 1975, pH was 9.0 at Bear Creek but unmeasured at Coal Creek below the plant. These consistencies in the occurrence of high pH values support the possibility of the pH meter being out of calibration. It seems unlikely that any other factor would have influenced all 3 sites simultaneously.

Parameters associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, calcium, magnesium, hardness, dissolved chloride and unfiltered sulfate results at this site all show this pattern, with values generally lower during May and June than at other times of year.

Sen slope analysis showed a decreasing trend for dissolved chloride of 2.7 mg/L per year that was significant at the 95% confidence level. Sen slope analysis also showed a decreasing trend of 30 mg/L per year for unfiltered sulfate that was significant at the 95% confidence level. Available information does not suggest an explanation for this apparent trend. If this site was upgradient from coal mining and processing operations, as believed, these operations are unlikely to have been an influence. Perhaps the trend is a consequence of the small size of the data set.

The remaining parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results for any valid patterns or trends to be evident.

The available data suggest that water at this site had acceptable quality except for occasional high values of pH, which is a concern for aquatic life.

**Table 9. Summary of results for Coal Creek upstream from Dutch Creek.**

| Parameter  | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Calcium (mg/L)   | 14                | 14                   | 66            | 166           | 124          | No                 | NA <sup>2</sup>         |
| Chloride, dissolved (mg/L)                                 | 8                 | 8                    | 0.5           | 2             | 1.25         | ↓ <sup>3</sup>     | 0                       |
| Hardness (mg/L as CaCO <sub>3</sub> )                      | 14                | 14                   | 102           | 262           | 217          | No                 | NA                      |
| Iron, total recoverable (µg/L)                             | 5                 | 5                    | 15            | 280           | 40           | No                 | 0                       |
| Magnesium (mg/L)   | 14                | 14                   | 36            | 144           | 83           | No                 | NA                      |
| Nitrate, dissolved (mg/L as NO <sub>3</sub> <sup>-</sup> ) | 3                 | 3                    | 0.1           | 0.2           | 0.13         | No                 | NA                      |
| Oxygen, dissolved (mg/L)                                   | 2                 | 2                    | 10            | 11            | 10.5         | No                 | 0                       |
| pH   | 10                | 10                   | 8.2           | 9.3           | 9.0          | No                 | 2                       |
| Specific conductance (µS/cm)                               | 9                 | 9                    | 230           | 540           | 460          | No                 | NA                      |
| Sulfate, unfiltered (mg/L)                                 | 13                | 13                   | 5             | 80            | 33           | ↓                  | 0                       |
| Temperature (°C)   | 10                | 10                   | 1.1           | 15            | 6.4          | No                 | 0                       |

| Parameter       | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|-----------------|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Turbidity (NTU) | 14                | 14                   | 1.5           | 430           | 22           | No                 | NA                      |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ↓: Decreasing trend

## 5.7 Coal Creek downstream of Dutch Creek (Site 7)

Coal Creek was sampled at the downstream extent of coal mining operations in Coal Basin. This site is approximately 3.5 river miles downstream of Site 6 (Coal Creek above Dutch Creek) and 3.5 road miles northwest of Redstone on County Road 307. The creek was sampled on 17 occasions at irregular intervals by the USFS from May 1973 to April 1977. Sampling was also conducted by RFC staff on 35 occasions, monthly in 2000 and then roughly quarterly through December 2006.

The classification and standards for Coal Creek are found under Region 12, Roaring Fork Basin, Segment 9 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The creek is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 10 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard.

Three temperature measurements were greater than the MWAT standard of 9.0°C for the months October through May: 12°C on 4 October 2000, 12°C on 23 May 2001, and 10°C on 30 March 2004. Two measurements exceeded the MWAT standard of 17.0°C for the months June through September: 18°C on 15 June 2000 and 20°C on 9 August 2000. However, being a single result rather than an average of several samples taken over a week, each of these results presents the possibility of noncompliance with the standard but is not proof of noncompliance.

Two values of pH exceeded the upper limit of 9.0 specified in the standards: 9.25 on 25 July 1974, and 9.5 on 23 July 1976. However, the pH values recorded on those same dates by the same organization at Bear Creek (Site 8), were also greater than 9.0. This consistency in the occurrence of high pH values suggests the possibility that the pH meter was out of calibration. It seems unlikely that any other factor would have influenced both sites simultaneously.

Two dissolved oxygen measurements were less than the minimum value of 7.0 mg/L required during spawning periods: 6.6 mg/L on 9 August 2000 and 6 mg/L on 19 August 2002. These results do comply with the standard of 6.0 mg/L for non-spawning periods. The value of 6.6 mg/L occurred when water temperature was measured to be 20°C. At this temperature and for



this site's approximate elevation of 7,700 feet, the saturation concentration for DO is about 6.8 mg/L.

Five results for total recoverable iron were greater than the chronic standard of 1,000 µg/L: 3,534 µg/L on 13 April 2000; 1,081 on 23 May 2001; 1,770 µg/L on 22 May 2003; 2,601 µg/L on 25 February 2005; and 1.645µg/L on 26 May 2005. All but one of these results occurred in April or May during the spring runoff. The Colorado water quality regulations specify that 1,000 µg/L is not to be exceeded more than once every 3 years on the average. Five results greater than 1,000 µg/L over a period of 7 years exceeds this limit.

One result for dissolved iron, 736 µg/L on 22 May 2003, exceeded the standard for dissolved iron of 300 µg/L. Two results for selenium were greater than the chronic standard of 4.6 µg/L: 5.4 µg/L on 23 November 2005 and 5.9 µg/L on 16 February 2006. The Colorado water quality standards specify that 4.6 µg/L is not to be exceeded more than once every 3 years on average. Samples from this site were analyzed for selenium in 6 different years. Two results greater than 4.6 µg/L over 6 years, averages to 1 exceedance every 3 years, which does not exceed this limit.

Parameters associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, alkalinity, calcium, hardness, both dissolved and unfiltered chloride, unfiltered sulfate, and dissolved selenium show this pattern, with values generally lower during May and June than at other times of year.

Sen slope analysis showed decreasing trends at the 95% confidence level for 3 parameters: pH (0.015 pH units per year), calcium (1.7 mg/L per year), and magnesium (1.0 mg/L per year). Available information does not suggest an explanation for these apparent trends.

The available data suggest that water at this site had acceptable quality except for temperature and total recoverable iron.

**Table 10. Summary of results for Coal Creek downstream of Dutch Creek.**

| Parameter                               | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Alkalinity (mg/L as CaCO <sub>3</sub> ) | 30                | 30                   | 65            | 598           | 344          | No                 | NA <sup>2</sup>         |
| Aluminum, dissolved (mg/L)              | 7                 | 7                    | 15            | 349           | 23           | No                 | NA                      |
| Aluminum, unfiltered (mg/L)             | 29                | 29                   | 27            | 1490          | 157          | No                 | NA                      |

| Parameter   | Number of Samples | Number of Detections | Minimum Value   | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|-----------------|---------------|--------------|--------------------|-------------------------|
| Ammonia, unfiltered (mg/L as N)                       | 1                 | 1                    | 0.02            | 0.02          | 0.02         | No                 | 0                       |
| Ammonia plus organic nitrogen, unfiltered (mg/L as N) | 25                | 6                    | ND <sup>3</sup> | 2.2           | ND           | No                 | NA                      |
| Cadmium, dissolved (µg/L)                             | 2                 | 2                    | 0.17            | 0.19          | 0.18         | No                 | 0                       |
| Calcium (mg/L)  | 43                | 43                   | 18              | 162           | 56           | ↓ <sup>4</sup>     | NA                      |
| Chloride, dissolved (mg/L)                            | 9                 | 9                    | 0.5             | 9.5           | 3.5          | No                 | 0                       |
| Chloride, unfiltered (mg/L)                           | 8                 | 8                    | 1.1             | 14            | 4.2          | No                 | 0                       |
| Copper, dissolved (µg/L)                              | 6                 | 6                    | 1.1             | 2.7           | 1.2          | No                 | 0                       |
| Discharge (cfs)                                       | 4                 | 4                    | 8               | 75            | 35           | No                 | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> )                 | 48                | 48                   | 75              | 262           | 155          | No                 | NA                      |
| Iron, dissolved (µg/L)                                | 14                | 14                   | 11              | 736           | 17           | No                 | 1                       |
| Iron, recoverable (µg/L)                              | 33                | 33                   | 40              | 3545          | 296          | No                 | 5                       |
| Magnesium (mg/L)                                      | 43                | 43                   | 7.5             | 118           | 16           | ↓                  | NA                      |
| Manganese, dissolved (µg/L)                           | 6                 | 6                    | 6.6             | 37            | 15           | No                 | 0                       |

| Parameter                                  | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Manganese, recoverable (µg/L)              | 20                | 20                   | 5.5           | 81            | 13           | No                 | NA                      |
| Nitrate, dissolved (mg/L as N)             | 4                 | 4                    | 0.01          | 0.6           | 0.49         | No                 | 0                       |
| Oxygen, dissolved (mg/L)                   | 33                | 33                   | 6.0           | 11.5          | 9.0          | No                 | 2                       |
| pH   | 45                | 45                   | 7.9           | 9.5           | 8.6          | ↓                  | 2                       |
| Phosphate, dissolved (mg/L as P)           | 4                 | 4                    | 0.0065        | 0.095         | 0.021        | No                 | NA                      |
| Phosphorous, total, unfiltered (mg/L as P) | 6                 | 6                    | 0.014         | 0.1           | 0.03         | No                 | 0                       |
| Selenium, dissolved (µg/L)                 | 7                 | 7                    | 2             | 5.9           | 3            | No                 | 2                       |

|                                |    |    |     |     |     |    |    |
|--------------------------------|----|----|-----|-----|-----|----|----|
| Selenium, unfiltered (µg/L)    | 7  | 7  | 3   | 6.9 | 3.4 | No | NA |
| Solids, total suspended (mg/L) | 9  | 9  | 16  | 165 | 69  | No | NA |
| Specific conductance (µS/cm)   | 13 | 13 | 225 | 950 | 470 | No | NA |
| Sulfate, unfiltered (mg/L)     | 24 | 24 | 13  | 140 | 38  | No | 0  |
| Temperature (°C)               | 41 | 41 | 0   | 20  | 8   | No | 5  |

|                         |    |    |     |      |     |    |    |
|-------------------------|----|----|-----|------|-----|----|----|
| Turbidity (NTU)         | 17 | 17 | 5.4 | 3280 | 74  | No | NA |
| Zinc, dissolved (µg/L)  | 7  | 7  | 2.7 | 14   | 4   | No | 0  |
| Zinc, unfiltered (µg/L) | 9  | 9  | 3.4 | 48   | 7.2 | No | NA |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ND: Not detected

<sup>4</sup> ↓: Decreasing trend

## 5.8 Bear Creek at Coal Creek (Site 8)

Bear Creek was sampled above its confluence with Coal Creek, which is located immediately downstream from Sites 7 and 8. The USFS collected samples on 16 occasions at irregular intervals between May 1973 and January 1978.

The classification and standards for Bear Creek are found under Region 12, Roaring Fork Basin, Segment 9 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. Bear Creek is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 11 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All results met standards except for pH.

Two values for pH exceeded the upper limit of 9.0 specified in the standards: 9.25 on 25 July 1974 and 9.2 on 23 July 1976. Given that there was little or no coal mining activity in this basin, the high pH values may be a reflection of the geochemistry of the site. However, the pH values recorded on those same dates by the same organization at Coal Creek downstream from Dutch Creek (Site 7), were also greater than 9.0. This consistency in the occurrence of high pH values suggests the possibility that the pH meter was out of calibration. It seems unlikely that any other factor would have influenced both sites simultaneously.

Parameters associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see Sections 4.4, 4.6, and 4.7*). Specific conductance, calcium, magnesium, hardness, and sulfate results at this site show this pattern, with values generally lower during May and June than at other times of year. Other parameters associated with specific conductance were not sampled often enough to show this pattern.

The remaining parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results for any valid patterns or trends to be evident.

The available data suggest that water at this site had acceptable quality except for occasional high values of pH, which is a concern for aquatic life.

**Table 11. Summary of results for Bear Creek at Coal Creek.**

| Parameter  | Number of Samples | Number of Detections | Minimum Value   | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|-----------------|---------------|--------------|--------------------|-------------------------|
| Calcium (mg/L)   | 13                | 13                   | 32              | 182           | 90           | No                 | NA <sup>2</sup>         |
| Chloride, dissolved (mg/L)                                 | 4                 | 4                    | 1.5             | 8             | 4.9          | No                 | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> )                      | 15                | 15                   | 47              | 276           | 136          | No                 | NA                      |
| Iron, total recoverable (µg/L)                             | 6                 | 6                    | 40              | 200           | 110          | No                 | 0                       |
| Magnesium (mg/L)   | 12                | 12                   | 15              | 106           | 46           | No                 | NA                      |
| Nitrate, dissolved (mg/L as NO <sub>3</sub> <sup>-</sup> ) | 5                 | 5                    | 0.1             | 0.8           | 0.4          | No                 | NA                      |
| Oxygen, dissolved (mg/L)                                   | 3                 | 3                    | 10              | 11            | 10.7         | No                 | 0                       |
| pH   | 12                | 12                   | 7.7             | 9.25          | 8.95         | No                 | 2                       |
| Specific conductance (µS/cm)                               | 11                | 11                   | 46              | 650           | 480          | No                 | NA                      |
| Sulfate, unfiltered (mg/L)                                 | 13                | 12                   | ND <sup>3</sup> | 72            | 23           | No                 | 0                       |
| Temperature (°C)   | 11                | 11                   | 0               | 14            | 5            | No                 | 0                       |

| Parameter       | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|-----------------|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Turbidity (NTU) | 15                | 15                   | 1.2           | 415           | 45           | No                 | NA                      |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ND: Not detected

## 5.9 Coal Creek at Crystal River (Site 9)

Coal Creek was sampled immediately above its confluence with the Crystal River. This site is approximately 3.5 miles downstream from Site 7, Coal Creek downstream of Dutch Creek. CDPHE collected samples on 26 occasions between May 1998 and June 2007. Ten of these events were in 2001 and the rest occurred at irregular intervals during the other years, except for 2004 and 2005, when no samples were collected. RFC staff and River Watch students collected samples on 57 occasions between January 2000 and June 2012. Samples were collected monthly in 2000, then quarterly in all other years except for 3 samples in 2005 and 2009, 5 samples in 2010, and 2 samples in 2012. This report considers all 83 samples that were collected between May 1998 and June 2012.

The classification and standards for Coal Creek are found under Region 12, Roaring Fork Basin, Segment 9 in the Stream Classification and Water Quality Standards listed in CWQCC Regulation 33. The creek is classified as Aquatic Life Cold 1, Recreation E, Water Supply, and Agriculture.

Table 12 shows each parameter that was studied, along with the number of samples, the number of samples in which the parameter was detected, the minimum, maximum, and median values, whether there was a statistically significant trend, and the number of samples whose result compared unfavorably with a standard. All of the results were below standards except for the following:

- The MWAT standard of 9.0°C for October through May was exceeded on 4 out of 24 occasions: 13°C on 19 May 1998, 9.9°C on 12 April 2000, 11.6°C on 26 April 2001, and 13.5°C on 23 May 2001. The 23 May 2001 temperature also exceeded the daily maximum standard of 13°C for October through May. The MWAT standard of 17.0°C for June through September was exceeded on 2 of 18 occasions: 18.1°C on 19 September 2000 and 18.1°C on 23 August 2001. However, being single results rather than an average of several samples taken over a week, these results present the possibility of an exceedance, but are not proof of an exceedance.
- The sum of nitrate and nitrite was quantified instead of the individual substances. If the entire sum was due to nitrate, there would be no exceedances of the nitrate standard of 10 mg/L as nitrogen. If the entire sum was nitrite, the nitrite standard of 0.05 mg/L as nitrogen would be exceeded on 14 out of 35 occasions, but it is very

unlikely for this to be the case. The dissolved oxygen results indicate that Coal Creek is well-oxygenated at this site, and under these conditions nitrogen tends to occur as nitrate rather than nitrite.

- The water quality goal for total phosphorous of 0.11 mg/L was exceeded by 3 out of 37 individual results: 0.17 mg/L on 19 May 1998, 0.16 mg/L on 12 April 2000, and 0.78 mg/L on 26 April 2001. However, compliance with the water quality goal is based on annual medians, with the annual medians not to exceed 0.11 mg/L more than once in every 5-year period. Of the 13 annual medians for this site, only the 1998 median exceeded 0.11 mg/L, so the water quality goal for total phosphorous has been met.
- The chronic standard of 1,000 µg/L for total recoverable iron was exceeded by 8 out of 47 results. These values ranged from 1,200 µg/L to 22,000 µg/L, with 7 occurring during the spring runoff (3 in April, 2 in May, 2 in June). This standard is not to be exceeded more than once every 3 years on average. Eight exceedances within a span of 12 years does not comply with this limitation. The exceedances do occur throughout the period: 1 each in 1998, 2007, 2008, and 2011; 1 in 2000; and 3 in 2001.
- The chronic standard of 0.02 µg/L for recoverable arsenic was exceeded on 3 out of 23 occasions: 1.3 µg/L on 19 May 1998; 250 µg/L on 7 February 2008; and 23 µg/L on 17 September 2008. This standard is not to be exceeded more than once every 3 years on average. Three exceedances within a span of 9 years complies with this limitation.
- One result out of 46 for dissolved copper, 200 µg/L on 20 June 2001, was greater than both the acute standard of 11.8 µg/L and chronic standard of 8.0 µg/L, which were calculated using the hardness value of 87 mg/L that was measured for this sample. This standard is not to be exceeded more than once every 3 years on average. One exceedance over a span of 12 years complies with this limitation.
- Three results out of 46 exceeded the chronic standard for dissolved lead: 6 µg/L on 29 September 2003; 6.4 µg/L on 7 February 2008; and 4.5 µg/L on 17 September 2008. The hardness-specific chronic standards of 3.3 µg/L, 2.6 µg/L, and 4.0 µg/L, respectively, were calculated using the hardness value measured for each sample. This standard is not to be exceeded more than once every 3 years on average. Three exceedances over a span of 12 years complies with this limitation.
- One out of 46 results exceeded the chronic standard of 4.6 µg/L for dissolved selenium: 5.9 µg/L on 17 September 2008. One exceedances over a span of 14 years complies with the limitation of no more than 1 exceedance every 3 years on average.

As expected, dissolved oxygen concentrations are slightly lower during the summer months when water temperature is higher (*see* Section 4.5). This behavior is consistent with oxygen having a lower solubility at higher water temperatures.

Parameters associated with specific conductance are expected to show lower concentrations during runoff from snowmelt and storms (*see* [Sections 4.4, 4.6, and 4.7](#)). All such parameters at this site—specific conductance, total dissolved solids, alkalinity, calcium, magnesium, hardness, chloride, and sulfate—show this pattern, with values generally lower during April, May, and June than at other times of year.

The analysis for total phosphorous (unfiltered), total recoverable iron, and recoverable arsenic includes not only the amount of these elements dissolved in the water, but the amounts occurring in particulate form as well (*see* [Section 4.14](#)). Occasional elevated concentrations of particulates are likely to be a result of natural events and/or human actions that cause a large input of eroded soil or sediment to the river over a short time. Intense or extended storms and spring runoff are examples of such natural events; clearing of vegetation from the land surface and earthmoving are examples of such human actions. The analysis for TSS gives particulate concentrations. All 3 phosphorous exceedances, 7 of 8 iron exceedances, and 1 of 3 arsenic exceedances occurred on dates when TSS was found to be high relative to most TSS values, which supports the expectation that high values of these 3 parameters are a result of high sediment loads in the stream.

Sen slope analysis showed a statistically significant decreasing trend at the 95% confidence level for several parameters: dissolved aluminum (1.0 µg/L per year), dissolved copper (0.010 µg/L per year), dissolved iron (0.88 µg/L per year), recoverable manganese (1.2 µg/L per year), and total phosphorous in unfiltered samples (0.0016 µg/L per year). Perhaps the cessation of coal mining in the Coal Creek watershed is responsible for these trends. In contrast, Sen slope analysis showed a statistically significant increasing trend at the 95% confidence level for total dissolved solids (45 mg/L per year) and hardness (4.4 mg/L per year). The contrasting trends are somewhat of a surprise given that aluminum, copper, iron, manganese, and some phosphorous-containing chemicals will contribute to total dissolved solids, albeit only at the microgram per liter level.

Other parameters analyzed showed no obvious patterns or statistically significant trends over time. In many cases, there were too few results above the detection limit for any patterns or trends to be evident.

The available data suggest that water quality in Coal Creek is occasionally impaired for aquatic life by high water temperatures and total recoverable iron.



**Table 12. Summary of results for Coal Creek at Crystal River.**

| Parameter                               | Number of Samples | Number of Detections | Minimum Value   | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|---|-------------------|----------------------|-----------------|---------------|--------------|--------------------|-------------------------|
| Alkalinity (mg/L as CaCO <sub>3</sub> ) | 21                | 21                   | 96              | 400           | 338          | No                 | NA <sup>2</sup>         |
| Aluminum, dissolved (mg/L)              | 45                | 7                    | ND <sup>3</sup> | 170           | ND           | ↓ <sup>4</sup>     | NA                      |
| Aluminum, unfiltered (mg/L)             | 25                | 25                   | ND              | 2916          | 157          | No                 | NA                      |
| Ammonia, total (mg/L as N)              | 10                | 3                    | ND              | 0.03          | ND           | No                 | 0                       |
| Ammonia plus ammonium (mg/L)            | 26                | 2                    | ND              | 0.1           | ND           | No                 | NA                      |
| Ammonia plus organic nitrogen (mg/L)    | 25                | 6                    | ND              | 2.2           | ND           | No                 | NA                      |
| Arsenic, dissolved (µg/L)               | 44                | 4                    | ND              | 290           | ND           | No                 | 0                       |
| Arsenic, recoverable (µg/L)             | 23                | 3                    | ND              | 250           | ND           | No                 | 3                       |
| Cadmium, dissolved (µg/L)               | 47                | 3                    | ND              | 0.4           | ND           | No                 | 0                       |
| Calcium (mg/L)                          | 22                | 22                   | 23              | 85            | 43           | No                 | NA                      |
| Chloride, unfiltered (mg/L)             | 13                | 12                   | ND              | 7.5           | 1.6          | No                 | 0                       |
| Copper, dissolved (µg/L)                | 46                | 7                    | ND              | 200           | ND           | ↓                  | 1                       |

| Parameter                                  | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Discharge (cfs)                            | 2                 | 22                   | 4.0           | 9             | 6.5          | No                 | NA                      |
| Hardness (mg/L as CaCO <sub>3</sub> )      | 45                | 45                   | 87            | 226           | 140          | ↑                  | NA                      |
| Iron, dissolved (µg/L)                     | 48                | 22                   | ND            | 270           | 12           | ↓                  | 0                       |
| Iron, total recoverable (µg/L)             | 47                | 47                   | 17            | 22,000        | 259          | No                 | 8                       |
| Lead, dissolved (µg/L)                     | 46                | 4                    | ND            | 6.4           | ND           | No                 | 3                       |
| Magnesium (mg/L)                           | 22                | 22                   | 6.0           | 22            | 16           | No                 | NA                      |
| Manganese, dissolved (µg/L)                | 46                | 7                    | ND            | 10            | ND           | No                 | 0                       |
| Manganese, recoverable (µg/L)              | 25                | 14                   | ND            | 120           | 9.3          |                    | NA                      |
| Nitrate plus nitrite, total (mg/L as N)    | 35                | 16                   | ND            | 1.7           | ND           | No                 | NA                      |
| Oxygen, dissolved (mg/L)                   | 40                | 40                   | 7.0           | 12            | 9.4          | No                 | 0                       |
| pH   | 42                | 42                   | 6.6           | 9.1           | 8.5          | No                 | 0                       |
| Phosphorous, total, unfiltered (mg/L as P) | 37                | 27                   | ND            | 0.78          | 0.02         | ↓                  | 3                       |
| Selenium, dissolved (µg/L)                 | 46                | 2                    | ND            | 5.9           | ND           | No                 | 1                       |

| Parameter                      | Number of Samples | Number of Detections | Minimum Value | Maximum Value | Median Value | Trend <sup>1</sup> | Exceedances of Standard |
|--------------------------------|-------------------|----------------------|---------------|---------------|--------------|--------------------|-------------------------|
| Selenium, unfiltered (µg/L)    | 23                | 3                    | ND            | 11            | ND           | No                 | NA                      |
| Solids, total dissolved (mg/L) | 22                | 22                   | 160           | 690           | 480          | ↑                  | NA                      |
| Solids, total suspended (mg/L) | 34                | 25                   | ND            | 1260          | 17           | No                 | NA                      |
| Specific conductance (µS/cm)   | 24                | 24                   | 240           | 940           | 669          | No                 | NA                      |
| Sulfate, unfiltered (mg/L)     | 38                | 38                   | 16            | 161           | 57           | No                 | 0                       |
| Temperature (°C)               | 42                | 42                   | -0.1          | 18            | 6.1          | No                 | 6                       |
| Zinc, dissolved (µg/L)         | 47                | 17                   | ND            | 53            | ND           | No                 | 0                       |
| Zinc, unfiltered (µg/L)        | 25                | 13                   | ND            | 27            | 5            | No                 | NA                      |

<sup>1</sup> Assessed using the Sen slope method and 95% confidence level

<sup>2</sup> NA: Not applicable (there is no standard for this parameter)

<sup>3</sup> ND: Not detected

<sup>4</sup> ↑: Increasing trend

<sup>5</sup> ↓: Decreasing trend

## 6.0 Site-to-Site comparisons

The available data provide an opportunity to identify similarities and differences in water quality among the various study sites. Given that comparisons are possible only when the parameter of interest is common to both sites, not every water quality parameter can be compared. In order for comparisons to be valid, they are further limited to those date ranges that are common to both sites for the parameter in question. These two considerations reduce the possible comparisons to a relatively small number. These limitations must be kept in mind when interpreting the results of comparisons. True differences may exist in parameters that were not measured at the sites being compared, and if there was only a limited period of time available for comparison, true

differences may also exist for a longer time period even if no difference was found for the shorter time period, and *vice versa*.

The Wilcoxon rank sum test provided in the WQSTAT II software package was used to determine if there was a difference in a given parameter between two sites at the 95% confidence level. The Wilcoxon test is a non-parametric method that does not require data sets to have a normal (bell-shaped) distribution and thus is well-suited for the available data. In order for this test to be used, there must be at least 4 values for the parameter of interest at each site.

Of all the possible combinations of two sites, the four combinations described below are of greatest interest. The results of the comparisons are presented in [Tables 13](#) through [16](#). Each Table shows those parameters for which valid comparisons could be made, the date range of the comparison, whether there is a difference at the 95% confidence level, and for those parameters with a statistically significant difference, the median value for each site.

### **6.1 Crystal River at Genter Mine Bridge (Site 1) versus Crystal River upstream of Coal Creek (Site 2)**

Comparison of these two sites shows any significant changes in water quality in the Crystal River between the Genter Mine Bridge on County Road 3 near Marble and the Crystal River in Redstone before the confluence with Coal Creek, a distance of approximately 8.6 river miles. Comparisons were possible for 14 parameters. Results are summarized in [Table 13](#).

Only 3 parameters had statistically significant differences. Dissolved iron and dissolved manganese concentrations were slightly greater at Redstone than near Marble, while the pH was lower at Redstone than near Marble. These differences may be the result of small changes in the geochemistry of the Crystal River in this reach as compared with the area upstream of the Genter Mine Bridge.

The statistical comparisons suggest that there is little change in water quality between these two sites. This result is reasonable if there is no significant change in the geochemistry of the watershed and no significant human-driven inputs between the sites.

### **6.2 Crystal River upstream of Coal Creek (Site 2) versus Coal Creek at Crystal River (Site 9)**

This comparison shows any significant differences in water quality between the Crystal River and Coal Creek immediately above their confluence. Comparisons were possible for 22 parameters. Results are summarized in [Table 14](#).

Six parameters had statistically significant differences. Total recoverable iron, pH, total dissolved solids, suspended solids, and specific conductance were all considerably greater in Coal Creek than in the Crystal River. Total phosphorous in unfiltered samples was slightly greater in Coal Creek.

**Table 13. Crystal River at Genter Mine Bridge (Site 1) compared to Crystal River upstream of Coal Creek (Site 2).**

| Parameter                      | Date Range Covered by Comparison |          | Different at 95% Confidence Level? | Difference in Medians     |                          |
|--------------------------------|----------------------------------|----------|------------------------------------|---------------------------|--------------------------|
|                                |                                  |          |                                    | Crystal at GMB:           | Crystal above Coal:      |
| Aluminum, dissolved (µg/L)     | 12/7/00                          | 2/20/02  | No                                 |                           |                          |
| Arsenic, dissolved (µg/L)      | 6/14/00                          | 2/20/02  | No                                 |                           |                          |
| Cadmium, dissolved (µg/L)      | 12/7/00                          | 2/20/02  | No                                 |                           |                          |
| Copper, dissolved (µg/L)       | 12/7/00                          | 2/20/02  | No                                 |                           |                          |
| Dissolved oxygen (mg/L)        | 12/7/00                          | 2/20/02  | No                                 |                           |                          |
| Hardness (mg/L)                | 1/13/99                          | 2/20/02  | No                                 |                           |                          |
| Iron, dissolved (µg/L)         | 1/13/99                          | 2/20/02  | Yes                                | Crystal at GMB: <i>ND</i> | Crystal above Coal: 5    |
| Iron, total recoverable (µg/L) | 1/13/99                          | 2/20/02  | No                                 |                           |                          |
| Lead, dissolved (µg/L)         | 2/9/99                           | 2/20/02  | No                                 |                           |                          |
| Manganese, dissolved (µg/L)    | 8/23/01                          | 2/20/02  | Yes                                | Crystal at GMB: <i>ND</i> | Crystal above Coal: 7    |
| pH                             | 2/9/99                           | 2/20/02  | Yes                                | Crystal at GMB: 8.12      | Crystal above Coal: 7.70 |
| Selenium, dissolved (µg/L)     | 12/7/00                          | 2/20/02  | No                                 |                           |                          |
| Temperature (°C)               | 2/9/99                           | 2/20/02  | No                                 |                           |                          |
| Zinc, dissolved (µg/L)         | 4/26/01                          | 12/18/01 | No                                 |                           |                          |

The statistical comparisons suggest that Coal Creek is significantly different than the Crystal River upstream of the Coal Creek confluence. Higher concentrations of suspended solids, total recoverable iron, and total phosphorous in unfiltered samples are all associated with a high sediment input to the stream. The extensive unvegetated slopes that occur both naturally and from past mining operations in the Coal Creek basin are a source of suspended solids. The total recoverable iron is a naturally-occurring component of these sediments. The source of the phosphorous is unclear, but when it is present phosphorous tends to be sorbed to sediments and thus also may be linked with a high sediment input. It may also be that the geochemistry of soil and rock in this basin includes more iron and phosphorous than the geochemistry in the Crystal River watershed upstream from Redstone.

Higher values of specific conductance and pH in Coal Creek are also likely to be a consequence of differences in the geochemistry of the two watersheds, with Coal Creek perhaps having sedimentary deposits richer in salts that are readily dissolved in water and that make the pH more basic.

### **6.3 Crystal River upstream of Coal Creek (Site 2) versus Crystal River below Redstone (Site 3)**

Site 3, the Crystal River below Redstone, is located at the downstream end of Redstone, approximately 1.7 river miles downstream from Site 2, the Crystal River upstream of Coal Creek. Comparison of these two sites shows how water quality in the Crystal River changes as a result of inflow from Coal Creek and any inputs that may be associated with Redstone. Results are summarized in [Table 15](#).

Comparisons were possible for 14 parameters of which 7 showed statistically significant differences. Dissolved cadmium, dissolved copper, dissolved iron, total recoverable iron, dissolved manganese, pH, and dissolved selenium were all greater below Redstone than above.

The influence of Coal Creek on the chemistry of the Crystal River is apparent for total recoverable iron and pH, both of which had statistically greater values in Coal Creek than in the Crystal River upstream of Coal Creek. Values for both of these parameters were greater in the Crystal River below Redstone than in the Crystal River site upstream of Coal Creek.

For dissolved iron, the difference between Coal Creek and the Crystal River upstream of Coal Creek was not statistically significant, but the median Coal Creek concentration was greater than the median Crystal River concentration (12 µg/L versus 5 µg/L). Thus it appears that Coal Creek contributed to the increase in dissolved iron observed between the Crystal River site above Coal Creek and the site below Redstone. The data for dissolved cadmium, dissolved manganese, and dissolved selenium do not show this same pattern, which suggests that there may be additional sources of these elements in the Redstone area.

## **6.4 Crystal River below Redstone (Site 3) versus Crystal River above Avalanche Creek (Site 5)**

Site 5, the Crystal River above Avalanche Creek, represents the downstream limit of the data included in this study. Comparisons were possible for 17 parameters, of which 4 showed statistically significant differences: total recoverable iron, pH, specific conductance, and temperature. Results are summarized in [Table 16](#).

Total recoverable iron concentrations and specific conductance were both greater in the Crystal River above Avalanche Creek than in the Crystal River below Redstone. These results suggest that this portion of the Crystal River watershed contributes a significant amount of additional iron-laden sediment to the river from surface runoff. Any human actions that result in increased soil erosion would contribute to this effect. The results also suggest a significant addition of dissolved salts to the river through contact between the water and salt-rich soil and rock.

Temperature was slightly greater above Avalanche Creek than below Redstone. This increase may be a combination of two factors. Inflow of warmer water from the Penny Hot Springs occurs in this reach. Also, water temperature is typically warmer downstream than upstream due to the opportunity for the water to absorb more heat from sunlight during the time it takes to flow through that distance.

The pH of the Crystal River decreased from 8.30 at Site 3 below Redstone to 7.83 at Site 5 above Avalanche Creek. The pH above Avalanche Creek was similar to the river pH of 7.70 above Coal Creek, while the pH of the Coal Creek tributary was much higher at 8.50. This suggests that the high pH below Redstone is a result of the high pH Coal Creek water joining the Crystal River at Redstone. As the river flows further downstream, the influence of the soil and rock geochemistry in the Crystal River valley lowers the pH toward the value it had above the confluence with Coal Creek.

**Table 14. Crystal River upstream of Coal Creek (Site 2) compared to Coal Creek at Crystal River (Site 9).**

| <b>Parameter</b>                     | <b>Date Range Covered by Comparison</b> |          | <b>Different at 95% Confidence Level?</b> | <b>Difference in Medians</b> |                      |
|--------------------------------------|---|----------|---|------------------------------|----------------------|
| Aluminum, dissolved (µg/L)           | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Ammonia plus ammonium (mg/L)         | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Ammonia plus organic nitrogen (mg/L) | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Arsenic, dissolved (µg/L)            | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Cadmium, dissolved (µg/L)            | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Copper, dissolved (µg/L)             | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Dissolved oxygen (mg/L)              | 12/21/00                                | 12/21/02 | No  |                              |                      |
| Hardness (mg/L)                      | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Iron, dissolved (µg/L)               | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Iron, total recoverable (µg/L)       | 5/19/98                                 | 2/21/02  | Yes                                       | Crystal above Coal: 31       | Coal at Crystal: 288 |
| Lead, dissolved (µg/L)               | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Manganese, dissolved (µg/L)          | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Nitrate plus nitrite (mg/L)          | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| pH                                   | 5/19/98                                 | 2/21/02  | Yes                                       | Crystal above Coal: 7.7      | Coal at Crystal: 8.5 |
| Selenium, dissolved (µg/L)           | 5/19/98                                 | 2/20/02  | No  |                              |                      |
| Solids, total dissolved (mg/L)       | 5/19/98                                 | 2/20/02  | Yes                                       | Crystal above Coal: 310      | Coal at Crystal: 475 |



| <b>Parameter</b>                     | <b>Date Range Covered by Comparison</b> |         | <b>Different at 95% Confidence Level?</b> | <b>Difference in Medians</b> |                        |
|--------------------------------------|---|---------|---|------------------------------|------------------------|
| Solids, suspended (mg/L)             | 5/19/98                                 | 2/20/02 | Yes                                       | Crystal above Coal: 5        | Coal at Crystal: 20    |
| Specific conductance (µS/cm)         | 5/19/98                                 | 2/20/02 | Yes                                       | Crystal above Coal: 405      | Coal at Crystal: 712   |
| Sulfate, unfiltered (mg/L)           | 5/19/98                                 | 2/21/02 | No  |                              |                        |
| Temperature (°C)                     | 5/19/98                                 | 2/21/02 | No  |                              |                        |
| Total phosphorous, unfiltered (mg/L) | 5/19/98                                 | 2/21/02 | Yes                                       | Crystal above Coal: 0.015    | Coal at Crystal: 0.023 |
| Zinc, dissolved (µg/L)               | 5/19/98                                 | 2/20/02 | No  |                              |                        |

**Table 15. Crystal River upstream of Coal Creek (Site 2) compared to Crystal River below Redstone (Site 3).**

| Parameter                      | Date Range Covered by Comparison |          | Different at 95% Confidence Level? | Difference in Medians |             |
|--------------------------------|----------------------------------|----------|------------------------------------|-----------------------|-------------|
|                                |                                  |          |                                    | Below Redstone:       | Above Coal: |
| Aluminum, dissolved (µg/L)     | 5/19/98                          | 1/23/02  | No                                 |                       |             |
| Cadmium, dissolved (µg/L)      | 5/19/98                          | 4/26/01  | Yes                                | 0.31                  | 0.15        |
| Copper, dissolved (µg/L)       | 5/19/98                          | 2/21/02  | Yes                                | 2.1                   | 1.5         |
| Dissolved oxygen (mg/L)        | 12/6/00                          | 3/20/02  | No                                 |                       |             |
| Hardness (mg/L)                | 5/19/98                          | 3/20/02  | No                                 |                       |             |
| Iron, dissolved (µg/L)         | 5/19/98                          | 2/20/02  | Yes                                | 24                    | 5           |
| Iron, total recoverable (µg/L) | 5/19/98                          | 3/20/02  | Yes                                | 129                   | 31          |
| Lead, dissolved (µg/L)         | 5/19/98                          | 12/21/02 | No                                 |                       |             |
| Manganese, dissolved (µg/L)    | 5/19/98                          | 11/20/02 | Yes                                | 14                    | 2           |
| pH                             | 5/19/98                          | 2/21/02  | Yes                                | 8.28                  | 7.70        |
| Selenium, dissolved (µg/L)     | 5/19/98                          | 3/20/02  | Yes                                | 2.4                   | 0.5         |
| Sulfate, unfiltered (mg/L)     | 5/19/98                          | 2/21/02  | No                                 |                       |             |
| Temperature (°C)               | 5/19/98                          | 3/20/02  | No                                 |                       |             |

**Table 16. Crystal River below Redstone (Site 3) compared to Crystal River above Avalanche Creek (Site 5).**

| <b>Parameter</b>                      | <b>Date Range Covered by Comparison</b> |          | <b>Different at 95% Confidence Level?</b> | <b>Difference in Medians</b>               |
|---------------------------------------|---|----------|---|--|
| Cadmium, dissolved (µg/L)             | 10/15/96                                | 5/21/03  | No  |  |
| Calcium (mg/L)                        | 10/21/98                                | 9/17/10  | No  |  |
| Copper, dissolved (µg/L)              | 10/15/96                                | 9/4/03   | No  |  |
| Dissolved oxygen (mg/L)               | 10/15/96                                | 6/29/05  | No  |  |
| Hardness (mg/L as CaCO <sub>3</sub> ) | 10/15/96                                | 6/29/05  | No  |  |
| Iron, total recoverable (µg/L)        | 10/15/96                                | 7/19/04  | Yes                                       | Below Redstone: 88 Above Avalanche: 297    |
| Lead, dissolved (µg/L)                | 10/15/96                                | 12/6/00  | No  |  |
| Magnesium (mg/L)                      | 12/16/98                                | 12/26/05 | No  |  |
| Manganese, dissolved (µg/L)           | 10/15/96                                | 5/29/02  | No  |  |
| Manganese, recoverable (µg/L)         | 5/12/98                                 | 12/22/05 | No  |  |
| pH                                    | 10/15/96                                | 12/22/05 | Yes                                       | Below Redstone: 8.30 Above Avalanche: 7.83 |
| Specific conductance (µS/cm)          | 5/4/79                                  | 4/9/92   | Yes                                       | Below Redstone: 380 Above Avalanche: 418   |
| Selenium, dissolved (µg/L)            | 10/15/96                                | 12/22/05 | No  |  |
| Sulfate, unfiltered (mg/L)            | 10/15/96                                | 12/22/05 | No  |  |
| Temperature (°C)                      | 5/15/79                                 | 10/4/10  | Yes                                       | Below Redstone: 7 Above Avalanche: 8       |
| Total phosphorous, unfiltered (µg/L)  | 10/15/96                                | 12/22/05 | No  |  |
| Zinc, dissolved (µg/L)                | 10/15/96                                | 9/4/03   | No  |  |

## **7.0 Recommendations for future monitoring**

### **7.1 General water quality parameters and sampling locations**

The primary water quality problem in the Crystal River and Coal Basin is the iron content in sediments that are washed into the river and creeks, which is reflected in the results for samples analyzed for total recoverable iron. Approximately 15% of the samples analyzed for total recoverable iron exceeded the water quality standard, which is designed to protect aquatic life.

Approximately 7% of the water temperature results were found to be higher than the temperature limits designated in the water quality standards, which are also based on protection of aquatic life. However, these temperature measurements were not conducted in the manner specified in the Colorado water quality regulations so they do not represent definite exceedances of the standard.

Dissolved oxygen results fell below the aquatic life-based water quality standard in approximately 8% of all samples. The majority of these low results occurred in one place and during one period, the Crystal River at Penny Hot Springs from 1994 through 1997, thus this appears to be a localized problem.

Recoverable arsenic results exceeded the water quality standard in approximately 8% of samples. This standard is based on the use of the stream as a domestic water supply, which is not taking place in the Crystal River or Coal Creek at this time.

Several other parameters exceeded standards less frequently than those described above and are not judged to be a widespread or on-going problem. These parameters include pH, nitrate, cadmium, copper, lead, and selenium.

The purpose of monitoring water quality parameters is to compare conditions against state standards and to detect any trends or patterns that are occurring, such as improvements due to restoration work or degradation due to the occurrence of new problems. If sufficient funds are available, all parameters having state standards could be monitored. Alternatively, monitoring could be limited to a subset that includes those parameters that reveal basic aspects of water quality plus those that are of the most concern based on historical data and current issues. This list could include temperature, pH, dissolved oxygen, total phosphorous, dissolved iron, total recoverable iron, and selenium. Although there are no state water quality standards for specific conductance, this parameter should also be measured because it is an easy, indirect way to monitor changes in total dissolved solids. Unexpected values for specific conductance would be an indication that conditions have changed and a more detailed study is warranted. Quarterly sampling should be frequent enough to establish a baseline for water quality across the variety of conditions that occur during a typical year.

The following locations are recommended:

- Coal Creek immediately upstream from its confluence with the Crystal River;

- Crystal River immediately above the confluence with Coal Creek; and
- Crystal River at a suitable location downstream from the confluence with Coal Creek.

## 7.2 Sediment load

There is considerable concern about large inputs of sediment into Coal Basin from disturbed areas within its watershed, and input of sediment from Coal Creek into the Crystal River. Existing data are inadequate to determine the extent of the issue because 1) we do not have good reference data, and 2) existing sampling efforts obtain data that reflect conditions at the time of sampling, but may miss conditions caused by episodic events. Reference data is useful to determine background conditions, without major human impacts. This would represent the upper end of what could be expected. In this area, there is a lack of the two basic types of reference data—baseline data that indicate conditions before major impacts and reference data obtained from a similar area with few impacts. Future efforts should be designed to fill these basic data gaps.

Sediment input is high during the spring runoff and during intense rainfall events that occur at other times of year. Channel instability and degradation of aquatic habitat result. One approach to monitoring sediment is to focus on physical effects of excessive sediment input, which can be tracked by periodic depth measurements at selected channel cross-sections, and by periodic measurement of cobble and boulder embeddedness at selected locations in the stream bed. An experienced fluvial geomorphologist should be consulted on methodology and selection of measurement locations.

Sediment input can also be characterized by focusing on sediment suspended in the water. The proper way to characterize suspended sediment over time is to monitor sediment load, which is the mass of sediment transported past a given point during a specific time period. Suspended sediment load is the product of suspended sediment concentration multiplied by stream flow and thus requires simultaneous measurement of both quantities. The ideal situation is to collect year-round, real-time streamflow measurements using a stream gage equipped with a turbidity/ TSS sensor, and a specific conductivity sensor. Obtaining companion meteorological gaging equipment for the station will allow relationships to be developed between precipitation events and flow and suspended sediment. This is crucial to determining the effectiveness of restoration activities.

Although not ideal, measurements can be targeted for high-flow periods, when sediment loads are expected to be greater. Relatively few measurements are needed during low-flow periods. A starting point is biweekly measurements during the rising and receding periods of the spring runoff, with three additional measurements spread over the low-flow portion of the year. Modification of this schedule should be considered after year three, depending on results. This scenario is not intended to capture sediment delivery from summer monsoonal events.

One approach to flow measurement in wadeable streams is to use an AA or pygmy meter to determine water velocity, and a wading rod and measuring tape to determine cross-sectional area. This approach may be appropriate for medium and low flows, but safety considerations dictate an alternate method for higher flows, such as making analogous measurements from a

bridge. If funds are available to install a stream gauge, a rating curve relating water height to stream flow could be developed over time, which would simplify future measurements of flow. RFC installed instrumentation on Coal Creek about 1 mile upstream from its mouth at the Crystal River in 2013. This station collects measurements of stream flow, turbidity, and precipitation and is tied to an automated sediment sampler.

Quantification of suspended sediment in streams is problematic. Suspended sediment concentration varies greatly with changes in stream flow. At a given high stream flow, there is also significant point-to-point and moment-to-moment variability within any cross-section, so care must be taken to obtain a representative value of sediment concentration. The silt and clay fraction of the suspended sediment is considered to be evenly distributed throughout a cross-section, and can be characterized using a single grab sample taken near the water surface in the center of the stream. If larger particle sizes (*e.g.*, sand) are a significant part of the suspended sediment load, then use of a depth-integrating sampler (*e.g.*, DH-48 sampler) is better. Depth-integrated samples are collected by moving the sampler up and down from bed to surface to collect water from all depths. Depth-integrated samples from several locations within a cross-section are combined. The logistics of this operation are reminiscent of measuring stream flow, and safety again dictates that sampling would have to occur from a bridge during high flow periods. Analysis for suspended sediment is simple – a known volume of water is filtered, and the mass of the sediment collected on the filter is measured.

In order to characterize suspended sediment loads, simultaneous collection of water samples and stream flow measurement should take place at the following locations:

- Coal Creek immediately upstream from its confluence with the Crystal River;
- Coal Creek at other locations bracketing disturbed areas prior to and following restoration, sited so as to quantify the effect of restoration efforts on suspended sediment load;
- Crystal River immediately above the confluence with Coal Creek; and
- Crystal River at a suitable location downstream from the confluence with Coal Creek.

### **7.3 Macroinvertebrates**

Annual collections of macroinvertebrates and pebble counts are also recommended for this area. RFC partnered with the USFS and Timberline Aquatics and collected macroinvertebrates on the Crystal River and in Coal Basin in the fall of 2011 and 2012. An experienced aquatic ecologist should be consulted on methodology and selection of measurement locations. Because of their limited mobility, relatively long aquatic life stage, high population densities, and sensitivity to disturbance, benthic macroinvertebrates have become a preferred biological indicator for the assessment of biological integrity (Herricks 1995, Ward *et al.* 2002). They are particularly useful to capture the impacts from episodic events, such as intense rainfall, that routine sampling may miss.

## 8.0 References

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